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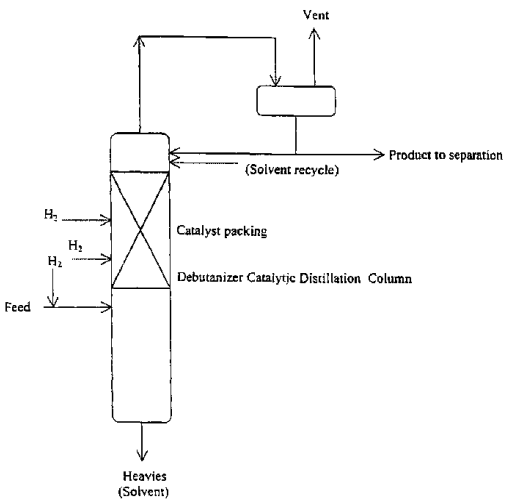
(54)【発明の名称】アルキン類の選択的水素化方法及びそのための触媒

(57)【要約】
混合１，３－ブタジエンのようなオレフィン流れ中のアセチレン型化合物を、アルミナ、シリカ等のような高度に多孔質の担体表面の担持型銅触媒上で選択的に水素化した。好ましい担体は、約２００オングストロームよりも大きな平均細孔直径を有し、ミクロ細孔を有せず、約０．６５cc/gよりも大きな総細孔容積及び好ましくは約２３０m^2/g未満のＢＥＴ表面積を有する。銅触媒を、好ましくはパラジウムのようなＶＩＩＩ族金属を用いて促進して、銅触媒の低い活性を改良する。生成物流れは、典型的には２０ppm未満の全アルキン類を含む。また銅触媒及びパラジウム促進銅触媒を、酸化亜鉛を用いて調整して、触媒の性能を改良してよい。異なるレベルのパラジウムを用いて促進された２種以上の銅触媒を反応器に装填した。また好ましくは銅触媒を、銀、金または銀及び金の両方を用いて調整して、触媒の銅成分によるポリマー形成を低減し、１，３－ブタジエンのようなオレフィン類の収率を改良し、炭化水素の液相中に浸出することによる銅及び／またはパラジウムの損失を防ぐ。



【特許請求の範囲】
【請求項１】
２００オングストロームよりも大きな平均細孔直径または約０．７０g/cm^{3}未満の見かけの嵩密度の特性のうちの少なくとも１つを含むアルミナ担体上の、銅成分及び少なくとも１種のＶＩＩＩ族金属成分、Ａｇ、Ａｕ成分またはこれらの混合物の成分を含む、アセチレン類の選択的水素化のための触媒。
【請求項２】
Ａｇ、Ａｕ成分またはこれらの混合物の成分を含む、請求項１に記載の触媒。
【請求項３】
少なくとも１種のＶＩＩＩ族金属成分を含む、請求項１に記載の触媒。
【請求項４】
少なくとも１種のＶＩＩＩ族金属成分及びＡｇ、Ａｕまたはこれらの混合物成分の成分を含む、請求項１に記載の触媒。
【請求項５】
少なくとも１種のＶＩＩＩ族金属成分、Ａｇ成分及びＡｕ成分の成分を含む、請求項１に記載の触媒。
【請求項６】
前記ＶＩＩＩ族成分はＰｄを含む、請求項２、３、４または５に記載の触媒。
【請求項７】
Ｚｎ成分を含む、請求項２、３、４または５に記載の触媒。
【請求項８】
２００オングストロームよりも大きな平均細孔直径を有するアルミナ担体を含む、請求項１に記載の触媒。
【請求項９】
約０．７０g/cm^{3}未満の見かけの嵩密度を有するアルミナ担体を含む、請求項１に記載の触媒。
【請求項１０】
銅成分、少なくとも１種のＶＩＩＩ族金属成分及びＺｎ成分を含む、アセチレン類の選択的水素化のための触媒。
【請求項１１】
Ａｇ、Ａｕまたはこれらの混合物の成分を含む、請求項１０に記載の触媒。
【請求項１２】
約０．１～２５重量％のＣｕを含む、請求項１０に記載の触媒。
【請求項１３】
少なくとも部分的に液相中のアセチレン類を含む供給物と請求項１に記載の触媒とを、前記アセチレン類を選択的に水素化する条件下で接触させることを含む、アセチレン類の選択的水素化方法。
【請求項１４】
可溶性ポリマーは、前記水素化の間中前記触媒に連続的に堆積して、アセチレン類の選択的水素化のための前記触媒の低下した活性をもたらし、前記水素化は間欠的に中断し、前記可溶性ポリマーの溶媒は前記触媒と接触し、前記ポリマーの一部を除去し、前記選択的水素化のための前記触媒の活性の一部を回復する、請求項１３に記載の方法。
【請求項１５】
前記溶媒は、テトラヒドロフラン、フラン、１，４－ジオキサン、エーテル類、ガンマ－ブチロラクトン、ベンゼンまたはトルエンのうちの少なくとも１つを含む、請求項１４に記載の方法。
【請求項１６】
少なくとも部分的に液相中のアセチレン類を含む供給物と請求項１０に記載の触媒とを、前記アセチレン類を選択的に水素化する条件下で接触させることを含む、アセチレン類の選択的水素化方法。

【請求項１７】
可溶性ポリマーは、前記水素化の間中前記触媒に連続的に堆積して、アセチレン類の選択的水素化のための前記触媒の低下した活性をもたらし、前記水素化は間欠的に中断し、前記可溶性ポリマーの溶媒は前記触媒と接触し、前記ポリマーの一部を除去し、前記選択的水素化のための前記触媒の活性の一部を回復する、請求項１６に記載の方法。
【請求項１８】
前記溶媒は、テトラヒドロフラン、フラン、１，４－ジオキサン、エーテル類、ガンマ－ブチロラクトン、ベンゼンまたはトルエンのうちの少なくとも１つを含む、請求項１７に記載の方法。
【発明の詳細な説明】
【技術分野】
【０００１】
本発明は、不飽和化合物の混合物からのより高度に不飽和な化合物の選択的除去に関する。より詳細には、本発明は、１，３－ブタジエンのようなジエン類との混合物からのアセチレン型化合物の選択的水素化に関する。本発明は、新規な触媒及び他の不飽和化合物と混和しているアセチレン類の選択的水素化方法の両方を提供する。
【背景技術】
【０００２】
担持型銅触媒及びパラジウム触媒は、オレフィン流れ中のアセチレン型不純物を選択的水素化によって取り除く際の好ましい触媒とされてきた。銅触媒は、オレフィン類及びジオレフィン類の実質的な水素化無しにアセチレン型化合物を選択的に水素化する（本明細書において、オレフィン類を保持するための選択性と呼ぶ）が、主に触媒表面へのポリマー堆積が理由となって比較的に低い活性及び短いサイクル時間を有する。パラジウム触媒は、優れた活性及び銅に基づく触媒よりもはるかに長いサイクル時間を有するが、アセチレン類に対するより低い選択性を有する。パラジウム触媒のオレフィン選択性を改良するために、少量の銀または金を調整剤としてパラジウム触媒に加えてきた。
【０００３】
Fr 1 253 947（１９６０）は、ジオレフィンまたはモノオレフィン流れ中のアセチレン型化合物の選択的水素化のための銅触媒を開示した。選択的水素化を、蒸気相中で実行した。純度９９．９～９９．９９９％の銅を、ガンマアルミナのような高表面積（２５～３００m^2/g）担体表面に担持させた。触媒の銅含量は、５～２０％の範囲内だった。触媒は、０．１％未満の他の金属（触媒の金属含量を基準として）の例えばＦｅ、Ｎｉ、Ｒｕ、Ｒｈ、Ｐｄ、ＩｒまたはＰｔを助触媒として含んでよい。選択的水素化を、蒸気相中及び液相中の両方で実行した。米国特許第4,440,956号（１９８４）及び同第4493906号（１９８５）は、アルミニウムアルコキシドから製造したガンマアルミナのような非常に特殊なアルミナ表面に担持された改良された銅触媒であって、液体炭化水素流れ中のアルキン類を除去するために有用な銅触媒を開示した。特許権者は、ガンマアルミナを、細孔の６０～９０％が細孔直径約４０オングストローム～１２０オングストロームを有するはずであり、２５％以下でかつ２％以上が細孔直径１０００オングストローム～１０，０００オングストロームを有したとキャラクタリゼーションした。アルミナの窒素表面積は、約６８～３５０m^2/gだった。触媒は、３～１３重量％のＣｕを含んだ。触媒は、銀、マンガン、コバルト、ニッケル及びクロムからなる群から選択される少量の少なくとも１つの多価活性化剤金属を含んだ。高純度のアルミナ（特にナトリウム（０．１５重量％未満であるべきである）及びFe_2O_3（０．０６重量％未満）含量の点で）は、頻繁な触媒再生によって引き起こされる表面積の収縮が理由となって、必要要件であると主張された。
【０００４】
Ger 2 109 070（１９７０）は、蒸気相中の１，３－ブタジエン流れ中のアセチレン型化合物の選択的水素化のための銅（２６％）－酸化亜鉛触媒を開示した。
米国特許第4,174,355号（１９７９）は、ジオレフィン流れからα－アセチレンを非選択的水素化によって除去する方法を開示した。水素も酸素も無い状態で、供給物蒸気とα－

アルミナ表面に担持されたＣｕＯ及び／またはＡｇ$_2$Ｏとを接触させることで、アルキン類を除去した。

【０００５】

米国特許第4,533,779号（１９８５）は、アセチレン型化合物の選択的水素化のための、アルミナ（１～１００㎡/g）のような担体表面に担持されたパラジウム／金触媒を開示した。触媒中のパラジウム及び金の含量は、それぞれ０．０３～１重量％及び０．００３～０．３重量％の範囲内だった。

【０００６】

米国特許第4,831,200号（１９８９）は、１，３－ブタジエンとの混合物のようなオレフィン流れ中のアルキン類の選択的水素化方法を開示した。選択的水素化を、２段階で順次実行した。第一の段階において、炭化水素供給物を、水素と共に、少なくとも部分的に液相中で、上記に検討した米国特許第4,533,779号において開示したもののようなパラジウム触媒上を通過させた。第２の段階において、第１の段階から生じた生成物流れを再度、水素と共に、少なくとも部分的に液相中で、上記に検討した米国特許第4,493,906号及び同第4,440,956号において開示したもののような銅触媒上を通過させて、製造最終生成物流れ中のかなり低下したアルキン濃度を生じた。

【０００７】

米国特許第5,877,363号（１９９９）は、Ｐｔ及びＰｄのような担持型水素化触媒を使用することによる、混合オレフィン濃厚Ｃ$_4$流れ中のアセチレン型不純物及び１，２－ブタジエンの選択的水素化方法を開示した。

【０００８】

一般に、オレフィン蒸気中のアセチレン型化合物の選択的水素化のために、パラジウム触媒は銅触媒と比較して非常に活性がある。しかし、流れ中の高濃度（＞２０００ppm）の全アルキン類～約５００ppm未満の全アルキン類を除去しようと試みると、特にアセチレン類が２００ppm未満に低減すると、パラジウム触媒は、１，３－ブタジエンのようなジオレフィン類を保持するための低い選択性を示す。工業的実施においては、パラジウム触媒の非選択性は、１，３－ブタジエンの損失をもたらすので望ましくない。

【０００９】

一方、銅触媒は、アセチレン類の水素化に対して非常に選択的であることによって、１，３－ブタジエンのようなジオレフィン類を保持する際に高度に選択的である。しかし、銅触媒の活性は低い。また、触媒表面へのポリマー材料の堆積によって引き起こされる急速な失活が理由となって、触媒のサイクル時間は、約２０００ppmよりも高い全アルキン類を含む供給物流れにとっては望ましくない程短い。たとえ水素化を液相中で実行しても、銅触媒表面に堆積したポリマーの幾らかは、選択的水素化条件下で液体生成物流れ中への溶解度をほとんど有しない。こうした２つの理由によって、銅触媒は、比較的に高濃度の全アルキン類を含む混合オレフィン供給物の選択的水素化に対する改良を必要とする。

【発明の開示】

【００１０】

本発明は、約０．１～２５重量％、好ましくは０．２～２０重量％のＣｕを含む銅成分を含む触媒を含み；パラジウム助触媒は０～２重量％、好ましくは０～１重量％の範囲内であり；銀調整剤または金調整剤は０～１５重量％、好ましくは０～１０重量％の範囲内であり；酸化亜鉛調整剤は０～２５重量％、好ましくは０～約１５重量％の範囲内である。銀調整剤は、触媒活性を適度にし、オレフィン収率及びサイクル時間を改良する。酸化亜鉛調整剤は、１，３－ブタジエンのようなオレフィンの収率を改良し、触媒活性をわずかに改良する。酸化亜鉛調整銅触媒は、１，３－ブタジエンの極めて高い収率を有しながらビニルアセチレン不純物を除去するために、特に非常に有効である。好適な具体例においては、触媒成分を担体表面に堆積させる。

【００１１】

好ましい担体は、約２００オングストロームよりも大きな平均細孔直径を有し、ミクロ細孔を有せず、約０．６５cc/gよりも大きな総細孔容積及び好ましくは約２３０㎡/g未満の

ＢＥＴ表面積を有する。銅触媒を、好ましくはパラジウムのようなＶＩＩＩ族金属を用いて促進して、銅触媒の低い活性を改良する。生成物流れは、典型的には２０ppm未満の全アルキン類を含む。また銅触媒及びパラジウム促進銅触媒を、酸化亜鉛を用いて調整して、触媒の性能を改良してよい。異なるレベルのパラジウムを用いて促進された２種以上の銅触媒を反応器に装填した。また好ましくは銅触媒を、銀、金または銀及び金の両方を用いて調整して、触媒の銅成分によるポリマー形成を低減し、１，３－ブタジエンのようなオレフィン類の収率を改良し、炭化水素の液相中に浸出することによる銅及びパラジウムの損失を防ぐ。

【００１２】

少量のアセチレン型化合物を含む炭化水素流れと様々な配置及び形状の本発明の触媒とを接触させることでアセチレン型化合物を除去する方法もまた、本発明の一部である。

【発明を実施するための最良の手段】

【００１３】

選択的水素化を、少なくとも部分的に液相中で、例えば単数または複数の接触蒸留（ＣＤ）ユニットを用いることで実行することが好ましい。従って、選択的水素化を、より高いスループット率で１段階で実行することができ、しかもなおジエン類のようなオレフィン類を保持する高い選択性及び長い触媒寿命を維持するように、新規な方法及び改良された銅触媒を提供することが非常に望ましい。本発明においては、この目的は、選択的水素化を、高度に活性がありしかもなお高度に選択的な銅触媒を有する単一の反応器中で実行することで成し遂げられる。選択的水素化を、少なくとも部分的に液相中で、接触蒸留（ＣＤ）ユニットを用いることで実行することが好ましい。異なるレベルのＶＩＩＩ族の元素の例えばパラジウム、ルテニウム、ニッケル等を用いて促進され、また酸化亜鉛及びＩＢ族の元素を用いて調整された２種以上の銅触媒を蒸留塔に装填する。好ましい助触媒は、パラジウムである。銅触媒をパラジウムを用いて促進することは、高アセチレン型不純物含有供給物を取り扱う際に非常に望ましい。本データは、銅は、パラジウムとの合金にすることではるかに高活性になり、しかも１，３－ブタジエンまたは１－ブテンのようなオレフィン類を保持する選択性の損失はわずかであることを示す。銅をパラジウムとの合金にすることで、本銅－パラジウム触媒の化学的性質は、従来のパラジウムまたはパラジウム－銀触媒から変化する。変化の性質を実施例１２において証明する。本発明から得られる生成物流れ中のエチルアセチレン対ビニルアセチレンの比は、従来のパラジウム触媒から得られる生成物よりもはるかに高く、というのは、本銅－パラジウム触媒は、ビニルアセチレン及びエチルアセチレンに対する化学反応性が従来のパラジウムまたはパラジウム－銀触媒とはかなり異なるからである。従って、C_4アセチレン類の所定の転化における比の差は、本銅－パラジウム触媒の化学的な触媒の性質を従来のパラジウム触媒と区別する指紋である。

【００１４】

清浄な１，３－ブタジエン濃厚生成物を製造するために混合C_4供給物流れを取り扱う際に、銅触媒を脱ブタン塔蒸留塔中に装填して、ＣＤ反応器を提供してよい。接触蒸留塔に至る供給物を、好ましくは触媒床よりも下の、塔の中央区画に供給する。生成物を塔頂留出物として回収する。より重質の生成物をボトム生成物として回収する。ＣＤ反応器中に装填する銅触媒のパラジウム含量は、触媒床の底部区画から頂部区画へと上昇するにつれて徐々に減少する。触媒を、蒸留塔への供給箇所よりも上に装填する。水素を、炭化水素供給物と一緒に、または別個に蒸留塔の底部区画における位置に供給する。触媒反応帯域中の水素対全アルキン類の最適比は、触媒のＣｕ含量のみならずＣｕ／Ｐｄ重量比に依存する。従って、反応器中の触媒の組成に依存して、好ましくは水素を、接触蒸留塔または固定床に沿って２つ以上の位置に供給する。また触媒のパラジウム成分は、触媒のサイクル時間を改良する。Ｐｄを用いて促進された銅触媒のこの追加の利益がどのようにして生じるかは知られてないが、ポリマー材料に至る不飽和前駆体がより有効に水素化されて、銅触媒表面へのポリマー材料の堆積がより遅いかまたはほとんどないのかもしれない。ポリマー材料は、非促進銅触媒表面に形成されたポリマーよりも、生成物蒸気中への高い溶

解度を有することができる。従って、前駆体及びポリマー材料を触媒から接触蒸留塔の底部へと有効に洗い流して、連続的に再生されるより清浄な触媒表面をもたらす。好ましくは触媒の銅成分を、ＩＢ族の元素の例えば銀及び／または金または両方を用いて調整して、ポリマー形成をさらに低減してジエンの選択性を改良し、触媒から銅及びパラジウム金属が徐々に浸出する点を改良する。

【００１５】

触媒を、酸化亜鉛を用いてさらに調整して、触媒活性、１，３－ブタジエンのようなオレフィン類の収率、触媒のサイクル時間を改良し、触媒から徐々に浸出することによる銅及びパラジウムの損失を低減してよい。硝酸塩類の混合溶液の共沈によって製造したＣｕ－Ｚｎ－Ａｌメタノール合成触媒の場合には、Ｃｕ（ＩＩ）イオンは、銅－酸化亜鉛－アルミナ触媒（共沈手法によって製造した）の酸化亜鉛相中に溶解し、その濃度は、約２５原子％もの高さになる可能性がある（T. M. Yurieva, et al. React. Kinet. Catal. Lett., 29, pp. 55-61, 1985）。本発明において開示する全ての銅触媒は、触媒が酸化亜鉛を含むかどうかにかかわらず、水素の無い状態でオレフィン類を水素化することができる活性水素種の高い含量を有することが観察された。

【００１６】

水素化を、２段階で実行してよい。例えば、選択的水素化を、２つのＣＤ反応器、またはＣＤ反応器及び固定床反応器の組合せ、または２つの固定床反応器を用いて図２に示すように実行することができる。固定床反応器の稼働においては、第１の反応器から生じた反応器流出液流れを第２の反応器に入る前に冷却することで、水素化反応の発熱による熱を除去するために、２つ以上の反応器が必要かもしれない。固定床反応器の稼働における反応器流出液を再循環して、水素化反応の熱を希釈することもできるかもしれない。所望により、反応性蒸留態様またはストレートパス態様で、触媒表面に堆積したポリマーが可溶であるような材料を使用して、ポリマーを触媒から洗い流してよい。このような溶媒の例としては、テトラヒドロフラン、フラン、１，４－ジオキサン、エーテル類、ガンマ－ブチロラクトン、ベンゼン、トルエンまたはこれらの混合物が挙げられる。図１に示すように、生成物を溶媒から分離した後に、溶媒を再循環して反応器に戻す。触媒寿命を長くする別の手法は、触媒を、液体溶媒を用いて、約４０℃～３５０℃の範囲内の温度で間欠的に洗浄して、堆積したポリマーを触媒から除去することである。ポリマーを触媒から洗い流す最中に、所望により少量の水素ガスを、溶媒と共に触媒床を通過させる。C_4流れ中のアクテリエン類（actelyenes）の選択的水素化をＣＤ態様で実行する際に、溶媒の沸点が約１００°Fよりも高い場合、溶媒を接触蒸留反応器の触媒帯域の頂部に加えることができ、溶媒は塔の底部に下降流で流れる。ストレートパス反応器においては溶媒（solve）を反応物供給流れと共に反応器に供給してよい。両方の実施態様の間中、供給物流れ中の少なくとも０．２モル％のアセチレン類が、反応帯域中の溶媒及び炭化水素を含む液相中にあるように、十分な圧力をかけることが望ましい。

【００１７】

本発明における触媒の製造のために使用される好ましい担体は、メソ細孔性材料（mesoporous material）であり、比較的に大きな細孔容積を有するべきである。担持材料の平均細孔直径が増大するにつれて、細孔容積も同様に増大するが、材料の表面積及びＡＢＤ（見かけの嵩密度（apparent bulk density）、しばしば充填密度（packed density）と呼ばれる）の両方は減少する。好ましくは担体はミクロ細孔を有せず、好ましくは直径約３０オングストローム未満の細孔を有しないだろう。触媒表面への重質材料の堆積が、触媒失活及び過度の反応による所望の材料の選択性の低下を引き起こす場合に、一般に細孔の孔径分布及びサイズは触媒性能にとって重要な役割を果たす。本発明において好ましい担体のうちの１つは、遷移アルミナである。所望のアルミナの細孔は、１００オングストロームよりも大きな直径を有する細孔で主に構成される。細孔の約８５％、好ましくは約９０％は、窒素ポロシメトリーによって測定して１００オングストロームよりも大きな細孔直径を有しよう。好ましいアルミナは、約１００オングストロームよりも大きく、好ましくは１２０オングストロームよりも大きな平均細孔直径、約０．６５cc/gよりも大きく（

窒素ポロシメトリーによって測定して）、好ましくは０．７０cc/gよりも大きな総細孔容積、好ましくは約２３０m^2/g未満、最も好ましくは３０～２００m^2/gのＢＥＴ表面積、約０．７０g/cm^3未満の見かけの嵩密度（ＡＢＤ）を有しよう。アルミナの細孔は、様々なサイズの細孔直径で構成される。アルミナ表面積の特定の範囲内で、どのようにしてアルミナを製造し、か焼したかに依存してアルミナの細孔分布を操作することができる。米国特許第4,440,956号において開示されているアルミナとは異なり、本発明において好ましいアルミナは、細孔の少なくとも３０％、好ましくは少なくとも５０％が１００オングストロームよりも大きな直径を有する細孔を有し、約０．６５cc/gよりも大きく、好ましくは約０．７５cc/gの総細孔容積を有しよう。

【００１８】

本発明において開示する好ましいアルミナを、いわゆる活性アルミナを製造する当業者には周知の多数の手法によって製造することができる。本発明において開示する好ましいアルミナのうちの１つを、いわゆる油滴下ゲル化手法（oil dropping gelatiion technique）によって製造することができる。従来技術の例は、米国特許第2,620,314号（１９５２）、及び同第4,273,735号（１９８１）において開示されている。球形のアルミナを、水性塩酸溶液中でアルミニウム金属を温浸する（digest）ことで製造したアルミニウムヒドロキシクロリドゾルから製造する。小滴の形態の球形のアルミナゾル材料を、塩基性液体油相中でゲル化し、続いてエージング、洗浄、乾燥、及びか焼して（アルミナの所望の特性に依存して様々な温度で）、遷移状態アルミナにする。他に、好ましい球形のアルミナを、油滴下ゲル化手法によって分散型ベーマイトまたは擬ベーマイトアルミナゾルを使用して製造することもできる。従来技術の例は、米国特許第4,179,408号（１９７９）において開示されている。アルミナゾルは、適切なベーマイト、擬ベーマイト、またはベーマイトと擬ベーマイトアルミナとの混合物を酸性の水の中に分散させることで製造される。擬ベーマイトまたはベーマイト原料は、アルミニウムアルコキシドを加水分解し、結晶化するか、または、アルミン酸ナトリウムと硫酸アルミニウムのようなアルミニウム塩類とを反応させ、結晶化することで得られる。様々なベーマイトアルミナまたは分散型ベーマイトアルミナゾルが、市場で入手可能である。コンデア（Condea）は、供給者のうちの１つである。本発明において細孔構造が開示される好ましい球形のアルミナを製造するために、ディスペラル　ＨＰ　１４／２（Disperal HP 14/2）、ディスパル　１１Ｎ７－８０（Dispal 11N7-80）、ディスパル　２３Ｎ４－２０、ディスペラル　ＨＰ１４、デペラル　４０（Deperal 40）、プラル　２００（Pural 200）、プラル　１００、プラル　ＮＧ等またはこうしたものの混合物を使用できる。他のベーマイトアルミナの例えばカタパル　Ｃ１（Catapal C1）、プラル　ＳＢ、ディスペラル　Ｐ２等は、本発明において開示する好ましいアルミナの製造のための好ましい原料ではない。こうした材料は、米国特許第4,493,906号及び同第4,440,956号において開示されている同様なアルミナを与える。

【００１９】

押出物形態の好ましいアルミナを、上記に検討した好ましいベーマイトアルミナを押出し、約５５０℃～１２００℃の高温でか焼することで製造することもできる。一般に、遷移アルミナは、結晶性アルミナの例えば非晶質、γ、χ、δ、η、ρ、θ、α等の様々な混合物であり、その表面積は、高温雰囲気に繰り返しさらすことによって、より安定な結晶形に至るゆっくりとした結晶化が原因となって収縮する傾向がある。特にこの表面積の収縮は、雰囲気中の水分またはアルミナ中の微量のナトリウムまたは両方の存在下で加速される。ガンマアルミナが所望の形である場合、か焼を、通常約５５０℃～７００℃の温度で実行する。米国特許第4,493,906号及び同第4,440,956号において開示されているアルミナとは異なり、アルミナ担体を、非常に少量の塩素を含むアルミニウムヒドロキシクロリドゾルを使用して本油滴下ゲル化手法において製造した。本発明において開示するアルミナ中の少量のナトリウムまたは塩素は、溶媒を用いた接触蒸留の稼働または固定床の稼働の場合は、長い触媒のサイクル時間が理由となって通常は重大な問題を引き起こさない。

【００２０】

本発明において好ましいアルミナの物理的形状は、球、押出物、ペレット及び顆粒であり

、これらは、直径約１／４インチ未満、好ましくは１／８インチを有し、押出物またはペレットの場合長さ約１／２インチ未満、好ましくは長さ１／４インチ未満を有する。

【００２１】

触媒の銅成分を、硝酸第二銅、酢酸第二銅等のような第二銅塩類の水溶液を用いた様々な含浸手法によって、好ましいアルミナ表面に置く。含浸生成物を、約１００～５００℃、好ましくは２００～４００℃でか焼して、塩類を分解して、酸化銅－アルミナ生成物を得る。銀調整剤及び酸化亜鉛調整剤を、硝酸銀のような銀塩及び硝酸亜鉛のような亜鉛塩と銅塩との同時含浸（co-impregnation）によって触媒中に取り入れる。所望により、これらを、二重含浸（double impregnation）によって銅触媒中に取り入れる。酸化亜鉛調整剤または銀調整剤及び酸化亜鉛調整剤の両方を、銅化合物の溶液の含浸の前にアルミナ担体表面に置く。含浸生成物を、約１００～６５０℃、好ましくは１００～６００℃でか焼して、酸化銅－酸化銀－アルミナ触媒または酸化銅－酸化銀－酸化亜鉛－アルミナ触媒を得る。さらに別の手法を使用して酸化亜鉛調整銅触媒を製造することができ、これは、所望の量の亜鉛塩または亜鉛塩及び銅塩の両方を含むアルミナゾルを塩基性油相中に滴下してゲルを形成し、続いてエージングし、洗浄し、４５０～１２００℃の温度範囲でか焼することによる。

【００２２】

パラジウム助触媒を、硝酸パラジウム（ＩＩ）、酢酸パラジウム（ＩＩ）、パラジウム（ＩＩ）アセチルアセトナート等のようなパラジウム化合物溶液と銅塩溶液または銅塩及び銀塩を含む溶液との同時含浸によって触媒中に取り入れる。様々な含浸手法を使用できるが、パラジウム化合物溶液、またはパラジウム化合物と銅化合物との、若しくはパラジウム化合物と銅化合物と銀化合物との、若しくはパラジウム化合物と銅化合物と銀化合物と亜鉛化合物との混合溶液の好ましい含浸手法は、アトマイザーを使用した噴霧コーティング含浸（spray coating impregnation）である。担体表面に溶液を均一に噴霧することは非常に望ましい。また、圧縮ガスアトマイザーを使用してパラジウム溶液の微細なミストを生成することは非常に望ましい。アルミナのような担体表面に様々なパラジウム溶液を噴霧コーティングする場合に、溶液の所望の体積は、含浸される担体の総細孔容積（担体の重量に、担体の単位重量当りの細孔容積をかける）の約９０体積％未満、好ましくは約８５体積％未満である。

【００２３】

パラジウムを用いて促進された高度に活性がある銅触媒を製造する場合に、触媒成分の含浸を１段階でまたは２段階で実行することができる。２段階含浸においては、第１の段階の含浸手法では、通常、初期細孔含浸手法（incipient pore impregnation technique）を使用して、アルミナ担体に、銅化合物の溶液、または銅及び亜鉛化合物、若しくは銅、亜鉛及び銀化合物、若しくは亜鉛及び銀化合物を含む混合溶液を含浸させ、続いて約１００～２５０℃の温度で乾燥し、２５０～７００℃、好ましくは３００～５５０℃の温度でか焼する。第２の段階において、第１の段階から生じた生成物に、パラジウム化合物の溶液、好ましくはパラジウムと銅化合物との、またはパラジウムと銅と銀化合物との、またはパラジウムと銅と亜鉛と銀化合物との、またはパラジウムと銀と亜鉛化合物との混合溶液を、アトマイザーを用いた噴霧コーティング手法によって含浸させ、続いて１００～２５０℃の温度で乾燥し、約２５０～６５０℃、好ましくは３００～５５０℃の温度でか焼する。

【００２４】

パラジウムを銅触媒中に取り入れる別の好ましい手法は、パラジウム化合物の溶液または硝酸パラジウムのようなパラジウム化合物と硝酸銀のような銀化合物との混合溶液の、酸化銅－アルミナ触媒、酸化銅－アルミナ、酸化銅－酸化亜鉛－アルミナ触媒または酸化銅－酸化銀－酸化亜鉛アルミナ触媒表面への噴霧コーティング含浸であり、その間、銅触媒球は、適切な角度で傾けた平坦な表面上を転がり落ちる。銅触媒表面へのパラジウムの比較的に高い負荷（＞０．１５重量％）は、比較的に高い含量（＞～４０００ppm）の全アセチレン型化合物を含む供給物を処理するために望ましい。同時含浸及び噴霧コーティン

グ含浸の組合せは、触媒表面への高パラジウム負荷のために最も望ましい手法である。噴霧コーティング含浸のためにパラジウム溶液の微細なミストを生成することは非常に重要である。約０．１５％を超えるＰｄを用いて促進された銅触媒が望ましい場合、同時含浸及び噴霧コーティング含浸の組合せが一般に好ましい。含浸生成物を、空気中、約１００～４００℃、好ましくは１００～３５０℃でか焼して、パラジウムを用いて促進された、銅、銅－銀または銅－銀－亜鉛触媒を製造する。

【００２５】

所望により、上記に説明した好ましい担体の物理特性を有するアルミナ粉末表面に、金属塩類の混合溶液を含浸させることで、触媒を製造することができる。このようなアルミナ粉末を製造する原料は、適切なベーマイト粉末及び擬ベーマイト粉末の例えばディスペラル　ＨＰ　１４／２である。原料を、含浸する前に約４００℃～約７５０℃の温度でか焼する。含浸生成物を、約２５０～５５０℃の温度で空気中でか焼し、成形して所望のサイズの押出物またはペレットにする。所望により、含浸生成物を成形して押出物またはペレットにし、次に、成形済み材料を、約２５０℃～５５０℃の高温で空気中でか焼する。

【００２６】

触媒活性化を、約６０～４００℃、好ましくは１００～３５０℃で、水素を含むガス流中で実行する。ガス中の水素の含量は、活性化の間中、窒素のような不活性ガス中で約５体積％～５０体積％以上まで徐々に増大する。触媒活性化の最中に、十分な量のガス流は、触媒表面の水蒸気凝縮が生じないと思われるので好ましい。活性化の長さは、反応器中の触媒の量、ガス中の水素含量及び活性化温度に依存する。実験室においては、約１００グラム未満の触媒の場合には、３０分～約１０時間で十分である。工業的実施においては、一般にはるかに長い活性化時間が必要であると思われる。触媒活性化の後に、反応帯域中に残存している水素を、不活性ガスを用いてフラッシングする。選択的水素化の開始時に、飽和炭化水素のような不活性希釈剤を使用することによって、供給物流れ中の不飽和化合物の含量を触媒反応帯域中で非常に低いレベルで保つべきであり、これを、活性化された触媒中の水素含量の大部分が消費されるまで行う。触媒表面の銅の比較的に高い含量が理由となって、活性化された触媒は、触媒床中で暴走温度（run away temperature）を生じる可能性がある比較的に多量の活性水素を含む。

【００２７】

工業的実施において実際の供給物流れを取り扱う際には、銅触媒のような選択的水素化触媒を、アルキルメルカプタン類のような硫黄化合物による毒作用から保護することが必要である。選択的水素化触媒を、供給物流れ中のアルキルメルカプタン類による毒作用から保護するために、Ｐｄ、Ｎｉ等の触媒または本発明において開示するがメルカプタン反応を最大にするために選択的水素化触媒とは別の仕方で最適化された所望による触媒上で、硫黄不純物を、オレフィン類、アセチレン型化合物またはジエン類と反応させることで、より重質の硫黄化合物に転化する。より重質の硫黄生成物を、単蒸留によって軽質成分から除去する。このメルカプタン除去稼働の最中に硫黄化合物からH_2Sを生成しないことが非常に重要であり、というのは、H_2Sは選択的水素化銅触媒に毒作用をするであろうからである。ＣＤユニットにおいては、メルカプタン類のこの除去を、単一の蒸留塔中で選択的水素化と同時に実行することができる。米国特許第5,510,568号、同第5,595,643号、同第5,597,476号または同第5,807,477号において開示されているもののような、メルカプタン類からより高沸点の有機スルフィド類を形成するための触媒を、ＣＤ塔中の選択的水素化触媒床の底部に装填する。より重質の硫黄化合物を、選択的水素化反応帯域に入る前にＣＤ塔からボトム生成物として除去し、それによって選択的水素化触媒を硫黄不純物から保護する。硫化水素を生成しないために、このメルカプタン反応帯域中で最小量の水素を維持することは重要である。過剰の水素が利用可能な場合、メルカプタン類の幾らかは、アルキルメルカプタン類またはスルフィドの水素化脱硫によって硫化水素に転化することがある。硫化水素の形成を防ぐために、メルカプタン反応帯域中の水素含量を、接触選択的水素化反応帯域中のものとは別の仕方で調節することが必要かもしれない。

【００２８】

対照実施例１
銅触媒を、米国特許第4,440,956号の実施例１に従って製造した。ガンマアルミナ（ＵＣＩから得たＣＳ　３３１－１、１／１６インチの押出物であり、表面積２６５m^2/g）を、使用前に、７００℃で３時間、周囲雰囲気中でか焼した。か焼の前及び後で、ＡＢＤはほとんど変化しなかった。か焼したアルミナは、０．７９２g/ccのＡＢＤを有した。１１０mlの脱イオン水中の２８．７gのＣｕ（NO_3）$_2$．２．５H_2O、Ｎｉ（NO_3）$_2$．６H_2O、０．０４gの$AgNO_3$、０．３４gのＣｒ（NO_3）$_3$．９H_2O及び０．３４gのＣｏ（NO_3）$_2$．６H_2Oの溶液を作製した。ロータリーエバポレーターを使用して、６０gのＵＣＩアルミナに上記の溶液を含浸させた。含浸生成物を、１１０℃、真空オーブン中で一晩乾燥した後に、４００℃、マッフル炉中で３時間か焼した。触媒のＡＢＤは、０．８７g/ccだった。２２gのこの触媒を、１００mlの直径３mmのガラス球とブレンドし、従来の反応器として使用する垂直ステンレス反応器（直径１インチ×長さ２０インチ）中に装填した。以下の手順によって触媒を活性化した；（１）反応器を、１００cc／分のN_2ガス流中で２３０°Fに加熱し、（２）２００cc／分のH_2をN_2ガス流に加え、次に３時間２３０°Fで保持し、（３）N_2ガスを止め、H_2ガス流を３００cc／分に増大させ、（４）反応器温度６６２°Fにまで加熱し、３時間６６２°Fで保持し、次に反応器を３０cc／分のH_2ガス流中で１４７°Fに冷却した。

【００２９】
２８重量ppmのメチルアセチレン、１０３４重量ppmのビニルアセチレン及び５４９重量ppmのエチルアセチレン、４５．２３重量％の１，３－ブタジエン、０．１０重量％の１，２－ブタジエン、６．０５重量％のｔ－２－ブテン、４．２２重量％のｃ－２－ブテン、１５．３６重量％の１－ブテン、１８．０５重量％のイソブテン、９．３４重量％のｎ－ブタン、１．３０重量％のイソブタン、並びに０．１９重量％の他のもので構成される混合C_4流れを選択的に水素化して、アセチレン型不純物を圧力１１９psigで除去した。最初の２６時間の運転時間の間、供給炭化水素及び水素速度は、それぞれ２．２cc／分（３．６ＷＨＳＶ）及び３１．４scc／分だった。次いで、次の２４時間の運転時間の間、供給速度を、炭化水素の場合に３cc／分（５．０ＷＨＳＶ）、水素速度の場合に２７scc／分に変更した。この後、ランの終了まで、供給速度は、炭化水素の場合に２．２cc／分（３．６ＷＨＳＶ）、水素速度の場合に３１．４scc／分だった。

【００３０】
対照実施例２
１８グラムのパラジウム触媒（ＵＣＩから得た２４６４Ｆであるアルミナの表面の０．７％のＰｄ／１．４％のＡｇ）を、１１０mlの直径３mmのガラス球と混合し、対照実施例１において使用したものと同じ反応器中に装填した。Ｈｅ中の１ml／分（周囲温度で測定して）のイソブタン及び１０cc／分の１０体積％のH_2ガスを２００psigで１時間通過させることで、触媒を１８０°Fで活性化した。３９重量ppmのメチルアセチレン、５９７４重量ppmのビニルアセチレン及び１１１９重量ppmのエチルアセチレン、４６．０５重量％の１，３－ブタジエン、０．１５重量％の１，２－ブタジエン、５．６８重量％のｔ－２－ブテン、３．９５重量％のｃ－２－ブテン、１４．３８重量％の１－ブテン、１７．９８重量％のイソブテン、９．２４重量％のｎ－ブタン、１．３２重量％のイソブタン、並びに０．５４重量％の他のもので構成される混合C_4流れを選択的に水素化して、その中のアセチレン型不純物を除去した。選択的水素化を、１４７°Fの一定温度で実行した。しかしながら、最初の７９時間の運転時間の間、炭化水素及び水素供給速度は、反応器圧力１１９psigでそれぞれ３ml／分（６．１ＷＨＳＶ）及び３６．８scc／分であり、次に、反応器圧力１０８psigでそれぞれ４．９ml／分（９．９ＷＨＳＶ）及び６０scc／分に変更された。

【００３１】
対照実施例３
１８グラムのパラジウム触媒（ＵＣＩから得たＣＤＴ－３であるアルミナの表面の０．２％のＰｄ／０．１％のＡｇ）を、１１０mlの直径３mmのガラス球と混合し、対照実施例１

において使用したものと同じ反応器中に装填した。Ｈｅ中の１ｍｌ／分（周囲温度で測定して）のイソブタン及び１０cc／分の１０体積％のH_2ガスを２００psigで１時間通過させることで、触媒を１８０°Fで活性化した。

【００３２】

３９重量ppmのメチルアセチレン、５９７４重量ppmのビニルアセチレン及び１１１９重量ppmのエチルアセチレン、４６．０５重量％の１，３－ブタジエン、０．１５重量％の１，２－ブタジエン、５．６８重量％のｔ－２－ブテン、３．９５重量％のｃ－２－ブテン、１４．３８重量％の１－ブテン、１７．９８重量％のイソブテン、９．２４重量％のｎ－ブタン、１．３２重量％のイソブタン、並びに０．５４重量％の他のもので構成される混合C_4流れを選択的に水素化した。

【００３３】

対照実施例４

活性アルミナ（アルファ　３１２６８（Alfa 31268）、３．２mmのペレットであり、表面積９０m^2/g）を粉砕して１０～２０メッシュの顆粒にした。顆粒状アルミナは、約１g/ccのＡＢＤを有した。１００mlの脱イオン水中の２８．７gのＣｕ（NO_3）$_2$．２．５H_2O、Ｎｉ（NO_3）$_2$．６H_2O、及び０．０４gの$AgNO_3$の溶液を作製した。ロータリーエバポレーターを使用して、６０gの顆粒状アルミナに上記の溶液を含浸させた。含浸生成物を、１１０℃、真空オーブン中で一晩乾燥した後に、４００℃、マッフル炉中で３時間か焼した。１８gのこの触媒を、１１０mlの直径３mmのガラス球とブレンドし、対照実施例１におけるものと同じ反応器中に装填した。以下の手順によって触媒を活性化した；（１）反応器を、１００cc／分のN_2ガス流中で２３０°Fに加熱し、（２）２００cc／分のH_2をN_2ガス流に加え、次に３時間２３０°Fで保持し、（３）N_2ガスを止め、H_2ガス流を３００cc／分に増大させ、（４）反応器温度６６２°Fにまで加熱し、３時間６６２°Fで保持し、次に反応器を３０cc／分のH_2ガス流中で１４７°Fに冷却した。

【００３４】

対照実施例１において使用したものと同じ供給物を選択的に水素化して、アセチレン型不純物を圧力１１９psigで除去した。最初の２６．５時間の運転時間の間、供給炭化水素及び水素速度は、それぞれ１．８cc／分（３．６ＷＨＳＶ）及び２５．７scc／分だった。次いで、次の２４時間の運転時間の間、供給速度を、炭化水素の場合に２．４cc／分（４．９ＷＨＳＶ）、水素速度の場合に２２．１scc／分に変更した。この後、供給速度を再度、炭化水素の場合に１．８cc／分（３．６ＷＨＳＶ）及び２５．７scc／分に変更した。

【００３５】

実施例５

銅触媒を、油滴下ゲル化手法によって製造したアルミナ（直径１／１６インチの球形）を使用して、本発明に従って製造した。アルミナの物理的性質を表１に要約する。アルミナの孔径分布を図１に示す。約９０％を超える細孔は、直径が１００オングストロームよりも大きかった。１１０mlの脱イオン水中の２８．７gのＣｕ（NO_3）$_2$．２．５H_2O、Ｎｉ（NO_3）$_2$．６H_2O、０．０４gの$AgNO_3$、０．３４gのＣｒ（NO_3）$_3$．９H_2O及び０．３４gのＣｏ（NO_3）$_2$．６H_2Oの溶液を作製した。ロータリーエバポレーターを使用して、６０gのアルミナに上記の溶液を含浸させた。含浸生成物を、１１０℃、真空オーブン中で一晩さらに乾燥した後に、４００℃、マッフル炉中で３時間か焼した。触媒の物理的性質を表２に要約する。図１に示すように、銅触媒の細孔構造はアルミナ担体からわずかに変化したのみだった。２２gのこの触媒を、１００mlの直径３mmのガラス球とブレンドし、対照実施例１において使用したものと同じ反応器中に装填した。触媒活性化を、対照実施例１において説明したものと同じ方法で実行した。

【００３６】

対照実施例１において使用したものと同じ供給物を選択的に水素化して、アセチレン型不純物を１１９psigで除去した。最初の２６時間の運転時間の間、供給炭化水素及び水素速度は、それぞれ２．２cc／分（３．６ＷＨＳＶ）及び３１．４scc／分だった。次いで、

次の２４時間の運転時間の間、供給速度を、炭化水素の場合に３cc／分（５．０ＷＨＳＶ）、水素速度の場合に２７scc／分に変更した。この後、供給炭化水素及び水素速度は２．２cc／分（３．６ＷＨＳＶ）だったが、水素速度２７scc／分をランの終了まで維持した。

【００３７】

実施例５及び対照実施例１における銅触媒の試験結果を、図４及び５に示す。図３は、本発明において開示する触媒の、従来技術に勝る優れた触媒活性及び安定性を証明する。図５は、従来技術に勝る本発明の優れたブタジエン収率を証明する。本発明において開示する触媒上での全アルキン類の同じ転化における１，３－ブタジエンの収率は、従来技術において開示するものよりも高い。また実施例５は、供給物流れ中の全てのアセチレン型化合物を転化した後に過剰の水素が利用可能な場合、過剰の水素が過度の水素化による１，３－ブタジエンの損失を引き起こすことを示し、過剰の水素を選択的水素化帯域中で最小に保つべきであることを示唆する。

【００３８】

【表１】

表１

ＡＢＤ、g/cc	0.53
一点ＢＥＴ、m^2/g	157.5
多点ＢＥＴ、m^2/g	170.2
メソ細孔面積、m^2/g	170.2
ミクロ細孔面積、m^2/g	0
累積吸着表面積、m^2/g	172.6
累積脱着表面積、m^2/g	230.4
Ｐ／Ｐ$_o$＝０．９８０１において４９３オングストローム未満の半径を有する細孔の総細孔容積（cc/g）	0.912
細孔（半径２０～３００オングストローム）の累積吸着細孔容積	0.852
細孔（半径１７．５～３００オングストローム）の累積脱着細孔容積	0.930
平均細孔直径、オングストローム	214.4

【００３９】

【表２】

表２

ＡＢＤ、g/cc	0.58
一点ＢＥＴ、m^2/g	137.5
メソ細孔面積、m^2/g	147.7
ミクロ細孔面積、m^2/g	0
細孔（半径１７．５～３００オングストローム）の累積脱着細孔容積	0.790

【００４０】

実施例６
実施例５において使用したアルミナを、７００℃で３時間、空気中でか焼した。銅触媒を、このか焼したアルミナを使用して製造した。１２８mlの脱イオン水中の３０gのＣｕ（NO_3）$_2$．２．５H_2O、Ｎｉ（NO_3）$_2$．６H_2O、０．０４７gのＡｇNO_3、０．３９６gのＣｒ（NO_3）$_3$．９H_2O及び０．３９６gのＣｏ（NO_3）$_2$．６H_2Oの溶液を作製した。ロータリーエバポレーターを使用して、７０gのアルミナに上記の溶液を含浸させた。含浸生成物を、１１０℃、真空オーブン中で一晩さらに乾燥した後に、４００℃、マッフル炉中で３時間、空気中でか焼した。触媒のＡＢＤは、０．５７g/ccだった。１８gのこの触媒を、１００mlの直径３mmのガラス球とブレンドし、対照実施例１におけるものと同じ反応器中に装填した。対照実施例１におけるものと同一の方法で、触媒を活性化した。

【００４１】
４４４重量ppmのメチルアセチレン、８２５重量ppmのビニルアセチレン及び６３４重量ppmのエチルアセチレン、５５．３６重量％の１，３－ブタジエン、０．１２重量％の１，２－ブタジエン、６．３９重量％のｔ－２－ブテン、４．１３重量％のｃ－２－ブテン、１６．８４重量％の１－ブテン、１２．３８重量％のイソブテン、３．５３重量％のｎ－ブタン、０．９７重量％のイソブタン、並びに０．０９重量％の他のもので構成される混合C_4流れを選択的に水素化して、アセチレン型不純物を１１９psigで除去した。この実施例においては、炭化水素及び水素速度を、炭化水素の場合に３cc／分、水素の場合に２７scc／分の一定速度で維持した。実施例６及び対照実施例１における銅触媒の試験結果を、実施例５から得られた結果と共に図４及び５に示す。

【００４２】
図４及び５は、本発明において開示する銅触媒の、従来技術に勝る優れた性能を明確に証明する。

【００４３】
実施例７
この実施例においては、接触蒸留塔を、混合C_4流れ中のアセチレン型不純物の選択的水素化のために使用する。より大きなバッチの触媒を、実施例５において説明したものと正確に同じ方法で、２４０グラムのアルミナを使用して製造した。触媒（９９．８８グラム）を、接触蒸留塔（直径１インチ×高さ２５フィート）中に装填した。塔中の触媒床の高さは、６フィートだった。触媒床の頂部及び底部の８０インチに１／４インチの鞍状物を充填した。対照実施例１において説明したものと同じ方法で、ただしガスの流量を触媒重量を基準として比例させて増大させて、触媒を活性化した。

【００４４】
実施例６において使用したものと同じ供給物中のアセチレン型不純物を、接触蒸留態様で選択的水素化を実行することで除去した。炭化水素供給速度は、１．２ポンド／時だった。水素速度はランの初めに１scf／時だったが、ランの最中により高い速度に変更された。炭化水素及び水素供給物を、鞍状物充填材よりも下の箇所において供給した。結果を図６に示す。３scf／時以上の水素速度で、供給物中のエチルアセチレン及びビニルアセチレンは事実上全て除去された。１，３－ブタジエンのほぼ完全な回収が得られた。図６に示すように、触媒は、固定床稼働よりも接触稼働態様下ではるかに安定だった。

【００４５】
実施例８
本発明において開示する銅触媒中に銅触媒の性能を改良するために酸化亜鉛を取り入れることの有益な効果を証明するために、この実験を実行した。銅触媒を、実施例５において使用したものと同一の手順に従って製造した。１００mlの脱イオン水中の２２．６gのＣｕ（NO_3）$_2$．２．５H_2O、Ｎｉ（NO_3）$_2$．６H_2O、０．０４gのＡｇNO_3、及び４．０gのＺｎ（NO_3）$_2$．６H_2Oの混合溶液を作製した。ロータリーエバポレーターを使用して、実施例５において使用したものと同じ６０gのアルミナに上記の溶液を含浸させた。含浸生成物を、１１０℃、真空オーブン中で一晩さらに乾燥した後に、４００℃、マ

ッフル炉中で３時間か焼した。１８gのこの触媒を、１００mlの直径３mmのガラス球とブレンドし、対照実施例１において使用したものと同じ反応器中に装填した。触媒活性化を、対照実施例１において説明したものと同じ方法で実行した。

【００４６】

４７５ppmのメチルアセチレン、９５９重量ppmのビニルアセチレン及び７３１重量ppmのエチルアセチレン、５４．８７重量％の１，３－ブタジエン、０．１２重量％の１，２－ブタジエン、６．４２重量％のｔ－２－ブテン、４．１６重量％のｃ－２－ブテン、１６．７６重量％の１－ブテン、１２．５３重量％のイソブテン、３．５６重量％のｎ－ブタン、１．２７重量％のイソブタン、並びに０．０９重量％の他のもので構成される混合C_4流れを選択的に水素化して、その中のアセチレン型不純物を除去した。選択的水素化を、１４７°Fの一定温度及び１１９psigで実行した。一定の炭化水素及び水素供給速度である３ml／分（６．１WHSV）及び２７．１scc／分をランの間中使用した。このランの結果を、図７及び８に要約する。銅触媒中に取り入れられた酸化亜鉛が触媒性能に及ぼす有益な効果が、この実施例において明確に証明される。

【００４７】

実施例９

この実施例においては、本発明において開示する好ましい溶媒のうちの１つであるテトラヒドロフラン（ＴＨＦ）の有用性を証明する。実施例５において製造した銅触媒（３６グラム）を、対照実施例１において使用したものと同じ反応器中に装填した。この実施例において使用する混合C_4供給物は、以下の組成を有した；２０ppmのメチルアセチレン、５８８ppmのビニルアセチレン、５９９ppmのエチルアセチレン、４４．５１重量％の１，３－ブタジエン、０．０７重量％の１，２－ブタジエン、６．２９重量％のｔ－２－ブテン、４．３３重量％のｃ－２－ブテン、１５．９７重量％の１－ブテン、１８．０４重量％のイソブテン、９．３６重量％のｎ－ブタン、１．３０重量％のイソブタン、並びに０．０１重量％の他のものである。１７６時間の運転時間の後、反応器を、N_2ガスを用いてフラッシングした後に、１４７°F、２００psigで１時間、次に１５７°Fで５時間、１０cc／分のＴＨＦ、６６．９scc／分のH_2で、触媒を、ＴＨＦを用いて洗浄して、触媒表面に堆積したポリマーを除去した。反応器を、N_2ガスを用いてフラッシングした後に、選択的な水素を継続した。一定温度（１４７°F）及び圧力（１１９psig）をランの間中維持した。この実験の最中のランの条件を表３に列記する。

【００４８】

この実験の結果を、図９に示す。図９に示すように、アセチレン型不純物の漏出が１２８時間の運転時間で起きた。しかし、触媒をＴＨＦを用いて洗浄した後に、漏出の場合と同じ条件下で得られた生成物は、検出可能な量のアセチレン型不純物を含まなかった。

【００４９】

【表３】

表３

147°F及び119 psig

運転時間(時)	0－26	26－50	50－74	74－98	98－128	128－152	152－176	THF 176－188.5	
HC供給速度, ml/min	2.9	5.8	2.9	2.9	5.8	7	7	洗浄	7
H_2速度, scc/min	45	45	45	15	10	45	45	54	45

アセチレン類の漏出

【００５０】

従って、ＴＨＦは、触媒再生のための好ましい溶媒のうちの１つである。またＴＨＦは、接触蒸留塔を使用して選択的水素化を実行するために使用される好ましい溶媒のうちの１つである。ＴＨＦをＣＤ選択的水素化において溶媒として使用する場合に、ＴＨＦを触媒床よりも上で蒸留塔に供給することができ、またはこれを混合C_4供給物流れと共に塔に供給することができる。こうした２つの場合には、塔稼働のための異なる条件が必要とな

ろう。後者の場合、塔は、ＴＨＦに関して全内部還流（total internal reflux）条件下で稼働しよう。両方の場合に、ＴＨＦはボトム生成物として塔から除去され、塔に再循環されよう。しかしながら、再循環ＴＨＦ流れの一部は、再循環流れ中の重質成分の蓄積を避けるために、塔に戻る前に分離器中で精製されよう。

【００５１】

実施例１０Ａ

対照実施例２において使用した混合C_4供給物中のアセチレン型不純物（７１３２ppmの全アセチレン類）の選択的水素化に関して、実施例５において製造した銅触媒を試験した。１８gの触媒を、１００mlの直径３mmのガラス球とブレンドし、対照実施例１におけるものと同じ反応器中に装填した。対照実施例１におけるものと同一の方法で、触媒を活性化した。選択的水素化を、１４７°Fの一定温度及び１１９psigで実行した。最初の６６．５時間の運転時間の間、炭化水素及び水素供給速度は、それぞれ２．９ml／分（５．８７ＷＨＳＶ）及び４５scc／分であり、次に、それぞれ１．４ml／分（２．８３ＷＨＳＶ）及び２４．１scc／分に変更された。

【００５２】

実施例１０Ｂ

パラジウムを用いて促進された銅触媒を、本発明に従って製造した。実施例５において使用したアルミナを、９００℃で３時間、空気中でか焼した。１１０mlの脱イオン水中に２８．７gの$Cu(NO_3)_2.2.5H_2O$、$Ni(NO_3)_2.6H_2O$、０．０４gの$AgNO_3$、０．３４gの$Cr(NO_3)_3.9H_2O$及び０．３４gの$Co(NO_3)_2.6H_2O$を溶解させることで、混合溶液を作製した。ロータリーエバポレーターを使用して、上記のか焼したアルミナ（６０g）にこの溶液を含浸させた。含浸生成物を、１１０℃、真空オーブン中で一晩さらに乾燥した後に、これを、４００℃、マッフル炉中で３時間、空気中でか焼した。５．４６９グラムの水性硝酸パラジウム（ＩＩ）溶液（オールドリッチ　３８，００４－０（Aldrich 38,004-0）；１０重量％の硝酸中の１０重量％の$Pd(NO_3)_2$）を、アトマイザーを使用して銅触媒球（２９．７６２グラム）表面に噴霧し、その間、銅触媒球は平坦な表面上をあちらこちらに転がり回って、球はパラジウム溶液で一様にコーティングされた。パラジウム塩溶液の微細なミストを生成することが非常に重要である。パラジウム溶液噴霧済みの生成物を、２５０℃で２時間、空気中でか焼した。Ｃｕ／Ｐｄ触媒のＡＢＤは、０．５２g/ccだった。この触媒の分析は、８．２０％のＣｕ、０．７１％のＰｄ、０．２０％のＮｉ、０．１１％のＣｒ、及び０．１７％のＡｇを示す。

【００５３】

２２gのこの触媒を、１００mlの直径３mmのガラス球とブレンドし、対照実施例１において使用したものと同じ反応器中に装填した。以下の手順によって触媒を活性化した；（１）反応器を、１００cc／分のN_2ガス流中で２３０°Fに加熱し、（２）２００cc／分のH_2をN_2ガス流に加え、３時間２３０°Fで保持し、（３）N_2ガスを止め、H_2ガス流を３００cc／分に増大させ、（４）反応器温度５７２°Fにまで加熱し、３時間５７２°Fで保持し、次に反応器を３０cc／分のH_2ガス流中で１４７°Fに冷却した。

【００５４】

実施例１０Ａにおいて使用したものと同じ供給物中のアセチレン型不純物を、選択的水素化によって除去した。選択的水素化を、１４２°Fの一定温度で実行した。しかしながら、最初の７３時間の運転時間の間、炭化水素及び水素供給速度は、反応器圧力１１９psigでそれぞれ３．７ml／分（６．１ＷＨＳＶ）及び４５scc／分であり、次に、１０８psigでそれぞれ６．１ml／分（１０．１ＷＨＳＶ）及び７４．２scc／分に変更された。１４５時間の運転時間の後に、触媒を、１００℃及び１０８psigで、７４．２scc／分のH_2流中で５時間、ベンゼン（１０ml／分）を用いて洗浄した。選択的水素化を、ベンゼン洗浄の直前と同じ条件で２４時間続けたが、ベンゼン（０．６ml／分）を混合C_4供給物と同時に反応器に供給した。この後、次の１８時間、供給速度を、１０ml／分の混合C_4供給物、１ml／分のベンゼン、及び９０scc／分のH_2に変更した。次いで、次の３０時間、供給速度を、反応器圧力９５psigで１５ml／分の混合C_4供給物、１．５ml／分のベンゼン

、及び１１２scc／分のH_2に増大させた。この後、選択的水素化を、水素速度を９５scc／分に低下させて２４時間実行し、その間、他のプロセスパラメータを同じ条件で保った。次いで、次の６６時間、供給速度を、１０ml／分の混合C_4供給物、１ml／分のベンゼン、及び５４scc／分のH_2に低下させ、その間、他のプロセスパラメータを同じ条件で保った。

【００５５】

実施例１０A及び１０Bの結果を、対照実施例２と共に図１０及び１１に示す。図８に示すように、パラジウムを用いて促進しなかった銅触媒は、高濃度のアセチレン型不純物を取り扱う際に非常に低い活性を有した。しかし、本発明において開示する手法において銅触媒をパラジウムを用いて促進した場合、触媒活性は劇的に改良された。驚くべきことに、本パラジウム促進銅触媒は、市販のＰｄ選択的水素化触媒よりもはるかに優れた活性を有する。さらに驚くべきことに、本パラジウム促進触媒はまた、そのはるかに高い活性にもかかわらず、アセチレン類の同じ転化において、市販のパラジウム触媒に勝る優れた１，３－ブタジエン収率を有する。また、本パラジウム促進触媒の失活速度は、市販のＰｄ触媒または非促進銅触媒よりもはるかに良好だった。この実施例は、高アセチレン型供給物の選択的水素化のための本パラジウム促進銅触媒の、パラジウム触媒または非促進銅触媒に勝る優れた性能を明確に証明する。

【００５６】

実施例１１

ガンマアルミナ（ＵＣＩから得たもので、１／８インチの押出物であり、表面積約２６０m^2/g）を粉砕して１０～２０メッシュの顆粒にした。このアルミナの供給者によれば、このアルミナの原料は、対照実施例１において使用したアルミナと同一だった。しかし、この顆粒状アルミナは、対照実施例１において使用したアルミナ（０．７９２g/ccのＡＢＤ）よりも低いＡＢＤ（０．５０g/cc）を有する。１２８mlの脱イオン水中の３０gの$Cu(NO_3)_2.6H_2O$、０．９３gの$Ni(NO_3)_2.6H_2O$、０．０４７gの$AgNO_3$、０．３９６$Cr(NO)_3.9H_2O$及び０．３９６$Co(NO_3)_2.6H_2O$の溶液を作製した。ロータリーエバポレーターを使用して、７０gの顆粒状アルミナに上記の溶液を含浸させた。含浸生成物を、１１０℃、真空オーブン中で一晩乾燥した後に、４００℃、マッフル炉中で３時間か焼した。１８gのこの触媒を、１１０mlの直径３mmのガラス球とブレンドし、対照実施例１におけるものと同じ反応器中に装填した。以下の手順によって触媒を活性化した；（１）反応器を、１００cc／分のN_2ガス流中で２３０°Fに加熱し、（２）２００cc／分のH_2をN_2ガス流に加え、次に３時間２３０°Fで保持し、（３）N_2ガスを止め、H_2ガス流を３００cc／分に増大させ、（４）反応器温度６６２°Fにまで加熱し、３時間６６２°Fで保持し、次に反応器を３０cc／分のH_2ガス流中で１４７°Fに冷却した。

【００５７】

対照実施例１において使用したものと同じ供給物を選択的に水素化して、アセチレン型不純物を圧力１１９psigで除去した。最初の２９時間の運転時間の間、供給炭化水素及び水素速度は、それぞれ１．８cc／分（３．６WHSV）及び２５．７sc.／分だった。次いで、次の２４時間の運転時間の間、供給速度を、炭化水素の場合に２．４cc／分（４．９WHSV）、水素速度の場合に３４．３sc.／分に増大させた。この後、ランの終了まで、供給速度を炭化水素の場合に３cc／分（６．１WHSV）にさらに増大させたが、水素供給速度を３０sc.／分に低下させた。

【００５８】

この実験の試験結果と対照実施例１及び４の試験結果との比較を、担体アルミナのＡＢＤが触媒性能に及ぼす効果を証明するために、図１２及び１３に示す。この実施例におけるより低いＡＢＤのアルミナ（より高い多孔性を意味する）を使用して製造した触媒は、対照実施例１及び４において使用したより高いＡＢＤのアルミナよりも優れていた。この実施例及び対照実施例１におけるアルミナは同じ原料から製造された。しかし、この実施例において使用するより低いＡＢＤのアルミナは、アセチレン型不純物を除去する際により

有効な触媒をもたらす。この実施例における触媒は、対照実施例１におけるものよりも良好な１，３－ブタジエン収率を有する。対照実施例４における触媒を製造するために使用したアルミナは、本発明において開示する表面積の好ましい範囲に入る表面積を有する。しかし、対照実施例４におけるアルミナのＡＢＤは０．９８g/ccであり、本発明において開示する好ましいＡＢＤ（＜０．６５g/cm^3）よりも高い。対照実施例４における触媒がアセチレン型不純物を除去する際の有効性は、ほぼ対照実施例１と実施例１１との間に入る。実施例１１と対照実施例４とで、１，３－ブタジエンの収率の差はほとんどない。

【００５９】

実施例１２

比較的に高濃度のアセチレン型不純物を含む供給物の選択的水素化のためのパラジウム促進銅触媒の優れた性能を証明するために、この実施例を実行した。

【００６０】

パラジウムを用いて促進された銅触媒を、本発明に従って製造した。実施例５において使用したアルミナを、９００℃で３時間、空気中でか焼した。１０重量％の硝酸中の４．６１gの１０重量％のＰｄ（NO_3）$_2$溶液（オールドリッチ　３８，００４－０：１０重量％のＰｄ（NO_3）$_2$）を、６．３７８gの脱イオン水を用いて希釈することで作製した硝酸パラジウム溶液中に、１．８６６gのＣｕ（NO_3）$_2$２．５H_2Oを溶解させることで、混合溶液を作製した。５．５６gのこの混合溶液を、アトマイザーを使用して３０gのか焼したアルミナ球表面に噴霧し、その間、アルミナ球は平坦な表面上をあちらこちらに転がり回り、次に、噴霧済みの生成物を１１５℃、真空オーブン中で乾燥した。乾燥した生成物を、２５０℃で２時間、空気中でか焼した。

【００６１】

１８gのこの触媒を、１１０mlの直径３mmのガラス球と混合し、対照実施例１において使用したものと同じ反応器中に装填した。実施例１１において説明したものと同じ方法で、触媒を活性化した。対照実施例３において使用したものと同じ供給物中のアセチレン型化合物を、選択的水素化を実行することで除去した。選択的水素化を、１４２°Fの一定温度及び１０８psigで実行した。炭化水素供給速度を、ランの終了まで１０ml／分（２０．２ＷＨＳＶ）で保った。しかしながら、４４scc／分～９０scc／分の範囲内の水素流量の変動がランの最中に生じた。

【００６２】

この実施例１２及び対照実施例３の結果を、図１４及び１５に示す。本パラジウム促進銅触媒の、従来のパラジウム触媒に勝る優れた触媒活性が明確に証明される。実施例１２における供給速度は対照実施例３のものよりも少なくとも４倍高いにもかかわらず、本パラジウム促進銅触媒は、対照実施例３における従来のパラジウム触媒に勝る１，３－ブタジエンの優れた収率（図１４において回収率として表す）を有しながら、２０ppm未満のC_4アセチレン類を含む生成物を生じることができる。C_4アセチレン類の回収率を、１００％対C_4アセチレン類の％転化によって定義する。例えばC_4アセチレン類の０％回収率は、C_4アセチレン類の１００％除去に等しく、１００％の１，３－ブタジエン回収率は、１，３－ブタジエンの０％転化に等しい。

【００６３】

生成物中のエチルアセチレン対ビニルアセチレンの比を、図１５に示す。本パラジウム促進銅触媒は、ビニルアセチレンに対する反応性が従来のパラジウム触媒よりもはるかに高い。本パラジウム促進銅触媒は、非促進銅触媒よりも約１桁高い活性を有する。本パラジウム促進銅触媒が、従来のＰｄ触媒よりも数倍高い活性を有し、しかもなおこれが１，３－ブタジエンを保持する優れた選択性を有することは予想外である。

【図面の簡単な説明】

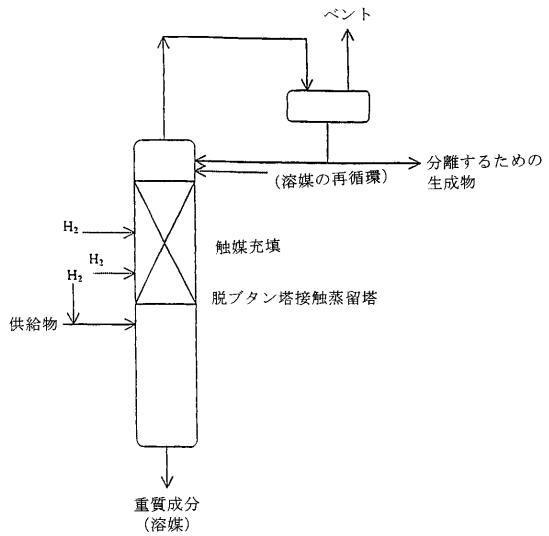
【００６４】

【図１】アセチレン類の選択的水素化のために上部に本銅触媒を有するＣＤ反応器の略図である。

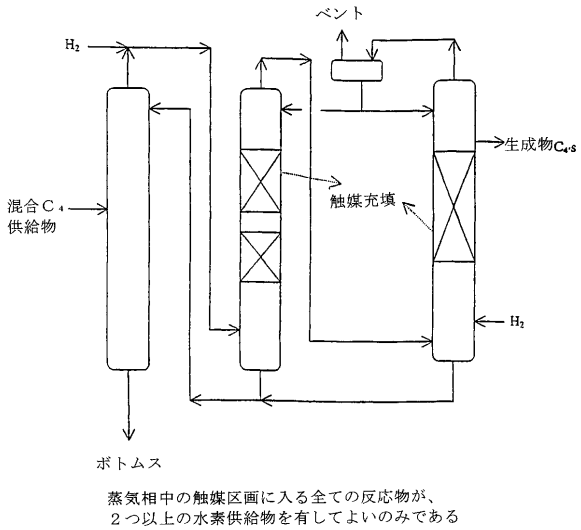
【図２】アセチレン類の選択的水素化のために上部に本銅触媒を有し、メルカプタン類及

びジオレフィン類を反応させるために下部にＶＩＩＩ族触媒を有するＣＤ反応器の略図である。
【図３】実施例５のアルミナ担体及び触媒の細孔分布のグラフ図である。
【図４】実施例の対照１、実施例５及び実施例６の生成物中の全生成物アルキン類のグラフ図である。
【図５】実施例の対照１、実施例５及び実施例６の全１，３－ブタジエン生成物の収率のグラフ図である。
【図６】ＣＤにおける実施例７の結果のグラフ図である。
【図７】実施例５（非ＣＤ）及び実施例８（ＣＤ）の生成物中の全アルキン類のグラフ図である。
【図８】実施例５（非ＣＤ）の１，３－ブタジエン生成物及び実施例８（ＣＤ）を比較するグラフ図である。
【図９】使用された触媒の溶媒処理の利益のグラフ図である。
【図１０】Ｐｄ促進Ｃｕの利益を示すために実施例１０Ａ及び１０Ｂを比較するグラフ図である。
【図１１】１，３－ブタジエン製造に及ぼすＰｄ促進Ｃｕの利益を示すために実施例１０Ａ及び１０Ｂを比較するグラフ図である。
【図１２】アセチレン類の除去の場合の本発明によるＡＢＤの利益のグラフ図であり、対照実施例１及び４並びに実施例１１を比較したものである。
【図１３】１，３－ブタジエン生成物の場合の本発明によるＡＢＤの利益のグラフ図であり、対照実施例１及び４並びに実施例１１を比較したものである。
【図１４】本パラジウム促進銅触媒の利益のグラフ図であり、実施例１２と対照実施例３とを比較したものである。
【図１５】実施例１２と対照実施例３とを比較することによる、本パラジウム促進銅触媒を従来のパラジウム触媒と区別する化学的指紋のグラフ図である。

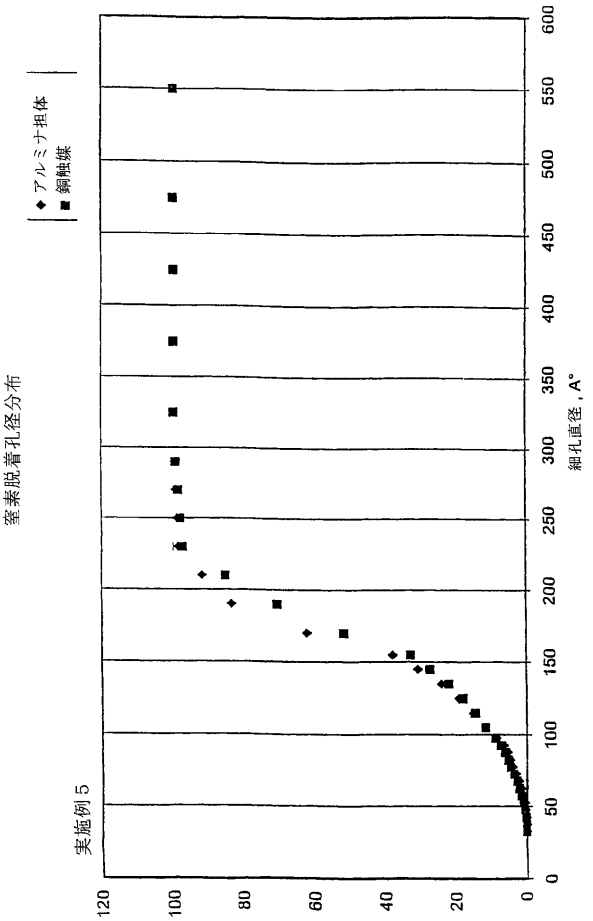
【図１】



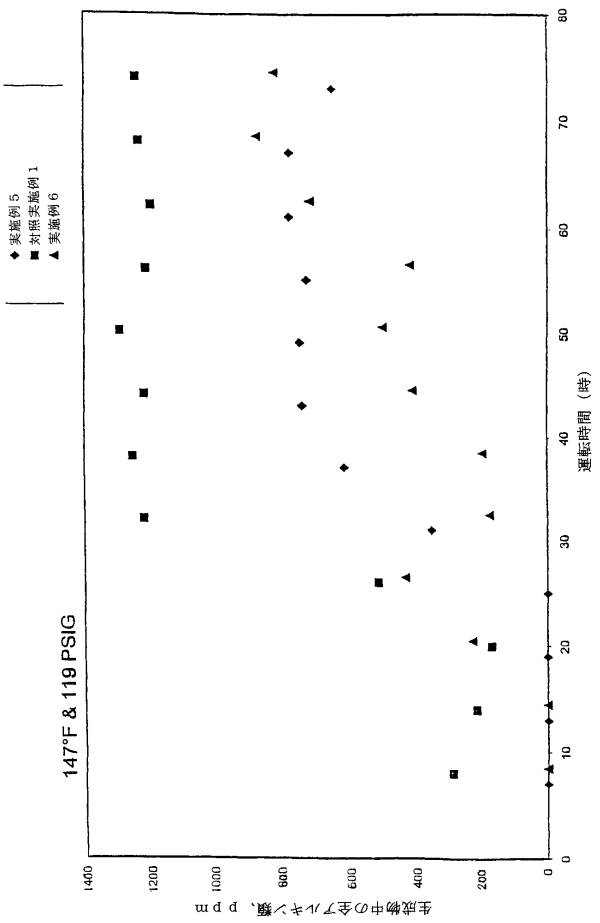
【図２】



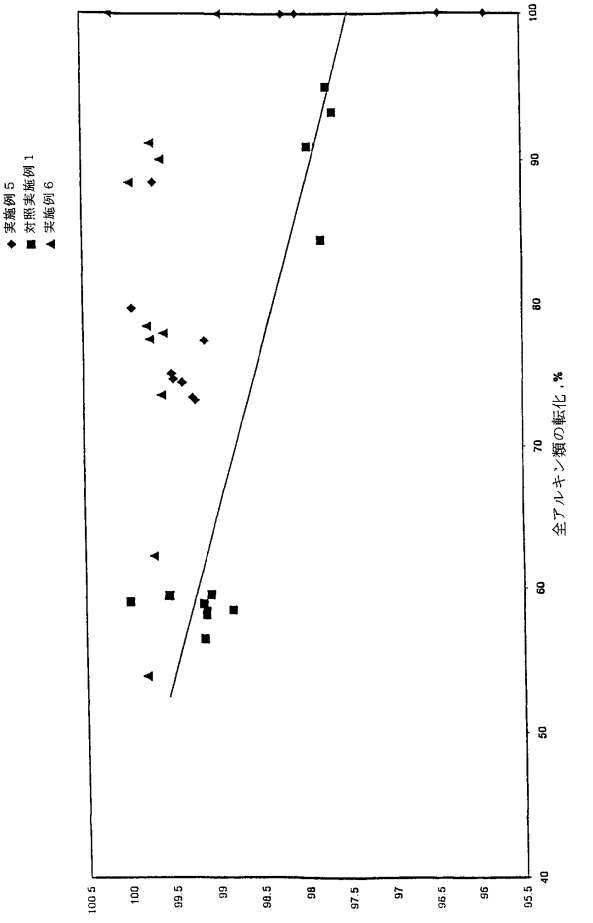
【図３】


窒素脱着孔径分布
実施例５
◆ アルミナ担体
■ 銅触媒
細孔直径，A°

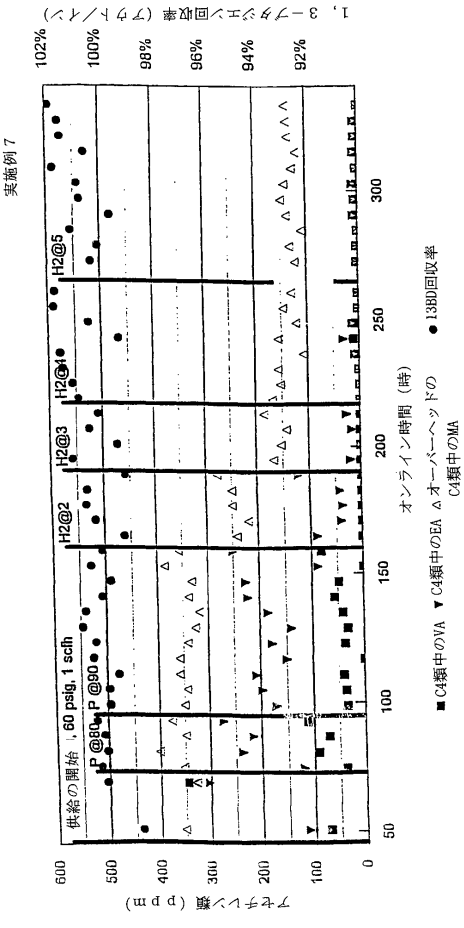
【図４】


147°F & 119 PSIG
◆ 実施例５
■ 対照実施例１
▲ 実施例６
運転時間（時）
生成物中の全アルキン類，ｐｐｍ

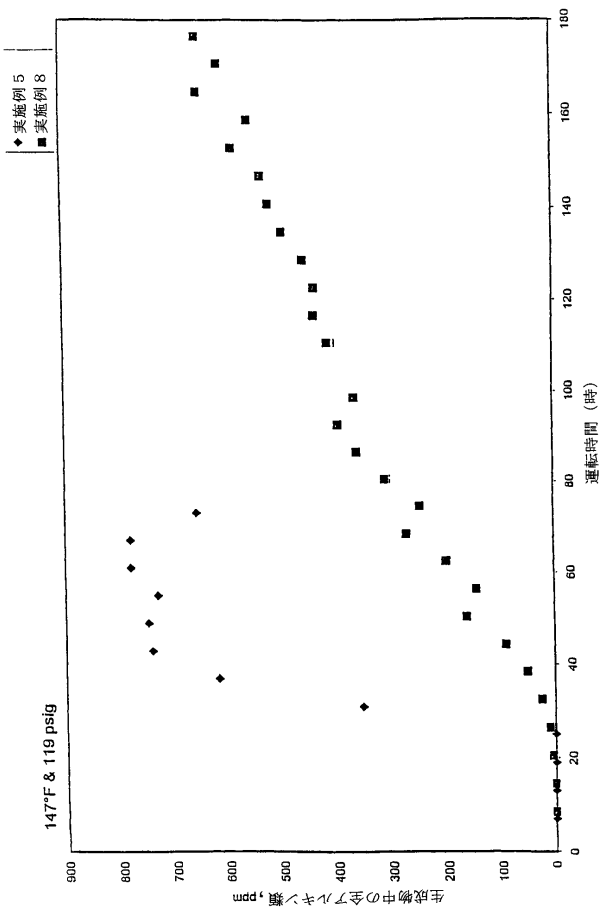
【図５】


◆ 実施例５
■ 対照実施例１
▲ 実施例６
全アルキン類の転化，%

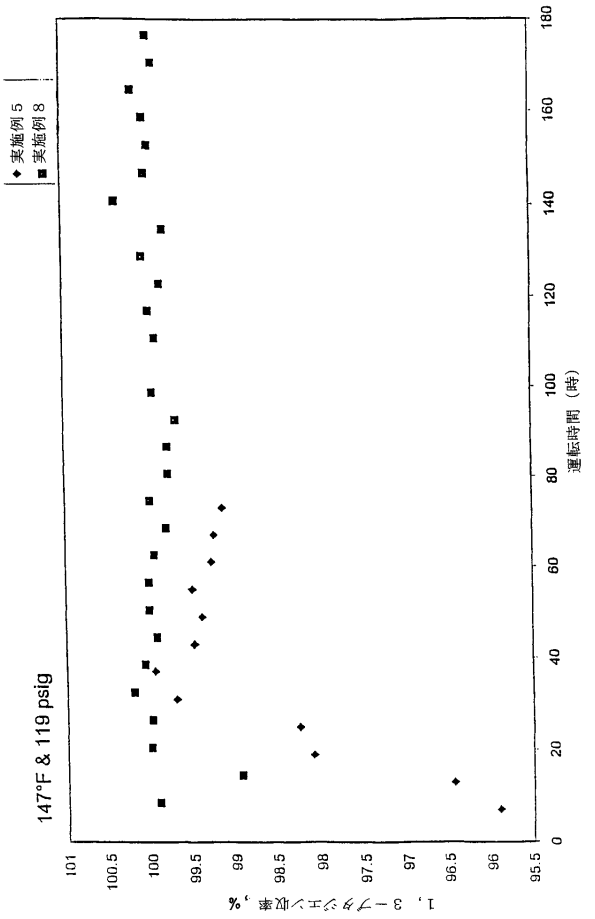
【図６】


実施例７
供給の開始 1, 60 psig, 1 scfh
P @80
P @90
H2@2
H2@3
H2@4
H2@5
オンライン時間（時）
■ C4類中のVA ▼ C4類中のEA △ オーバーヘッドのC4類中のMA
● 13BD回収率
アセチレン類（ｐｐｍ）
1，3－ブタジエン回収率（ブウト／イン）

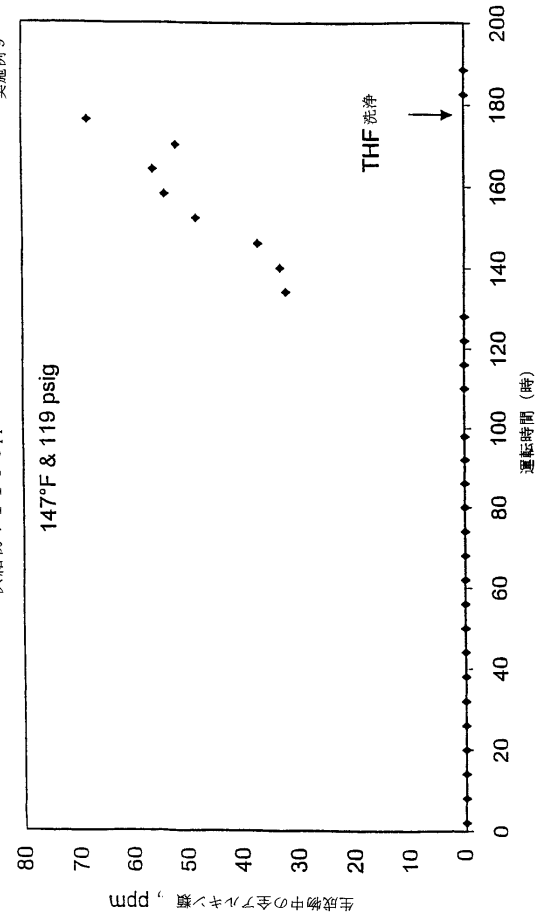
【図７】


◆実施例５
■実施例８
147°F & 119 psig
生成物中の全アルキン類，ppm
運転時間（時）

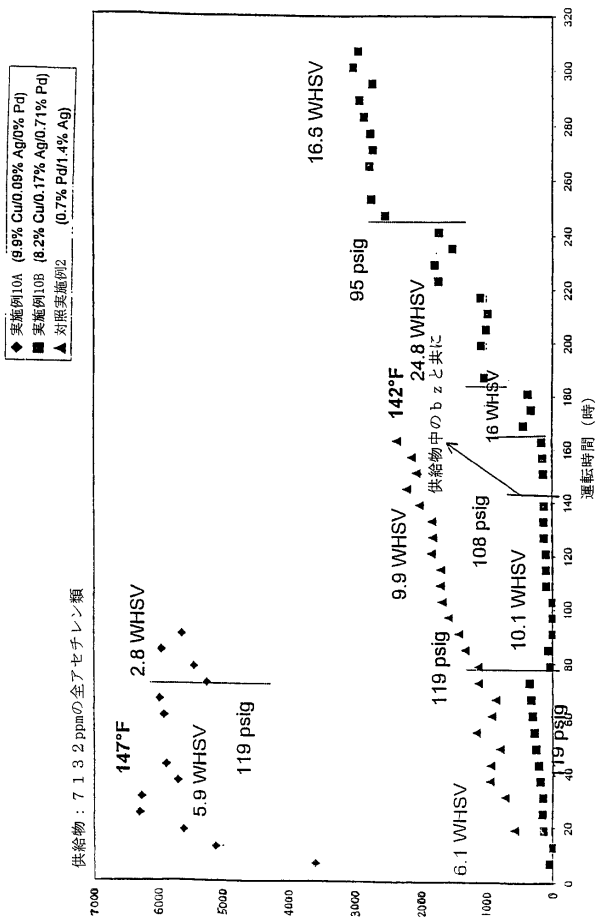
【図８】


◆実施例５
■実施例８
147°F & 119 psig
1，３－ブタジエン収率，%
運転時間（時）

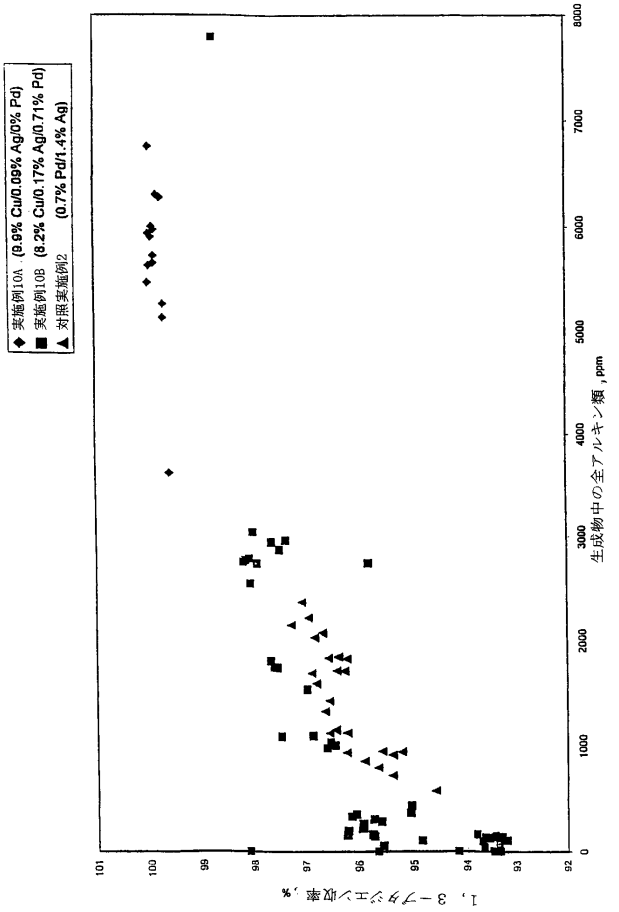
【図９】


供給物：１１９６ppmの全アルキン類
実施例９
147°F & 119 psig
THF 洗浄
生成物中の全アルキン類，ppm
運転時間（時）

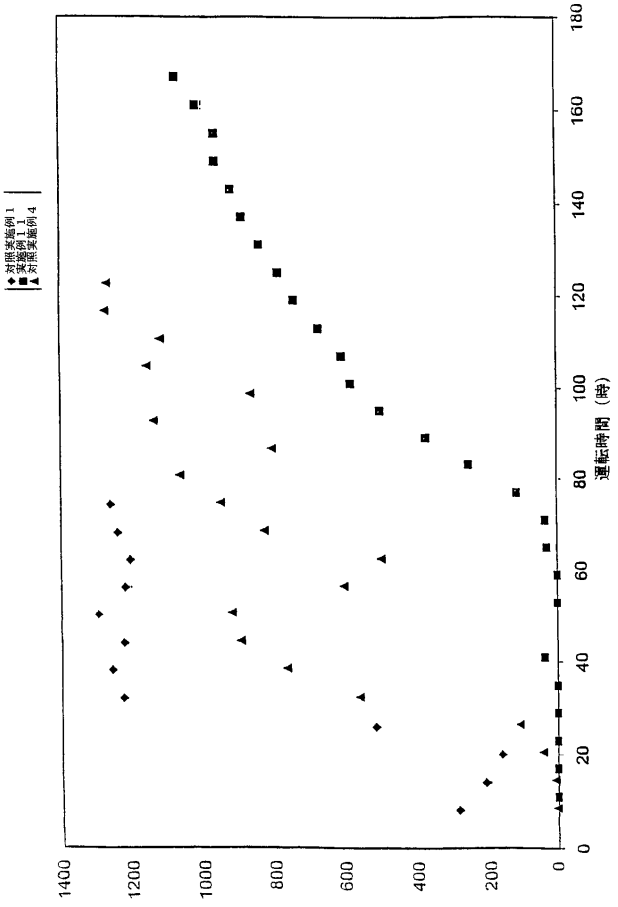
【図１０】


◆実施例10A (9.9% Cu/0.09% Ag/0% Pd)
■実施例10B (8.2% Cu/0.17% Ag/0.71% Pd)
▲対照実施例2 (0.7% Pd/1.4% Ag)
供給物：７１３２ppmの全アセチレン類
147°F
2.8 WHSV
5.9 WHSV
119 psig
16.6 WHSV
95 psig
142°F
24.8 WHSV
供給物中のｂｚと共に
9.9 WHSV
119 psig
108 psig
16 WHSV
10.1 WHSV
6.1 WHSV
運転時間（時）

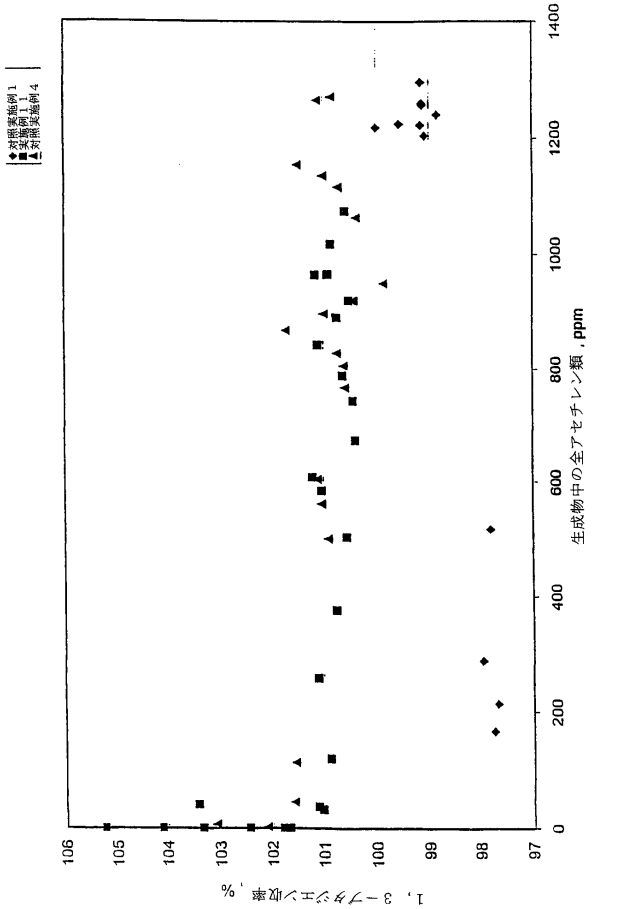
【図１１】



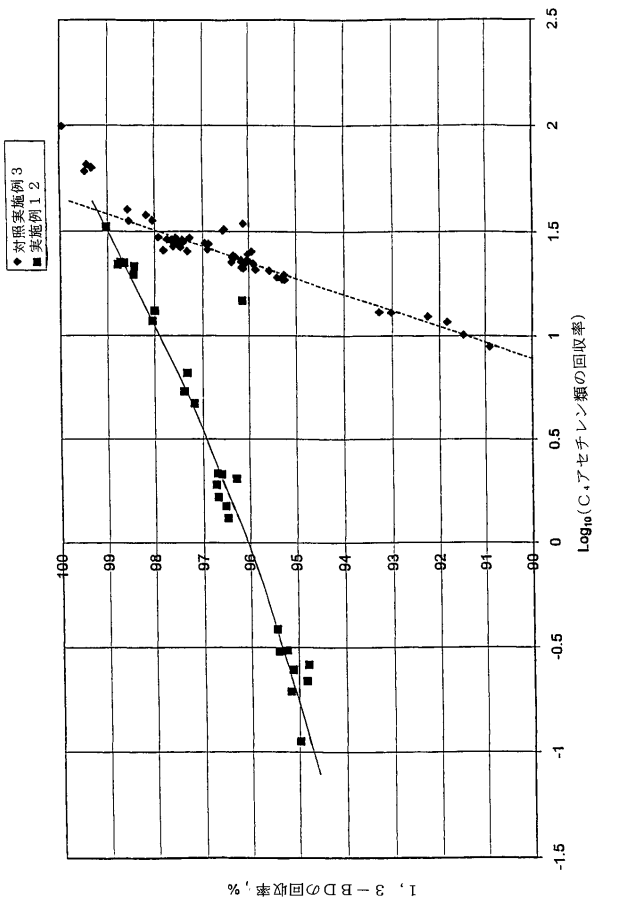
【図１２】



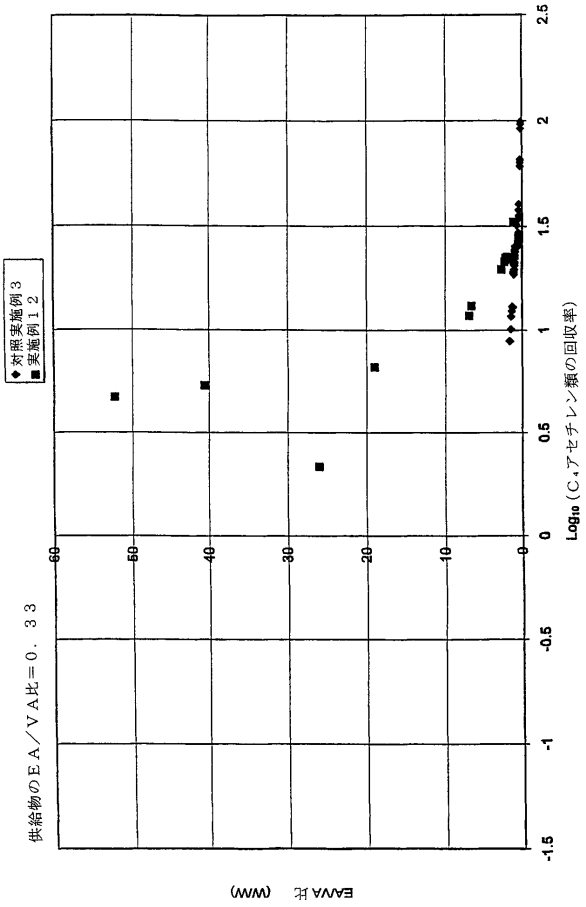
【図１３】



【図１４】



【図１５】


◆対照実施例３
■実施例１２
供給物のＥＡ／ＶＡ比＝０．３３
EAVA比 (wt%)
60
50
40
30
20
10
0
-0.5
-1
-1.5
0.5
1
1.5
2
2.5
Log10 (C4アセチレン類の回収率)

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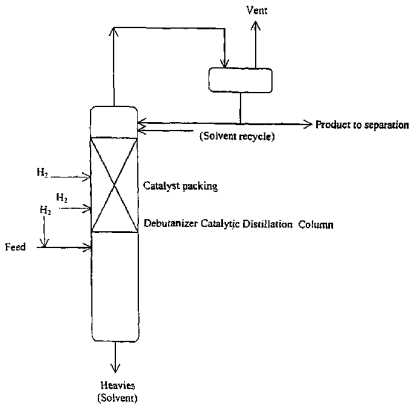
(54) Title: PROCESS FOR SELECTIVE HYDROGENATION OF ALKYNES AND CATALYST THEREFOR



(57) Abstract: Acetylenic compounds in olefin streams such as mixed 1,3-butadiene were selectively hydrogenated over the supported copper catalysts on highly porous supports such as alumina, silica, etc. The preferred supports have the average pore diameter larger than about 200Å, no micro pores, total pore volume larger than about 0.65 cc/g, and preferably less than about 230 m^2/g BET surface area. The copper catalysts were preferably promoted with the group VIII metal such as palladium to improve low activity of copper catalyst. The product stream typically contains less than 20 ppm total alkynes. Also the copper catalysts and the palladium promoted copper catalysts may be modified with zinc oxide to improve the performance of the catalysts. The reactor was loaded with two or more copper catalysts promoted with different levels of palladium. Preferably the copper catalysts were also modified with silver, gold or both silver and gold to reduce polymer formation by the copper component of the catalyst, improve the yield of olefins such as 1,3-butadiene, and prevent the loss of copper and/or palladium due to leaching out into the liquid phase of hydrocarbon.

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Process For Selective Hydrogenation of Alkynes and Catalyst Therefor

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to the selective removal of more highly unsaturated compounds from mixtures of unsaturated compounds. More particularly the invention is concerned with the selective hydrogenation of acetylenic compounds from mixtures with dienes, such as 1,3-butadiene. The invention provides both novel catalysts and process for the selective hydrogenation of acetylenes in admixture with other unsaturated compounds.

Related Information

Supported copper catalysts and palladium catalysts have been preferred catalysts in cleaning up acetylenic impurities in olefin streams by selective hydrogenation. Copper catalysts selectively hydrogenate acetylenic compounds without substantial hydrogenation of the olefins and diolefins (designated herein as selectivity for retaining olefins), but have relatively low activity and short cycle time due to primarily polymer deposition on the catalyst surface. Palladium catalysts have excellent activity and much longer cycle time, but lower selectivity for the acetylenes than copper-based catalysts. To improve olefin selectivity of palladium catalyst, silver or gold has been added to palladium catalyst in minor amounts as modifier.

Fr 1 253 947 (1960) disclosed the copper catalyst for selective hydrogenation of acetylenic compounds in diolefin or monoolefin streams. The selective hydrogenation was carried out in vapor phase. 99.9 - 99.999% purity copper was supported on high surface area (25-300 m^2/g) supports such as gamma alumina. Copper content of the catalyst was in a range of 5 to 20%. The catalyst may contain less than 0.1% other metals (based on metal content of the catalyst) such as Fe, Ni, Ru, Rh, Pd, Ir or Pt as promoter. The selective hydrogenation was carried out in both vapor and liquid phase. U.S. Pat. Nos. 4,440, 956 (1984) and 4 493 906 (1985) disclosed the improved copper catalysts supported on the very specific alumina such as gamma alumina prepared from aluminum alkoxides, which are useful for

removing alkynes in liquid hydrocarbon streams. The patentee characterized the gamma alumina as having 60 to 90% of pores which should have a pore diameter between about 40 Å and 120 Å, and not more than 25% nor less than 2% had pore diameter between l000 Å to l 0,000 Å. The nitrogen surface area of the alumina was from about 68 to 350 m^2/g. The catalyst contained 3 to 13 weight % Cu. The catalyst contained minor amounts of at least one polyvalent activator metal selected from the group consisting of silver, manganese, cobalt, nickel and chromium. High purity of alumina, especially in terms of sodium (should be less than 0.15 wt %) and Fe_2O_3 (less than 0.06 wt %) contents, was claimed to be critical due to shrinkage of the surface area caused by frequent catalyst regeneration.

Ger 2 109 070 (1970) disclosed copper (26%)-zinc oxide catalyst for selective hydrogenation of acetylenic compounds in 1,3-butadiene stream in vapor phase.

U.S. patent 4,174,355 (1979) disclosed a process for removing (α-acetylenes from diolefin streams by nonselective hydrogenation. The alkynes were removed by contacting the feed steams with CuO and or Ag_2O supported on (α-alumina in the absence of hydrogen or oxygen.

U.S. patent 4,533,779 (1985) disclosed palladium/gold catalyst supported on supports such as alumina (l to l00m^2/g) for selective hydrogenation of acetylenic compounds. The contents of palladium and gold in the catalysts were in the range of 0.03 to l weight % and 0.003 to 0.3 weight %, respectively.

U.S. patent 4,831,200 (1989) disclosed the process for the selective hydrogenation of alkynes in olefin streams such as mixtures with 1,3-butadiene. The selective hydrogenation was carried out in two steps in sequence. In the first step, the hydrocarbon feed was passed at least partially in liquid phase with hydrogen over the palladium catalyst such as that disclosed in U.S. 4,533,779 discussed above. In the second step, the product stream from the first step was passed again at least partially in liquid phase with hydrogen over the copper catalyst such as that disclosed U.S. patents 4,493,906 and 4,440,956 discussed above to produce significantly reduced alkyne concentration in the final product stream.

U.S. patent 5,877,363 (1999) disclosed the process for the selective hydrogenation of acetylenic impurities and 1,2-butadiene in mixed olefin rich C_4 streams by using supported hydrogenation catalysts such as Pt and Pd.

In general, the palladium catalysts are very active compared with the copper catalysts for selective hydrogenation of acetylenic compounds in the olefinic steams. But the palladium catalysts exhibit low selectivity for retaining diolefins, such as 1,3-butadiene, when one is trying to remove high concentrations (>2000 ppm) of total alkynes to less than about 500 ppm total alkynes in the streams, especially when the acetylenes are reduced to less than 200 ppm. The non selectivity of palladium catalysts is not desirable in commercial practice, because it resulting in a loss of 1,3-butadiene.

On the other hand, the copper catalysts are highly selective in retaining diolefins such as 1,3-butadiene by being very selective to acetylenes hydrogenation. But the activity of copper catalysts is slow. And the catalyst cycle time is undesirably short for the feed streams, which contain higher than about 2000 ppm total alkynes due to fast deactivation caused by the deposition of polymeric material on the catalyst surface, Even though the hydrogenation is carried out in liquid phase, some of the polymers deposited on the copper catalyst has little solubility in the liquid product stream under the selective hydrogenation condition. Due to these two reasons, the copper catalysts need improvement for the selective hydrogenation of the mixed olefin feeds, which contain relatively high concentration of total alkynes.

SUMMARY OF THE INVENTION

The present invention includes a catalyst comprising a copper component containing from about 0.1 to 25 wt percent Cu, preferably 0.2 to 20 wt %; a palladium promoter in a range of 0 to 2 wt %, preferably 0 to 1 wt %; a silver or gold modifier is in a range of 0 to 15 wt %, preferably 0 to 10 wt %; and a zinc oxide modifier is in a range of 0 to 25 wt %, preferably from 0 to about 15 wt %. The silver modifier moderates the catalyst activity, and improves the olefin yield and the cycle time. The zinc oxide modifier improves the olefin yield such as 1,3-butadiene with small improvement in the catalyst activity. The zinc oxide modified copper catalysts is especially very effective for removing vinyl acetylene impurity with extremely high yield of 1,3-butadiene. In a preferred embodiment the catalyst components are deposited on a support.

The preferred supports have the average pore diameter larger than about 200Å, no micro pores, total pore volume larger than about 0.65 cc/g, and preferably

less than about 230 m^2/g BET surface area. The copper catalysts are preferably promoted with the Group VIII metal such as palladium to improve low activity of copper catalyst. The product stream typically contains less than 20 ppm total alkynes. Also the copper catalysts and the palladium promoted copper catalysts may be modified with zinc oxide to improve the performance of the catalysts. The reactor was loaded with two or more copper catalysts promoted with different levels of palladium. Preferably the copper catalysts were also modified with silver, gold or both silver and gold to reduce polymer formation by the copper component of the catalyst, improve the yield of olefins such as 1,3-butadiene, and prevent the loss of copper and palladium due to leaching out into the liquid phase of hydrocarbon.

The process of removing acetylenic compounds by contact hydrocarbon streams containing small amounts of acetylenic compounds with the catalyst of the invention in various arrangements and configurations is also part of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic presentation of CD reactor having the present copper catalyst in the upper portion for selective hydrogenation of acetylenes.

Fig. 2 is a schematic presentation of CD reactor having the present copper catalyst in the upper portion for selective hydrogenation of acetylenes and group VIII catalyst in the lower portion to react mercaptans and diolefins.

Fig. 3 is a graphic presentation of the pore distribution of alumina support and catalyst of Example 5.

Fig. 4 is a graphic presentation of the total product alkynes in the products of Examples Control 1, 5 and 6.

Fig. 5 is a graphic presentation of the total 1,3-butadiene product yield of Examples Control 1, 5 and 6.

Fig. 6 is a graphic presentation of the results of Example 7 in CD.

Fig. 7 is a graphic presentation of total alkynes in the products of Example 5 (non CD) and Example 8 (CD).

Fig. 8 is a graphic presentation comparing Example 5 (non CD) 1.3-butadiene product and Examples 8 (CD).

Fig. 9 is a graphic presentation of the benefit of solvent treatment of the used catalyst.

Fig. 10 is a graphic presentation comparing Examples 10A an 10B to show the benefit of Pd promoted Cu.

Fig. 11 is a graphic presentation comparing Examples 10A and 10B to show the benefit of Pd promoted Cu on 1,3-butadiene production.

Fig. 12 is a graphic presentation of the benefits of ABD according to the present invention for acetylenes removal comparing Control Examples 1 and 4 and Example 11.

Fig. 13 is a graphic presentation of the benefits of ABD according to the present invention for 1,3-butadiene product comparing Control Examples 1 and 4 and Example 11.

Fig. 14 is a graphic presentation of the benefits of the palladium promoted copper catalyst comparing Example 12 with Control Example 3.

Fig. 15 is a graphic presentation of the chemical fingerprint differentiating the palladium promoted copper catalyst from traditional palladium catalyst by comparing Example 12 with Control Example 3.

DETAILED DESCRIPTION

The selective hydrogenation is preferably carried out at least partially in liquid phase for example by employing a catalytic distillation (CD) unit(s). Therefore, it is highly desirable to provide a new process and improved copper catalysts so that the selective hydrogenation can be carried out in a single step with higher throughput rate and yet maintaining high selectivity retaining olefins such as dienes and long catalyst life. In this invention, this objective is accomplished by carrying out the selective hydrogenation in a single reactor with the highly active, yet highly selective copper catalysts. The selective hydrogenation is preferably carried out at least partially in liquid phase by employing a catalytic distillation (CD) unit. The distillation column is loaded with two or more copper catalysts promoted with different levels of elements in the Group VIII such as palladium, ruthenium, nickel, etc and also modified with zinc oxide and an element in the Group IB. The preferred promoter is palladium. Promoting copper catalyst with palladium is very desirable in dealing with high acetylenic impurities containing feeds. The present data indicates that copper

becomes much more active by alloying with palladium with small loss in the selectivity retaining olefins such as 1,3-butadiene or 1-butene. By alloying copper with palladium, the chemical nature of the copper-palladium catalyst is changed from the traditional palladium or palladium-silver catalysts. The nature of change is demonstrated in the Example 12. The ratio of ethyl acetylene to vinyl acetylene in the product stream from this invention is much higher than the product from the traditional palladium catalysts, because the copper-palladium catalyst has quite different chemical reactivity toward to vinyl acetylene and ethyl acetylene from the traditional palladium or palladium-silver catalyst. Therefore, the difference in the ratios at a given conversion of C_4 acetylenes is the fingerprint differentiating the chemical catalytic nature of the copper-palladium catalyst from the traditional palladium catalysts.

The copper catalysts may be loaded in the debutanizer distillation column to provide a CD reactor, in dealing with a mixed C_4 feed stream to produce a clean 1,3-butadiene rich product. The feed stream to the catalytic distillation column is preferably fed to the middle section of the column below the catalyst bed. The product is recovered as overhead product. The heavier product is recovered as bottom product. The palladium content of the copper catalysts loaded in the CD reactor gradually decrease as moving up from the bottom section to the top section of the catalyst bed. The catalysts are loaded above the feed point to the distillation column. Hydrogen is fed together with hydrocarbon feed or separately to a position at the bottom section of the distillation column. The optimum ratio of hydrogen to the total alkynes in the catalytic reaction zone depends on the Cu content of the catalyst as wells Cu/Pd weight ratio. Therefore, preferably hydrogen is fed to two or more positions along the catalytic distillation column or the fixed bed depending on the compositions of the catalysts in reactor. Also the palladium component of the catalyst improves the catalyst cycle time. Although it is not known how this additional benefit of the copper catalysts promoted with Pd occur, it may be that unsaturated precursors to polymeric materials are more effectively hydrogenated resulting in slower or little deposition of polymeric material on the copper catalysts. The polymeric materials may have a higher solubility in the product steam than the polymers formed on the unpromoted copper catalysts. Consequently, the precursors

and polymeric materials are effectively washed off from the catalysts to the bottom of the catalytic distillation column resulting in continuously renewed, cleaner catalyst surface. Preferably the copper component of the catalyst is modified with an element of Group IB such as silver and/or gold or both to reduce further polymer formation to improve the selectivity of diene and improve slowly leaching out the copper and palladium metals from the catalyst.

The catalyst may be modified further with zinc oxide to improve the catalyst activity, the yield of olefins such as 1,3-butadiene, the catalyst cycle time, and reduce the loss of copper and palladium due to slowly leaching out from the catalyst. In the case of the Cu-Zn-Al methanol synthesis catalyst prepared by co-precipitation of mixed solution of nitrate salts, Cu(II) ions dissolves into zinc oxide phase of the copper-zinc oxide-alumina catalyst (prepared by co-precipitation technique) and their concentration could be as high as about 25 at. % (T. M. Yurieva, et al. React. Kinet. Catal. Lett., 29, pp. 55-61, 1985). It was observed that all the copper catalysts disclosed in this invention have high content of active hydrogen species that can hydrogenate olefins in the absence of hydrogen regardless of whether or not the catalysts contain zinc oxide.

The hydrogenation may be carried out in two steps. For example, the selective hydrogenation can be carried out with two CD reactors, or a combination of a CD reactor and a fixed bed reactor, or two fixed bed reactors as shown in Figure 2. In the fixed bed reactor operation, two or more reactors may be needed, to remove the exothermic heat of the hydrogenation reaction by cooling the reactor effluent stream from the first reactor prior to entering the second reactor. One may recycle the reactor effluent in fixed bed reactor operation to dilute the heat of the hydrogenation reaction. Optionally, material in which the polymer deposited on the catalyst surface is soluble may be used to wash off the polymer from the catalyst in either the reactive distillation mode or the straight pass mode. Examples of such solvents include tetrahydrofuran, furan, 1,4-dioxane, ethers, gamma-butyrolactone, benzene, toluene or mixtures of thereof. After separating products from the solvent, the solvent is recycled back to the reactor as shown in the Figure 1. Another technique to prolong the catalyst life is washing the catalyst intermittently with a liquid solvent at temperatures in the range of about 40°C to 350°C to remove deposited polymers

from the catalyst. Optionally a small amount of hydrogen gas is passed through the catalyst bed with solvent during washing off the polymers from the catalyst. When the selective hydrogenation of actelyenes in the C_4 streams is carried out in the CD mode, if the boiling point of the solvent is higher than about 100°F, the solvent can be added to the top of the catalyst zone of the catalytic distillation reactor and the solvent flows down to the bottom of the column. In a straight pass reactor the solve may be fed with the reactant feed stream to the reactor. During both modes of operation, it is desirable to apply sufficient pressure so that at least 0.2 mole% of the acetylenes in the feed stream is in the liquid phase which comprises solvent and hydrocarbons in the reaction zone.

The preferred supports to be used for the preparation of the catalyst in this invention are mesoporous materials and should have relatively large pore volume. As the average pore diameter of a supporting material increases, the pore volume increases as well, but both the surface area and ABD (apparent bulk density often called packed density) of the material decrease. Preferably the supports will have no micro pores, preferably no pores less than about 30Å diameter. When the deposition of heavy material on the catalyst surface causes the catalyst deactivation and deterioration of the selectivity of a desired material due to over-reaction, generally pore size distribution and size of pores play important roles for the catalyst performance. One of preferred supports in this invention is transition alumina. The pores of the desired alumina are mostly composed of pores larger than 100Å diameter. About 85%, preferably about 90% of pores will have the pore diameter larger than 100Å determined by nitrogen porosimetry. The preferred alumina will have the average pore diameter larger than about 100Å, preferably larger than 120Å, total pore volume larger than about 0.65 cc/g (determined by nitrogen porosimetry), preferably larger than 0.70 cc/g, and preferably the BET surface area of less than about 230 m^2/g, most preferably from 30 to 200 m^2/g, and the apparent bulk density (ABD) less than about 0.70 g/cm^3. The pores of alumina are composed of various size pore diameters. Within a certain range of alumina surface area, the pore distribution of alumina can be manipulated depending on how the aluminas are prepared and calcined. Unlike the alumina disclosed in U.S. patent 4,440,956, the preferred alumina in this invention will have at least 30% , preferably at least 50% of

the pores larger than 100Å diameter, and a total pore volume larger than about 0.65 cc/g, preferably about 0.75 cc/g.

The preferred alumina disclosed in this invention can be prepared by a number of techniques well known to whom skilled in arts preparing so called active aluminas. One of the preferred aluminas disclosed in this invention can be prepared by so-called oil dropping gelation technique. The examples of the prior arts are disclosed in U.S. 2,620,314 (1952), and 4,273,735 (1981). The spherically shaped alumina is prepared from aluminum hydroxychloride sol prepared by digesting aluminum metal in aqueous hydrochloric acid solution. Spherically shaped alumina sol materials, in the form of droplets, are gelled in basic liquid oil phase followed by aging, washing, drying, and calcining to transition state aluminas at various temperatures depending on the desired property of alumina. Alternatively the preferred spherically shaped alumina also can be prepared by oil dropping gelation technique using the dispersed boehmite or pseudoboehmite alumina sols. The example of the prior art is disclosed in U.S. 4,179,408 (1979). The alumina sols are prepared by dispersing suitable boehmite, pseudoboehmite or mixtures of boehmite and pseudoboehmite aluminas in acidic water. The pseudoboehmite or boehmite raw materials are obtained by hydrolyzing aluminum alkoxides and crystallizing or reacting sodium aluminate with aluminum salts such as aluminum sulfate and crystallizing. Various boehmite aluminas or dispersed boehmite aluminas sols are available in market place. Condea is one of the suppliers. To prepare the preferred spherical alumina whose pore structure is disclosed in this invention, Disperal HP 14/2, Dispal 11N7-80, Dispal 23N4-20, Disperal HP 14, Deperal 40, Pural 200, Pural 100, Pural NG, etc. or mixtures of these can be used. Other boehmite aluminas such as Catapal C1, Pural SB, Disperal P2, etc are not preferred raw materials for the preparation of the preferred alumina disclosed in this invention. These materials yield the like aluminas disclosed in the U.S. patents 4,493,906 and 4,440,956.

The preferred alumina in extrudate form can also prepared by extruding the preferred boehmite aluminas discussed above and calcining at elevated temperatures from about 550°C to 1200°C. Generally transition aluminas are various mixtures of crystalline aluminas such as amorphous, γ, χ δ, η, ρ, θ, α, etc and their surface area tends to shrink by repeated exposures to high temperature

atmosphere due to slow crystallization to more stable crystal forms. Especially this surface area shrinkage accelerates in the presence of moisture in atmosphere or trace amount of sodium in alumina or both. If gamma alumina is the desired form, the calcination is usually carried out at temperatures from about 550°C to 700°C. Unlike the aluminas disclosed in U.S. 4,493,906 and 4,440,956, the alumina supports prepared in this oil dropping gelation technique using aluminum hydroxychloride sols contain a very small amount of chlorine. A small amount of sodium or chlorine in alumina disclosed in this invention usually doesn't cause serious problem for the catalytic distillation operation or fixed bed operation with solvent, because of long catalyst cycle time.

The physical shapes of the preferred aluminas in this invention are spheres, extrudates, pellets and granules which have diameter of less than about ¼ inches, preferably 1/8 inches and less than about ½ inches length, preferably less than ¼ inches length for extrudates or pellets.

The copper component of the catalyst is put on the preferred alumina by various impregnation techniques with aqueous solution of cupric salts such as cupric nitrate, cupric acetate, etc. The impregnation product is calcined at from about 100 to 500°C, preferably from 200 to 400°C to decompose the salts resulting in copper oxide-alumina product. The silver and zinc oxide modifiers are incorporated into the catalyst by co-impregnation of a silver salt such as silver nitrate and a zinc salt such as zinc nitrate with copper salt. Optionally they are incorporated into the copper catalyst by double impregnation. The zinc oxide or both silver and zinc oxide modifiers are put on alumina support prior to impregnating the solution of a copper compound. The impregnation product is calcined at from about 100 to 650°C, preferably from 100 to 600°C to obtain the copper oxide-silver oxide-alumina catalyst or the copper oxide-silver oxide-zinc oxide-alumina catalyst. Still another technique can be used to prepare the zinc oxide modified copper catalyst by dropping the alumina sols, which contain a desired amount of zinc salt or both zinc and copper salts, into basic oil phase to form gels, followed by aging, washing and calcining at a temperature range of 450° to 1200°C.

The palladium promoter is incorporated into the catalyst by co-impregnating the palladium compound solution such as palladium (II) nitrate, palladium (II) acetate,

palladium (II) acetylacetonate, etc. with copper salt solution or a solution containing copper salt and silver salt. Although various impregnation techniques can be used, the preferred impregnation technique of the palladium compound solution or the mixed solutions of palladium compound and copper compound or palladium compound, copper compound and silver compound or palladium compound, copper compound, silver compound and zinc compound is spray coating impregnation by using an atomizer. It is highly desirable to spraying the solutions uniformly on supports. It is also highly desirable to create a fine mist of the palladium solutions using a compressed gas atomizer. When various palladium solutions are spray coated on supports such as alumina, the desired volume of the solution is less than about 90 volume % of the total pore volume (weight of support multiplied by the pore volume per unit weight of support) of the support to be impregnated, preferably less than about 85 volume %.

When highly active copper catalyst promoted with palladium is prepared, the impregnation of catalyst components can be carried out in either a single step or two steps. In the two step impregnation, the impregnation technique, for the first step, alumina support is impregnated with a solution of copper compound or a mixed solution containing copper and zinc compounds or copper, zinc and silver compounds or zinc and silver compounds by using usually incipient pore impregnation technique, followed by drying at a temperature from about 100 to 250°C and calcination at a temperature from 250 to 700, preferably from 300 to 550°C. In the second step the product from the first step is impregnated with a solution of palladium compound, preferably a mixed solution of palladium and copper compounds or palladium, copper and silver compounds or palladium, copper, zinc and silver compounds or palladium, silver and zinc compounds by using spray coating technique with an atomizer, followed by drying at a temperature from 100 to 250°C and calcining at a temperature from about 250 to 650°C, preferably from 300 to 550°C.

Another preferred technique incorporating palladium into the copper catalyst is the spray-coating impregnation of a solution of a palladium compound or a mixed solution of a palladium compound such as palladium nitrate and a silver compound such as silver nitrate, while the copper catalyst spheres are rolling down a flat

surface tilted at a proper angle, on the copper oxide-alumina catalyst, the copper oxide-alumina, the copper oxide-zinc oxide-alumina catalyst or the copper oxide-silver oxide-zinc oxide alumina catalyst. Relatively high loading (>0.15 wt %) of palladium on the copper catalyst is desired for processing the feeds which contain relatively high content (>~4000 ppm) of total acetylenic compounds. A combination of co-impregnation and the spray-coating impregnation is the most desired technique for high palladium loading on the catalyst. It is very important to produce a fine mist of the palladium solution for the spay-coating impregnation. If the copper catalyst, which is promoted with more than about 0.15% Pd, is desired, a combination of co-impregnation and spray coating impregnation is generally preferred. The impregnation product is calcined in air at from about 100 to 400°C, preferably from 100 to 350°C to prepare the copper, the copper-silver or the copper-silver-zinc catalysts promoted with palladium.

Optionally the catalysts can be prepared by impregnating mixed solutions of metal salts on the alumina powders which have the physical characteristics of preferred supports described above. The raw materials preparing such alumina powders are suitable boehmite powder and pseudoboehmite powders such as Disperal HP 14/2. The raw materials are calcined at temperatures from about 400°C to about 750° prior to the impregnation. The impregnation products are calcined at temperature from about 250° to 550°C in air and shaped to desired size of extrudates or pellets. Optionally the impregnation products are shaped to extrudates or pellets and then the shaped materials are calcined in air at elevated temperature from about 250°C to 550°C in air.

The catalyst activation is carried out at from about 60 to 400°C, preferably from 100 to 350°C in the gas flow containing hydrogen. The content of hydrogen in the gas is gradually increased during the activation from about 5 volume % to 50 volume % or more in the inert gas such as nitrogen. During the catalyst activation, a sufficient amount of gas flow is preferred so that no water vapor condensation on the catalyst would occur. The length of activation depends on the amount of the catalyst in reactor, the hydrogen content in the gas and the activation temperature. In laboratory, from 30 minutes to about 10 hours is sufficient for less than about 100 grams catalyst. In commercial practice, generally much longer activation time would

be needed. After the catalyst activation, the residual hydrogen in the reaction zone is flushed out with inert gas. At the start-up of the selective hydrogenation, the content of unsaturated compounds in the feed stream should be kept at very low level in the catalytic reaction zone by using inert diluent such as saturated hydrocarbons until most of hydrogen content in the activated catalyst is consumed. Due to relatively high content of copper on the catalyst, the activated catalyst contains relatively large amount of active hydrogen, which could cause run away temperature in the catalyst bed.

Protecting the selective hydrogenation catalysts such as copper catalysts from poisoning by the sulfur compounds such as alkyl mercaptans is necessary in dealing with real feed streams in commercial practice. To protect the selective hydrogenation catalyst from the poisoning by alkyl mercaptans in feed streams, the sulfur impurities are converted to heavier sulfur compounds by reacting with olefins, acetylenic compounds or dienes over Pd, Ni, etc. catalysts or optionally the catalyst disclosed in this invention, but optimized differently from the selective hydrogenation catalysts to maximize the mercaptan reaction. The heavier sulfur products are removed from light components by simple distillation. It is critically important not to produce H_2S from sulfur compounds during this mercaptan removing operation, because H_2S will poison the selective hydrogenation copper catalysts. In a CD unit, this removal of mercaptans can be carried out concurrently with the selective hydrogenation in a single distillation column. The catalyst for forming higher boiling organic sulfides from mercaptans such as that disclosed in U.S. Pat. Nos. 5,510,568; 5,595,643, 5,597,476 or 5,807,477 is loaded at the bottom of the selective hydrogenation catalyst bed in the CD column. The heavier sulfur compounds is removed as bottom product from the CD column prior to entering to selective hydrogenation reaction zone so that the selective hydrogenation catalysts is protected from the sulfur impurities. It is important to maintain a minimal amount of hydrogen in this mercaptan reaction zone not to produce hydrogen sulfide. If too much hydrogen is available, some of mercaptans may be converted to hydrogen sulfide by hydrodesulfurization of alkyl mercaptans or sulfides. To prevent the formation of hydrogen sulfide, it may be necessary to adjust the hydrogen content in the mercaptan reaction zone differently from that in the catalytic selective hydrogenation reaction zone.

Control Example 1

A copper catalyst was prepared according to the Example 1 in U.S. 4,440,956. Gamma alumina (CS 331-1 obtained from UCI, 1/16 inch extrudates and 265 m^2/g surface area) was calcined at 700°C for 3 hours in the ambient atmosphere before use. There was little change in ABD before and after calcination. The calcined alumina had 0.792 g/cc ABD. A solution of 28.7g $Cu(NO_3)_2.2.5H_2O$, $Ni(NO_3)_2.6H_2O$, 0.04g $AgNO_3$, 0.34g $Cr(NO_3)_3.9H_2O$ and 0.34g $Co(NO_3)_2.6H_2O$ in 110 ml deionized water was prepared. 60g UCI alumina was impregnated with above solution by using a rotary evaporator. After drying the impregnation product in 110°C in vacuum oven overnight, calcined at 400°C in a muffle furnace for 3 hours. The ABD of the catalyst was 0.87 g/cc. 22g of this catalyst was blended with 100 ml 3 mm diameter glass balls and loaded in a vertical stainless reactor (1 inch diameter x 20 inch long) used as a conventional reactor. The catalyst was activated by the following procedure; (1) heating the reactor to 230°F in 100 cc/min N_2 gas flow, (2) adding 200 cc/min H_2 to the N_2 gas flow and then holding for 3 hours at 230°F, (3) shut off N_2 gas and increasing H_2 gas flow to 300 cc/min, (4) heating the reactor temperature to 662°F and holding for 3 hours at 662°F and then cooled the reactor to 147°F in 30 cc/min H_2 gas flow.

A mixed C_4 stream composed of 28 wt ppm methyl acetylene, 1034 wt ppm vinyl acetylene and 549 wt ppm ethyl acetylene, 45.23 wt % 1,3-butadiene, 0.10 wt % 1,2-butadiene, 6.05 wt % t-2-butene, 4.22 wt % c-2-butene, 15.36 wt % 1-butene, 18.05 wt % isobutene, 9.34 wt % n-butane, 1. 30 wt % isobutane, and 0.19 wt % others was selectively hydrogenated to remove acetylenic impurities at 119 psig pressure. For the first 26 hours on stream time, the feed hydrocarbon and hydrogen rates were 2.2 cc/min (3.6 WHSV) and 31.4 scc/min, respectively. Then the feed rates were changed to 3 cc/min for hydrocarbon (5.0 WHSV) and 27 scc/min for hydrogen rate for the next 24 hours on stream. After that, the feed rates were 2.2 cc/min for hydrocarbon (3.6 WHSV) and 31.4 scc/min for hydrogen rate until the end of the run.

Control Example 2

18 grams of the palladium catalyst (0.7% Pd/1.4% Ag on alumina, 2464F obtained from UCI) was mixed with 110 ml 3 mm diameter glass balls and loaded in

the following procedure; (1) heating the reactor to 230°F in 100 cc/min N_2 gas flow, (2) adding 200 cc/min H_2 to the N_2 gas flow and then holding for 3 hours at 230°F, (3) shut off N_2 gas and increasing H_2 gas flow to 300 cc/min, (4) heating the reactor temperature to 662°F and holding for 3 hours at 662°F and then cooled the reactor to 147°F in 30 cc/min H_2 gas flow.

The same feed used in the Control Example 1 was selectively hydrogenated to remove acetylenic impurities at 119 psig pressure. For the first 26.5 hours on stream time, the feed hydrocarbon and hydrogen rates were 1.8 cc/min (3.6 WHSV) and 25.7 scc/min, respectively. Then the feed rates were changed to 2.4 cc/min for hydrocarbon (4.9 WHSV) and 22.1 scc/min for hydrogen rate for the next 24 hours on stream. After that, the feed rates were changed again to 1.8 cc/min for hydrocarbon carbon (3.6 WHSV) and 25.7 scc/min.

Example 5

A copper catalyst was prepared according to this invention using the alumina (1/16" diameter spherically shaped) prepared by the oil dropping gelation technique. The physical property of the alumina is summarized in Table 1. The pore size distribution of the alumina is illustrated in Figure 1. More than about 90% of the pores were larger than 100Å diameter. The solution of 28.7g $Cu(NO_3)_2.2.5H_2O$, $Ni(NO_3)_2.6H_2O$, 0.04g $AgNO_3$, 0.34g $Cr(NO_3)_3.9H_2O$ and 0.34g $Co(NO_3)_2.6H_2O$ in 110 ml deionized water was prepared. 60g alumina was impregnated with above solution by using a rotary evaporator. After drying further the impregnation product in 110°C in vacuum oven overnight, calcined at 400°C in a muffle furnace for 3 hours. The physical property of the catalyst is summarized in Table 2. There is only a minor change in the pore structure of the copper catalyst from the alumina support as shown in Figure 1. 22g of this catalyst was blended with 100 ml 3 mm diameter glass balls and loaded in the same reactor used in the Control Example 1. The catalyst activation was carried out in the same manner described in the Control Example 1.

The same feed used in the Control Example 1 was selectively hydrogenated to remove acetylenic impurities at 119 psig. For the first 26 hours on stream time, the feed hydrocarbon and hydrogen rates were 2.2 cc/min (3.6 WHSV) and 31.4 scc/min, respectively. Then the feed rates were changed to 3 cc/min for hydrocarbon (5.0 WHSV) and 27 scc/min for hydrogen rate for the next 24 hours on

stream time. After that, the feed hydrocarbon and hydrogen rates were 2.2 cc/min (3.6 WHSV), but maintained the hydrogen rate at 27 scc/min until the end of the run.

The test results of copper catalyst in the Example 5 and the Control Example 1 are illustrated in Figure 4 and 5. The Figure 3 demonstrates the superior catalyst activity and stability of the catalyst disclosed in this invention over the prior art. The Figure 5 demonstrates a superior butadiene yield of this invention over the prior art. The yields of 1,3-butadiene at the same conversion of the total alkynes over the catalyst disclosed in this invention are higher than those disclosed in the prior art. Also the Example 5 indicates that, if excess hydrogen is available after converting all the acetylenic compounds in the feed stream, the excess hydrogen causes the loss of 1,3-butadiene due to over-hydrogenation, suggesting that the excess hydrogen should be kept to minimal in the selective hydrogenation zone.

Table 1

ABD, g/cc	0.53
Single-point BET, m^2/g	157.5
Multiple-point BET, m^2/g	170.2
Meso Pore Area, m^2/g	170.2
Micro Pore Area, m^2/g	0
Cumulative Adsorption Surface area, m^2g	172.6
Cumulative Desorption Surface area, m^2/g	230.4
Total Pore Volume (cc/g)	
for pores less than 493 A° radius at P/P_0 = 0.9801	0.912
Cumulative Adsorption Pore Volume for pores (20 – 300Åradius)	0.852
Cumulative Desorption Pore Volume for pores (17.5 – 300Å radius)	0.930
Average Pore diameter,Å	214.4

Table 2

ABD, g/cc	0.58
Single-point BET, m^2/g	137.5
Meso Pore Area, m^2/g	147.7
Micro Pore Area, m^2/g	0
Cumulative Desorption Pore Volume for pores (17.5 – 300Å radius)	0.790

Example 6

The alumina used in the Example 5 was calcined at 700°C for 3 hours in air. A copper catalyst was prepared using this calcined alumina. The solution of 30g $Cu(NO_3)_2.2.5H_2O$, $Ni(NO_3)_2.6H_2O$, 0.047g $AgNO_3$, 0.396g $Cr(NO_3)_3.9H_2O$ and 0.396g $Co(NO_3)_2.6H_2O$ in 128 ml deionized water was prepared. 70g alumina was impregnated with above solution by using a rotary evaporator. After drying further the impregnation product at 110°C in a vacuum oven overnight, calcined it at 400°C in a muffle furnace for 3 hours in air. The ABD of the catalyst was 0.57 g/cc. 18g of this catalyst was blended with 100 ml 3 mm diameter glass balls and loaded in the same reactor in the Control Example. The catalyst was activated in the identical manner as in the Control Example 1.

A mixed C_4 stream composed of 444 wt ppm methyl acetylene, 825 wt ppm vinyl acetylene and 634 wt ppm ethyl acetylene, 55.36 wt % 1,3-butadiene, 0.12 wt % 1,2-butadiene, 6.39 wt % t-2-butene, 4.13 wt % c-2-butene, 16.84 wt % 1-butene, 12.38 wt % isobutene, 3.53 wt % n-butane, 0.97 wt % isobutane, and 0.09 wt % others was selectively hydrogenated to remove acetylenic impurities at 119 psig. In this example, the hydrocarbon and hydrogen rates were maintained at constant rates; 3 cc/min for hydrocarbon and 27 scc/min hydrogen. The test results of copper catalyst in the Example 6 and the Control Example 1 are illustrated in Figure 4 and 5 along the result from Example 5.

The Figures 4 and 5 clearly demonstrate the superior performance of the copper catalysts disclosed in this invention over the prior art.

Example 7

In this example, a catalytic distillation column is used for the selective hydrogenation of the acetylenic impurities in a mixed C_4 stream. A larger batch catalyst was prepared by using 240 grams of alumina in the exactly same manner described in the Example 5. The catalyst (99.88 grams) was loaded in a catalytic distillation column (1" diameter x 25' height). The height of the catalyst bed in the column was 6 feet. 80 inches of top and bottom of the catalyst bed was packed with ¼" saddles. The catalyst was activated in the same manner described in the Control Example 1 except that the flow rate of gases were increased proportionally based on the catalyst weight.

The acetylenic impurities in the same feed used in the Example 6 were removed by carrying out the selectively hydrogenation in the catalytic distillation mode. The hydrocarbon feed rate was 1.2 pounds per hour. The hydrogen rate was 1 scf per hour at the beginning of the run, but during the run it was changed to higher rates. The hydrocarbon and hydrogen feeds were fed at point of below the saddle packing. The result is illustrated in Figure 6. At the hydrogen rate of 3 scf per hour or higher, ethyl acetylene and vinyl acetylene in the feed were practically all removed. Near complete recovery of 1,3-butadiene was obtained. As shown in Figure 6, the catalyst was much more stable under the catalytic operation mode than the fixed bed operation.

Example 8

This experiment was carried out to demonstrate the beneficial effect of zinc oxide incorporation into the copper catalyst disclosed in this invention to improve the performance of the copper catalyst. A copper catalyst was prepared according to the identical procedure used in the Example 5. The mixed solution of 22.6g $Cu(NO_3)_2.2.5H_2O$, $Ni(NO_3)_2.6H_2O$, 0.04g $AgNO_3$, and 4.0g Zn $(NO_3)_2.6H_2O$ in 100 ml deionized water was prepared. 60g of the same alumina used in the Example 5 was impregnated with above solution by using a rotary evaporator. After drying further the impregnation product in 110°C in vacuum oven overnight, calcined at 400°C in a muffle furnace for 3 hours. 18g of this catalyst was blended with 100 ml 3 mm diameter glass balls and loaded in the same reactor used in the Control Example 1. The catalyst activation was carried out in the same manner described in the Control Example 1.

A mixed C_4 stream composed of 475 ppm methyl acetylene, 959 wt ppm vinyl acetylene and 731 wt ppm ethyl acetylene, 54.87 wt % 1,3-butadiene, 0.12 wt % 1,2-butadiene, 6.42 wt % t-2-butene, 4.16 wt % c-2-butene, 16.76 wt % 1-butene, 12.53 wt % isobutene, 3.56 wt % n-butane, 1.27 wt % isobutane, and 0.09 wt % others was selectively hydrogenated to remove the acetylenic impurities in it. The selective hydrogenation was carried out at the constant temperature 147°F and 119 psig. The constant hydrocarbon and hydrogen feed rates were used throughout the run; 3 ml/min (6.1 WHSV) and 27.1 scc/min. The result of this run is summarized in Figures

7 and 8. The beneficial effects of the zinc oxide incorporated into the copper catalyst on the catalyst performance are clearly demonstrated in this example.

Example 9

In this example, the usefulness of one of the preferred solvents disclosed in this invention, tetrahydrofuran (THF), is demonstrated. The copper catalyst (36 grams) prepared in Example 5 was loaded in the same reactor used in the Control Example 1. The mixed C_4 feed used in this example had the following composition; 20 ppm methyl acetylene, 588 ppm vinyl acetylene, 599 ppm ethyl acetylene, 44.51 wt % 1,3-butadiene, 0.07 wt % 1,2-butadiene, 6.29 wt % t-2-butene, 4.33 wt % c-2-butene, 15.97 wt % 1-butene, 18.04 wt % isobutene, 9.36 wt % n-butane, 1. 30 wt % isobutane, and 0.01 wt % others. After on 176 hours on stream time, the catalyst was washed to remove the polymers deposited on the catalyst with THF after flushing out the reactor with N_2 gas; 10 cc/min THF, 66.9 scc/min H_2 at 147°F and 200 psig for 1 hour and then at 157°F for 5 hours. After flushing out the reactor with N_2 gas, the selective hydrogen was continued. The constant temperature (147°F) and pressure (119 psig) were maintained during the run. The run conditions during this experiment are listed in Table 3.

The result of this experiment is illustrated in Figure 9. The break through of the acetylenic impurities occurred on 128 hours on stream as shown in Figure 9. But after washing the catalyst with THF, the product obtained under the same condition for the break-through contained no detectable amount of acetylenic impurities. Therefore, THF

Table 3

147°F and 119 psig

Hours on stream	0 – 26	26 – 50	50 – 74	74 – 98	98 – 128	128 – 152	152 – 176	THF	176 – 188.5
HC Feed rate, ml/min	2.9	5.8	2.9	2.9	5.8	7	7	wash	7
H_2 rate, scc/min	45	45	45	15	10	45	45	54.	45
					Break through of acetylenes				

is one of the preferred solvents for the catalyst regeneration. Also THF is one of the preferred solvents to be used for carrying out the selective hydrogenation using catalytic distillation column. When THF is used as the solvent in CD selective hydrogenation, THF can be fed to the distillation column above the catalyst bed or it can be feed to the column with the mixed C_4 feed stream. The different conditions

for the column operation will be needed for these two cases. In the latter case, the column will be operated under the total internal reflux condition with respect to THF. THF will be removed from the column as the bottom product for both cases and recycled to the column. However, a part of the recycle THF stream will be purified in a separator to avoid the heavies build-up in the recycle stream before returning to the column.

Example 10A

The copper catalyst prepared in the Example 5 was tested for the selective hydrogenation of the acetylenic impurities (7132 ppm total acetylenes) in the mixed C_4 feed used in the Control Example 2.18g of the catalyst was blended with 100 ml 3 mm diameter glass balls and loaded in the same reactor in the Control Example 1. The catalyst was activated in the identical manner as in the Control Example 1. The selective hydrogenation was carried out at a constant temperature 147°F and 119 psig. The hydrocarbon and hydrogen feed rates were 2.9 ml/min (5.87 WHSV) and 45 scc/min, respectively, for the first 66.5 hours on stream, and then changed to 1.4 ml/min (2.83 WHSV) and 24.1 scc/min, respectively.

Example 10B

A copper catalyst promoted with palladium was prepared according this invention. The alumina used in the Example 5 was calcined at 900°C for 3 hours in air. A mixed solution was prepared by dissolving 28.7g $Cu(NO_3)_2.2.5H_2O$, $Ni(NO_3)_2.6H_2O$, 0.04g $AgNO_3$, 0.34g $Cr(NO_3)_3.9H_2O$ and 0.34g $Co(NO_3)_2.6H_2O$ in 110 ml deionized water. The above calcined alumina (60g) was impregnated with this solution by using a rotary evaporator. After further drying the impregnation product at 110° in a vacuum oven overnight, it was calcined at 400°C in a muffle furnace for 3 hours in air. 5.469 grams of aqueous palladium(II) nitrate solution (Aldrich 38,004-0; 10 wt % $Pd(NO_3)_2$ in 10 wt % nitric acid) was sprayed on the copper catalyst spheres (29.762 grams) by using an atomizer, while the copper catalyst spheres were rolling around on the flat surface, to evenly coat the spheres with the palladium solution. It is very important to produce a fine mist of the palladium salt solution. The palladium solution sprayed product was calcined at 250°C for 2 hours in air. The ABD of the Cu/Pd catalyst was 0.52 g/cc. The analysis of this catalyst indicates 8.20% Cu, 0.71% Pd, 0.20% Ni, 0.11%Cr, and 0.17% Ag.

22g of this catalyst was blended with 100 ml 3 mm diameter glass balls and loaded in the same reactor used in the Control Example 1. The catalyst was activated by the following procedure; (1) heating the reactor to 230°F in 100 cc/min N_2 gas flow, (2) adding 200 cc/min H_2 to the N_2 gas flow and holding for 3 hours at 230°F, (3) shut off N_2 gas and increasing H_2 gas flow to 300 cc/min, (4) heating the reactor temperature to 572°F, holding for 3 hours at 572°F and then cooled the reactor to 147°F in 30 cc/min H_2 gas flow.

The acetylenic impurities in the same feed used in the Example 10A were removed by selective hydrogenation. The selective hydrogenation was carried out at a constant temperature 142°F. However, the hydrocarbon and hydrogen feed rates were 3.7 ml/min (6.1 WHSV) and 45 scc/min at the reactor pressure of 119 psig, respectively, for the first 73 hours on stream, and then changed to 6.1 ml/min (10.1 WHSV) and 74.2 scc/min at 108 psig, respectively. After 145 hours on stream, the catalyst was washed with benzene(10 ml/min) at 100°C and 108 psig in 74.2 scc/min H_2 flow for 5 hours. The selective hydrogenation was continued at the same condition just before the benzene wash for 24 hours, but benzene (0.6 ml/min) was co-fed to the reactor with the mixed C_4 feed. After that, the feed rates were changed to 10 ml/min mixed C_4 feed, 1 ml/min benzene, and 90 scc/min H_2 for the next 18 hours. And then the feed rates were increased to 15 ml/min mixed C_4 feed, 1.5 ml/min benzene, and 112 scc/min H_2 at the reactor pressure 95 psig for the next 30 hours. After that, the selective hydrogenation was carried out at a reduced hydrogen rate of 95 scc/min for 24 hours, while keeping other process parameters at the same condition. And then the feed rate was reduced to 10 ml/min mixed C_4 feed, 1 ml/min benzene, and 54 scc/min H_2 for the next 66 hours, while keeping other process parameters at the same condition.

The results of the Examples 10A and 10B are illustrated in Figure 10 and 11 along with the Control Example 2. As shown in Figure 8, the copper catalyst, which was not promoted with palladium, had very low activity in dealing with the high concentration of acetylenic impurities. But when the copper catalyst was promoted with palladium in the technique disclosed in this invention, the catalyst activity was dramatically improved. Surprisingly, the palladium promoted copper catalyst has far superior activity than the commercial Pd selective hydrogenation catalyst. Yet more

surprisingly the present palladium promoted catalyst has also a superior 1,3-butadiene yield at the same conversion of the acetylenes over the commercial palladium catalyst despite of its much higher activity. Also the deactivation rate of the palladium promoted catalyst was much better than the commercial Pd catalyst or the unpromoted copper catalyst. This example clearly demonstrates the superior performance of the palladium promoted copper catalyst for the selective hydrogenation of high acetylenic feeds over the palladium catalyst or unpromoted copper catalyst.

Example 11

Gamma alumina (obtained from UCI, 1/8 inch extrudates and about 260 m^2/g surface area) was ground to 10-20 mesh granules. According to the supplier of this alumina, the raw material of this alumina is identical to the alumina used in the Control Example 1. But this granular alumina has lower ABD (0.50 g/cc) than the alumina (0.792 g/cc ABD) used in the Control Example 1. A solution of 30g $Cu(NO_3)_2.6H_2O$, 0.93g $Ni(NO_3)_2.6H_2O$, 0.047g $AgNO_3$, 0.396 $Cr(NO_3)_3.9H_2O$ and 0.396 $Co(NO_3)_2.6H_2O$ in 128 ml deionized water was prepared. 70g of the granular alumina were impregnated with above solution by using a rotary evaporator. After drying the impregnation product in 110°C in vacuum oven overnight, calcined at 400°C in a muffle furnace for 3 hours. 18g of this catalyst was blended with 110 ml 3 mm diameter glass balls and loaded in the same reactor in the Control Example 1. The catalyst was activated by the following procedure; (1) heating the reactor to 230°F in 100 cc/min N_2 gas flow, (2) adding 200 cc/min H_2 to the N_2 gas flow and then holding for 3 hours at 230°F, (3) shut off N_2 gas and increasing H_2 gas flow to 300 cc/min, (4) heating the reactor temperature to 662°F and holding for 3 hours at 662°F and then cooled the reactor to 147°F in 30 cc/min H_2 gas flow.

The same feed used in the Control Example 1 was selectively hydrogenated to remove acetylene impurities at 119 pig pressure. For the first 29 hours on stream time, the feed hydrocarbon and hydrogen rates were 1.8 cc/min (3.6 WHSV) and 25.7 sc./min, respectively. Then the feed rates were increased to 2.4 cc/min for hydrocarbon (4.9 WHSV) and 34.3 sc./min for hydrogen rate for the next 42 hours on stream. After that, the feed rates was further increased to 3 cc/min for

hydrocarbon (6.1 WHSV), but hydrogen feed rate was lowered to 30 sc./min, until the end of the run.

The comparison of the test result of this experiment with those of Control Examples 1 and 4 is illustrated in Figures 12 and 13 to demonstrate of the effect of ABD of support aluminas on the catalyst performance. The catalyst prepared using lower ABD alumina, which means higher porosity, in this example outperformed the higher ABD aluminas used in Control Examples 1 and 4. The aluminas in this example and the Control Example 1 were prepared from the same raw materials. But the lower ABD alumina used in this example results in more effective catalyst in removing acetylenic impurities. The catalyst in this example has a better 1,3-butadiene yield than in the Control Example 1. The alumina used to prepare the catalyst in the Control Example 4 has the surface area falling in the preferred range of surface area disclosed in this invention. But the ABD of the alumina in the Control Example 4 is 0.98 g/cc, which is higher than the preferred ABD (<0.65g/cm^3) disclosed in this invention. The effectiveness of the catalyst in the Control Example 4 in removing acetylenic impurities approximately falls in between the Control Example 1 and the Example 11. There is little difference in the yield of the 1,3-Butadiene in the Example 11 and the Control Example 4.

Example 12

To demonstrate the superior performance of the palladium promoted copper catalyst for the selective hydrogenation of a feed containing relatively high concentration of acetylenic impurities, this example was carried out.

A copper catalyst promoted with palladium was prepared according to this invention. The alumina used in the Example 5 was calcined at 900°C for 3 hours in air. A mixed solution was prepared by dissolving 1.866g $Cu(NO_3)_2$ $2.5H_2O$ in a palladium nitrate solution prepared by diluting 4.61g 10 wt % $Pd(NO_3)_2$ solution in 10 wt % nitric acid (Aldrich 38,004-0: 10 wt % $Pd(NO_3)_2$) with 6.378g deionized water. 5.56g of this mixed solution was sprayed on 30g of calcined alumina spheres by using an atomizer, while the alumina spheres were rolling around on a flat surface and then the sprayed product was dried at 115°C in a vacuum oven. The dried product was calcined at 250°C for 2 hours in air.

18 g of this catalyst was mixed with 110 ml of 3 mm diameter glass balls and loaded in the same reactor used in the Control Example 1. The catalyst was activated in the same manner described in Example 11. The acetylenic compounds in the same feed used in the Control Example 3 were removed by carrying out the selective hydrogenation. The selective hydrogenation was carried out at the constant temperature of 142°F and 108 psig. The hydrocarbon feed rate was kept at 10 ml/min (20.2 WHSV) until the end of the run. However, variations of hydrogen flow rate in the range of from 44 scc/min to 90 scc/min were made during the run.

The results of this Example 12 and the Control Example 3 are illustrated in Figures 14 and 15. The superior catalytic activity of the palladium promoted copper catalyst over the traditional palladium catalyst is clearly demonstrated. Despite a higher feed rate in Example 12 of at least 4 times greater than that of Control Example 3, the palladium promoted copper catalyst is able to produce product containing less than 20 ppm C_4 acetylenes with a superior yield (expressed as recovery in Figure 14) of 1,3-butadiene over the traditional palladium catalyst in Control Example 3. The recovery of C_4 acetylenes is defined by 100% vs % conversion of C_4 acetylenes; e.g. 0 percent recovery of C_4 acetylenes is equivalent to 100% removal of C_4 acetylenes and 100%1,3-butadiene recovery is equivalent to 0% conversion of 1,3-butadiene.

The ratios of ethyl acetylene to vinyl acetylene in the products are illustrated in Figure 15. The palladium promoted copper catalyst has much higher reactivity toward to vinyl acetylene than the traditional palladium catalyst. The palladium promoted copper catalyst has approximately an order higher activity than the unpromoted copper catalyst. It was unexpected that the palladium promoted copper catalyst has several times higher activity than the traditional Pd catalyst and yet it has a superior selectivity retaining 1,3-butadiene.

The invention claimed is:

1. A catalyst for selective hydrogenation of acetylenes comprising a copper component and a component of at least one Group VIII metal component, a Ag, Au component or mixtures thereof on an alumina support comprising at least one of the properties of average pore diameter larger than 200Å or apparent bulk density of less than about 0.70g/cm^3.

2. The catalyst according to claim 1 comprising a component of Ag, Au component or a mixture thereof.

3. The catalyst according to claim 1 comprising at least one Group VIII metal component.

4. The catalyst according to claim 1 comprising a component of at least one Group VIII metal component and a Ag, Au or mixtures thereof component.

5. The catalyst according to claim 1 comprising a component of at least one Group VIII metal component, a Ag component and a Au component.

6. The catalyst according to claim 2, 3, 4 or 5 wherein the Group VIII component comprises Pd.

7. The catalyst according to claim 2, 3, 4 or 5 comprising a Zn component.

8. The catalyst according to claim 1 comprising an alumina support having average pore diameter larger than 200Å.

9. The catalyst according to claim 1 comprising an alumina support having an apparent bulk density of less than about 0.70g/cm^3.

10. A catalyst for the selective hydrogenation of acetylenes comprising a copper component at least one Group VIII metal component and a Zn component.

11. The catalyst according to claim 10 comprising a component of Ag, Au or mixture thereof.

12. The catalyst according to claim 10 comprising about 0.1 to 25 Wt% Cu.

13. A process for the selective hydrogenation of acetylenes comprising contacting a feed containing acetylenes in at least partial liquid phase with a catalyst according to claim 1 under conditions to selectively hydrogenate said acetylenes.

14. The process according to claim 13 wherein a soluble polymer is continuously deposited on said catalyst during said hydrogenation to reduced activity of said catalyst for the selective hydrogenation of acetylenes, and said hydrogenation

is intermittently interrupted and a solvent for said soluble polymer is contacted with said catalyst and remove a portion of said polymer and restore a portion of the activity of said catalyst for said selective hydrogenation.

15. The process according to claim 14 wherein said solvent comprises at least one of tetrahydrofuran, furan, 1,4-dioxane, ethers, gamma-butyrolactone, benzene or toluene.

16. A process for the selective hydrogenation of acetylenes comprising contacting a feed containing acetylenes in at least partial liquid phase with a catalyst according to claim 10 under conditions to selectively hydrogenate said acetylenes.

17. The process according to claim 16 wherein a soluble polymer is continuously deposited on said catalyst during said hydrogenation to reduced activity of said catalyst for the selective hydrogenation of acetylenes, and said hydrogenation is intermittently interrupted and a solvent for said soluble polymer is contacted with said catalyst and remove a portion of said polymer and restore a portion of the activity of said catalyst for said selective hydrogenation.

18. The process according to claim 17 wherein said solvent comprises at least one of tetrahydrofuran, furan, 1,4-dioxane, ethers, gamma-butyrolactone, benzene or toluene.

Figure 1

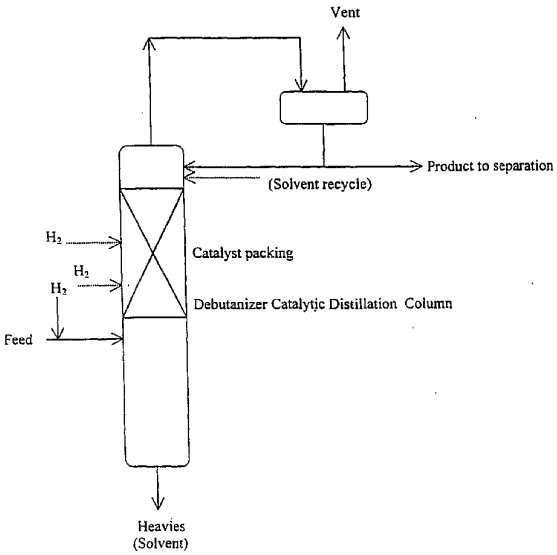
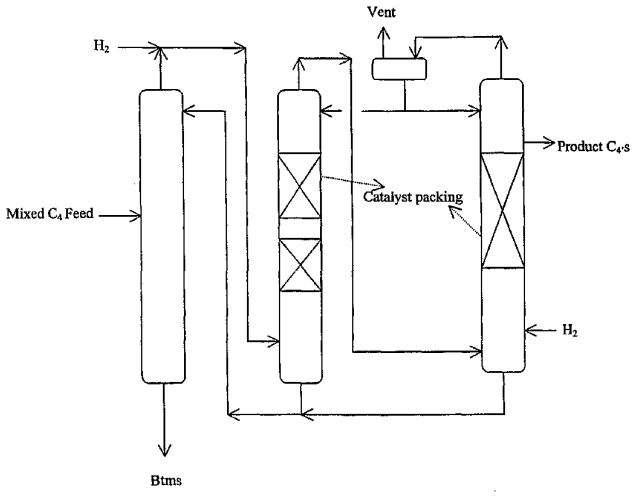

Vent
Product to separation
(Solvent recycle)
H_2
H_2
H_2
Catalyst packing
Debutanizer Catalytic Distillation Column
Feed
Heavies
(Solvent)

Figure 2



All reactants enter the catalyst sections in vapor phase only
May have two or more hydrogen feed

Figure 3
Nitrogen Desorption Pore Size Distribution
Example 5

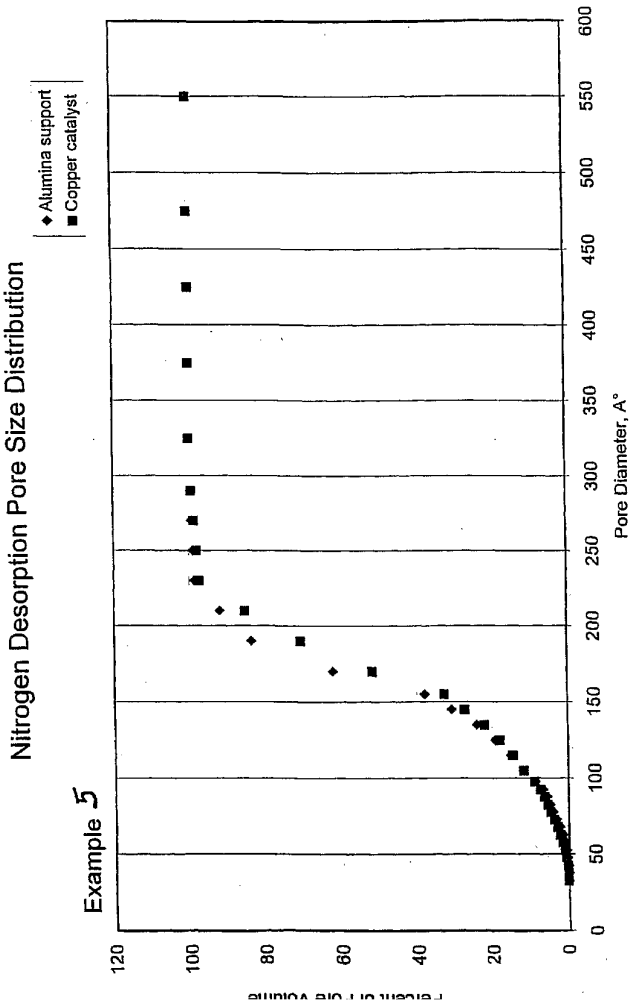


Figure 4

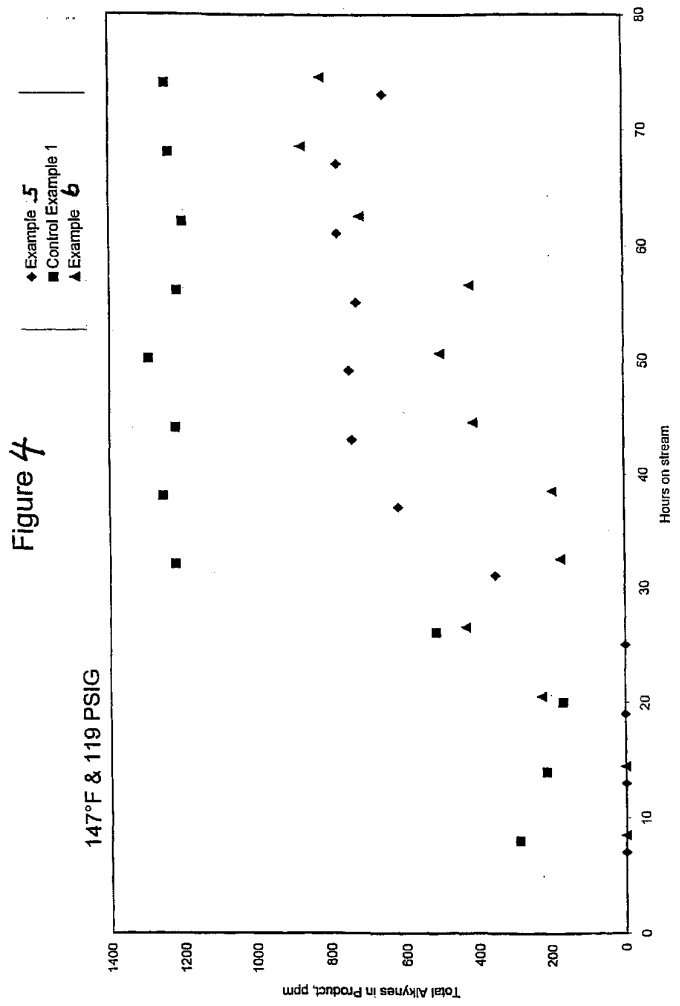

◆Example 5
■Control Example 1
▲Example 6
147°F & 119 PSIG
Total Alkynes in Product, ppm
Hours on stream
0
200
400
600
800
1000
1200
1400
0
10
20
30
40
50
60
70
80

Figure 5

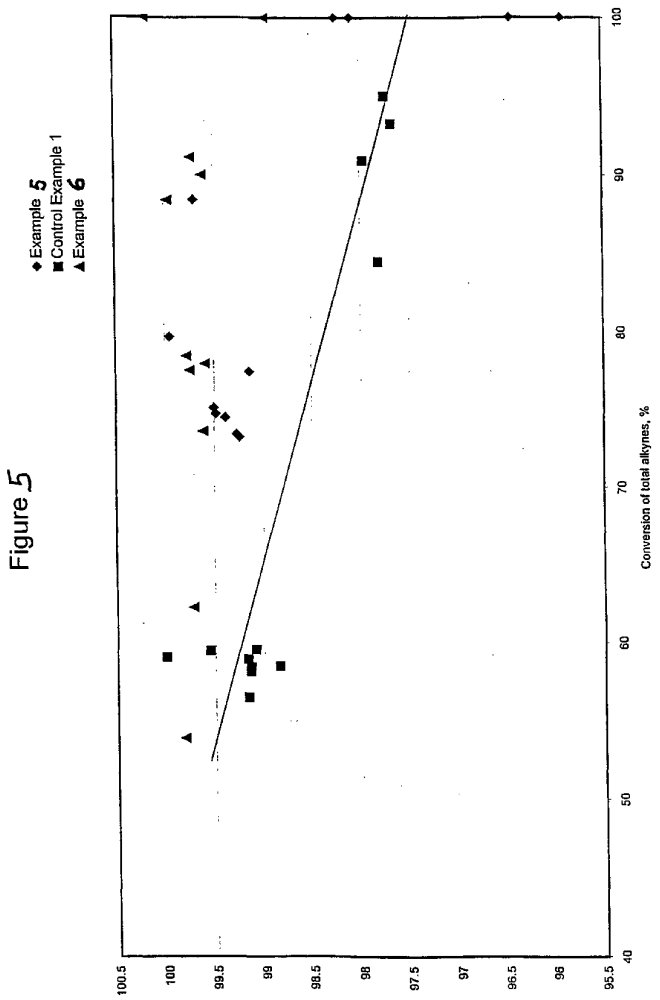
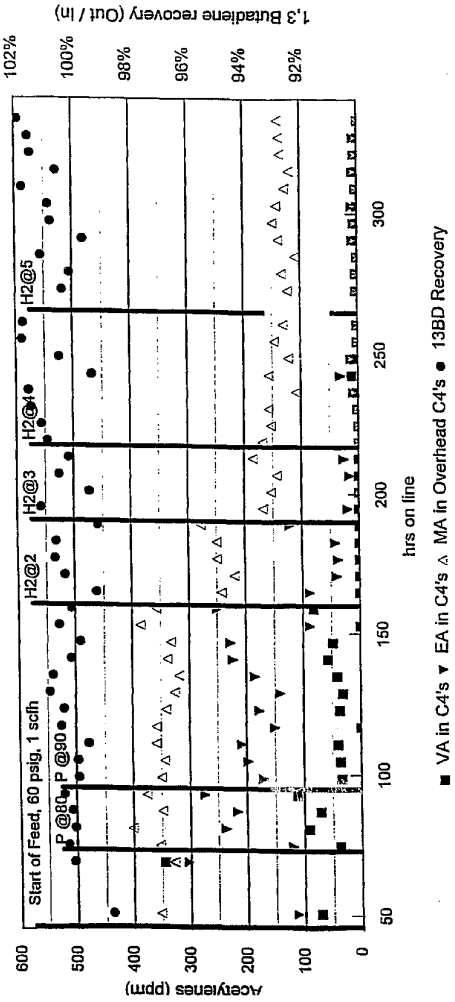

◆Example 5
■Control Example 1
▲Example 6
Conversion of total alkynes, %
100.5
100
99.5
99
98.5
98
97.5
97
96.5
96
95.5
100
90
80
70
60
50
40

Figure 6

Example 7



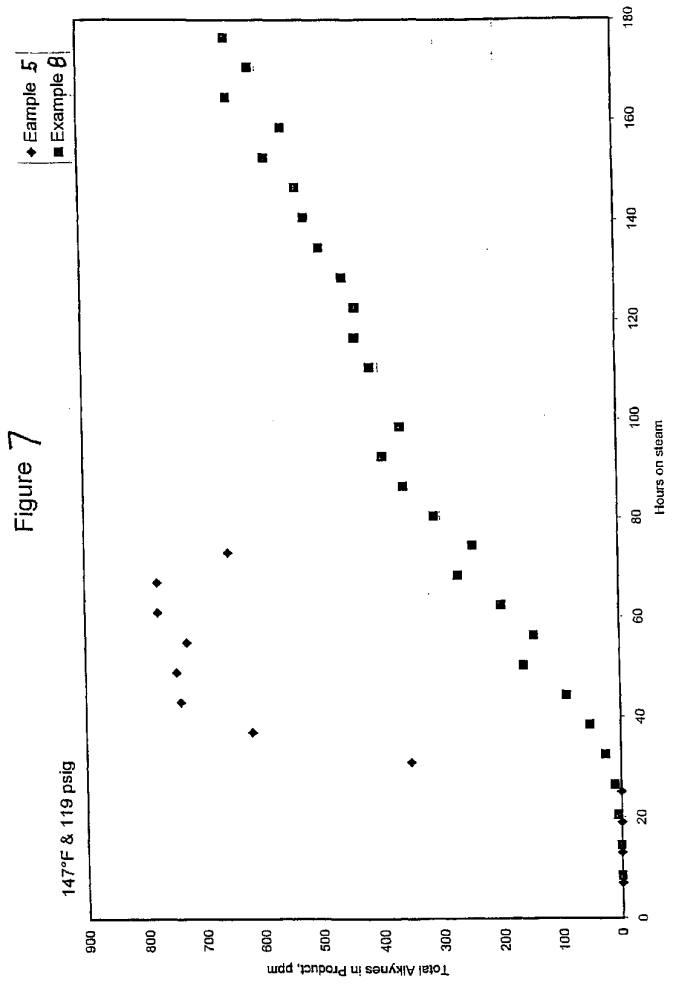

Example 5
Example 6
147°F & 119 psig
Total Alkynes in Product, ppm
Hours on steam
0
100
200
300
400
500
600
700
800
900
0
20
40
60
80
100
120
140
160
180

Figure 7

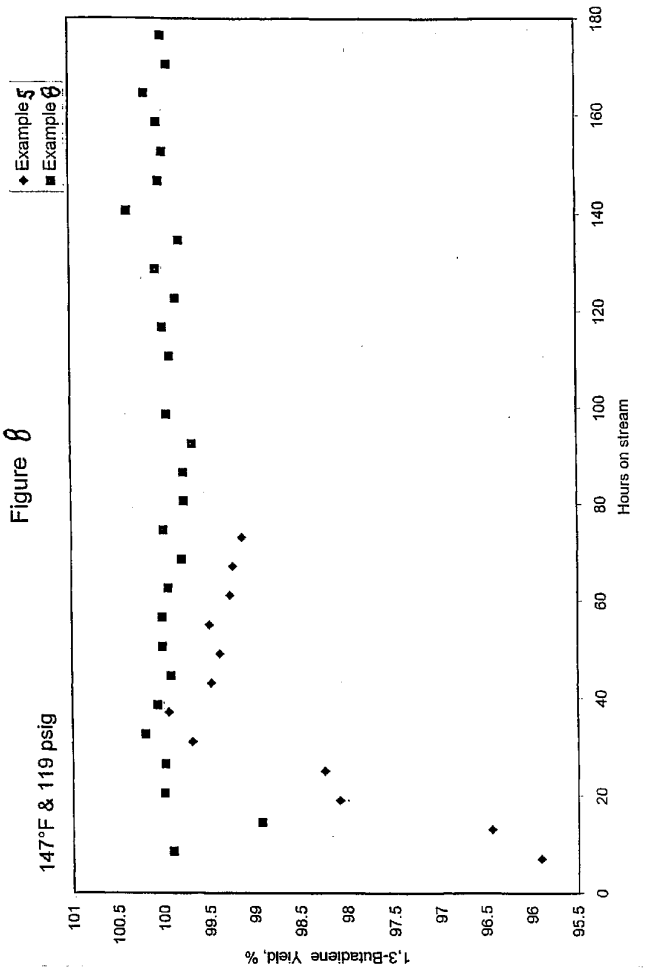

Example 5
Example 6
147°F & 119 psig
1,3-Butadiene Yield, %
Hours on stream
101
100.5
100
99.5
99
98.5
98
97.5
97
96.5
96
95.5
0
20
40
60
80
100
120
140
160
180

Figure 6

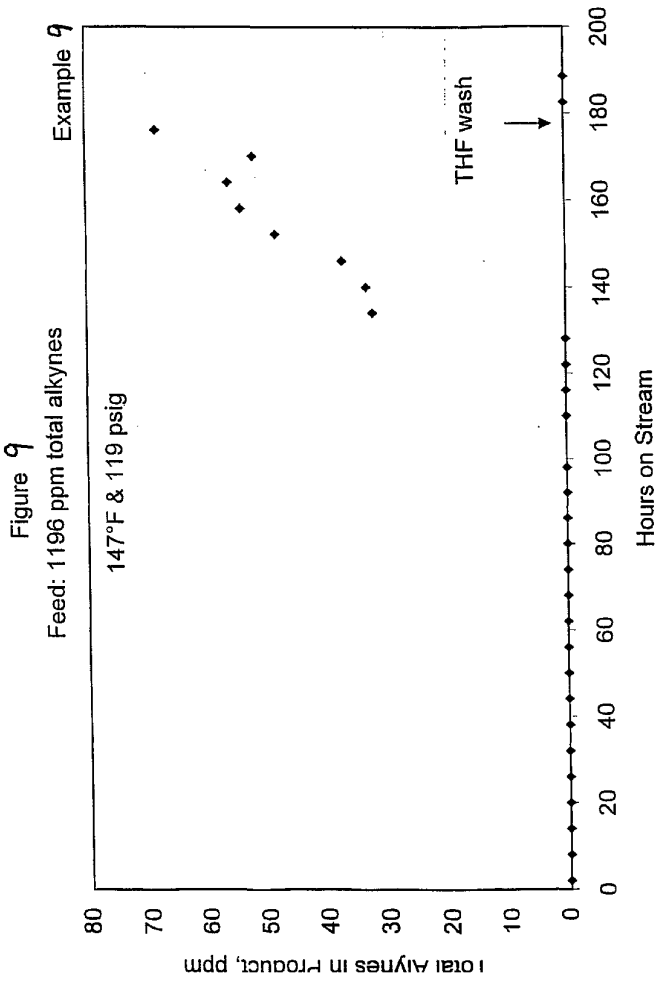
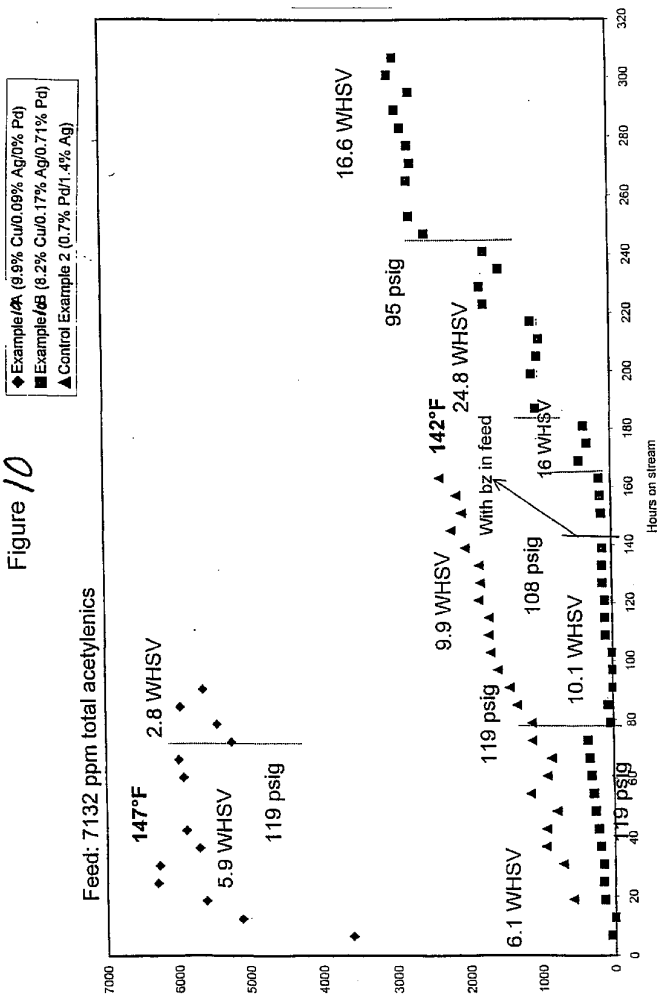

Example 9
Feed: 1196 ppm total alkynes
147°F & 119 psig
THF wash
Total Alynes in Product, ppm
Hours on Stream
0
10
20
30
40
50
60
70
80
0
20
40
60
80
100
120
140
160
180
200

Figure 9

Figure 10


◆Example/A (9.9% Cu/0.09% Ag/0% Pd)
■Example/B (8.2% Cu/0.17% Ag/0.71% Pd)
▲Control Example 2 (0.7% Pd/1.4% Ag)
Feed: 7132 ppm total acetylenics
147°F
2.8 WHSV
5.9 WHSV
119 psig
6.1 WHSV
119 psig
9.9 WHSV
142°F
With bz in feed
119 psig
10.1 WHSV
108 psig
16 WHSV
24.8 WHSV
95 psig
16.6 WHSV
Hours on stream

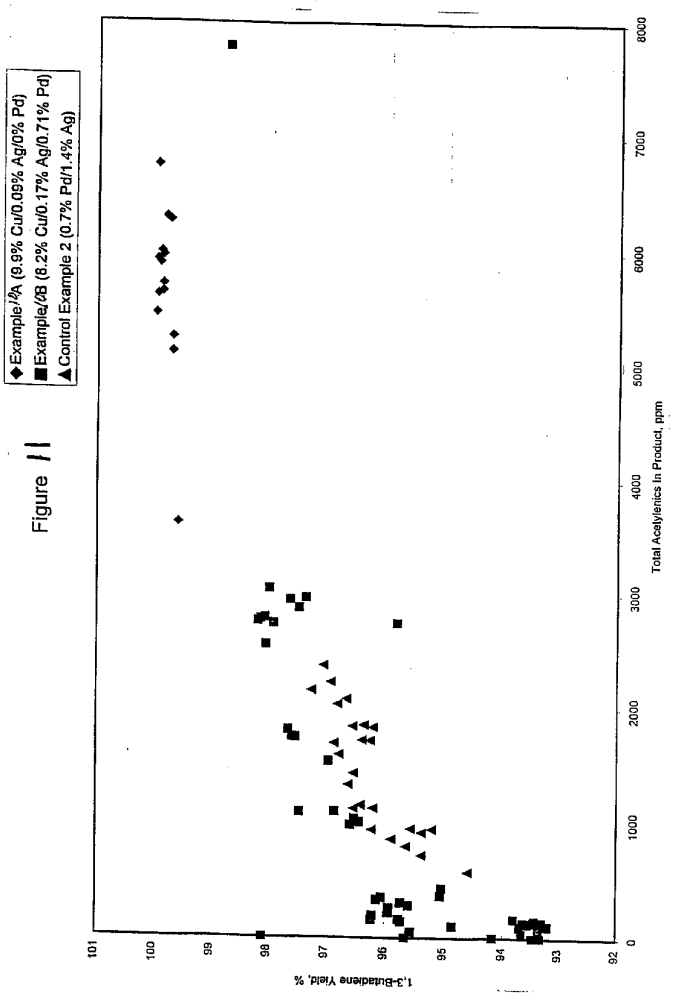

◆Example 4A (9.9% Cu/0.09% Ag/0% Pd)
■Example 4B (8.2% Cu/0.17% Ag/0.71% Pd)
▲Control Example 2 (0.7% Pd/1.4% Ag)
1,3-Butadiene Yield, %
Total Acetylenics In Product, ppm
101
100
99
98
97
96
95
94
93
92
0
1000
2000
3000
4000
5000
6000
7000
8000

Figure 11

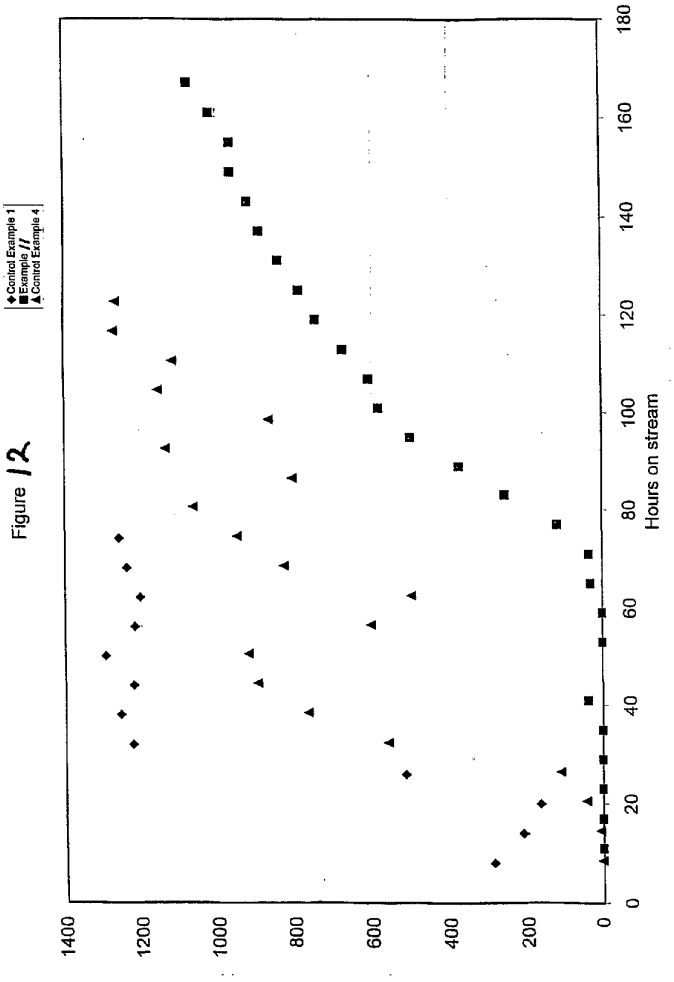

◆Control Example 1
■Example 11
▲Control Example 4
1400
1200
1000
800
600
400
200
0
0
20
40
60
80
100
120
140
160
180
Hours on stream

Figure 12

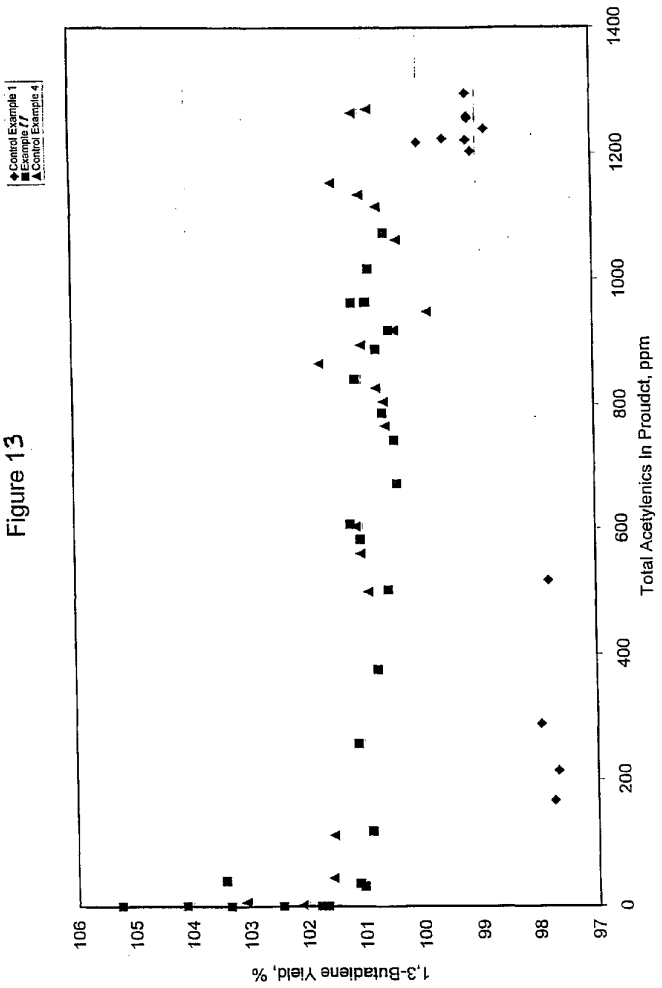

◆Control Example 1
■Example 11
▲Control Example 4
1,3-Butadiene Yield, %
106
105
104
103
102
101
100
99
98
97
0
200
400
600
800
1000
1200
1400
Total Acetylenics In Prouddt, ppm

Figure 13

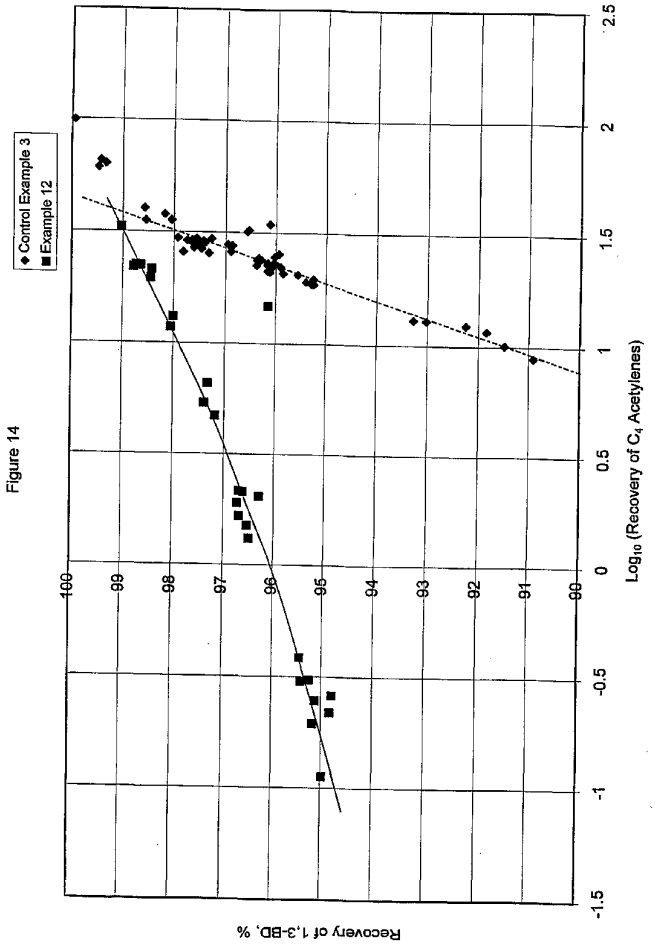

◆Control Example 3
■Example 12
Recovery of 1,3-BD, %
Log10 (Recovery of C4 Acetylenes)
100
99
98
97
96
95
94
93
92
91
90
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5

Figure 14

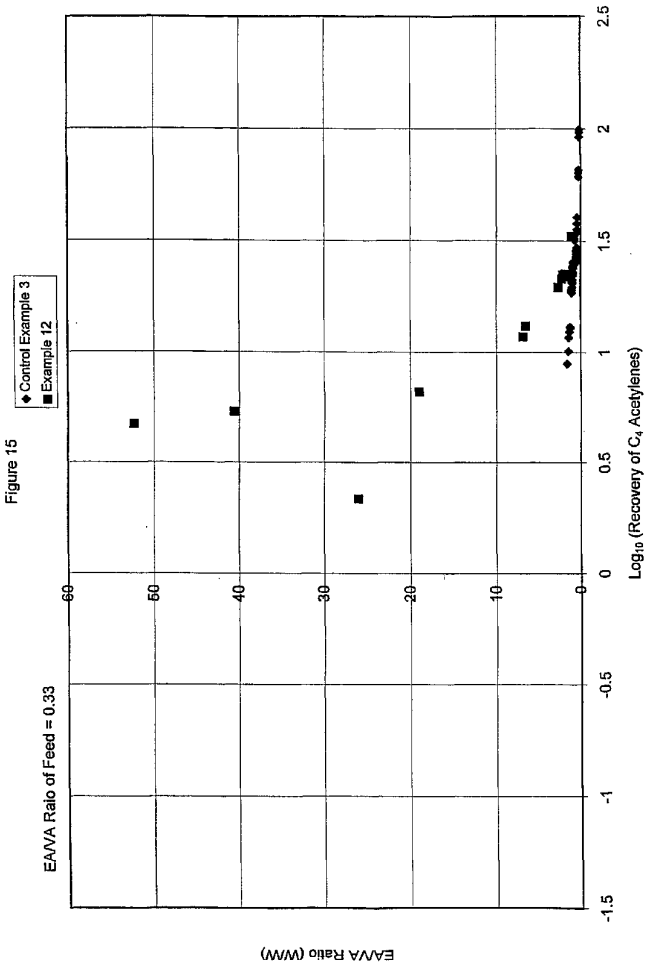

◆ Control Example 3
■ Example 12
EA/VA Ratio of Feed = 0.33
EA/VA Ratio (W/W)
Log10 (Recovery of C4 Acetylenes)
60
50
40
30
20
10
0
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5

Figure 15

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(74) Agent: JOHNSON, Kenneth, H.; P.O. Box 630708, Houston, TX 77263 (US).

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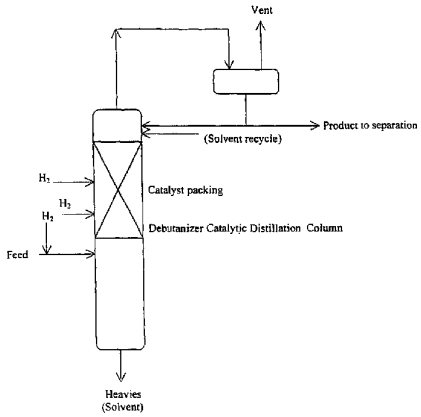
(54) Title: PROCESS FOR SELECTIVE HYDROGENATION OF ALKYNES AND CATALYST THEREFOR



(57) Abstract: Acetylenic compounds in olefin streams such as mixed 1,3-butadiene were selectively hydrogenated over the supported copper catalysts on highly porous supports such as alumina, silica, etc. The preferred supports have the average pore diameter larger than about 200Å, no micro pores, total pore volume larger than about 0.65 cc/g, and preferably less than about 230 m^2/g BET surface area. The copper catalysts were preferably promoted with the group VIII metal such as palladium to improve low activity of copper catalyst. The product stream typically contains less than 20 ppm total alkynes. Also the copper catalysts and the palladium promoted copper catalysts may be modified with zinc oxide to improve the performance of the catalysts. The reactor was loaded with two or more copper catalysts promoted with different levels of palladium. Preferably the copper catalysts were also modified with silver, gold or both silver and gold to reduce polymer formation by the copper component of the catalyst, improve the yield of olefins such as 1,3-butadiene, and prevent the loss of copper and/or palladium due to leaching out into the liquid phase of hydrocarbon.

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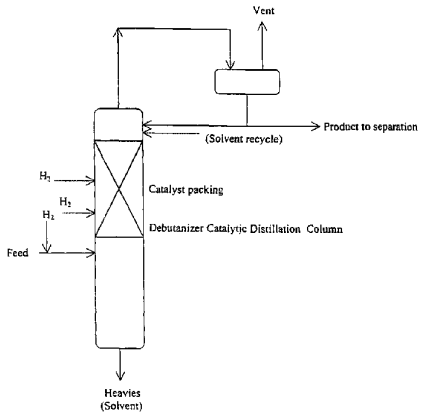

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CDT 1723/1702

Process For Selective Hydrogenation of Alkynes and Catalyst Therefor

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to the selective removal of more highly unsaturated compounds from mixtures of unsaturated compounds. More particularly the invention is concerned with the selective hydrogenation of acetylenic compounds from mixtures with dienes, such as 1,3-butadiene. The invention provides both novel catalysts and process for the selective hydrogenation of acetylenes in admixture with other unsaturated compounds.

Related Information

Supported copper catalysts and palladium catalysts have been preferred catalysts in cleaning up acetylenic impurities in olefin streams by selective hydrogenation. Copper catalysts selectively hydrogenate acetylenic compounds without substantial hydrogenation of the olefins and diolefins (designated herein as selectivity for retaining olefins), but have relatively low activity and short cycle time due to primarily polymer deposition on the catalyst surface. Palladium catalysts have excellent activity and much longer cycle time, but lower selectivity for the acetylenes than copper-based catalysts. To improve olefin selectivity of palladium catalyst, silver or gold has been added to palladium catalyst in minor amounts as modifier.

Fr 1 253 947 (1960) disclosed the copper catalyst for selective hydrogenation of acetylenic compounds in diolefin or monoolefin streams. The selective hydrogenation was carried out in vapor phase. 99.9 - 99.999% purity copper was supported on high surface area (25-300 m^2/g) supports such as gamma alumina. Copper content of the catalyst was in a range of 5 to 20%. The catalyst may contain less than 0.I% other metals (based on metal content of the catalyst) such as Fe, Ni, Ru, Rh, Pd, Ir or Pt as promoter. The selective hydrogenation was carried out in both vapor and liquid phase. U.S. Pat. Nos. 4,440, 956 (1984) and 4 493 906 (1985) disclosed the improved copper catalysts supported on the very specific alumina such as gamma alumina prepared from aluminum alkoxides, which are useful for

removing alkynes in liquid hydrocarbon streams. The patentee characterized the gamma alumina as having 60 to 90% of pores which should have a pore diameter between about 40 Å and 120 Å, and not more than 25% nor less than 2% had pore diameter between 1000 Å to 10,000 Å. The nitrogen surface area of the alumina was from about 68 to 350 m^2/g. The catalyst contained 3 to 13 weight % Cu. The catalyst contained minor amounts of at least one polyvalent activator metal selected from the group consisting of silver, manganese, cobalt, nickel and chromium. High purity of alumina, especially in terms of sodium (should be less than 0.15 wt %) and Fe_2O_3 (less than 0.06 wt %) contents, was claimed to be critical due to shrinkage of the surface area caused by frequent catalyst regeneration.

Ger 2 109 070 (1970) disclosed copper (26%)-zinc oxide catalyst for selective hydrogenation of acetylenic compounds in 1,3-butadiene stream in vapor phase.

U.S. patent 4,174,355 (1979) disclosed a process for removing (α-acetylenes from diolefin streams by nonselective hydrogenation. The alkynes were removed by contacting the feed steams with CuO and or Ag_2O supported on (α-alumina in the absence of hydrogen or oxygen.

U.S. patent 4,533,779 (1985) disclosed palladium/gold catalyst supported on supports such as alumina (1 to 100m^2/g) for selective hydrogenation of acetylenic compounds. The contents of palladium and gold in the catalysts were in the range of 0.03 to 1 weight % and 0.003 to 0.3 weight %, respectively.

U.S. patent 4,831,200 (1989) disclosed the process for the selective hydrogenation of alkynes in olefin streams such as mixtures with 1,3-butadiene. The selective hydrogenation was carried out in two steps in sequence. In the first step, the hydrocarbon feed was passed at least partially in liquid phase with hydrogen over the palladium catalyst such as that disclosed in U.S. 4,533,779 discussed above. In the second step, the product stream from the first step was passed again at least partially in liquid phase with hydrogen over the copper catalyst such as that disclosed U.S. patents 4,493,906 and 4,440,956 discussed above to produce significantly reduced alkyne concentration in the final product stream.

U.S. patent 5,877,363 (1999) disclosed the process for the selective hydrogenation of acetylenic impurities and 1,2-butadiene in mixed olefin rich C_4 streams by using supported hydrogenation catalysts such as Pt and Pd.

In general, the palladium catalysts are very active compared with the copper catalysts for selective hydrogenation of acetylenic compounds in the olefinic steams. But the palladium catalysts exhibit low selectivity for retaining diolefins, such as 1,3-butadiene, when one is trying to remove high concentrations (>2000 ppm) of total alkynes to less than about 500 ppm total alkynes in the streams, especially when the acetylenes are reduced to less than 200 ppm. The non selectivity of palladium catalysts is not desirable in commercial practice, because it resulting in a loss of 1,3-butadiene.

On the other hand, the copper catalysts are highly selective in retaining diolefins such as 1,3-butadiene by being very selective to acetylenes hydrogenation. But the activity of copper catalysts is slow. And the catalyst cycle time is undesirably short for the feed streams, which contain higher than about 2000 ppm total alkynes due to fast deactivation caused by the deposition of polymeric material on the catalyst surface, Even though the hydrogenation is carried out in liquid phase, some of the polymers deposited on the copper catalyst has little solubility in the liquid product stream under the selective hydrogenation condition. Due to these two reasons, the copper catalysts need improvement for the selective hydrogenation of the mixed olefin feeds, which contain relatively high concentration of total alkynes.

SUMMARY OF THE INVENTION

The present invention includes a catalyst comprising a copper component containing from about 0.1 to 25 wt percent Cu, preferably 0.2 to 20 wt %; a palladium promoter in a range of 0 to 2 wt %, preferably 0 to 1 wt %; a silver or gold modifier is in a range of 0 to 15 wt %, preferably 0 to 10 wt %; and a zinc oxide modifier is in a range of 0 to 25 wt %, preferably from 0 to about 15 wt %. The silver modifier moderates the catalyst activity, and improves the olefin yield and the cycle time. The zinc oxide modifier improves the olefin yield such as 1,3-butadiene with small improvement in the catalyst activity. The zinc oxide modified copper catalysts is especially very effective for removing vinyl acetylene impurity with extremely high yield of 1,3-butadiene. In a preferred embodiment the catalyst components are deposited on a support.

The preferred supports have the average pore diameter larger than about 200Å, no micro pores, total pore volume larger than about 0.65 cc/g, and preferably

less than about 230 m^2/g BET surface area. The copper catalysts are preferably promoted with the Group VIII metal such as palladium to improve low activity of copper catalyst. The product stream typically contains less than 20 ppm total alkynes. Also the copper catalysts and the palladium promoted copper catalysts may be modified with zinc oxide to improve the performance of the catalysts. The reactor was loaded with two or more copper catalysts promoted with different levels of palladium. Preferably the copper catalysts were also modified with silver, gold or both silver and gold to reduce polymer formation by the copper component of the catalyst, improve the yield of olefins such as 1,3-butadiene, and prevent the loss of copper and palladium due to leaching out into the liquid phase of hydrocarbon.

The process of removing acetylenic compounds by contact hydrocarbon streams containing small amounts of acetylenic compounds with the catalyst of the invention in various arrangements and configurations is also part of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic presentation of CD reactor having the present copper catalyst in the upper portion for selective hydrogenation of acetylenes.

Fig. 2 is a schematic presentation of CD reactor having the present copper catalyst in the upper portion for selective hydrogenation of acetylenes and group VIII catalyst in the lower portion to react mercaptans and diolefins.

Fig. 3 is a graphic presentation of the pore distribution of alumina support and catalyst of Example 5.

Fig. 4 is a graphic presentation of the total product alkynes in the products of Examples Control 1, 5 and 6.

Fig. 5 is a graphic presentation of the total 1,3-butadiene product yield of Examples Control 1, 5 and 6.

Fig. 6 is a graphic presentation of the results of Example 7 in CD.

Fig. 7 is a graphic presentation of total alkynes in the products of Example 5 (non CD) and Example 8 (CD).

Fig. 8 is a graphic presentation comparing Example 5 (non CD) 1.3-butadiene product and Examples 8 (CD).

Fig. 9 is a graphic presentation of the benefit of solvent treatment of the used catalyst.

Fig. 10 is a graphic presentation comparing Examples 10A an 10B to show the benefit of Pd promoted Cu.

Fig. 11 is a graphic presentation comparing Examples 10A and 10B to show the benefit of Pd promoted Cu on 1,3-butadiene production.

Fig. 12 is a graphic presentation of the benefits of ABD according to the present invention for acetylenes removal comparing Control Examples 1 and 4 and Example 11.

Fig. 13 is a graphic presentation of the benefits of ABD according to the present invention for 1,3-butadiene product comparing Control Examples 1 and 4 and Example 11.

Fig. 14 is a graphic presentation of the benefits of the palladium promoted copper catalyst comparing Example 12 with Control Example 3.

Fig. 15 is a graphic presentation of the chemical fingerprint differentiating the palladium promoted copper catalyst from traditional palladium catalyst by comparing Example 12 with Control Example 3.

DETAILED DESCRIPTION

The selective hydrogenation is preferably carried out at least partially in liquid phase for example by employing a catalytic distillation (CD) unit(s). Therefore, it is highly desirable to provide a new process and improved copper catalysts so that the selective hydrogenation can be carried out in a single step with higher throughput rate and yet maintaining high selectivity retaining olefins such as dienes and long catalyst life. In this invention, this objective is accomplished by carrying out the selective hydrogenation in a single reactor with the highly active, yet highly selective copper catalysts. The selective hydrogenation is preferably carried out at least partially in liquid phase by employing a catalytic distillation (CD) unit. The distillation column is loaded with two or more copper catalysts promoted with different levels of elements in the Group VIII such as palladium, ruthenium, nickel, etc and also modified with zinc oxide and an element in the Group IB. The preferred promoter is palladium. Promoting copper catalyst with palladium is very desirable in dealing with high acetylenic impurities containing feeds. The present data indicates that copper

becomes much more active by alloying with palladium with small loss in the selectivity retaining olefins such as 1,3-butadiene or 1-butene. By alloying copper with palladium, the chemical nature of the copper-palladium catalyst is changed from the traditional palladium or palladium-silver catalysts. The nature of change is demonstrated in the Example 12. The ratio of ethyl acetylene to vinyl acetylene in the product stream from this invention is much higher than the product from the traditional palladium catalysts, because the copper-palladium catalyst has quite different chemical reactivity toward to vinyl acetylene and ethyl acetylene from the traditional palladium or palladium-silver catalyst. Therefore, the difference in the ratios at a given conversion of C_4 acetylenes is the fingerprint differentiating the chemical catalytic nature of the copper-palladium catalyst from the traditional palladium catalysts.

The copper catalysts may be loaded in the debutanizer distillation column to provide a CD reactor, in dealing with a mixed C_4 feed stream to produce a clean 1,3-butadiene rich product. The feed stream to the catalytic distillation column is preferably fed to the middle section of the column below the catalyst bed. The product is recovered as overhead product. The heavier product is recovered as bottom product. The palladium content of the copper catalysts loaded in the CD reactor gradually decrease as moving up from the bottom section to the top section of the catalyst bed. The catalysts are loaded above the feed point to the distillation column. Hydrogen is fed together with hydrocarbon feed or separately to a position at the bottom section of the distillation column. The optimum ratio of hydrogen to the total alkynes in the catalytic reaction zone depends on the Cu content of the catalyst as wells Cu/Pd weight ratio. Therefore, preferably hydrogen is fed to two or more positions along the catalytic distillation column or the fixed bed depending on the compositions of the catalysts in reactor. Also the palladium component of the catalyst improves the catalyst cycle time. Although it is not known how this additional benefit of the copper catalysts promoted with Pd occur, it may be that unsaturated precursors to polymeric materials are more effectively hydrogenated resulting in slower or little deposition of polymeric material on the copper catalysts. The polymeric materials may have a higher solubility in the product steam than the polymers formed on the unpromoted copper catalysts. Consequently, the precursors

and polymeric materials are effectively washed off from the catalysts to the bottom of the catalytic distillation column resulting in continuously renewed, cleaner catalyst surface. Preferably the copper component of the catalyst is modified with an element of Group IB such as silver and/or gold or both to reduce further polymer formation to improve the selectivity of diene and improve slowly leaching out the copper and palladium metals from the catalyst.

The catalyst may be modified further with zinc oxide to improve the catalyst activity, the yield of olefins such as 1,3-butadiene, the catalyst cycle time, and reduce the loss of copper and palladium due to slowly leaching out from the catalyst. In the case of the Cu-Zn-Al methanol synthesis catalyst prepared by co-precipitation of mixed solution of nitrate salts, Cu(II) ions dissolves into zinc oxide phase of the copper-zinc oxide-alumina catalyst (prepared by co-precipitation technique) and their concentration could be as high as about 25 at. % (T. M. Yurieva, et al. React. Kinet. Catal. Lett., 29, pp. 55-61, 1985). It was observed that all the copper catalysts disclosed in this invention have high content of active hydrogen species that can hydrogenate olefins in the absence of hydrogen regardless of whether or not the catalysts contain zinc oxide.

The hydrogenation may be carried out in two steps. For example, the selective hydrogenation can be carried out with two CD reactors, or a combination of a CD reactor and a fixed bed reactor, or two fixed bed reactors as shown in Figure 2. In the fixed bed reactor operation, two or more reactors may be needed, to remove the exothermic heat of the hydrogenation reaction by cooling the reactor effluent stream from the first reactor prior to entering the second reactor. One may recycle the reactor effluent in fixed bed reactor operation to dilute the heat of the hydrogenation reaction. Optionally, material in which the polymer deposited on the catalyst surface is soluble may be used to wash off the polymer from the catalyst in either the reactive distillation mode or the straight pass mode. Examples of such solvents include tetrahydrofuran, furan, 1,4-dioxane, ethers, gamma-butyrolactone, benzene, toluene or mixtures of thereof. After separating products from the solvent, the solvent is recycled back to the reactor as shown in the Figure 1. Another technique to prolong the catalyst life is washing the catalyst intermittently with a liquid solvent at temperatures in the range of about 40°C to 350°C to remove deposited polymers

from the catalyst. Optionally a small amount of hydrogen gas is passed through the catalyst bed with solvent during washing off the polymers from the catalyst. When the selective hydrogenation of actelyenes in the C_4 streams is carried out in the CD mode, if the boiling point of the solvent is higher than about 100°F, the solvent can be added to the top of the catalyst zone of the catalytic distillation reactor and the solvent flows down to the bottom of the column. In a straight pass reactor the solve may be fed with the reactant feed stream to the reactor. During both modes of operation, it is desirable to apply sufficient pressure so that at least 0.2 mole% of the acetylenes in the feed stream is in the liquid phase which comprises solvent and hydrocarbons in the reaction zone.

The preferred supports to be used for the preparation of the catalyst in this invention are mesoporous materials and should have relatively large pore volume. As the average pore diameter of a supporting material increases, the pore volume increases as well, but both the surface area and ABD (apparent bulk density often called packed density) of the material decrease. Preferably the supports will have no micro pores, preferably no pores less than about 30Å diameter. When the deposition of heavy material on the catalyst surface causes the catalyst deactivation and deterioration of the selectivity of a desired material due to over-reaction, generally pore size distribution and size of pores play important roles for the catalyst performance. One of preferred supports in this invention is transition alumina. The pores of the desired alumina are mostly composed of pores larger than 100Å diameter. About 85%, preferably about 90% of pores will have the pore diameter larger than 100Å determined by nitrogen porosimetry. The preferred alumina will have the average pore diameter larger than about 100Å, preferably larger than 120Å, total pore volume larger than about 0.65 cc/g (determined by nitrogen porosimetry), preferably larger than 0.70 cc/g, and preferably the BET surface area of less than about 230 m^2/g, most preferably from 30 to 200 m^2/g, and the apparent bulk density (ABD) less than about 0.70 g/cm^3. The pores of alumina are composed of various size pore diameters. Within a certain range of alumina surface area, the pore distribution of alumina can be manipulated depending on how the aluminas are prepared and calcined. Unlike the alumina disclosed in U.S. patent 4,440,956, the preferred alumina in this invention will have at least 30% , preferably at least 50% of

the pores larger than 100Å diameter, and a total pore volume larger than about 0.65 cc/g, preferably about 0.75 cc/g.

The preferred alumina disclosed in this invention can be prepared by a number of techniques well known to whom skilled in arts preparing so called active aluminas. One of the preferred aluminas disclosed in this invention can be prepared by so-called oil dropping gelation technique. The examples of the prior arts are disclosed in U.S. 2,620,314 (1952), and 4,273,735 (1981). The spherically shaped alumina is prepared from aluminum hydroxychloride sol prepared by digesting aluminum metal in aqueous hydrochloric acid solution. Spherically shaped alumina sol materials, in the form of droplets, are gelled in basic liquid oil phase followed by aging, washing, drying, and calcining to transition state aluminas at various temperatures depending on the desired property of alumina. Alternatively the preferred spherically shaped alumina also can be prepared by oil dropping gelation technique using the dispersed boehmite or pseudoboehmite alumina sols. The example of the prior art is disclosed in U.S. 4,179,408 (1979). The alumina sols are prepared by dispersing suitable boehmite, pseudoboehmite or mixtures of boehmite and pseudoboehmite aluminas in acidic water. The pseudoboehmite or boehmite raw materials are obtained by hydrolyzing aluminum alkoxides and crystallizing or reacting sodium aluminate with aluminum salts such as aluminum sulfate and crystallizing. Various boehmite aluminas or dispersed boehmite aluminas sols are available in market place. Condea is one of the suppliers. To prepare the preferred spherical alumina whose pore structure is disclosed in this invention, Disperal HP 14/2, Dispal 11N7-80, Dispal 23N4-20, Disperal HP 14, Deperal 40, Pural 200, Pural 100, Pural NG, etc. or mixtures of these can be used. Other boehmite aluminas such as Catapal C1, Pural SB, Disperal P2, etc are not preferred raw materials for the preparation of the preferred alumina disclosed in this invention. These materials yield the like aluminas disclosed in the U.S. patents 4,493,906 and 4,440,956.

The preferred alumina in extrudate form can also prepared by extruding the preferred boehmite aluminas discussed above and calcining at elevated temperatures from about 550°C to 1200°C. Generally transition aluminas are various mixtures of crystalline aluminas such as amorphous, γ, χ δ, η, ρ, θ, α, etc and their surface area tends to shrink by repeated exposures to high temperature

atmosphere due to slow crystallization to more stable crystal forms. Especially this surface area shrinkage accelerates in the presence of moisture in atmosphere or trace amount of sodium in alumina or both. If gamma alumina is the desired form, the calcination is usually carried out at temperatures from about 550°C to 700°C. Unlike the aluminas disclosed in U.S. 4,493,906 and 4,440,956, the alumina supports prepared in this oil dropping gelation technique using aluminum hydroxychloride sols contain a very small amount of chlorine. A small amount of sodium or chlorine in alumina disclosed in this invention usually doesn't cause serious problem for the catalytic distillation operation or fixed bed operation with solvent, because of long catalyst cycle time.

The physical shapes of the preferred aluminas in this invention are spheres, extrudates, pellets and granules which have diameter of less than about ¼ inches, preferably 1/8 inches and less than about ½ inches length, preferably less than ¼ inches length for extrudates or pellets.

The copper component of the catalyst is put on the preferred alumina by various impregnation techniques with aqueous solution of cupric salts such as cupric nitrate, cupric acetate, etc. The impregnation product is calcined at from about 100 to 500°C, preferably from 200 to 400°C to decompose the salts resulting in copper oxide-alumina product. The silver and zinc oxide modifiers are incorporated into the catalyst by co-impregnation of a silver salt such as silver nitrate and a zinc salt such as zinc nitrate with copper salt. Optionally they are incorporated into the copper catalyst by double impregnation. The zinc oxide or both silver and zinc oxide modifiers are put on alumina support prior to impregnating the solution of a copper compound. The impregnation product is calcined at from about 100 to 650°C, preferably from 100 to 600°C to obtain the copper oxide-silver oxide-alumina catalyst or the copper oxide-silver oxide-zinc oxide-alumina catalyst. Still another technique can be used to prepare the zinc oxide modified copper catalyst by dropping the alumina sols, which contain a desired amount of zinc salt or both zinc and copper salts, into basic oil phase to form gels, followed by aging, washing and calcining at a temperature range of 450° to 1200°C.

The palladium promoter is incorporated into the catalyst by co-impregnating the palladium compound solution such as palladium (II) nitrate, palladium (II) acetate,

palladium (II) acetylacetonate, etc. with copper salt solution or a solution containing copper salt and silver salt. Although various impregnation techniques can be used, the preferred impregnation technique of the palladium compound solution or the mixed solutions of palladium compound and copper compound or palladium compound, copper compound and silver compound or palladium compound, copper compound, silver compound and zinc compound is spray coating impregnation by using an atomizer. It is highly desirable to spraying the solutions uniformly on supports. It is also highly desirable to create a fine mist of the palladium solutions using a compressed gas atomizer. When various palladium solutions are spray coated on supports such as alumina, the desired volume of the solution is less than about 90 volume % of the total pore volume (weight of support multiplied by the pore volume per unit weight of support) of the support to be impregnated, preferably less than about 85 volume %.

When highly active copper catalyst promoted with palladium is prepared, the impregnation of catalyst components can be carried out in either a single step or two steps. In the two step impregnation, the impregnation technique, for the first step, alumina support is impregnated with a solution of copper compound or a mixed solution containing copper and zinc compounds or copper, zinc and silver compounds or zinc and silver compounds by using usually incipient pore impregnation technique, followed by drying at a temperature from about 100 to 250°C and calcination at a temperature from 250 to 700, preferably from 300 to 550°C. In the second step the product from the first step is impregnated with a solution of palladium compound, preferably a mixed solution of palladium and copper compounds or palladium, copper and silver compounds or palladium, copper, zinc and silver compounds or palladium, silver and zinc compounds by using spray coating technique with an atomizer, followed by drying at a temperature from 100 to 250°C and calcining at a temperature from about 250 to 650°C, preferably from 300 to 550°C.

Another preferred technique incorporating palladium into the copper catalyst is the spray-coating impregnation of a solution of a palladium compound or a mixed solution of a palladium compound such as palladium nitrate and a silver compound such as silver nitrate, while the copper catalyst spheres are rolling down a flat

surface tilted at a proper angle, on the copper oxide-alumina catalyst, the copper oxide-alumina, the copper oxide-zinc oxide-alumina catalyst or the copper oxide-silver oxide-zinc oxide alumina catalyst. Relatively high loading (>0.15 wt %) of palladium on the copper catalyst is desired for processing the feeds which contain relatively high content (>~4000 ppm) of total acetylenic compounds. A combination of co-impregnation and the spray-coating impregnation is the most desired technique for high palladium loading on the catalyst. It is very important to produce a fine mist of the palladium solution for the spay-coating impregnation. If the copper catalyst, which is promoted with more than about 0.15% Pd, is desired, a combination of co-impregnation and spray coating impregnation is generally preferred. The impregnation product is calcined in air at from about 100 to 400°C, preferably from 100 to 350°C to prepare the copper, the copper-silver or the copper-silver-zinc catalysts promoted with palladium.

Optionally the catalysts can be prepared by impregnating mixed solutions of metal salts on the alumina powders which have the physical characteristics of preferred supports described above. The raw materials preparing such alumina powders are suitable boehmite powder and pseudoboehmite powders such as Disperal HP 14/2. The raw materials are calcined at temperatures from about 400°C to about 750° prior to the impregnation. The impregnation products are calcined at temperature from about 250° to 550°C in air and shaped to desired size of extrudates or pellets. Optionally the impregnation products are shaped to extrudates or pellets and then the shaped materials are calcined in air at elevated temperature from about 250°C to 550°C in air.

The catalyst activation is carried out at from about 60 to 400°C, preferably from 100 to 350°C in the gas flow containing hydrogen. The content of hydrogen in the gas is gradually increased during the activation from about 5 volume % to 50 volume % or more in the inert gas such as nitrogen. During the catalyst activation, a sufficient amount of gas flow is preferred so that no water vapor condensation on the catalyst would occur. The length of activation depends on the amount of the catalyst in reactor, the hydrogen content in the gas and the activation temperature. In laboratory, from 30 minutes to about 10 hours is sufficient for less than about 100 grams catalyst. In commercial practice, generally much longer activation time would

be needed. After the catalyst activation, the residual hydrogen in the reaction zone is flushed out with inert gas. At the start-up of the selective hydrogenation, the content of unsaturated compounds in the feed stream should be kept at very low level in the catalytic reaction zone by using inert diluent such as saturated hydrocarbons until most of hydrogen content in the activated catalyst is consumed. Due to relatively high content of copper on the catalyst, the activated catalyst contains relatively large amount of active hydrogen, which could cause run away temperature in the catalyst bed.

Protecting the selective hydrogenation catalysts such as copper catalysts from poisoning by the sulfur compounds such as alkyl mercaptans is necessary in dealing with real feed streams in commercial practice. To protect the selective hydrogenation catalyst from the poisoning by alkyl mercaptans in feed streams, the sulfur impurities are converted to heavier sulfur compounds by reacting with olefins, acetylenic compounds or dienes over Pd, Ni, etc. catalysts or optionally the catalyst disclosed in this invention, but optimized differently from the selective hydrogenation catalysts to maximize the mercaptan reaction. The heavier sulfur products are removed from light components by simple distillation. It is critically important not to produce H_2S from sulfur compounds during this mercaptan removing operation, because H_2S will poison the selective hydrogenation copper catalysts. In a CD unit, this removal of mercaptans can be carried out concurrently with the selective hydrogenation in a single distillation column. The catalyst for forming higher boiling organic sulfides from mercaptans such as that disclosed in U.S. Pat. Nos. 5,510,568; 5,595,643, 5,597,476 or 5,807,477 is loaded at the bottom of the selective hydrogenation catalyst bed in the CD column. The heavier sulfur compounds is removed as bottom product from the CD column prior to entering to selective hydrogenation reaction zone so that the selective hydrogenation catalysts is protected from the sulfur impurities. It is important to maintain a minimal amount of hydrogen in this mercaptan reaction zone not to produce hydrogen sulfide. If too much hydrogen is available, some of mercaptans may be converted to hydrogen sulfide by hydrodesulfurization of alkyl mercaptans or sulfides. To prevent the formation of hydrogen sulfide, it may be necessary to adjust the hydrogen content in the mercaptan reaction zone differently from that in the catalytic selective hydrogenation reaction zone.

Control Example 1

A copper catalyst was prepared according to the Example 1 in U.S. 4,440,956. Gamma alumina (CS 331-1 obtained from UCI, 1/16 inch extrudates and 265 m^2/g surface area) was calcined at 700°C for 3 hours in the ambient atmosphere before use. There was little change in ABD before and after calcination. The calcined alumina had 0.792 g/cc ABD. A solution of 28.7g $Cu(NO_3)_2.2.5H_2O$, $Ni(NO_3)_2.6H_2O$, 0.04g $AgNO_3$, 0.34g $Cr(NO_3)_3.9H_2O$ and 0.34g $Co(NO_3)_2.6H_2O$ in 110 ml deionized water was prepared. 60g UCI alumina was impregnated with above solution by using a rotary evaporator. After drying the impregnation product in 110°C in vacuum oven overnight, calcined at 400°C in a muffle furnace for 3 hours. The ABD of the catalyst was 0.87 g/cc. 22g of this catalyst was blended with 100 ml 3 mm diameter glass balls and loaded in a vertical stainless reactor (1 inch diameter x 20 inch long) used as a conventional reactor. The catalyst was activated by the following procedure; (1) heating the reactor to 230°F in 100 cc/min N_2 gas flow, (2) adding 200 cc/min H_2 to the N_2 gas flow and then holding for 3 hours at 230°F, (3) shut off N_2 gas and increasing H_2 gas flow to 300 cc/min, (4) heating the reactor temperature to 662°F and holding for 3 hours at 662°F and then cooled the reactor to 147°F in 30 cc/min H_2 gas flow.

A mixed C_4 stream composed of 28 wt ppm methyl acetylene, 1034 wt ppm vinyl acetylene and 549 wt ppm ethyl acetylene, 45.23 wt % 1,3-butadiene, 0.10 wt % 1,2-butadiene, 6.05 wt % t-2-butene, 4.22 wt % c-2-butene, 15.36 wt % 1-butene, 18.05 wt % isobutene, 9.34 wt % n-butane, 1. 30 wt % isobutane, and 0.19 wt % others was selectively hydrogenated to remove acetylenic impurities at 119 psig pressure. For the first 26 hours on stream time, the feed hydrocarbon and hydrogen rates were 2.2 cc/min (3.6 WHSV) and 31.4 scc/min, respectively. Then the feed rates were changed to 3 cc/min for hydrocarbon (5.0 WHSV) and 27 scc/min for hydrogen rate for the next 24 hours on stream. After that, the feed rates were 2.2 cc/min for hydrocarbon (3.6 WHSV) and 31.4 scc/min for hydrogen rate until the end of the run.

Control Example 2

18 grams of the palladium catalyst (0.7% Pd/1.4% Ag on alumina, 2464F obtained from UCI) was mixed with 110 ml 3 mm diameter glass balls and loaded in

the same reactor used in the Control Example 1. The catalyst was activated at 180°F by passing 1 ml/min (measured at ambient temperature) isobutane and 10 cc/min 10 volume % H_2 gas in He under 200 psig for an hour. A mixed C_4 stream composed of 39 wt ppm methyl acetylene, 5974 wt ppm vinyl acetylene and 1119 wt ppm ethyl acetylene, 46.05 wt % 1,3-butadiene, 0.15 wt % 1,2-butadiene, 5.68 wt % t-2-butene, 3.95 wt % c-2-butene, 14.38 wt % 1-butene, 17.98 wt % isobutene, 9.24 wt % n-butane, 1. 32 wt % isobutane, and 0.54 wt % others was selectively hydrogenated to remove the acetylenic impurities in it. The selective hydrogenation was carried out at the constant temperature 147°F. However, the hydrocarbon and hydrogen feed rates were 3 ml/min (6.1 WHSV) and 36.8 scc/min at the reactor pressure 119 psig, respectively, for the first 79 hours on stream, and then changed to 4.9 ml/min (9.9 WHSV) and 60 scc/min at the reactor pressure 108 psig, respectively.

Control Example 3

18 grams of the palladium catalyst (0.2% Pd/0.1% Ag on alumina, CDT-3 obtained from UCI) was mixed with 110 ml 3 mm diameter glass balls and loaded in the same reactor used in the Control Example 1. The catalyst was activated at 180°F by passing 1 ml/min (measured at ambient temperature) isobutane and 10 cc/min 10 volume % H_2 gas in He under 200 psig for an hour.

A mixed C_4 stream composed of 39 wt ppm methyl acetylene, 5974 wt ppm vinyl acetylene and 1119 wt ppm ethyl acetylene, 46, 05 wt % 1,3-butadiene, 0.15 wt % 1,2-butadiene, 5.68 wt % t-2-butene, 3.95 wt % c-2-butene, 14.38 wt % 1-butene, 17.98 wt % isobutene, 9.24 wt % n-butane, 1. 32 wt % isobutane, and 0.54 wt % others was selectively hydrogenated.

Control Example 4

The activated alumina (Alfa 31268, 3.2 mm pellets; 90 m^2/g surface area) was ground to 10-20 mesh granules. This granular alumina had about 1 g/cc ABD. A solution of 28.7g $Cu(NO_3)_2.2.5H_2O$, $Ni(NO_3)_2.6H_2O$, and 0.04g $AgNO_3$ in 100 ml deionized water was prepared. 60g of the granular alumina were impregnated with above solution by using a rotary evaporator. After drying the impregnation product in 110°C in vacuum oven overnight, calcined at 400°C in a muffle furnace for 3 hours. 18g of this catalyst was blended with 110 ml 3 mm diameter glass balls and loaded in the same reactor in the Control Example 1. The catalyst was activated by

the following procedure; (1) heating the reactor to 230°F in 100 cc/min N_2 gas flow, (2) adding 200 cc/min H_2 to the N_2 gas flow and then holding for 3 hours at 230°F, (3) shut off N_2 gas and increasing H_2 gas flow to 300 cc/min, (4) heating the reactor temperature to 662°F and holding for 3 hours at 662°F and then cooled the reactor to 147°F in 30 cc/min H_2 gas flow.

The same feed used in the Control Example 1 was selectively hydrogenated to remove acetylenic impurities at 119 psig pressure. For the first 26.5 hours on stream time, the feed hydrocarbon and hydrogen rates were 1.8 cc/min (3.6 WHSV) and 25.7 scc/min, respectively. Then the feed rates were changed to 2.4 cc/min for hydrocarbon (4.9 WHSV) and 22.1 scc/min for hydrogen rate for the next 24 hours on stream. After that, the feed rates were changed again to 1.8 cc/min for hydrocarbon carbon (3.6 WHSV) and 25.7 scc/min.

Example 5

A copper catalyst was prepared according to this invention using the alumina (1/16" diameter spherically shaped) prepared by the oil dropping gelation technique. The physical property of the alumina is summarized in Table 1. The pore size distribution of the alumina is illustrated in Figure 1. More than about 90% of the pores were larger than 100Å diameter. The solution of 28.7g $Cu(NO_3)_2.2.5H_2O$, $Ni(NO_3)_2.6H_2O$, 0.04g $AgNO_3$, 0.34g $Cr(NO_3)_3.9H_2O$ and 0.34g $Co(NO_3)_2.6H_2O$ in 110 ml deionized water was prepared. 60g alumina was impregnated with above solution by using a rotary evaporator. After drying further the impregnation product in 110°C in vacuum oven overnight, calcined at 400°C in a muffle furnace for 3 hours. The physical property of the catalyst is summarized in Table 2. There is only a minor change in the pore structure of the copper catalyst from the alumina support as shown in Figure 1. 22g of this catalyst was blended with 100 ml 3 mm diameter glass balls and loaded in the same reactor used in the Control Example 1. The catalyst activation was carried out in the same manner described in the Control Example 1.

The same feed used in the Control Example 1 was selectively hydrogenated to remove acetylenic impurities at 119 psig. For the first 26 hours on stream time, the feed hydrocarbon and hydrogen rates were 2.2 cc/min (3.6 WHSV) and 31.4 scc/min, respectively. Then the feed rates were changed to 3 cc/min for hydrocarbon (5.0 WHSV) and 27 scc/min for hydrogen rate for the next 24 hours on

stream time. After that, the feed hydrocarbon and hydrogen rates were 2.2 cc/min (3.6 WHSV), but maintained the hydrogen rate at 27 scc/min until the end of the run.

The test results of copper catalyst in the Example 5 and the Control Example 1 are illustrated in Figure 4 and 5. The Figure 3 demonstrates the superior catalyst activity and stability of the catalyst disclosed in this invention over the prior art. The Figure 5 demonstrates a superior butadiene yield of this invention over the prior art. The yields of 1,3-butadiene at the same conversion of the total alkynes over the catalyst disclosed in this invention are higher than those disclosed in the prior art. Also the Example 5 indicates that, if excess hydrogen is available after converting all the acetylenic compounds in the feed stream, the excess hydrogen causes the loss of 1,3-butadiene due to over-hydrogenation, suggesting that the excess hydrogen should be kept to minimal in the selective hydrogenation zone.

Table 1

ABD, g/cc	0.53
Single-point BET, m^2/g	157.5
Multiple-point BET, m^2/g	170.2
Meso Pore Area, m^2/g	170.2
Micro Pore Area, m^2/g	0
Cumulative Adsorption Surface area, m^2g	172.6
Cumulative Desorption Surface area, m^2/g	230.4
Total Pore Volume (cc/g)	
for pores less than 493 A° radius at P/P_0 = 0.9801	0.912
Cumulative Adsorption Pore Volume for pores (20 – 300Åradius)	0.852
Cumulative Desorption Pore Volume for pores (17.5 – 300Å radius)	0.930
Average Pore diameter,Å	214.4

Table 2

ABD, g/cc	0.58
Single-point BET, m^2/g	137.5
Meso Pore Area, m^2/g	147.7
Micro Pore Area, m^2/g	0
Cumulative Desorption Pore Volume for pores (17.5 – 300Å radius)	0.790

Example 6

The alumina used in the Example 5 was calcined at 700°C for 3 hours in air. A copper catalyst was prepared using this calcined alumina. The solution of 30g $Cu(NO_3)_2.2.5H_2O$, $Ni(NO_3)_2.6H_2O$, 0.047g $AgNO_3$, 0.396g $Cr(NO_3)_3.9H_2O$ and 0.396g $Co(NO_3)_2.6H_2O$ in 128 ml deionized water was prepared. 70g alumina was impregnated with above solution by using a rotary evaporator. After drying further the impregnation product at 110°C in a vacuum oven overnight, calcined it at 400°C in a muffle furnace for 3 hours in air. The ABD of the catalyst was 0.57 g/cc. 18g of this catalyst was blended with 100 ml 3 mm diameter glass balls and loaded in the same reactor in the Control Example. The catalyst was activated in the identical manner as in the Control Example 1.

A mixed C_4 stream composed of 444 wt ppm methyl acetylene, 825 wt ppm vinyl acetylene and 634 wt ppm ethyl acetylene, 55.36 wt % 1,3-butadiene, 0.12 wt % 1,2-butadiene, 6.39 wt % t-2-butene, 4.13 wt % c-2-butene, 16.84 wt % 1-butene, 12.38 wt % isobutene, 3.53 wt % n-butane, 0.97 wt % isobutane, and 0.09 wt % others was selectively hydrogenated to remove acetylenic impurities at 119 psig. In this example, the hydrocarbon and hydrogen rates were maintained at constant rates; 3 cc/min for hydrocarbon and 27 scc/min hydrogen. The test results of copper catalyst in the Example 6 and the Control Example 1 are illustrated in Figure 4 and 5 along the result from Example 5.

The Figures 4 and 5 clearly demonstrate the superior performance of the copper catalysts disclosed in this invention over the prior art.

Example 7

In this example, a catalytic distillation column is used for the selective hydrogenation of the acetylenic impurities in a mixed C_4 stream. A larger batch catalyst was prepared by using 240 grams of alumina in the exactly same manner described in the Example 5. The catalyst (99.88 grams) was loaded in a catalytic distillation column (1" diameter x 25' height). The height of the catalyst bed in the column was 6 feet. 80 inches of top and bottom of the catalyst bed was packed with ¼" saddles. The catalyst was activated in the same manner described in the Control Example 1 except that the flow rate of gases were increased proportionally based on the catalyst weight.

The acetylenic impurities in the same feed used in the Example 6 were removed by carrying out the selectively hydrogenation in the catalytic distillation mode. The hydrocarbon feed rate was 1.2 pounds per hour. The hydrogen rate was 1 scf per hour at the beginning of the run, but during the run it was changed to higher rates. The hydrocarbon and hydrogen feeds were fed at point of below the saddle packing. The result is illustrated in Figure 6. At the hydrogen rate of 3 scf per hour or higher, ethyl acetylene and vinyl acetylene in the feed were practically all removed. Near complete recovery of 1,3-butadiene was obtained. As shown in Figure 6, the catalyst was much more stable under the catalytic operation mode than the fixed bed operation.

Example 8

This experiment was carried out to demonstrate the beneficial effect of zinc oxide incorporation into the copper catalyst disclosed in this invention to improve the performance of the copper catalyst. A copper catalyst was prepared according to the identical procedure used in the Example 5. The mixed solution of 22.6g $Cu(NO_3)_2.2.5H_2O$, $Ni(NO_3)_2.6H_2O$, 0.04g $AgNO_3$, and 4.0g Zn

$(NO_3)_2.6H_2O$ in 100 ml deionized water was prepared. 60g of the same alumina used in the Example 5 was impregnated with above solution by using a rotary evaporator. After drying further the impregnation product in 110°C in vacuum oven overnight, calcined at 400°C in a muffle furnace for 3 hours. 18g of this catalyst was blended with 100 ml 3 mm diameter glass balls and loaded in the same reactor used in the Control Example 1. The catalyst activation was carried out in the same manner described in the Control Example 1.

A mixed C_4 stream composed of 475 ppm methyl acetylene, 959 wt ppm vinyl acetylene and 731 wt ppm ethyl acetylene, 54.87 wt % 1,3-butadiene, 0.12 wt % 1,2-butadiene, 6.42 wt % t-2-butene, 4.16 wt % c-2-butene, 16.76 wt % 1-butene, 12.53 wt % isobutene, 3.56 wt % n-butane, 1.27 wt % isobutane, and 0.09 wt % others was selectively hydrogenated to remove the acetylenic impurities in it. The selective hydrogenation was carried out at the constant temperature 147°F and 119 psig. The constant hydrocarbon and hydrogen feed rates were used throughout the run; 3 ml/min (6.1 WHSV) and 27.1 scc/min. The result of this run is summarized in Figures

7 and 8. The beneficial effects of the zinc oxide incorporated into the copper catalyst on the catalyst performance are clearly demonstrated in this example.

Example 9

In this example, the usefulness of one of the preferred solvents disclosed in this invention, tetrahydrofuran (THF), is demonstrated. The copper catalyst (36 grams) prepared in Example 5 was loaded in the same reactor used in the Control Example 1. The mixed C_4 feed used in this example had the following composition; 20 ppm methyl acetylene, 588 ppm vinyl acetylene, 599 ppm ethyl acetylene, 44.51 wt % 1,3-butadiene, 0.07 wt % 1,2-butadiene, 6.29 wt % t-2-butene, 4.33 wt % c-2-butene, 15.97 wt % 1-butene, 18.04 wt % isobutene, 9.36 wt % n-butane, 1. 30 wt % isobutane, and 0.01 wt % others. After on 176 hours on stream time, the catalyst was washed to remove the polymers deposited on the catalyst with THF after flushing out the reactor with N_2 gas; 10 cc/min THF, 66.9 scc/min H_2 at 147°F and 200 psig for 1 hour and then at 157°F for 5 hours. After flushing out the reactor with N_2 gas, the selective hydrogen was continued. The constant temperature (147°F) and pressure (119 psig) were maintained during the run. The run conditions during this experiment are listed in Table 3.

The result of this experiment is illustrated in Figure 9. The break through of the acetylenic impurities occurred on 128 hours on stream as shown in Figure 9. But after washing the catalyst with THF, the product obtained under the same condition for the break-through contained no detectable amount of acetylenic impurities. Therefore, THF

Table 3

147°F and 119 psig

Hours on stream	0 – 26	26 – 50	50 – 74	74 – 98	98 – 128	128 – 152	152 – 176	THF 176 – 188.5
HC Feed rate, ml/min	2.9	5.8	2.9	2.9	5.8	7	7	wash 7
H_2 rate, scc/min	45	45	45	15	10	45	45	54. 45
							Break through of acetylenes	

is one of the preferred solvents for the catalyst regeneration. Also THF is one of the preferred solvents to be used for carrying out the selective hydrogenation using catalytic distillation column. When THF is used as the solvent in CD selective hydrogenation, THF can be fed to the distillation column above the catalyst bed or it can be feed to the column with the mixed C_4 feed stream. The different conditions

for the column operation will be needed for these two cases. In the latter case, the column will be operated under the total internal reflux condition with respect to THF. THF will be removed from the column as the bottom product for both cases and recycled to the column. However, a part of the recycle THF stream will be purified in a separator to avoid the heavies build-up in the recycle stream before returning to the column.

Example 10A

The copper catalyst prepared in the Example 5 was tested for the selective hydrogenation of the acetylenic impurities (7132 ppm total acetylenes) in the mixed C_4 feed used in the Control Example 2.18g of the catalyst was blended with 100 ml 3 mm diameter glass balls and loaded in the same reactor in the Control Example 1. The catalyst was activated in the identical manner as in the Control Example 1. The selective hydrogenation was carried out at a constant temperature 147°F and 119 psig. The hydrocarbon and hydrogen feed rates were 2.9 ml/min (5.87 WHSV) and 45 scc/min, respectively, for the first 66.5 hours on stream, and then changed to 1.4 ml/min (2.83 WHSV) and 24.1 scc/min, respectively.

Example 10B

A copper catalyst promoted with palladium was prepared according this invention. The alumina used in the Example 5 was calcined at 900°C for 3 hours in air. A mixed solution was prepared by dissolving 28.7g $Cu(NO_3)_2.2.5H_2O$, $Ni(NO_3)_2.6H_2O$, 0.04g $AgNO_3$, 0.34g $Cr(NO_3)_3.9H_2O$ and 0.34g $Co(NO_3)_2.6H_2O$ in 110 ml deionized water. The above calcined alumina (60g) was impregnated with this solution by using a rotary evaporator. After further drying the impregnation product at 110° in a vacuum oven overnight, it was calcined at 400°C in a muffle furnace for 3 hours in air. 5.469 grams of aqueous palladium(II) nitrate solution (Aldrich 38,004-0; 10 wt % $Pd(NO_3)_2$ in 10 wt % nitric acid) was sprayed on the copper catalyst spheres (29.762 grams) by using an atomizer, while the copper catalyst spheres were rolling around on the flat surface, to evenly coat the spheres with the palladium solution. It is very important to produce a fine mist of the palladium salt solution. The palladium solution sprayed product was calcined at 250°C for 2 hours in air. The ABD of the Cu/Pd catalyst was 0.52 g/cc. The analysis of this catalyst indicates 8.20% Cu, 0.71% Pd, 0.20% Ni, 0.11%Cr, and 0.17% Ag.

22g of this catalyst was blended with 100 ml 3 mm diameter glass balls and loaded in the same reactor used in the Control Example 1. The catalyst was activated by the following procedure; (1) heating the reactor to 230°F in 100 cc/min N_2 gas flow, (2) adding 200 cc/min H_2 to the N_2 gas flow and holding for 3 hours at 230°F, (3) shut off N_2 gas and increasing H_2 gas flow to 300 cc/min, (4) heating the reactor temperature to 572°F, holding for 3 hours at 572°F and then cooled the reactor to 147°F in 30 cc/min H_2 gas flow.

The acetylenic impurities in the same feed used in the Example 10A were removed by selective hydrogenation. The selective hydrogenation was carried out at a constant temperature 142°F. However, the hydrocarbon and hydrogen feed rates were 3.7 ml/min (6.1 WHSV) and 45 scc/min at the reactor pressure of 119 psig, respectively, for the first 73 hours on stream, and then changed to 6.1 ml/min (10.1 WHSV) and 74.2 scc/min at 108 psig, respectively. After 145 hours on stream, the catalyst was washed with benzene(10 ml/min) at 100°C and 108 psig in 74.2 scc/min H_2 flow for 5 hours. The selective hydrogenation was continued at the same condition just before the benzene wash for 24 hours, but benzene (0.6 ml/min) was co-fed to the reactor with the mixed C_4 feed. After that, the feed rates were changed to 10 ml/min mixed C_4 feed, 1 ml/min benzene, and 90 scc/min H_2 for the next 18 hours. And then the feed rates were increased to 15 ml/min mixed C_4 feed, 1.5 ml/min benzene, and 112 scc/min H_2 at the reactor pressure 95 psig for the next 30 hours. After that, the selective hydrogenation was carried out at a reduced hydrogen rate of 95 scc/min for 24 hours, while keeping other process parameters at the same condition. And then the feed rate was reduced to 10 ml/min mixed C_4 feed, 1 ml/min benzene, and 54 scc/min H_2 for the next 66 hours, while keeping other process parameters at the same condition.

The results of the Examples 10A and 10B are illustrated in Figure 10 and 11 along with the Control Example 2. As shown in Figure 8, the copper catalyst, which was not promoted with palladium, had very low activity in dealing with the high concentration of acetylenic impurities. But when the copper catalyst was promoted with palladium in the technique disclosed in this invention, the catalyst activity was dramatically improved. Surprisingly, the palladium promoted copper catalyst has far superior activity than the commercial Pd selective hydrogenation catalyst. Yet more

surprisingly the present palladium promoted catalyst has also a superior 1,3-butadiene yield at the same conversion of the acetylenes over the commercial palladium catalyst despite of its much higher activity. Also the deactivation rate of the palladium promoted catalyst was much better than the commercial Pd catalyst or the unpromoted copper catalyst. This example clearly demonstrates the superior performance of the palladium promoted copper catalyst for the selective hydrogenation of high acetylenic feeds over the palladium catalyst or unpromoted copper catalyst.

Example 11

Gamma alumina (obtained from UCI, 1/8 inch extrudates and about 260 m^2/g surface area) was ground to 10-20 mesh granules. According to the supplier of this alumina, the raw material of this alumina is identical to the alumina used in the Control Example 1. But this granular alumina has lower ABD (0.50 g/cc) than the alumina (0.792 g/cc ABD) used in the Control Example 1. A solution of 30g $Cu(NO_3)_2.6H_2O$, 0.93g $Ni(NO_3)_2.6H_2O$, 0.047g $AgNO_3$, 0.396 $Cr(NO_3)_3.9H_2O$ and 0.396 $Co(NO_3)_2.6H_2O$ in 128 ml deionized water was prepared. 70g of the granular alumina were impregnated with above solution by using a rotary evaporator. After drying the impregnation product in 110°C in vacuum oven overnight, calcined at 400°C in a muffle furnace for 3 hours. 18g of this catalyst was blended with 110 ml 3 mm diameter glass balls and loaded in the same reactor in the Control Example 1. The catalyst was activated by the following procedure; (1) heating the reactor to 230°F in 100 cc/min N_2 gas flow, (2) adding 200 cc/min H_2 to the N_2 gas flow and then holding for 3 hours at 230°F, (3) shut off N_2 gas and increasing H_2 gas flow to 300 cc/min, (4) heating the reactor temperature to 662°F and holding for 3 hours at 662°F and then cooled the reactor to 147°F in 30 cc/min H_2 gas flow.

The same feed used in the Control Example 1 was selectively hydrogenated to remove acetylene impurities at 119 pig pressure. For the first 29 hours on stream time, the feed hydrocarbon and hydrogen rates were 1.8 cc/min (3.6 WHSV) and 25.7 sc./min, respectively. Then the feed rates were increased to 2.4 cc/min for hydrocarbon (4.9 WHSV) and 34.3 sc./min for hydrogen rate for the next 42 hours on stream. After that, the feed rates was further increased to 3 cc/min for

hydrocarbon (6.1 WHSV), but hydrogen feed rate was lowered to 30 sc./min, until the end of the run.

The comparison of the test result of this experiment with those of Control Examples 1 and 4 is illustrated in Figures 12 and 13 to demonstrate of the effect of ABD of support aluminas on the catalyst performance. The catalyst prepared using lower ABD alumina, which means higher porosity, in this example outperformed the higher ABD aluminas used in Control Examples 1 and 4. The aluminas in this example and the Control Example 1 were prepared from the same raw materials. But the lower ABD alumina used in this example results in more effective catalyst in removing acetylenic impurities. The catalyst in this example has a better 1,3-butadiene yield than in the Control Example 1. The alumina used to prepare the catalyst in the Control Example 4 has the surface area falling in the preferred range of surface area disclosed in this invention. But the ABD of the alumina in the Control Example 4 is 0.98 g/cc, which is higher than the preferred ABD (<0.65g/cm^3) disclosed in this invention. The effectiveness of the catalyst in the Control Example 4 in removing acetylenic impurities approximately falls in between the Control Example 1 and the Example 11. There is little difference in the yield of the 1,3-Butadiene in the Example 11 and the Control Example 4.

Example 12

To demonstrate the superior performance of the palladium promoted copper catalyst for the selective hydrogenation of a feed containing relatively high concentration of acetylenic impurities, this example was carried out.

A copper catalyst promoted with palladium was prepared according to this invention. The alumina used in the Example 5 was calcined at 900°C for 3 hours in air. A mixed solution was prepared by dissolving 1.866g $Cu(NO_3)_2$ $2.5H_2O$ in a palladium nitrate solution prepared by diluting 4.61g 10 wt % $Pd(NO_3)_2$ solution in 10 wt % nitric acid (Aldrich 38,004-0: 10 wt % $Pd(NO_3)_2$) with 6.378g deionized water. 5.56g of this mixed solution was sprayed on 30g of calcined alumina spheres by using an atomizer, while the alumina spheres were rolling around on a flat surface and then the sprayed product was dried at 115°C in a vacuum oven. The dried product was calcined at 250°C for 2 hours in air.

18 g of this catalyst was mixed with 110 ml of 3 mm diameter glass balls and loaded in the same reactor used in the Control Example 1. The catalyst was activated in the same manner described in Example 11. The acetylenic compounds in the same feed used in the Control Example 3 were removed by carrying out the selective hydrogenation. The selective hydrogenation was carried out at the constant temperature of 142°F and 108 psig. The hydrocarbon feed rate was kept at 10 ml/min (20.2 WHSV) until the end of the run. However, variations of hydrogen flow rate in the range of from 44 scc/min to 90 scc/min were made during the run.

The results of this Example 12 and the Control Example 3 are illustrated in Figures 14 and 15. The superior catalytic activity of the palladium promoted copper catalyst over the traditional palladium catalyst is clearly demonstrated. Despite a higher feed rate in Example 12 of at least 4 times greater than that of Control Example 3, the palladium promoted copper catalyst is able to produce product containing less than 20 ppm C_4 acetylenes with a superior yield (expressed as recovery in Figure 14) of 1,3-butadiene over the traditional palladium catalyst in Control Example 3. The recovery of C_4 acetylenes is defined by 100% vs % conversion of C_4 acetylenes; e.g. 0 percent recovery of C_4 acetylenes is equivalent to 100% removal of C_4 acetylenes and 100%1,3-butadiene recovery is equivalent to 0% conversion of 1,3-butadiene.

The ratios of ethyl acetylene to vinyl acetylene in the products are illustrated in Figure 15. The palladium promoted copper catalyst has much higher reactivity toward to vinyl acetylene than the traditional palladium catalyst. The palladium promoted copper catalyst has approximately an order higher activity than the unpromoted copper catalyst. It was unexpected that the palladium promoted copper catalyst has several times higher activity than the traditional Pd catalyst and yet it has a superior selectivity retaining 1,3-butadiene.

The invention claimed is:

1. A catalyst for selective hydrogenation of acetylenes comprising a copper component and a component of at least one Group VIII metal component, a Ag, Au component or mixtures thereof on an alumina support comprising at least one of the properties of average pore diameter larger than 200Å or apparent bulk density of less than about 0.70g/cm^3.

2. The catalyst according to claim 1 comprising a component of Ag, Au component or a mixture thereof.

3. The catalyst according to claim 1 comprising at least one Group VIII metal component.

4. The catalyst according to claim 1 comprising a component of at least one Group VIII metal component and a Ag, Au or mixtures thereof component.

5. The catalyst according to claim 1 comprising a component of at least one Group VIII metal component, a Ag component and a Au component.

6. The catalyst according to claim 2, 3, 4 or 5 wherein the Group VIII component comprises Pd.

7. The catalyst according to claim 2, 3, 4 or 5 comprising a Zn component.

8. The catalyst according to claim 1 comprising an alumina support having average pore diameter larger than 200Å.

9. The catalyst according to claim 1 comprising an alumina support having an apparent bulk density of less than about 0.70g/cm^3.

10. A catalyst for the selective hydrogenation of acetylenes comprising a copper component at least one Group VIII metal component and a Zn component.

11. The catalyst according to claim 10 comprising a component of Ag, Au or mixture thereof.

12. The catalyst according to claim 10 comprising about 0.1 to 25 Wt% Cu.

13. A process for the selective hydrogenation of acetylenes comprising contacting a feed containing acetylenes in at least partial liquid phase with a catalyst according to claim 1 under conditions to selectively hydrogenate said acetylenes.

14. The process according to claim 13 wherein a soluble polymer is continuously deposited on said catalyst during said hydrogenation to reduced activity of said catalyst for the selective hydrogenation of acetylenes, and said hydrogenation

is intermittently interrupted and a solvent for said soluble polymer is contacted with said catalyst and remove a portion of said polymer and restore a portion of the activity of said catalyst for said selective hydrogenation.

15. The process according to claim 14 wherein said solvent comprises at least one of tetrahydrofuran, furan, 1,4-dioxane, ethers, gamma-butyrolactone, benzene or toluene.

16. A process for the selective hydrogenation of acetylenes comprising contacting a feed containing acetylenes in at least partial liquid phase with a catalyst according to claim 10 under conditions to selectively hydrogenate said acetylenes.

17. The process according to claim 16 wherein a soluble polymer is continuously deposited on said catalyst during said hydrogenation to reduced activity of said catalyst for the selective hydrogenation of acetylenes, and said hydrogenation is intermittently interrupted and a solvent for said soluble polymer is contacted with said catalyst and remove a portion of said polymer and restore a portion of the activity of said catalyst for said selective hydrogenation.

18. The process according to claim 17 wherein said solvent comprises at least one of tetrahydrofuran, furan, 1,4-dioxane, ethers, gamma-butyrolactone, benzene or toluene.

Figure 1

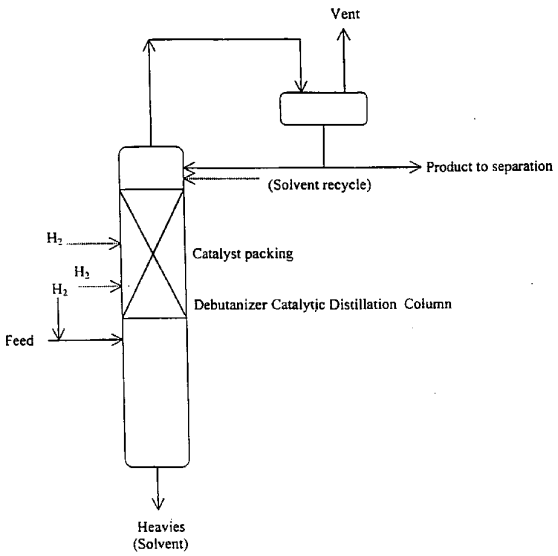
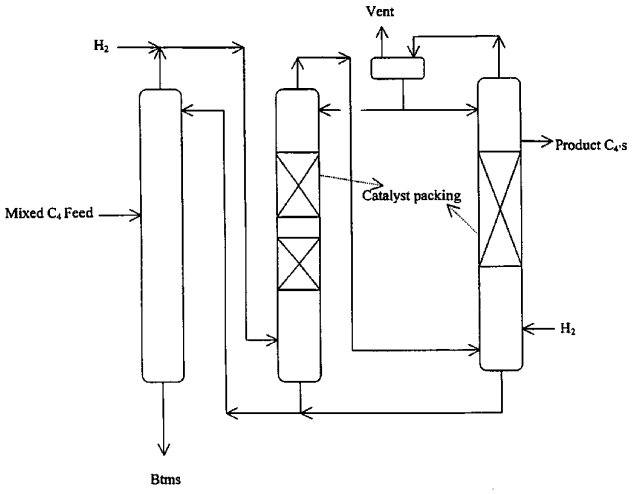

Vent
Product to separation
(Solvent recycle)
H_2
H_2
H_2
Catalyst packing
Debutanizer Catalytic Distillation Column
Feed
Heavies
(Solvent)

Figure 2



All reactants enter the catalyst sections in vapor phase only
May have two or more hydrogen feed

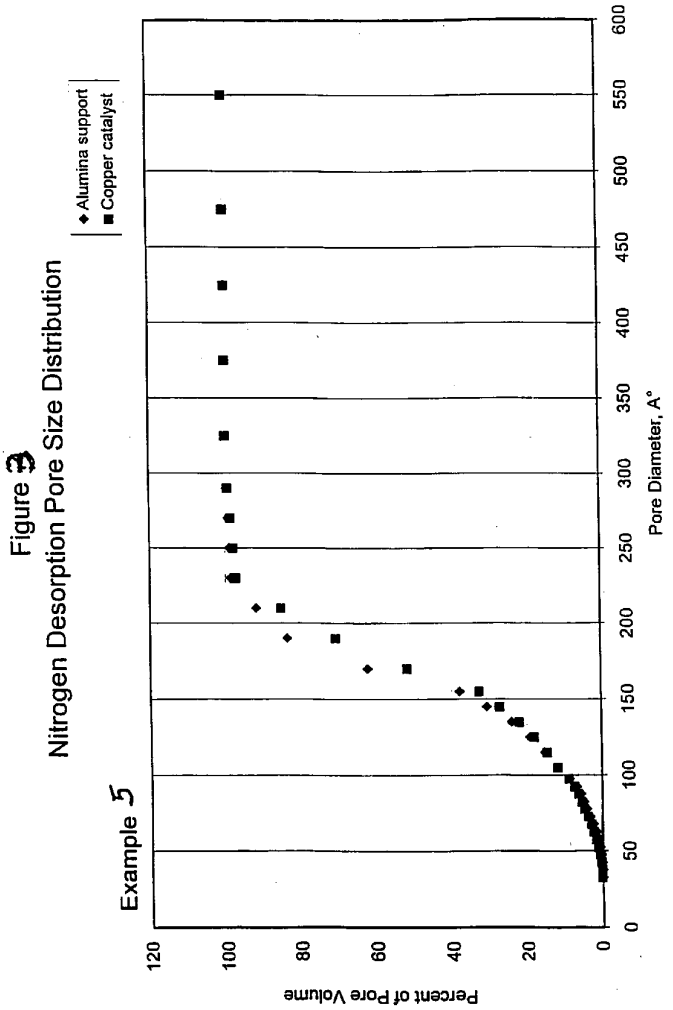


Figure 3
Nitrogen Desorption Pore Size Distribution
Example 5
◆ Alumina support
■ Copper catalyst
Percent of Pore Volume
0
20
40
60
80
100
120
Pore Diameter, A°
0
50
100
150
200
250
300
350
400
450
500
550
600

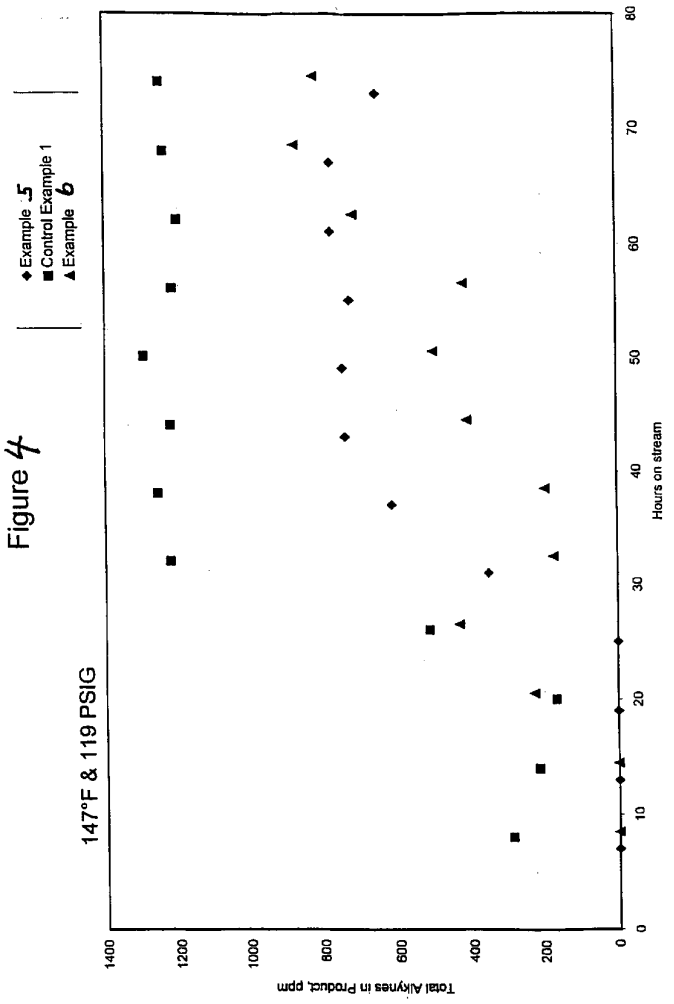

◆ Example 5
■ Control Example 1
▲ Example 6
147°F & 119 PSIG
Total Alkynes in Product, ppm
Hours on stream
0
200
400
600
800
1000
1200
1400
0
10
20
30
40
50
60
70
80

Figure 4

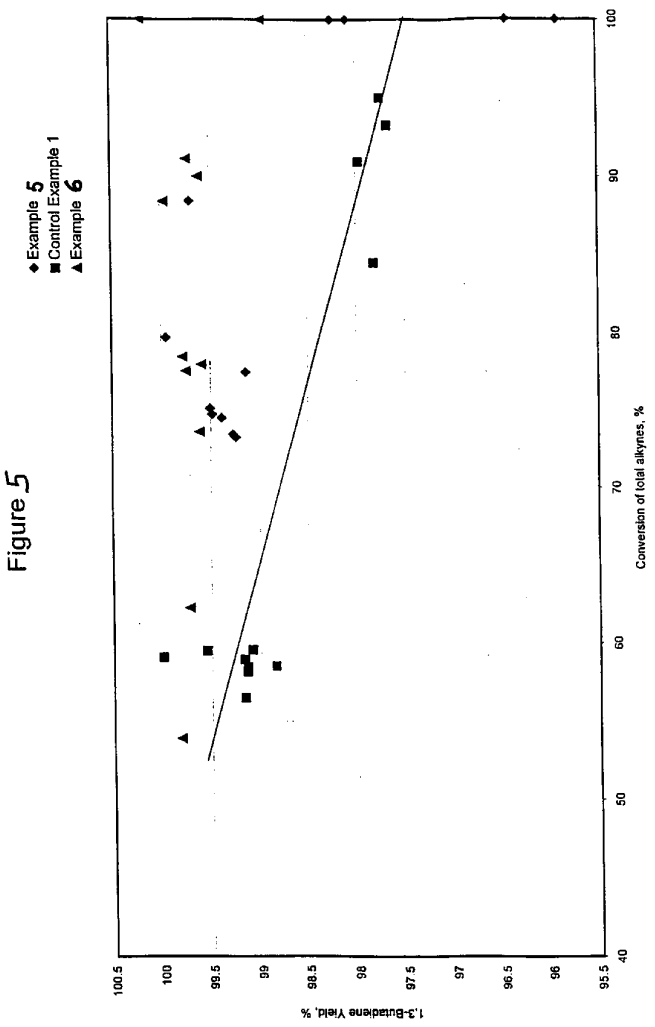
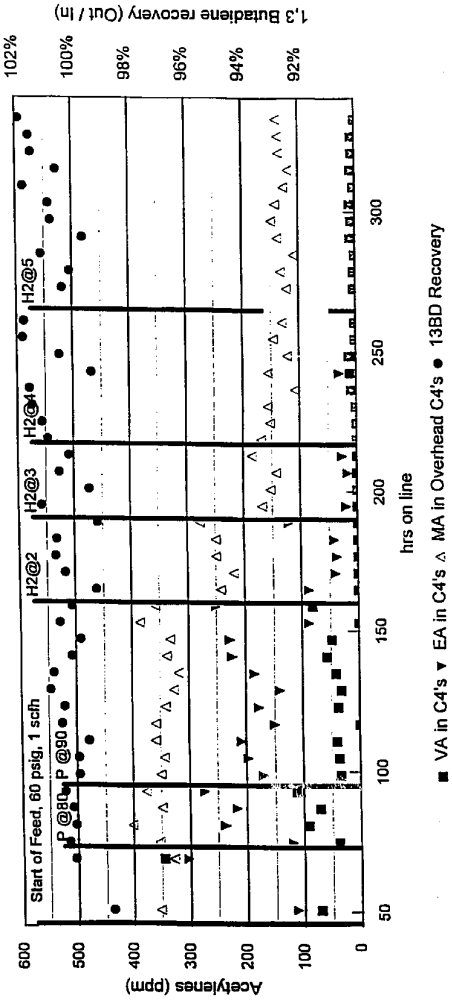

◆ Example 5
■ Control Example 1
▲ Example 6
1,3-Butadiene Yield, %
Conversion of total alkynes, %
100.5
100
99.5
99
98.5
98
97.5
97
96.5
96
95.5
100
90
80
70
60
50
40

Figure 5

Figure 6

Example 7



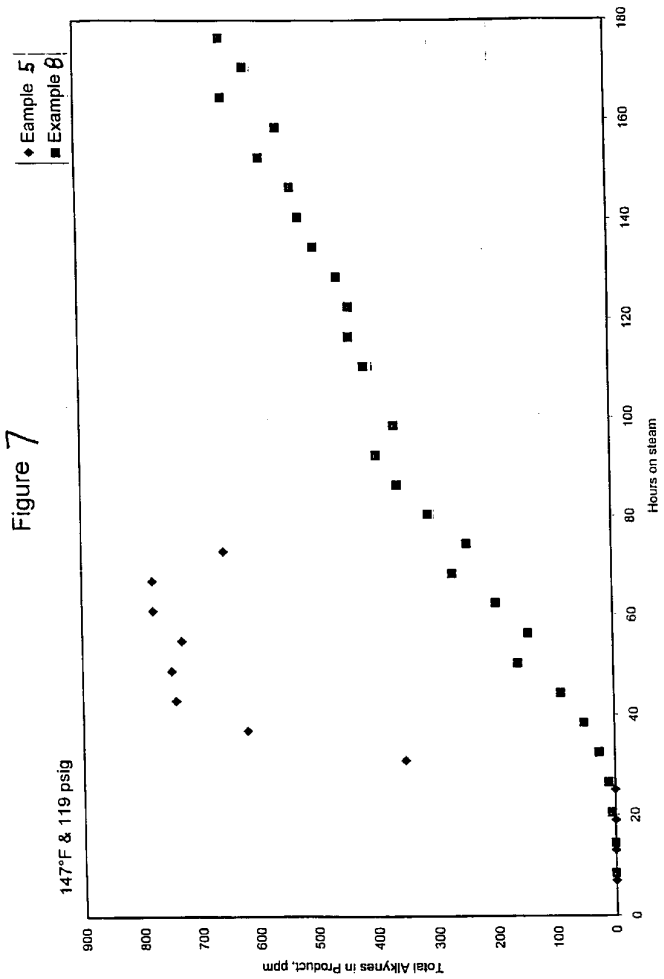

◆ Eample 5
■ Example 6
147°F & 119 psig
Total Alkynes in Product, ppm
Hours on steam
0
100
200
300
400
500
600
700
800
900
0
20
40
60
80
100
120
140
160
180

Figure 7

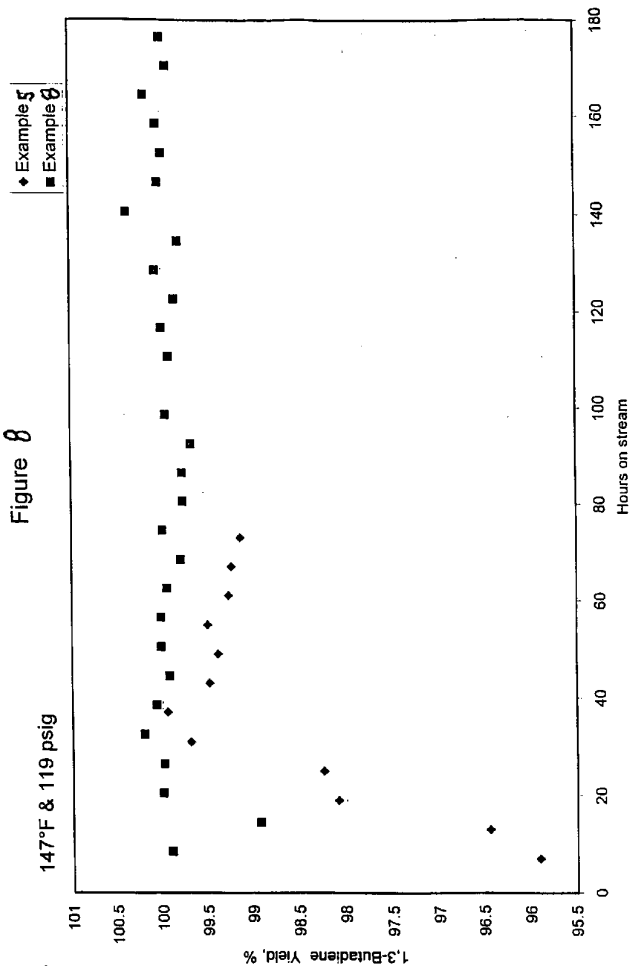

Example 5
Example 6
147°F & 119 psig
1,3-Butadiene Yield, %
Hours on stream
101
100.5
100
99.5
99
98.5
98
97.5
97
96.5
96
95.5
0
20
40
60
80
100
120
140
160
180

Figure 6

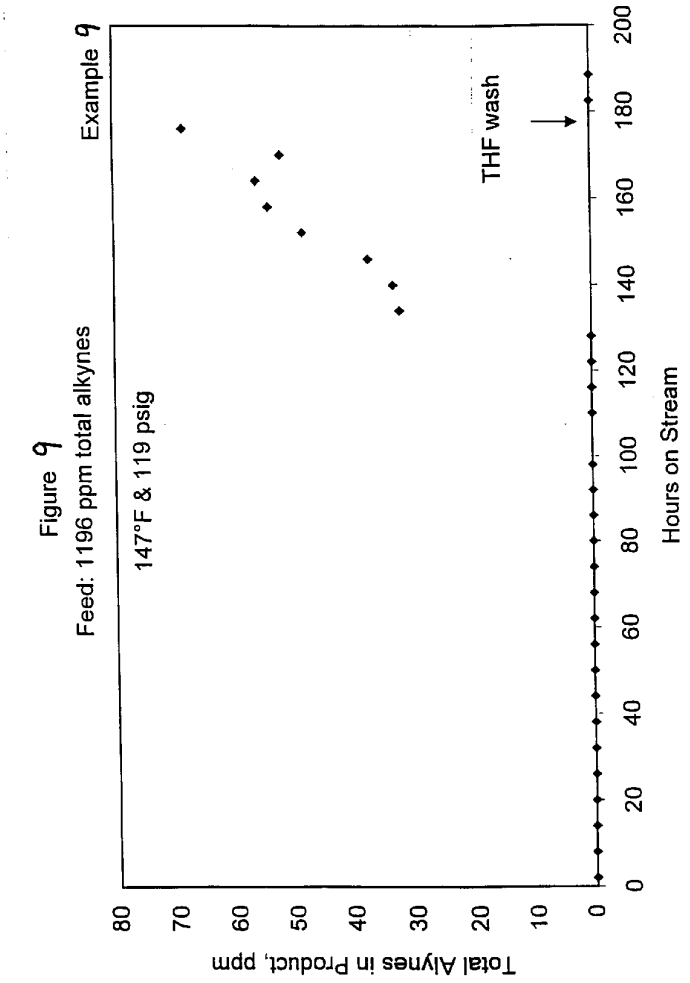
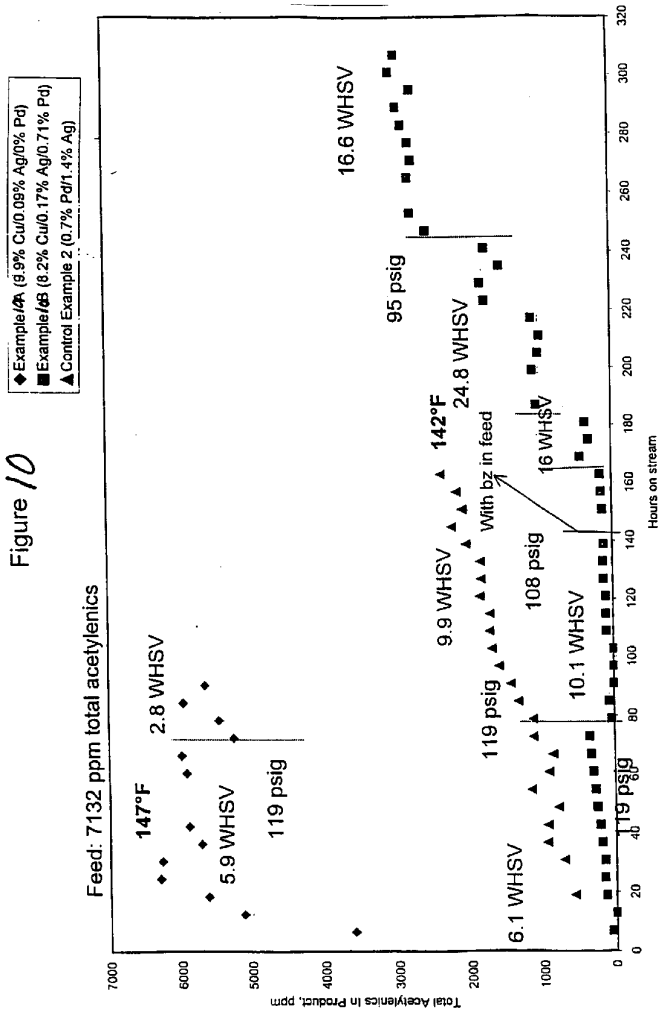

Example 9
Feed: 1196 ppm total alkynes
147°F & 119 psig
THF wash
Total Alynes in Product, ppm
Hours on Stream
0
10
20
30
40
50
60
70
80
0
20
40
60
80
100
120
140
160
180
200

Figure 9

Figure 10


◆Example 4A (3.9% Cu/0.09% Ag/0% Pd)
■Example 4B (8.2% Cu/0.17% Ag/0.71% Pd)
▲Control Example 2 (0.7% Pd/1.4% Ag)
Feed: 7132 ppm total acetylenics
147°F
2.8 WHSV
5.9 WHSV
119 psig
16.6 WHSV
95 psig
142°F
24.8 WHSV
With bz in feed
9.9 WHSV
119 psig
108 psig
16 WHSV
10.1 WHSV
6.1 WHSV
119 psig
Total Acetylenics In Product, ppm
Hours on stream

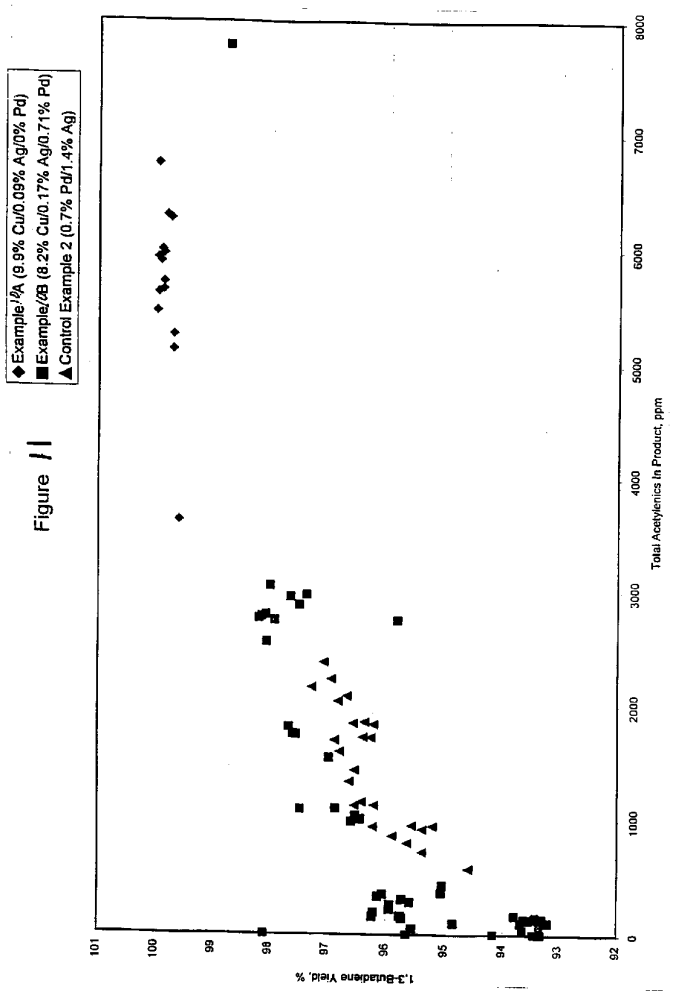
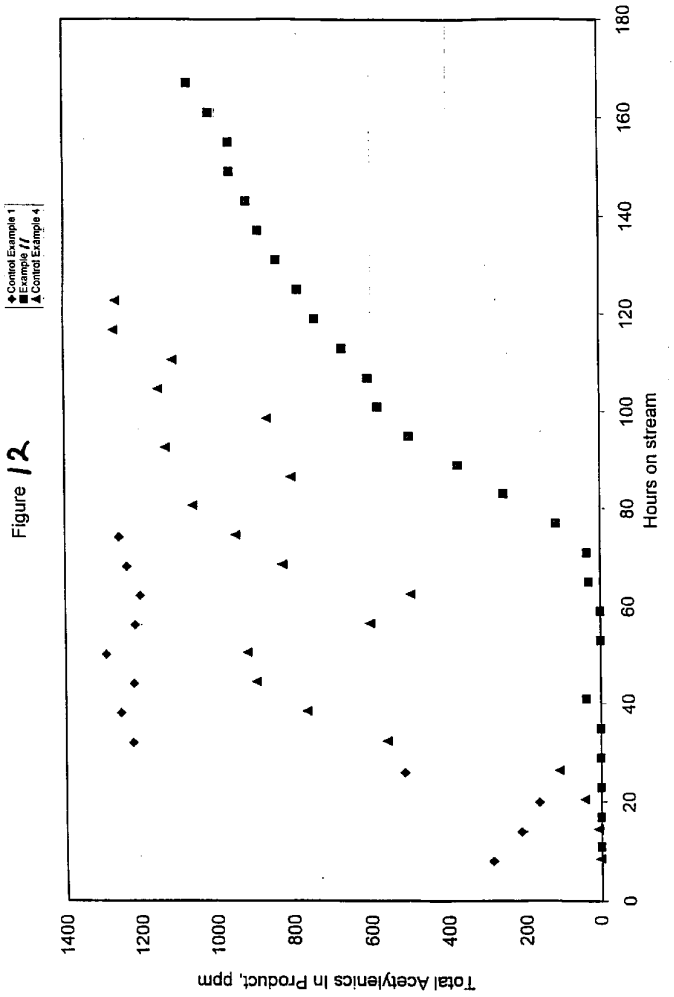

◆ Example 9A (9.9% Cu/0.09% Ag/0% Pd)
■ Example 8B (8.2% Cu/0.17% Ag/0.71% Pd)
▲ Control Example 2 (0.7% Pd/1.4% Ag)
1,3-Butadiene Yield, %
Total Acetylenics in Product, ppm
101
100
99
98
97
96
95
94
93
92
0
1000
2000
3000
4000
5000
6000
7000
8000

Figure 11

Figure 12


Control Example 1
Example 4
Control Example 4
Total Acetylenics In Product, ppm
0
200
400
600
800
1000
1200
1400
Hours on stream
0
20
40
60
80
100
120
140
160
180

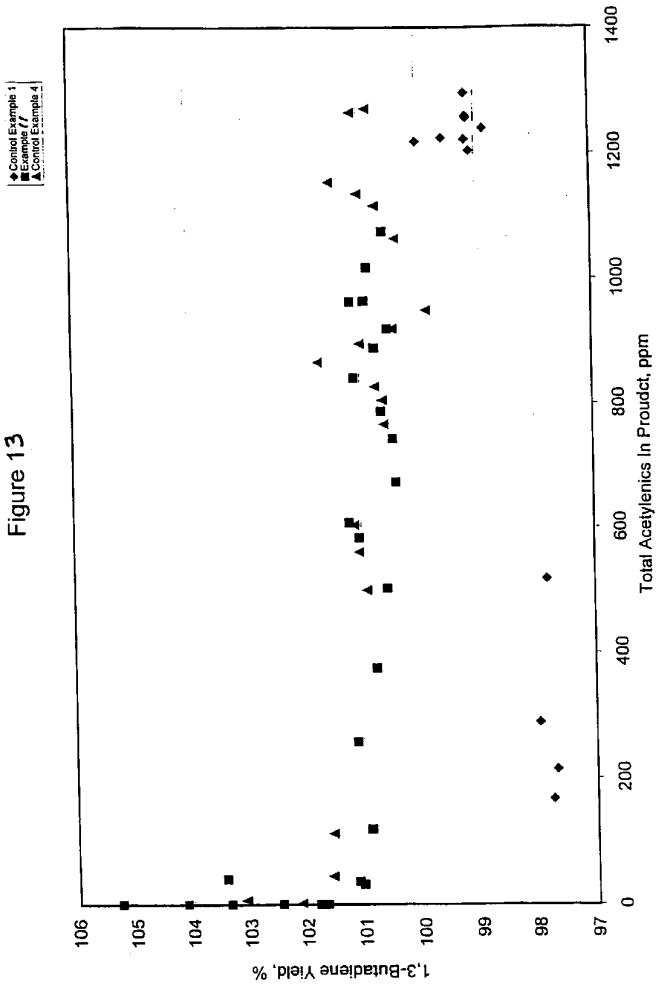

Control Example 1
Example 17
Control Example 4
1,3-Butadiene Yield, %
106
105
104
103
102
101
100
99
98
97
Total Acetylenics In Proudct, ppm
0
200
400
600
800
1000
1200
1400

Figure 13

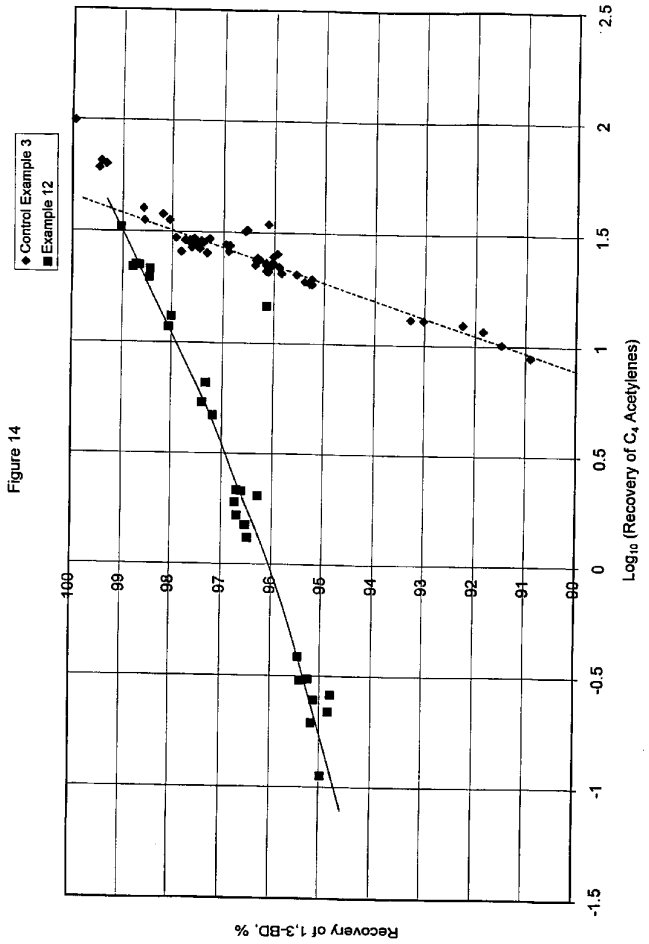

◆Control Example 3
■Example 12
Recovery of 1,3-BD, %
Log10 (Recovery of C4 Acetylenes)
100
99
98
97
96
95
94
93
92
91
90
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5

Figure 14

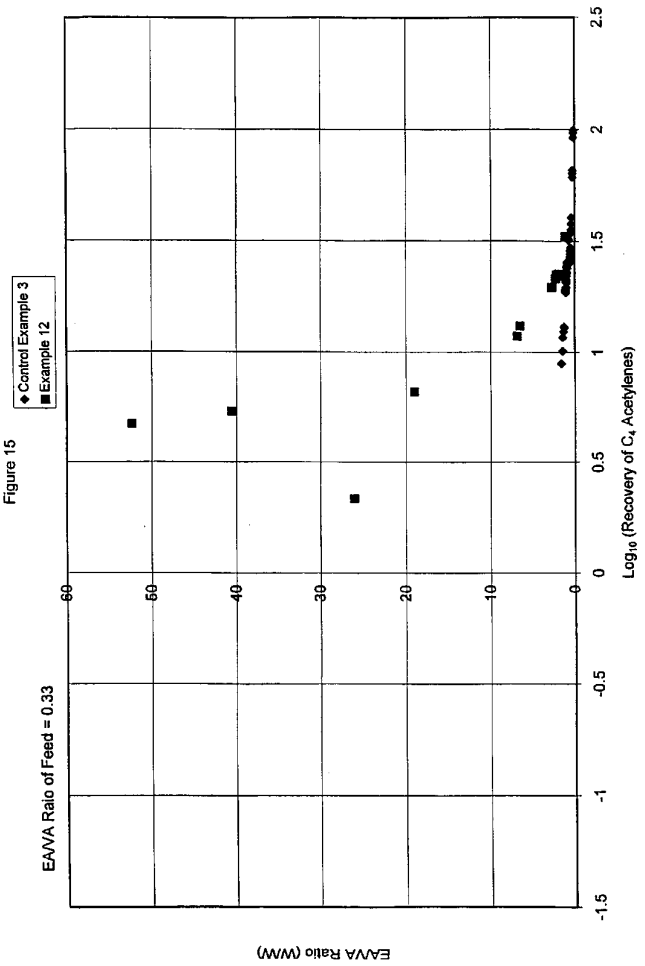

◆ Control Example 3
■ Example 12
EA/VA Ratio of Feed = 0.33
EA/VA Ratio (WM)
Log10 (Recovery of C4 Acetylenes)
60
50
40
30
20
10
0
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5

Figure 15

【国際調査報告】

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 02/07811

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01J23/89 B01J23/70 B01J23/80 B01J35/10 C07C7/167
C07C5/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01J C07C C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 440 956 A (COUVILLION MARK C) 3 April 1984 (1984-04-03) cited in the application	1-4,8,9, 13
Y	examples 3,5,7 figures 14,15	14,15
X	US 5 518 979 A (BONSE DIRK ET AL) 21 May 1996 (1996-05-21) examples 1-9	1,3,6,8
X	WO 94 20202 A (DARDA BETTINA ;KOCH VERONIKA (DE); BONSE DIRK (DE); BREHM AXEL (DE) 15 September 1994 (1994-09-15) examples 4,7	1,3,6,9

-/--

[X] Further documents are listed in the continuation of box C. [X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 December 2002	10. 12. 2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Zuurdeeg, B

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 02/07811

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 714 644 A (MIESEN ERNEST ET AL) 3 February 1998 (1998-02-03)	10,12,16
Y	column 2, line 23 -column 3, line 31 catalyst D	17,18
Y	EP 1 070 695 A (UOP LLC) 24 January 2001 (2001-01-24) claims 1,3-5,8,10 paragraphs '0004!,'0011!-'0019!	14,15, 17,18
A	FR 1 253 947 A (DOW CHEMICAL CO) 17 February 1961 (1961-02-17) cited in the application examples 1-3	1,3,6,13

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 02/07811

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☒ No protest accompanied the payment of additional search fees.

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FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-9, 13-15

Catalyst comprising a copper component and a component of at least one Group VIII metal component, a Ag, Au component or mixtures thereof on an alumina support comprising at least one of the properties of average pore diameter larger than 200 ANG or apparent bulk density of less than about 0.70 g/cm3 and a process for the selective hydrogenation of acetylenes using this catalyst

2. Claims: 10-12, 16-18

Catalyst comprising a copper component, at least one Group VIII metal component and a Zn component and a process for the selective hydrogenation of acetylenes using this catalyst.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 02/07811

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 4440956	A	03-04-1984	EP	0139051 A1	02-05-1985
			AU	559034 B2	19-02-1987
			AU	2030083 A	13-09-1984
			CA	1212373 A1	07-10-1986
			DE	3374666 D1	07-01-1988
			ES	8600081 A1	01-01-1986
			IN	161477 A1	12-12-1987
			JP	1679002 C	13-07-1992
			JP	3041212 B	21-06-1991
			JP	59162949 A	13-09-1984
			KR	9003942 B1	05-06-1990
			US	4493906 A	15-01-1985
			ZA	8307785 A	26-06-1985
US 5518979	A	21-05-1996	DE	4207961 A1	16-09-1993
			AT	133088 T	15-02-1996
			DE	59301480 D1	29-02-1996
			WO	9317786 A1	16-09-1993
			EP	0630288 A1	28-12-1994
			JP	7504357 T	18-05-1995
WO 9420202	A	15-09-1994	DE	4323085 A1	12-01-1995
			DE	4405202 A1	08-09-1994
			AT	148003 T	15-02-1997
			AT	180754 T	15-06-1999
			AT	153875 T	15-06-1997
			DE	4491188 D2	27-04-1995
			DE	4491189 D2	27-04-1995
			DE	4491190 D2	27-04-1995
			DE	59401659 D1	06-03-1997
			DE	59403026 D1	10-07-1997
			DE	59408365 D1	08-07-1999
			DK	687199 T3	14-07-1997
			WO	9420202 A1	15-09-1994
			WO	9420423 A1	15-09-1994
			WO	9420203 A1	15-09-1994
			EP	0687198 A1	20-12-1995
			EP	0690825 A1	10-01-1996
			EP	0687199 A1	20-12-1995
			JP	8506987 T	30-07-1996
			JP	8506988 T	30-07-1996
			JP	8506989 T	30-07-1996
			US	5736118 A	07-04-1998
			US	5676845 A	14-10-1997
			ZA	9401375 A	27-09-1994
US 5714644	A	03-02-1998	DE	4423738 A1	11-01-1996
			AU	688539 B2	12-03-1998
			AU	2981295 A	25-01-1996
			BR	9508232 A	19-05-1998
			CN	1151725 A ,B	11-06-1997
			DE	59506904 D1	28-10-1999
			WO	9601242 A1	18-01-1996
			EP	0770049 A1	02-05-1997
			ES	2138224 T3	01-01-2000
			HU	76706 A2	28-10-1997
			IL	113995 A	26-01-1999
			JP	10502363 T	03-03-1998

Form PCT/ISA/210 (patent family annex) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 02/07811

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 5714644	A		RU	2154527 C2	20-08-2000
EP 1070695	A	24-01-2001	US	6271428 B1	07-08-2001
			EP	1070695 A1	24-01-2001
			JP	2001058964 A	06-03-2001
FR 1253947	A	17-02-1961	NONE		

Form PCT/ISA/210 (patent family annex) (July 1992)

フロントページの続き

(81)指定国 AP(GH,GM,KE,LS,MW,MZ,SD,SL,SZ,TZ,UG,ZM,ZW),EA(AM,AZ,BY,KG,KZ,MD,RU,TJ,TM),EP(AT,BE,CH,CY,DE,DK,ES,FI,FR,GB,GR,IE,IT,LU,MC,NL,PT,SE,TR),OA(BF,BJ,CF,CG,CI,CM,GA,GN,GQ,GW,ML,MR,NE,SN,TD,TG),AE,AG,AL,AM,AT,AU,AZ,BA,BB,BG,BR,BY,BZ,CA,CH,CN,CO,CR,CU,CZ,DE,DK,DM,DZ,EE,ES,FI,GB,GD,GE,GH,GM,HR,HU,ID,IL,IN,IS,JP,KE,KG,KP,KR,KZ,LC,LK,LR,LS,LT,LU,LV,MA,MD,MG,MK,MN,MW,MX,MZ,NO,NZ,PL,PT,RO,RU,SD,SE,SG,SI,SK,SL,TJ,TM,TR,TT,TZ,UA,UG,UZ,VN,YU,ZA,ZW

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