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(54) Title: CATALYST COMPOSITION FOR SELECTIVE HYDROGENATION WITH IMPROVED CHARACTERISTICS

(57) Abstract: This invention relates to heterogeneous catalysts useful for selective hydrogenation of unsaturated hydrocarbons, comprising palladium and optionally a promoter, supported on a substrate, having an uncoated BET surface area of < 9 m^2/g, the surface being coated with an ionic liquid. Also described are methods of making the catalysts and methods of selective hydrogenation of acetylene in front-end mixed olefin feed streams.

CATALYST COMPOSITION FOR SELECTIVE HYDROGENATION WITH IMPROVED CHARACTERISTICS

FIELD OF THE INVENTION

The present invention is related to a catalyst composition for selective hydrogenations, for example for the selective hydrogenation of acetylene in the gaseous phase, comprising a heterogeneous catalyst with a BET surface area of ≤ 9 m^2/g and an ionic liquid applied to the surface of the same. The catalyst composition has improved characteristics such as, for example, improved selectivity in favor of the desired product and better thermal stability.

BACKGROUND OF THE INVENTION

Ethylene and propylene are important monomers for the production of plastics, such as for example polyethylene or polypropylene. Ethylene and propylene are primarily derived from petroleum and petroleum products by means of thermal or catalytic cracking of hydrocarbons. The ethylene or propylene derived with the aid of the cracking process does, however, contain an undesirably high proportion of acetylenic compounds such as acetylene or methyl acetylene (propyne), which can negatively influence downstream ethylene or propylene polymerization. Therefore prior to polymerization the ethylene or propylene must be freed from acetylenic compounds as far as possible.

Typically for the polymerization of ethylene the acetylene concentration must, for example, be reduced to a value of below 1 ppm. For this the acetylene is selectively hydrogenated into ethylene. High requirements are placed on the catalyst and the hydrogenation process. On the one hand, the acetylene must be removed as completely as possible by transformation into ethylene, while the hydrogenation of ethylene into ethane must be prevented, hence the term "selective hydrogenation". In order to ensure this result, the hydrogenation is carried out within a temperature range that is delimited by the so-called "clean-up" temperature and the so-called "run-away" temperature. In the present context the "clean-up" temperature is understood as the temperature from which an appreciable hydrogenation of acetylene into ethylene is observed, while "run-away" temperature is understood as the temperature at which an appreciable hydrogenation of ethylene into ethane commences. The said temperatures can be determined in that the hydrogen consumption of a defined gas mixture containing

acetylene, ethylene, and hydrogen is, for example, measured depending on the temperature.

Palladium shell catalysts, often using silver as a promoter, are primarily used as commercial catalysts for the selective hydrogenation of acetylene into ethylene in hydrocarbon streams. The palladium and the silver are supported on an inert, temperature-resistant substrate. The production of these catalysts is carried out in such a way that suitable salts of palladium and silver, for example palladium nitrate and silver nitrate, are applied to a substrate in form of an aqueous solution (impregnation). The impregnation can take place during separate steps with a palladium compound solution and a silver compound solution. It is, however, also possible to apply the solution of palladium compounds and the solution of silver compounds to the substrate simultaneously during a single impregnation step. The impregnated substrate is then calcined to transform the silver into silver oxide, or the palladium into palladium oxide, and is then subjected to a reduction in order to transfer the catalyst into the active form. During the reaction the silver and palladium are assumed to be transferred into the oxidation state "zero".

DE 31 19 850 A1 describes a method for the selective hydrogenation of a diolefin with at least 4 carbon atoms in a hydrocarbon mixture. Hydrogenation takes place with hydrogen on a catalyst containing palladium and silver. The silver/palladium weight ratio of the catalyst is 0.7:1 to 3:1. The production of the catalyst is by way of co-impregnation of a substrate with an aqueous solution of palladium and silver salts.

US 5,648,576 A describes a method for the selective gaseous phase hydrogenation of acetylenic hydrocarbons (C_2-C_3) into the corresponding ethylenic hydrocarbons. The production of the catalyst is realized by co-impregnating the substrate with an aqueous solution of the respective metal salts.

EP 0 064 301 A1 offers a catalyst for the selective gaseous phase hydrogenation of acetylene. The production of the catalyst is realized by means of a two-step application of palladium and silver.

EP 0 780 155 A1 describes the production of hydrogenation catalysts, whereby solutions of palladium nitrate and silver nitrate in a nitrogenous acid are used for the impregnation of the substrate.

Apart from the Pd/Ag catalysts described above, a number of further palladium based catalyst are described, which also provide improved selectivity and sometimes

also improved activity; the same include Pd/Zn, Pd/Cd, Pd/Ga and Pd/Au. The latter catalyst family is characterized primarily by a high "run-away" temperature.

According to the definition of Wasserscheid and Keim in "Angewandte Chemie" 2000, 112, pages 3926-3945, ionic liquids are salts, i.e. compounds of anions and cations that are externally neutral, which melt at low temperatures, usually at temperatures of below 100 °C. Ionic liquids are therefore already liquid at low temperatures. In addition they are generally not flammable and have an extremely low vapor pressure. Due to the high variation range of the structure of their cations and anions, their physical and chemical characteristics can be varied over a broad range.

The concept of coating heterogeneous catalysts with small quantities of an ionic liquid has already been described by Jess et al. and Claus et al. [U. Kernchen, B. Etzold, W. Korth, A. Jess, Chem. Eng. Technol. 2007, 30, 985-994; J. Arras, M. Steffan, Y. Shayeghi, P. Claus, Chem. Commun. 2008, 4058-4060]. In both cases an improved selectivity towards the desired product in the target reaction of the hydrogenation of citral or the hydrogenation of diolefins could be achieved than is possible with the uncoated catalyst. This catalyst family has also been named as SCILL – Solid Catalyst with Ionic Liquid Layer – catalysts by the authors.

US 2008/0269533 A1 describes the selective mono-hydrogenation of conjugated dienes with the aid of supported Pd nanoparticles coated with ionic liquids.

International patent application WO2007/124 896 relates to heterogeneous catalysts having a BET surface area of preferably 10 to 300 m^2/g. These catalysts may be covered with an ionic liquid and are used for the selective hydrogenation of unsaturated cyclic compounds.

A catalyst system for the selective hydrogenation of acetylene in the simultaneous presence of ethylene comprising a heterogeneous catalyst coated with ionic liquid has also already been described [M. Ruta, G. Laurenczy, P. J. Dyson, L. Kiwi-Minsker, J. Phys. Chem. C 2008, 112, 17814-17819]. However, these catalysts are prepared with support materials that are not suitable for industrial use, as the production of the same is too costly. The described turnovers are also far from realizable.

With all of the examples described so far support materials with a high specific surface area and a suitable pore volume were used. In order to achieve an even coating of the entire catalyst surface, and thus the best possible effect (selectivity increase etc.) a relatively large quantity of ionic liquid is required (10 - 17 wt. % in relation to the initial weight of the heterogeneous catalyst). This often results in a substantial pore

filling of the catalyst and the reduced activity connected with the same. Ionic liquids are also expensive, which results in substantial additional costs for the overall catalyst formulation.

SUMMARY OF THE INVENTION

There remains a need for further improving the selectivity of Pd/promoter catalysts for the hydrogenation of acetylenic hydrocarbons, while maintaining or even increasing catalyst activity.

It is therefore the object of this invention to provide a catalyst with high selectivity and activity for the hydrogenation of acetylenic hydrocarbons.

Surprisingly it has been found that conventional heterogeneous catalysts with a BET surface area of ≤ 9 m^2/g which are coated with a small amount of an ionic liquid (IL) have improved characteristics, such as improved selectivity in the hydrogenation of unsaturated hydrocarbons while retaining high activity.

With the catalyst system of the invention, known pre-formulated catalysts for the transformation of acetylene into ethylene with a BET surface area of ≤ 9 m^2/g are coated with one (or more) ionic liquid(s). The resulting catalyst formulations have a very high selectivity during the hydrogenation of acetylene in ethylene rich gas streams and are further surprisingly characterized by a higher "run-away" temperature. The catalyst formulations of the invention further may use very small quantities of ionic liquid (in the range of ≤ 3% by weight of the catalyst) to achieve these advantageous effects. The loss of catalyst activity is very small.

DETAILED DESCRIPTION OF THE INVENTION

The pre-formulated catalysts used for coating are, as already described above, supported palladium shell catalysts which preferably comprise at least one further promoter such as for example silver, gold, zinc, tin, lead, gallium, cadmium, copper, bismuth, or potassium. Preferred promoters are silver, gold and zinc, especially silver. Preferred metal or metal-alloy shell thicknesses are in the range of 100 to 500 µm. The Pd metal content in relation to the total weight of the catalyst without ionic liquid is preferably in the range of 10 to 1000 ppm, more preferably between 50 and 500 ppm. For the desired target reaction the catalysts are used either as shaped bodies such as for example tablets, rings, tri-holes, extrudates etc., or as a granulate or powder. The weight ratio of palladium to promoter metal for example lies within a range of 1:5 to 3:1, preferably within a range of 1:4 to 2:1, and particularly preferably within a range of 1:3 to 1:1.

Suitable carrier substrates are Al_2O_3, SiO_2, alumo silicates, TiO_2, ZrO_2, ZnO, MgO, Fe_2O_3 and CeO_2, or mixtures thereof. In order to increase activity or selectivity the substrates can further be doped with at least one of the following elements: Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr and/or Ba. Na, K and/or Ca are particularly suitable.

The BET surface area of the uncoated catalyst is ≤ 9 m^2/g, preferably in a range of 1 to 9 m^2/g, more preferably in a range of 2 to 8 m^2/g, and particularly preferably in a range of 3 to 5 m^2/g. The determination of the surface area may be carried out in accordance with ASTM D3663, Standard Test Method for Surface Area of Catalysts and Catalyst Carriers.

The integral pore volume of the catalyst (determined according to DIN 66134 of February 1998 (N_2 adsorption)) without the IL-coating preferably is in the range of 0.005 to 0.07 ml/g, more preferably in the range of 0.007 to 0.04 ml/g and particularly preferably within the range of 0.009 to 0.02 ml/g.

Suitable pre-formulated catalysts for use in preparing supported ionic liquid phase catalyst compositions of the invention include any commercially-available supported Pd or Pd/Ag catalysts supplied by, for example Süd-Chemie, AG, Munich, Germany, BASF, Johnson-Mathey, etc.

For the production of a catalyst composition of the invention a pre-formulated catalyst is loaded with ionic liquid. The ionic liquid to be used for this is not particularly restricted, and in principle, all known ionic liquids suitable for this purpose can be used. Preferred ionic liquids for use with this invention are compounds with the formula (I):

$$[A]_n^+ \; [Y]^{n-} \qquad (I),$$

wherein:

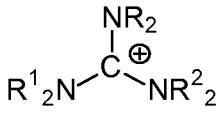
n = 1 or 2;

$[Y]^{n-}$ is selected from the group consisting of tetrafluoroborate ($[BF_4]^-$), hexafluorophosphate ($[PF_6]^-$), dicyanamide ($[N(CN)_2]^-$), halides (Cl^-, Br^-, F^-, I^-), hexafluoroantimonate ($[SbF_6]^-$), nitrate ($[NO_3]^-$), nitrite ($[NO_2]^-$), anionic metal complexes such as for example $[CuCl_4]^{2-}$, $[PdCl_4]^{2-}$ or $[AuCl_4]^-$, acetate ($[CH_3COO]^-$), trifluoracetate ($[F_3CCOO]^-$), hexafluoroarsenate ($[AsF_6]^-$), sulfate ($[SO_4]^{2-}$), hydrogen sulfate ($[HSO_4]^-$), alkyl sulfates ($[R'\text{-}SO_4]^-$), tosylate ($[C_7H_7SO_3]^-$), triflate ($[CF_3SO_3]^-$), nonaflate ($[C_4F_9SO_3]^-$), triperfluoroethylene trifluorophosphate ($[PF_3(C_2F_5)_3]^-$), tricyanomethide ($[C(CN)_3]^-$), tetracyanoborate ($[B(CN)_4]^-$, thiocyanate ($[SCN]^-$), carbonate ($[CO_3]^{2-}$), carboxylates ($[R'\text{-}COO]^-$), sulfonates ($[R'SO_3]^-$), dialkylphosphates

($[R'PO_4R"]^-$), alkyl phosphonates ($[R'HPO_3]^-$) and bissulfonylimides ($[(R'\text{-}SO_2)_2N]^-$), such as bis(trifluormethylsulfonyl)imide,

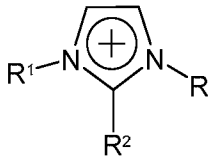
wherein R' and R" are the same or different, and each represents a linear or branched, 1 to 12 carbon atom-containing aliphatic or alicyclic alkyl group or a C_5-C_{18}-aryl, C_5-C_{18}-aryl-C_1-C_6-alkyl, or C_1-C_6-alkyl-C_5-C_{18}-aryl group that can be substituted with halogen atoms; and

$[A]^+$ is selected from the group consisting of quaternary ammonium cations with the formula $[NR^1R^2R^3R]^+$, phosphonium cations with the formula $[PR^1R^2R^3R]^+$, sulfonium cations with the formula $[SR^1R^2R]^+$, guadinium cations with the formula (II):



(II),

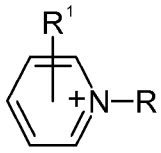
imidazolium cations with the formula (III)



(III),

wherein the imidazole core may additionally be substituted with one or more groups selected from C_1-C_6-alkyl, C_1-C_6-alkoxy, C_1-C_6-aminoalkyl, C_5-C_{12}-aryl, and C_5-C_{12}-aryl-C_1-C_6-alkyl groups,

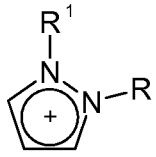
pyridinium cations with the formula (IV)



(IV),

wherein the pyridine core may additionally be substituted with one or more groups selected from C_1-C_6-alkyl, C_1-C_6-alkoxy, C_1-C_6-aminoalkyl, C_5-C_{12}-aryl, and C_5-C_{12}-aryl-C_1-C_6-alkyl groups,

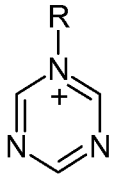
pyrazolium cations with the formula (V)



(V),

wherein the pyrazole core may additionally be substituted with one or more groups selected from C_1-C_6-alkyl, C_1-C_6-alkoxy, C_1-C_6-aminoalkyl, C_5-C_{12}-aryl, and C_5-C_{12}-aryl-C_1-C_6-alkyl groups,

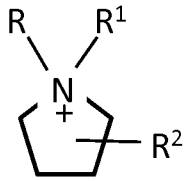
triazolium cations with the formula (VI)



(VI),

wherein the triazole core may additionally be substituted with one or more groups selected from C_1-C_6-alkyl, C_1-C_6-alkoxy, C_1-C_6-aminoalkyl, C_5-C_{12}-aryl, and C_5-C_{12}-aryl-C_1-C_6-alkyl groups,

and pyrrolidinium cations with the formula (VII)



(VII),

wherein the pyrrolidinium core may additionally be substituted with one or more groups selected from C_1-C_6-alkyl, C_1-C_6-alkoxy, C_1-C_6-aminoalkyl, C_5-C_{12}-aryl, and C_5-C_{12}-aryl-C_1-C_6-alkyl groups,

wherein R^1, R^2, and R^3 are selected independently from each other from the group consisting of: hydrogen; linear or branched, saturated or unsaturated, aliphatic or alicyclic alkyl groups with 1 to 20 carbon atoms, which may be interrupted by one or two of NH, O and/or S; heteroaryl groups with 3 to 8 carbon atoms and at least one hetero atom selected from N, O and S, wherein the heteroaryl groups can be substituted with one or more groups selected from C_1-C_6-alkyl groups and halogen atoms; heteroaryl-C_1-C_6-alkyl groups with 3 to 8 carbon atoms and at least one hetero atom selected from N, O and S in the heteroaryl moiety, wherein the heteroaryl moiety can be substituted with at least one group selected from C_1-C_6-alkyl groups and halogen atoms; polyethers with the formula $[-CH_2CH_2O]_nR^a$ with n = 1 to 50,000, wherein R^a is selected from the group consisting of linear or branched, saturated or unsaturated, aliphatic or alicyclic alkyl

groups with 1 to 20 carbon atoms; aryl groups with 5 to 12 carbon atoms, which may be substituted with one or more C_1-C_6-alkyl groups and/or halogen atoms; aryl-C_1-C_6-alkyl groups with 5 to 12 carbon atoms in the aryl moiety, which may be substituted with one or more C_1-C_6-alkyl groups and/or halogen atoms, and

wherein R is selected from the group consisting of: linear or branched, saturated or unsaturated, aliphatic or alicyclic alkyl groups with 1 to 20 carbon atoms; heteroaryl-C_1-C_6-alkyl groups with 4 to 8 carbon atoms and at least one hetero atom selected from N, O and S in the heteroaryl moiety, which may be substituted with one or more C_1-C_6-alkyl groups and/or halogen atoms; and aryl-C_1-C_6-alkyl groups with 4 to 12 carbon atoms in the aryl moiety, which may be substituted with one or more C_1-C_6-alkyl groups and/or halogen atoms.

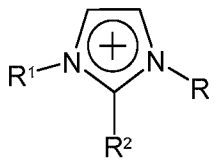
Further preferred ionic liquids for use with this invention are compounds with the formula (I):

$$[A]_n^+ \ [Y]^{n-} \qquad (I),$$

wherein:

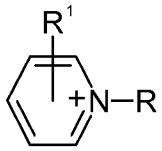
n and $[Y]^{n-}$ are as defined above, and

$[A]^+$ is selected from the group consisting of quaternary ammonium cations with the formula $[NR^1R^2R^3R]^+$, imidazolium cations with the formula (III)



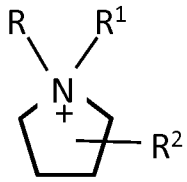
(III),

pyridinium cations with the formula (IV)



(IV),

and pyrrolidinium cations with the formula (VII)



(VII),

wherein R, R^1, R^2 and R^3 are selected independently from each other from the group consisting of hydrogen; linear or branched C_1-C_{12}-alkyl groups; linear or branched (C_1-C_6-alkyloxy)-C_1-C_6-alkyl groups; and aryl-C_1-C_6-alkyl groups with 5 to 12 carbon atoms in the aryl moiety, which may be substituted with one or more C_1-C_6-alkyl groups and/or halogen atoms.

More preferred ionic liquids for preparing supported ionic liquid phase catalysts of the invention include 1-butyl-3-methylimidazolium triflate, 1-ethyl-3-methylpyridinium ethylsulfate, 1-butyl-1-methylpyrrolidinium triflate, 1-butyl-2,3-dimethylimidazolium triflate, 1-butyl-3-methylimidazolium tricyanomethane, 1-butyl-3-methylimidazolium methylsulfate, 1-butyl-3-methylimidazolium octylsulfate, 1-butyl-3-methylimidazolium tetrafluoroborate, 1-ethyl-3-methylimidazolium ethylsulfate, 1-ethyl-3-methylimidazolium methylphosphonate, 1-ethyl-3-methylimidazolium triflate, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsufonyl)imide, 1-butyl-1-methylpyrrolidinium tetracyanoborate, 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate, 1-butyl-3-methylimidazolium bis(trifluoromethylsufonyl)imide, 1-butyl-3-methylimidazolium tricyanomethane, 1-ethyl-3-methylpyridinium bis(trifluoromethylsufonyl)imide, 1-ethyl-3-methylimidazolium tetracyanoborate, 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate, 1-ethyl-3-methylpyridinium bis(trifluoromethylsufonyl)imide, 1-methyl-3-octylimidazolium triflate, ethyldimethyl-(2-methoxyethyl)ammonium tris(pentafluoroethyl)trifluorophosphate, tributylmethylammonium dicyanamide, tricyclohexyltetradecylphosphonium tris(pentafluoroethyl)trifluorophosphate, 1-ethyl-3-methylimidazolium bis(trifluoromethylsufonyl)imide, and mixtures thereof.

More preferred ionic liquids further include those of the formula (I), wherein $[A]^+$ is selected from the group consisting of 1-butyl-1-methylpyrrolidinium, 1-butyl-2,3-dimethylimidazolium, 1-butyl-3-methylimidazolium, 1-ethyl-3-methylimidazolium, 1-ethyl-3-methylpyridinium, 1-methyl-3-octylimidazolium, ethyldimethyl-(2-methoxyethyl)ammonium, tributylmethylammonium, tricyclohexyltetradecylphosphonium, and mixtures thereof, and wherein $[Y]^{n-}$ is selected from the group consisting of bis(trifluoromethylsufonyl)imide, dicyanamide, ethylsulfate, methylphosphonate, methylsulfate, octylsulfate, tetracyanoborate, tetrafluoroborate, tricyanomethane, triflate, tris(pentafluoroethyl)trifluorophosphate, and mixtures thereof.

Especially preferred ionic liquids for use within this invention are compounds with the formula (I), wherein n =1, that is $[A]^+[Y]^-$.

For the production of catalyst compositions of the invention, the ionic liquid or mixtures of several ionic liquids are dissolved or suspended in a solution agent suitable for the purpose, such as for example water, alcohols, acetone etc., or in a solution agent mixture, and applied continuously onto the already pre-formed catalyst inside a reaction chamber with the aid of a nozzle. For this the solution agent is continuously removed from the reaction chamber during the process. In order to achieve an even coating of the substrate, the substrate material is continuously fluidized through a process gas in a process known as fluidized bed coating or through impregnation with a solution or suspension. Further suitable coating processes are dip coating or spray application with a spray pistol or a spray drying pistol.

The amount of ionic liquid relative to the total weight of the catalyst without ionic liquid is for example 0.1 – 10 wt%, preferably 0.2 – 3 wt%, and most preferably 0.3 – 1.5 wt%.

Apart from the application of ionic liquid by means of coating technologies, the same can also be applied by impregnating with a solution or suspension. For this the ionic liquid or mixtures of several ionic liquids are dissolved or suspended in a suitable solution agent (mixture) and subsequently brought into contact with the pre-formed catalyst. The solution agent is then removed under vacuum or at an increased temperature (or both), by resting in air, or by means of a gas stream. The quantity of solution agent used can be equal to or smaller or greater than the pore volume of the catalyst used.

The quantity of ionic liquid used is equal to or smaller than the pore volume of the catalyst used. After the application of the ionic liquid, one is left with an externally dry solid body coated with the desired quantity of ionic liquid. The pore volume of the resulting catalyst composition is reduced by the volume of the ionic liquid. Related to the total weight of the catalyst 0.1 – 5 wt. %, preferably 0.2 – 3 wt. %, and particularly preferably 0.3 – 1.5 wt. % of ionic liquid is used. The distribution of ionic liquid on the macroscopic substrate form body, granulate or powder is freely adjustable by selecting the coating conditions. Depending on the selection of the conditions, a formation of a so-called eggshell, egg-white, egg-yolk, or a uniform distribution of the ionic liquid may result on the substrate. In addition, any concentration gradient of ionic liquid can be created on the substrate. The ionic liquid is preferably applied to the substrate surface as a thin shell. The shell thickness of the ionic liquid on the substrate surface of this

invention usually lies within a range of 10 to 2000 µm, preferably within a range of 20 to 1000 µm, and particularly preferably within a range of 50 to 250 µm.

The resulting catalyst can be used without restricting the target reaction. The reduction of metal particles required for activating the catalyst can either take place prior to a coating with the ionic liquid or following the same.

The catalyst can for example be reduced prior to coating with an ionic liquid. The methods to be used for the same are known to the expert, and can for example include wet chemical methods through reduction such as for example $NaBH_4$, $LiAlH_4$, hydrazine (hydrate), hypophosphite, formic acid, or salts of the same (formates). In addition a reduction can be brought about in the gaseous phase with hydrogen (in all mixtures with an inert gas; preferably 5% in N_2) within a temperature range of 50-200°C, preferably at 80-120°C.

The reduced metal particles obtained in this way usually have a diameter within a range of 1 to 30 nm, preferably within a range of 1 to 10 nm, and particularly preferably within a range of 2 to 8 nm.

EXAMPLES

Example 1

Sample A contains 0.017 wt% Pd on 1-2 mm alumina spheres with a BET surface area of 4.0 m^2/g. In order to make Sample A, 1100 g Alpha Alumina was added to 1075 mL $PdCl_2$ solution (0.178 mg Pd/mL) heated at 70 °C. After the carrier was soaked in the solution for 1 hour, the solution was drained and then the catalyst was washed 10 times using 5 minute soak times with room temperature deionized water. After final wash, the catalyst was calcined in a muffle oven in air at 565 °C for 4 hours.

Sample A1 was made by adding 0.5 wt% of EMIM[$EtSO_4$] (1-ethyl-3-methylimidazolium ethylsulfate) on Sample A. In order to make Sample A1, Sample A (516.0 mg) was impregnated with an aqueous solution of 1-ethyl-3-methylimidazolium ethylsulfate (232 µL, 11.11 mg/mL) by incipient wetness. The catalyst was dried at 80 °C for 16 hours and reduced at 100 °C in 5% H_2/N_2 for 1 hour.

Sample A2 was made by adding 0.5 wt% of BMIM[OTf] (1-butyl-3-methylimidazolium triflate) on Sample A. In order to make Sample A2, Sample A (476.3 mg) was impregnated with an aqueous solution of 1-butyl-3-methylimidazolium triflate (214 µL, 11.11 mg/mL) by incipient wetness. The catalyst was dried at 80 °C for 16 hours and reduced at 100 °C in 5% H_2/N_2 for 1 hour.

Sample A3 was made by adding 0.5 wt% of BMPr[OTf] (1-butyl-1-methylpyrrolidinium triflate) on Sample A. In order to make Sample A3, Sample A (499.7 mg) was impregnated with an aqueous solution of 1-butyl-1-methylpyrrolidinium triflate (225 µL, 11.11 mg/mL) by incipient wetness. The catalyst was dried at 80 °C for 16 hours and reduced at 100 °C in 5% H_2/N_2 for 1 hour.

Sample A4 was made by adding 0.5 wt% of BMMIM[OTf] (1-Butyl-2,3-dimethylimidazolium triflate) on Sample A. In order to make Sample A4, Sample A (528.8 mg) was impregnated with an aqueous solution of 1-Butyl-2,3-dimethylimidazolium triflate (238 µL, 11.11 mg/mL) by incipient wetness. The catalyst was dried at 80 °C for 16 hours and reduced at 100 °C in 5 % H_2/N_2 for 1 hour.

Sample A5 was made by adding 0.5 wt% of BMIM[BF_4] (1-butyl-3-methylimidazolium tetrafluoroborate) on Sample A. In order to make Sample A5, Sample A (508.2 mg) was impregnated with an aqueous solution of 1-butyl-3-methylimidazolium tetrafluoroborate (229 µL, 11.11 mg/mL) by incipient wetness. The catalyst was dried at 80 °C for 16 hours and reduced at 100 °C in 5% H_2/N_2 for 1 hour.

Sample A6 was made by adding 0.5 wt% of BMIM[$MeSO_4$] (1-butyl-3-methylimidazolium methylsulfate) on Sample A. In order to make Sample A6, Sample A (511.8 mg) was impregnated with an aqueous solution of 1-butyl-3-methylimidazolium methylsulfate (230 µL, 11.11 mg/mL) by incipient wetness. The catalyst was dried at 80 °C for 16 hours and reduced at 100 °C in 5% H_2/N_2 for 1 hour.

Sample A7 was made by adding 0.5 wt% of BMIM[$C_8H_{17}SO_4$] (1-butyl-3-methylimidazolium octylsulfate) on Sample A. In order to make Sample A7, Sample A (485.7 mg) was impregnated with an aqueous solution of 1-butyl-3-methylimidazolium octylsulfate (218 µL, 11.11 mg/mL) by incipient wetness. The catalyst was dried at 80 °C for 16 hours and reduced at 100 °C in 5% H_2/N_2 for 1 hour.

Sample A8 was made by adding 0.5 wt% of EMIM[OTf] (1-ethyl-3-methylimidazolium triflate) on Sample A. In order to make Sample A8, Sample A (509.9 mg) was impregnated with an aqueous solution of 1-ethyl-3-methylimidazolium triflate (229 µL, 11.11 mg/mL) by incipient wetness. The catalyst was dried at 80 °C for 16 hours and reduced at 100 °C in 5% H_2/N_2 for 1 hour.

Sample A9 was made by adding 0.5 wt% of EMPy[$EtSO_4$] (1-ethyl-3-methylpyridinium ethylsulfate) on Sample A. In order to make Sample A9, Sample A (504.0 mg) was impregnated with an aqueous solution of 1-ethyl-3-methylpyridinium ethylsulfate (227 µL, 11.11 mg/mL) by incipient wetness. The catalyst was dried at 80 °C for 16 hours and reduced at 100 °C in 5% H_2/N_2 for 1 hour.

Sample A10 was made by adding 0.5 wt% of EMIM[$MePO_3$] (1-ethyl-3-methylimidazolium methylphosphonate) on Sample A. In order to make Sample A10, Sample A (517.1 mg) was impregnated with an aqueous solution of 1-ethyl-3-methylimidazolium methylphosphonate (233 µL, 11.11 mg/mL) by incipient wetness. The catalyst was dried at 80 °C for 16 hours and reduced at 100 °C in 5% H_2/N_2 for 1 hour.

Sample A11 was made by adding 0.5 wt% of BMIM[$C(CN)_3$] (1-butyl-3-methylimidazolium tricyanomethane) on Sample A. In order to make Sample A11, Sample A (504.0 mg) was impregnated with a solution of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide in 2-butanone (227 µL, 11.11 mg/mL) by incipient wetness. The catalyst was dried at 60 °C for 4 hours and reduced at 100 °C in 5% H_2/N_2 for 1 hour.

Sample A12 was made by adding 0.5 wt% of BMIM[NTf_2] (1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) on Sample A. In order to make

Sample A12, Sample A (513.4 mg) was impregnated with a solution of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide in 2-butanone (231 µL, 11.11 mg/mL) by incipient wetness. The catalyst was dried at 60 °C for 4 hours and reduced at 100 °C in 5% H_2/N_2 for 1 hour.

Sample A13 was made by adding 0.5 wt% of MOIM[OTf] (1-methyl-3-octylimidazolium triflate) on Sample A. In order to make Sample A13, Sample A (502.1 mg) was impregnated with a solution of 1-methyl-3-octylimidazolium triflate in 2-butanone (226 µL, 11.11 mg/mL) by incipient wetness. The catalyst was dried at 60 °C for 4 hours and reduced at 100 °C in 5% H_2/N_2 for 1 hour.

Sample A14 was made by adding 0.5 wt% of EMIM[NTf_2] (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) on Sample A. In order to make Sample A14, Sample A (490.3 mg) was impregnated with a solution of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide in 2-butanone (220 µL, 11.11 mg/mL) by incipient wetness. The catalyst was dried at 60 °C for 4 hours and reduced at 100 °C in 5% H_2/N_2 for 1 hour.

Sample A15 was made by adding 0.5 wt% of EMIM[$B(CN)_4$] (1-ethyl-3-methylimidazolium tetracyanoborate) on Sample A. In order to make Sample A15, Sample A (504.8 mg) was impregnated with a solution of 1-ethyl-3-methylimidazolium tetracyanoborate in 2-butanone (227 µL, 11.11 mg/mL) by incipient wetness. The catalyst was dried at 60 °C for 4 hours and reduced at 100 °C in 5% H_2/N_2 for 1 hour.

Sample A16 was made by adding 0.5 wt% of EMIM[$PF_3(C_2F_5)_3$] (1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate) on Sample A. In order to make Sample A16, Sample A (514.4 mg) was impregnated with a solution of 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate in 2-butanone (231 µL, 11.11 mg/mL) by incipient wetness. The catalyst was dried at 60 °C for 4 hours and reduced at 100 °C in 5% H_2/N_2 for 1 hour.

Sample A17 was made by adding 0.5 wt% of EMPy[NTf_2] (1-ethyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide) on Sample A. In order to make Sample A17, Sample A (531.6 mg) was impregnated with a solution of 1-ethyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide in 2-butanone (239 µL, 11.11 mg/mL) by incipient wetness. The catalyst was dried at 60 °C for 4 hours and reduced at 100 °C in 5% H_2/N_2 for 1 hour.

Sample A18 was made by adding 0.5 wt% of BMPr[NTf_2] (1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide) on Sample A. In order to make

Sample A18, Sample A (512.5 mg) was impregnated with a solution of 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide in 2-butanone (230 µL, 11.11 mg/mL) by incipient wetness. The catalyst was dried at 60 °C for 4 hours and reduced at 100 °C in 5% H_2/N_2 for 1 hour.

Sample A19 was made by adding 0.5 wt% of BMPr[$PF_3(C_2F_5)_3$] (1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate) on Sample A. In order to make Sample A19, Sample A (510.3 mg) was impregnated with a solution of 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate in 2-butanone (229 µL, 11.11 mg/mL) by incipient wetness. The catalyst was dried at 60 °C for 4 hours and reduced at 100 °C in 5% H_2/N_2 for 1 hour.

Sample A20 was made by adding 0.5 wt% of BMPr[$B(CN)_4$] (1-butyl-1-methylpyrrolidinium tetracyanoborate) on Sample A. In order to make Sample A20, Sample A (516.0 mg) was impregnated with a solution of 1-butyl-1-methylpyrrolidinium tetracyanoborate in 2-butanone (232 µL, 11.11 mg/mL) by incipient wetness. The catalyst was dried at 60 °C for 4 hours and reduced at 100 °C in 5% H_2/N_2 for 1 hour.

Sample A21 was made by adding 0.5 wt% of TBMA[$N(CN)_2$] (tributylmethylammonium dicyanamide) on Sample A. In order to make Sample A21, Sample A (474.2 mg) was impregnated with a solution of tributylmethylammonium dicyanamide in 2-butanone (213 µL, 11.11 mg/mL) by incipient wetness. The catalyst was dried at 60 °C for 4 hours and reduced at 100 °C in 5% H_2/N_2 for 1 hour.

Sample A22 was made by adding 0.5 wt% of {$EtMe_2(MeOEt)$}N[$PF_3(C_2F_5)_3$] (ethyldimethyl-(2-methoxyethyl)ammonium tris(pentafluoroethyl)trifluorophosphate) on Sample A. In order to make Sample A22, Sample A (477.6 mg) was impregnated with a solution of ethyldimethyl-(2-methoxyethyl)ammonium tris(pentafluoroethyl)trifluorophosphate in 2-butanone (215 µL, 11.11 mg/mL) by incipient wetness. The catalyst was dried at 60 °C for 4 hours and reduced at 100 °C in 5% H_2/N_2 for 1 hour.

Example 2

Sample B1 was made by adding 0.001 wt% of EMIM[$EtSO_4$] (1-ethyl-3-methylimidazolium ethylsulfate) on Sample A. In order to make Sample B1, Sample A (485.8 mg) was impregnated with an aqueous solution of 1-ethyl-3-methylimidazolium ethylsulfate (219 µL, 0.022 mg/mL) by incipient wetness. The catalyst was dried at 80°C for 16 hours and reduced at 100 °C in 5% H_2/N_2 for 1 hour.

Sample B2 was made by adding 0.007 wt% of EMIM[$EtSO_4$] (1-ethyl-3-methylimidazolium ethylsulfate) on Sample A. In order to make Sample B2, Sample A (505.1 mg) was impregnated with an aqueous solution of 1-ethyl-3-methylimidazolium ethylsulfate (227 µL, 0.16 mg/mL) by incipient wetness. The catalyst was dried at 80 °C for 16 hours and reduced at 100 °C in 5 % H_2/N_2 for 1 hour.

Sample B3 was made by adding 0.025 wt% of EMIM[$EtSO_4$] (1-ethyl-3-methylimidazolium ethylsulfate) on Sample A. In order to make Sample B3, Sample A (512.8 mg) was impregnated with an aqueous solution of 1-ethyl-3-methylimidazolium ethylsulfate (231 µL, 0.56 mg/mL) by incipient wetness. The catalyst was dried at 80 °C for 16 hours and reduced at 100 °C in 5% H_2/N_2 for 1 hour.

Sample B4 was made by adding 0.05 wt% of EMIM[$EtSO_4$] (1-ethyl-3-methylimidazolium ethylsulfate) on Sample A. In order to make Sample B4, Sample A (468.0 mg) was impregnated with an aqueous solution of 1-ethyl-3-methylimidazolium ethylsulfate (210 µL, 1.11 mg/mL) by incipient wetness. The catalyst was dried at 80 °C for 16 hours and reduced at 100 °C in 5 % H_2/N_2 for 1 hour.

Sample B5 was made by adding 0.1 wt% of EMIM[$EtSO_4$] (1-ethyl-3-methylimidazolium ethylsulfate) on Sample E. In order to make Sample B5, Sample A (497.3 mg) was impregnated with an aqueous solution of 1-ethyl-3-methylimidazolium ethylsulfate (224 µL, 2.22 mg/mL) by incipient wetness. The catalyst was dried at 80 °C for 16 hours and reduced at 100 °C in 5% H_2/N_2 for 1 hour.

Sample B6 was made by adding 0.25 wt% of EMIM[EtSO4] (1-ethyl-3-methylimidazolium ethylsulfate) on Sample A. In order to make Sample B6, Sample A (480.9 mg) was impregnated with an aqueous solution of 1-ethyl-3-methylimidazolium ethylsulfate (216 µL, 5.56 mg/mL) by incipient wetness. The catalyst was dried at 80 °C for 16 hours and reduced at 100 °C in 5% H_2/N_2 for 1 hour.

Comparative Example 3

Comparative Sample C contains 0.019 wt% Pd on 1-2 mm alumina spheres with a BET surface area of 50 m^2/g. In order to make Comparative Sample C, 10 g alumina was added to 11.4 mL $PdCl_2$ solution (0.1667 mg Pd/mL) heated at 70 °C. After the carrier was soaked in the solution for 1 hour, the solution was withdrawn and then the catalyst was washed 10 times using 5 minute soak times with room temperature deionized water. After the final washing step, the catalyst was calcined in muffle oven in air at 565 °C for 4 hours.

Comparative Sample C1 was made by adding 0.5 wt% of EMIM[$EtSO_4$] (1-ethyl-3-methylimidazolium ethylsulfate) on Comparative Sample C. In order to make Comparative Sample C1, Comparative Sample C (502.1 mg) was impregnated with an aqueous solution of 1-ethyl-3-methylimidazolium ethylsulfate (316 µL, 7.94 mg/mL) by incipient wetness. The catalyst was dried at 80 °C for 16 hours and reduced at 100 °C in 5% H_2/N_2 for 1 hour.

Comparative Sample C2 was made by adding 0.5 wt% of BMIM[OTf] (1-butyl-3-methylimidazolium triflate) on Comparative Sample C. In order to make Comparative Sample C2, Comparative Sample C (484.4 mg) was impregnated with an aqueous solution of 1-butyl-3-methylimidazolium triflate (305 µL, 7.94 mg/mL) by incipient wetness. The catalyst was dried at 80 °C for 16 hours and reduced at 100 °C in 5% H_2/N_2 for 1 hour.

Example 4

Sample A, Samples A1-A22, Samples B1-B6, and Comparative Samples C, C1and C2 were tested as prepared in a microreactor test unit at typical front-end hydrogenation conditions. In the test, a simulated de-propanizer feed containing 0.35 mol% acetylene, 15 mol% hydrogen, 0.02 mol% CO, 47 mol% ethylene, and balance nitrogen was passed over a 260 µl catalyst bed at 478 psig (34 bar) in total pressure and 7000 h^{-1} in Gas Hourly Space Velocity (GHSV), while the bed temperature was gradually increased from about 45ºC. The acetylene concentration at the reactor outlet was monitored with an on-line gas chromatograph (GC). The acetylene concentration at reactor outlet continued decreasing with increasing temperature until reaching <25 ppm. The temperature at this point was defined as the "clean up temperature" (T1). Catalyst bed temperature was further increased until 125ºC (the maximum temperature the test unit could reach) or a certain temperature (T2), at which the outlet ethane concentration was >2% due to the increased non-selective reaction of hydrogen with ethylene. The temperature range between T1 and T2 is called the "operation window". Test results of Sample A, Samples A1 to A22, Samples B1-B6, as well as of Comparative Sample C, C1-C2 are listed in the table below. For catalysts that did not run away at the maximum temperature the test unit could reach, T2 was calculated by fitting the data at temperatures above complete acetylene conversion with a first order kinetic model.

Test Results of Samples A, A1 to A22, B1 to B6, and Comparative Samples C and C1 to C2

	T1 [°C]	T2 [°C]	Operation Window [°C]	Selectivity at T1 [%]	Ethane Make at 125 °C
Sample A	63	84	21	92.8	10.439
Sample A1	68	176	108	96.1	0.429
Sample A2	68	137	69	96.9	0.714
Sample A3	61	113	52	89.0	3.316
Sample A4	62	113	51	85.6	3.228
Sample A5	69	164	95	94.5	0.462
Sample A6	68	167	99	97.6	0.390
Sample A7	68	157	89	95.5	0.594
Sample A8	65	141	76	96.2	1.139
Sample A9	65	100	35	95.8	9.45
Sample A10	82	188	106	90.1	0.194
Sample A11	68	157	89	90.0	0.637
Sample A12	61	100	39	89.5	4.668
Sample A13	67	115	48	66.1	3.005
Sample A14	60	110	50	99.8	3.477
Sample A15	71	149	78	90.6	0.821
Sample A16	67	145	78	90.1	1.199
Sample A17	62	86	24	93.0	10.23
Sample A18	64	101	37	88.9	4.836
Sample A19	62	120	58	74.8	2.382
Sample A20	69	150	81	98.9	0.906
Sample A21	65	153	88	85.2	0.982
Sample A22	66	122	56	93.2	2.315
Sample B1	62	82	20	47.3	10.444
Sample B2	63	101	38	69.0	8.691
Sample B3	60	113	53	96.3	9.122
Sample B4	61	119	58	95.5	5.378
Sample B5	65	121	56	98.4	3.838
Sample B6	67	123	56	100	2.428
Comparative Sample C	56	76	20	91.1	10.506
Comparative Sample C1	68	99	31	81.3	5.725
Comparative Sample C2	65	98	33	96.1	6.878

The operation window as well as the selectivity markedly increase with decrease in BET surface area (Samples A1 and A2 compared to Comparative Samples C1 and C2).

Example 5

Sample D is a commercial selective hydrogenation catalyst that is supplied by Süd-Chemie AG under trade name OleMax® 251. It contains 0.019 wt% Pd and 0.05 wt% Ag on 4 x 4 mm alumina tablets with a BET surface area of about 4.0 m^2/g.

Sample D1 was made by adding 0.5 wt% of BMMIM[OTf] (1-Butyl-2,3-dimethylimidazolium triflate) on Sample D. In order to make Sample D1, 0.6 g of the ionic liquid BMMIM[OTf] were dissolved in 150 ml deionized water. At the same time 120 g of the dry Sample D is fluidized in a reaction chamber with synthetic air as the process gas. The solution of BMMIM[OTf] in water was introduced into the reaction chamber at a flow rate of 5ml/min via a feed pump and sprayed onto the solid catalyst via a spray nozzle at a temperature of 80°C. Once the entire solution has been applied and the substrate is dry, the catalyst formulation is further dried at 80°C for 2 hours.

Sample D2 was made by adding 1.0 wt% of BMMIM[OTf] (1-Butyl-2,3-dimethylimidazolium triflate) on Sample D. In order to make Sample D2, 1.2 g of the ionic liquid BMMIM[OTf] were dissolved in 150 ml deionized water. At the same time 120 g of the dry Sample D is fluidized in a reaction chamber with synthetic air as the process gas. The solution of BMMIM[OTf] in water was introduced into the reaction chamber at a flow rate of 5ml/min via a feed pump and sprayed onto the solid catalyst via a spray nozzle at a temperature of 80°C. Once the entire solution has been applied and the substrate is dry, the catalyst formulation is further dried at 80°C for 2 hours.

Sample D3 was made by adding 2.0 wt% of BMMIM[OTf] (1-Butyl-2,3-dimethylimidazolium triflate) on Sample D. In order to make Sample D3, 2.4 g of the ionic liquid BMMIM[OTf] were dissolved in 150 ml deionized water. At the same time 120 g of the dry Sample D is fluidized in a reaction chamber with synthetic air as the process gas. The solution of BMMIM[OTf] in water was introduced into the reaction chamber at a flow rate of 5ml/min via a feed pump and sprayed onto the solid catalyst via a spray nozzle at a temperature of 80°C. Once the entire solution has been applied and the substrate is dry, the catalyst formulation is further dried at 80°C for 2 hours.

Sample D4 was made by adding 3.0 wt% of BMMIM[OTf] (1-Butyl-2,3-dimethylimidazolium triflate) on Sample D. In order to make Sample D4, 3.6 g of the ionic liquid BMMIM[OTf] were dissolved in 150 ml deionized water. At the same time 120 g of the dry Sample D is fluidized in a reaction chamber with synthetic air as the process gas. The solution of BMMIM[OTf] in water was introduced into the reaction chamber at a flow rate of 5ml/min via a feed pump and sprayed onto the solid catalyst via a spray

nozzle at a temperature of 80°C. Once the entire solution has been applied and the substrate is dry, the catalyst formulation is further dried at 80°C for 2 hours.

Sample D1' was made by impregnation of Sample D with a BMMIM[OTf] (1-Butyl-2,3-dimethylimidazolium triflate) solution containing 0.5 g of BMMIM[OTf] in 38 ml deionized water. The clear solution is added to 120 g of dry Sample D. The mixture is then mixed at room temperature for approx. 60 minutes. The catalyst formulation is then dried at 80°C for 16 h to finally obtain Sample D1'.

Example 6

Samples prepared in Example 5 were tested as prepared in a bench scale test unit at typical front-end hydrogenation conditions. In the test, a simulated de-ethanizer feed containing 0.35 mol% acetylene, 20 mol% hydrogen, 0.02 mol% CO, 45 mol% ethylene, and balance methane was passed over a 25 ml catalyst bed at 500 psig (35.5 bar) in total pressure and 7000 h^{-1} in Gas Hourly Space Velocity (GHSV), while the bed temperature was gradually increased from about 35ºC. The acetylene concentration at the reactor outlet was monitored with an on-line gas chromatograph (GC). The acetylene concentration at reactor outlet continued decreasing with increasing temperature until reaching <25 ppm. The temperature at this point was defined as the "clean up temperature" (T1). Catalyst bed temperature was further increased until 105ºC (the maximum temperature the water bath could reach) or a certain temperature (T2), at which the outlet ethane concentration was >2% due to the increased non-selective reaction of hydrogen with ethylene. The temperature range between T1 and T2 is called the "operation window". Test results of Sample D and Samples D1 to D4 and D1' are listed in the table below.

Front End Deethanizer Feed Test Results

	T1 [ºC]	T2 [ºC]	Operation Window [ºC]	Selectivity at T1 [%]
Sample D	52	57	5	-1
Sample D1	61	97	36	52
Sample D2	61	105	44	61
Sample D3	69	>105	>36	48
Sample D4	73	>105	>32	56
Sample D1'	67	99	32	38

The operation window as well as the selectivity markedly increase with increasing BMMIM[OTf] content. The optimum BMMIM[OTf] loading seems to be 0.5-1%. At higher loading, the runaway temperature continued to increase at the expense of a higher T1 temperature. Adding BMMIM[OTf] onto Sample D can be realized by coating or wet

impregnation; and both methods can generate a new catalyst with significantly improved operation window.

Example 7

Sample E is a commercial front end selective hydrogenation catalyst that is supplied by Süd-Chemie AG under the trade name OleMax® 250. It contains 0.018 wt% Pd on 4 x 4 mm alumina tablets with a BET surface area of about 4.0 m^2/g.

Sample E1 was made by adding 1.0 wt% of BMMIM[OTf] (1-Butyl-2,3-dimethylimidazolium triflate) on Sample E. In order to make Sample E1, 1.2 g of the ionic liquid BMMIM[OTf] were dissolved in 150 ml deionized water. At the same time 120 g of the dry Sample E is fluidized in a reaction chamber with synthetic air as the process gas. The solution of BMMIM[OTf] in water was introduced into the reaction chamber at a flow rate of 5ml/min via a feed pump and sprayed onto the solid catalyst via a spray nozzle at a temperature of 80°C. Once the entire solution has been applied and the substrate is dry, the catalyst formulation is further dried at 80°C for 2 hours.

Sample E2 was made by adding 2.0 wt% of BMMIM[OTf] (1-Butyl-2,3-dimethylimidazolium triflate) on Sample E. In order to make Sample E2, 2.4 g of the ionic liquid BMMIM[OTf] were dissolved in 150 ml deionized water. At the same time 120 g of the dry Sample E is fluidized in a reaction chamber with synthetic air as the process gas. The solution of BMMIM[OTf] in water was introduced into the reaction chamber at a flow rate of 5ml/min via a feed pump and sprayed onto the solid catalyst via a spray nozzle at a temperature of 80°C. Once the entire solution has been applied and the substrate is dry, the catalyst formulation is further dried at 80°C for 2 hours.

Sample E3 was made by adding 3.0 wt% of BMMIM[OTf] (1-Butyl-2,3-dimethylimidazolium triflate) on Sample E. In order to make Sample E3, 3.6 g of the ionic liquid BMMIM[OTf] were dissolved in 150 ml deionized water. At the same time 120 g of the dry Sample E is fluidized in a reaction chamber with synthetic air as the process gas. The solution of BMMIM[OTf] in water was introduced into the reaction chamber at a flow rate of 5ml/min via a feed pump and sprayed onto the solid catalyst via a spray nozzle at a temperature of 80°C. Once the entire solution has been applied and the substrate is dry, the catalyst formulation is further dried at 80°C for 2 hours.

Example 8

Sample E, Sample E1, Sample E2 and Sample E3 were tested after in-situ reduction at 94ºC for 1 hour in a bench scale test unit at typical front-end hydrogenation

conditions. In the test, a simulated de-ethanizer feed containing 0.35 mol% acetylene, 20 mol% hydrogen, 0.02 mol% CO, 45 mol% ethylene, and balance methane was passed over a 25 ml catalyst bed at 500 psig (35.5 bar) in total pressure and 7000 h^{-1} in Gas Hourly Space Velocity (GHSV), while the bed temperature was gradually increased from about 35ºC. The acetylene concentration at the reactor outlet was monitored with an on-line gas chromatograph (GC). The acetylene concentration at reactor outlet continued decreasing with increasing temperature until reaching <25 ppm. The temperature at this point was defined as the "clean up temperature" (T1). Catalyst bed temperature was further increased until 105ºC (the maximum temperature the water bath could reach) or a certain temperature (T2), at which the outlet ethane concentration was >2% due to the increased non-selective reaction of hydrogen with ethylene. The temperature range between T1 and T2 is called the "operation window". Test results of Sample E and Samples E1 to E3 are listed in the table below.

Test Results of Sample E and Samples E1 to E3

	T1 [ºC]	T2 [ºC]	Operation Window [ºC]	Selectivity at T1 [%]
Sample E	53	62	9	58
Sample E1	53	69	16	65
Sample E2	52	81	29	74
Sample E3	62	92	30	78

Upon addition of BMMIM[OTf] onto the Pd/alumina catalyst, the operation window increases linearly up to a loading of 2% and then stays constant at 30°C. At higher loading, both T1 and operation window increased.

Example 9

Comparative Sample F is a commercial selective hydrogenation catalyst that is supplied by Süd-Chemie AG under trade name OleMax® 201. It contains 0.03 wt% Pd and 0.18 wt% Ag on 2-4 mm alumina spheres with a BET surface area of about 35 m^2/g.

Comparative Sample F1' was made by adding 0.5 wt% of EMIM[$EtSO_4$] (1-ethyl-3-methylimidazolium ethylsulfate) onto Sample F by incipient wetness impregnation method. The EMIM[$EtSO_4$] solution contains 0.5 g of EMIM[$EtSO_4$] in 60 ml deionized water. The clear solution was added to 100 g of Comparative Sample F and mixed for about 5 min. The catalyst formulation is then dried at 80°C for 16 hr to obtain the final product.

Comparative Sample F2' was made by adding 1.0 wt% of EMIM[$EtSO_4$] (1-ethyl-3-methylimidazolium ethylsulfate) onto Sample F by incipient wetness impregnation

method. The EMIM[$EtSO_4$] solution contains 1 g of EMIM[$EtSO_4$] in 60 ml deionized water. The clear solution was added to 100 g of Comparative Sample F and mixed for about 5 min. The catalyst formulation is then dried at 80°C for 16 hr to obtain final product.

Sample D2' was made by adding 0.5 wt% EMIM[$EtSO_4$] (1-ethyl-3-methylimidazolium ethylsulfate) on Sample D by incipient wetness impregnation. The EMIM[$EtSO_4$] solution contains 0.5 g of EMIM[$EtSO_4$] in 24 ml deionized water. The clear solution was added to 100 g of Sample D and mixed for about 5 min. The catalyst formulation is then dried at 80°C for 16 hr to obtain final product.

Sample D3' was made by adding 1 wt% EMIM[$EtSO_4$] (1-ethyl-3-methylimidazolium ethylsulfate) on Sample D by incipient wetness impregnation. The EMIM[$EtSO_4$] solution contains 1 g of EMIM[$EtSO_4$] in 24 ml deionized water. The clear solution was added to 100 g of Sample D and mixed for about 5 min. The catalyst formulation is then dried at 80°C for 16 hr to obtain final product.

Example 10

Samples and Comparative Samples prepared in Example 9 were tested as prepared in a bench scale test unit at typical front-end hydrogenation conditions. In the test, a simulated de-ethanizer feed containing 0.35 mol% acetylene, 20 mol% hydrogen, 0.02 mol% CO, 45 mol% ethylene, and balance methane was passed over a 25 ml catalyst bed at 500 psig (35.5 bar) in total pressure and 7000 h^{-1} in Gas Hourly Space Velocity (GHSV), while the bed temperature was gradually increased from about 35ºC. The acetylene concentration at the reactor outlet was monitored with an on-line gas chromatograph (GC). The acetylene concentration at reactor outlet continued decreasing with increasing temperature until reaching <25 ppm. The temperature at this point was defined as the "clean up temperature" (T1). Catalyst bed temperature was further increased until 105ºC (the maximum temperature the water bath could reach) or a certain temperature (T2), at which the outlet ethane concentration was >2% due to the increased non-selective reaction of hydrogen with ethylene. The temperature range between T1 and T2 is called the "operation window". Test results of Sample F2' and F3' did not run away at the maximum temperature the test unit could reach: the ethane make was 0.35% at 102ºC for both catalysts. Their T2's for 2% ethane make were calculated by fitting the data at temperatures above complete acetylene conversion with a first order kinetic model.

Front End Deethanizer Feed Test Results

	T1 [°C]	T2 [°C]	T2-T1 [°C]	Selectivity at T1 [%]	Ethane Make at 102°C [%]
Sample F	51	53	2	-5	Not operable
Sample F1'	54	75	21	76	Not operable
Sample F2'	59	80	21	86	Not operable
Sample D	52	57	5	-1	Not operable
Sample D2'	65	148	83	91	0.35
Sample D3'	66	149	83	94	0.35

It appears that EMIM[$EtSO_4$] has much lower impact on Sample F than on Sample D.

CLAIMS

1. Heterogeneous catalyst, comprising Pd and optionally a promoter, on a support, wherein:

the catalyst is coated with an ionic liquid (IL), and

the BET surface area of the catalyst without the IL-coating is less than or equal to 9 m^2/g.

2. The catalyst according to claim 1, wherein the promoter is selected from one or more of silver, gold, zinc, tin, lead, gallium, cadmium, bismuth, potassium and copper, and mixtures thereof.

3. The catalyst according to claim 2, wherein the promoter is silver.

4. The catalyst according to any one of claims 1 to 3, wherein the BET surface area is within a range of 1 to 9 m^2/g, preferably within a range of 2 to 8 m^2/g, and most preferably within a range of 3 to 5 m^2/g.

5. The catalyst according to any one of claims 1 to 4, wherein the integral pore volume of the catalyst without the IL-coating is in the range of 0.005 to 0.07 ml/g, preferably in the range of 0.007 to 0.04 ml/g and more preferably in the range of 0.009 to 0.02 ml/g.

6. The catalyst according to any one of claims 1 to 5, wherein the total weight of Pd relative to the total weight of the catalyst without the IL-coating is in the range of 10 to 1000 ppm, preferably in the range of 50 to 500 ppm.

7. The catalyst according to any one of claims 1 to 6, wherein the weight ratio of palladium to promoter is in the range of 1:5 to 3:1, preferably in the range of 1:4 to 2:1, and more preferably in the range 1:3 to 1:1.

8. The catalyst according to any one of claims 1 to 7, wherein the ionic liquid is a compound of formula (I):

$$[A]_n^+ \ [Y]^{n-} \qquad (I),$$

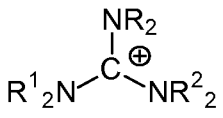
wherein:

n = 1 or 2;

$[Y]^{n-}$ is selected from the group consisting of tetrafluoroborate ($[BF_4]^-$), hexafluorophosphate ($[PF_6]^-$), dicyanamide ($[N(CN)_2]^-$), halides (Cl^-, Br^-, F^-, I^-), hexafluoroantimonate ($[SbF_6]^-$), nitrate ($[NO_3]^-$), nitrite ($[NO_2]^-$), anionic metal complexes such as $[CuCl_4]^{2-}$, $[PdCl_4]^{2-}$ or $[AuCl_4]^-$, acetate ($[CH_3COO]^-$), trifluoracetate ($[F_3CCOO]^-$), hexafluoroarsenate ($[AsF_6]^-$), sulfate ($[SO_4]^{2-}$), hydrogen sulfate ($[HSO_4]^-$), alkyl sulfates ($[R'\text{-}SO_4]^-$), tosylate ($[C_7H_7SO_3]^-$), triflate ($[CF_3SO_3]^-$), nonaflate ($[C_4F_9SO_3]^-$), triperfluoroethylene trifluorophosphate ($[PF_3(C_2F_5)_3]^-$), tricyanomethide ($[C(CN)_3]^-$), tetracyanoborate ($[B(CN)_4]^-$, thiocyanate ($[SCN]^-$), carbonate ($[CO_3]^{2-}$), carboxylates ($[R'\text{-}COO]^-$), sulfonates ($[R'SO_3]^-$), dialkylphosphates ($[R'PO_4R"]^-$), alkyl phosphonates ($[R'HPO_3]^-$) and bissulfonylimides ($[(R'\text{-}SO_2)_2N]^-$), such as bis(trifluormethylsulfonyl)imide,

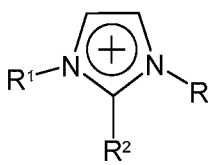
wherein R' and R" are the same or different, and each represents a linear or branched, 1 to 12 carbon atom-containing aliphatic or alicyclic alkyl group or a C_5-C_{18}-aryl, C_5-C_{18}-aryl-C_1-C_6-alkyl, or C_1-C_6-alkyl-C_5-C_{18}-aryl group that can be substituted with halogen atoms; and

$[A]^+$ is selected from the group consisting of quaternary ammonium cations with the formula $[NR^1R^2R^3R]^+$, phosphonium cations with the formula $[PR^1R^2R^3R]^+$, sulfonium cations with the formula $[SR^1R^2R]^+$, guadinium cations with the formula (II):



(II),

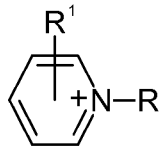
imidazolium cations with the formula (III)



(III),

wherein the imidazole core may additionally be substituted with one or more groups selected from C_1-C_6-alkyl, C_1-C_6-alkoxy, C_1-C_6-aminoalkyl, C_5-C_{12}-aryl, and C_5-C_{12}-aryl-C_1-C_6-alkyl groups,

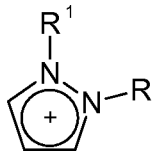
pyridinium cations with the formula (IV)



(IV),

wherein the pyridine core may additionally be substituted with one or more groups selected from C_1-C_6-alkyl, C_1-C_6-alkoxy, C_1-C_6-aminoalkyl, C_5-C_{12}-aryl, and C_5-C_{12}-aryl-C_1-C_6-alkyl groups,

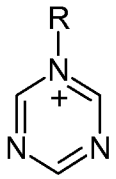
pyrazolium cations with the formula (V)



(V),

wherein the pyrazole core may additionally be substituted with one or more groups selected from C_1-C_6-alkyl, C_1-C_6-alkoxy, C_1-C_6-aminoalkyl, C_5-C_{12}-aryl, and C_5-C_{12}-aryl-C_1-C_6-alkyl groups,

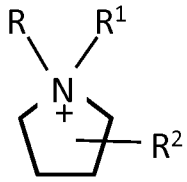
triazolium cations with the formula (VI)



(VI),

wherein the triazole core may additionally be substituted with one or more groups selected from C_1-C_6-alkyl, C_1-C_6-alkoxy, C_1-C_6-aminoalkyl, C_5-C_{12}-aryl, and C_5-C_{12}-aryl-C_1-C_6-alkyl groups,

and pyrrolidinium cations with the formula (VII)



(VII),

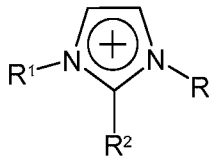
wherein the pyrrolidinium core may additionally be substituted with one or more groups selected from C_1-C_6-alkyl, C_1-C_6-alkoxy, C_1-C_6-aminoalkyl, C_5-C_{12}-aryl, and C_5-C_{12}-aryl-C_1-C_6-alkyl groups,

wherein R^1, R^2, and R^3 are selected independently from each other from the group consisting of: hydrogen; linear or branched, saturated or unsaturated, aliphatic or alicyclic alkyl groups with 1 to 20 carbon atoms, which may be interrupted by one or two of NH, O and/or S; heteroaryl groups with 3 to 8 carbon atoms and at least one hetero atom selected from N, O and S, wherein the heteroaryl groups can be substituted with one or more groups selected from C_1-C_6-alkyl groups and halogen atoms; heteroaryl-C_1-C_6-alkyl groups with 3 to 8 carbon atoms and at least one hetero atom selected from N, O and S in the heteroaryl moiety, wherein the heteroaryl moiety can be substituted with at least one group selected from C_1-C_6-alkyl groups and halogen atoms; polyethers with the formula $[-CH_2CH_2O]_nR^a$ with n = 1 to 50,000, wherein R^a is selected from the group consisting of linear or branched, saturated or unsaturated, aliphatic or alicyclic alkyl groups with 1 to 20 carbon atoms; aryl groups with 5 to 12 carbon atoms, which may be substituted with one or more C_1-C_6-alkyl groups and/or halogen atoms; aryl-C_1-C_6-alkyl groups with 5 to 12 carbon atoms in the aryl moiety, which may be substituted with one or more C_1-C_6-alkyl groups and/or halogen atoms, and

wherein R is selected from the group consisting of: linear or branched, saturated or unsaturated, aliphatic or alicyclic alkyl groups with 1 to 20 carbon atoms; heteroaryl-C_1-C_6-alkyl groups with 4 to 8 carbon atoms and at least one hetero atom selected from N, O and S in the heteroaryl moiety, which may be substituted with one or more C_1-C_6-alkyl groups and/or halogen atoms; and aryl-C_1-C_6-alkyl groups with 4 to 12 carbon atoms in the aryl moiety, which may be substituted with one or more C_1-C_6-alkyl groups and/or halogen atoms.

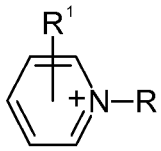
9. The catalyst according to claim 8, wherein the ionic liquid is a compound of formula (I), wherein

$[A]^+$ is selected from the group consisting of quaternary ammonium cations with the formula $[NR^1R^2R^3R]^+$, imidazolium cations with the formula (III)



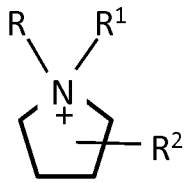
(III),

pyridinium cations with the formula (IV)



(IV),

and pyrrolidinium cations with the formula (VII)



(VII),

wherein R, R^1, R^2 and R^3 are selected independently from each other from the group consisting of hydrogen; linear or branched C_1-C_{12}-alkyl groups; linear or branched (C_1-C_6-alkyloxy)-C_1-C_6-alkyl groups; and aryl-C_1-C_6-alkyl groups with 5 to 12 carbon atoms in the aryl moiety, which may be substituted with one or more C_1-C_6-alkyl groups and/or halogen atoms.

10. The catalyst according to claim 9, wherein the ionic liquid is a compound of formula (I), wherein

$[A]^+$ is selected from the group consisting 1-butyl-3-methylimidazolium, 1-ethyl-3-methylpyridinium, 1-butyl-1-methylpyrrolidinium, 1-butyl-2,3-dimethylimidazolium, 1-ethyl-3-methylimidazolium, 1-methyl-3-octylimidazolium triflate, ethyldimethyl-(2-methoxyethyl)ammonium, tributylmethylammonium, and tricyclohexyltetradecylphosphonium; and

$[Y]^{n-}$ is selected from the group consisting of triflate, ethylsulfate, tricyanomethane, methylsulfate, octylsulfate, tetrafluoroborate, methylphosphonate, bis(trifluoromethylsufonyl)imide, tetracyanoborate, tris(pentafluoroethyl)trifluorophosphate, and dicyanamide.

11. The catalyst according to claim 9 or 10, wherein the ionic liquid is selected from 1-butyl-3-methylimidazolium triflate, 1-ethyl-3-methylpyridinium ethylsulfate, 1-butyl-1-methylpyrrolidinium triflate, 1-butyl-2,3-dimethylimidazolium triflate, 1-butyl-3-methylimidazolium tricyanomethane, 1-butyl-3-methylimidazolium methylsulfate, 1-butyl-3-methylimidazolium octylsulfate, 1-butyl-3-methylimidazolium tetrafluoroborate, 1-ethyl-3-methylimidazolium ethylsulfate, 1-ethyl-3-methylimidazolium methylphosphonate, 1-ethyl-3-methylimidazolium triflate, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsufonyl)imide, 1-butyl-1-methylpyrrolidinium tetracyanoborate, 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate, 1-butyl-3-methylimidazolium bis(trifluoromethylsufonyl)imide, 1-butyl-3-methylimidazolium tricyanomethane, 1-ethyl-3-methylpyridinium bis(trifluoromethylsufonyl)imide, 1-ethyl-3-methylimidazolium tetracyanoborate, 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate, 1-ethyl-3-methylpyridinium bis(trifluoromethylsufonyl)imide, 1-methyl-3-octylimidazolium triflate, ethyldimethyl-(2-methoxyethyl)ammonium tris(pentafluoroethyl)trifluorophosphate, tributylmethylammonium dicyanamide, tricyclohexyltetradecylphosphonium tris(pentafluoroethyl)trifluorophosphate, 1-ethyl-3-methylimidazolium bis(trifluoromethylsufonyl)imide, and mixtures thereof.

12. The catalyst according to any one of claims 1 to 11, wherein the amount of ionic liquid relative to the total weight of the catalyst without ionic liquid is 0.1 - 10 wt%, preferably 0.2 – 3 wt%, and most preferably 0.3 – 1.5 wt%.

13. A method for preparing a catalyst composition according to any one of claims 1 to 12, comprising the steps

a) providing a heterogenous catalyst, comprising Pd and optionally a promoter, on a support, having a BET surface area of less than or equal to 9 m^2/g,

b) coating of the catalyst with a mixture of ionic liquid and solvent, and

c) removing the solvent during or after coating the catalyst.

14. The method according to Claim 13, comprising the additional step of reducing the heterogeneous catalyst prior to step b) or after step c).

15. The method according to Claim 13 or 14, wherein the coating step b) is carried out by fluidized bed coating or by a coating through impregnation with a solution or suspension.

16. Use of a catalyst according to any one of the Claims 1 to 12 in the selective hydrogenation of acetylene, preferably in the gas phase or in the liquid phase.

17. A method of selective hydrogenation of acetylene, preferably in front-end mixed olefin feed streems, comprising catalyzing said hydrogenation with a catalyst according to any one of the Claims 1 to 12.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/070747

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J31/02 B01J23/44 B01J37/02 C07C5/09 C07C7/167
ADD.

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)
B01J C07C

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 practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2011/050953 A2 (SUED CHEMIE AG [DE]; SZESNI NORMEN [DE]; KAISER MELANIE [DE]; FISCHER) 5 May 2011 (2011-05-05) page 2, line 17 - line 25 page 11, line 22; claim 15 page 16, line 4 - line 6 -----	1-17
A	ARRAS ET AL: "Regioselective catalytic hydrogenation of citral with ionic liquids as reaction modifiers", GREEN CHEMISTRY, ROYAL SOCIETY OF CHEMISTRY, CAMBRIDGE, GB, vol. 11, 1 January 2009 (2009-01-01), pages 716-723, XP009150913, ISSN: 1463-9262 table 1 ----- -/--	1-17

[X] Further documents are listed in the continuation of Box C.

[X] See patent family 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 application or patent 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
13 December 2012	21/12/2012

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, Fax: (+31-70) 340-3016	Klaes, Daphne

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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JÜRGEN ARRAS ET AL: "The promoting effect of a dicyanamide based ionic liquid in the selective hydrogenation of citral", CHEMICAL COMMUNICATIONS, no. 34, 1 January 2008 (2008-01-01), page 4058, XP55047529, ISSN: 1359-7345, DOI: 10.1039/b810291k scheme 2 page 4058, column 2, last paragraph -----	1-17
A	RANTING TAO ET AL: "Pd nanoparticles immobilized on sepiolite by ionic liquids: efficient catalysts for hydrogenation of alkenes and Heck reactions", GREEN CHEMISTRY, vol. 11, no. 1, 1 January 2009 (2009-01-01), page 96, XP055047524, ISSN: 1463-9262, DOI: 10.1039/b811587g cited in the application table 2 page 17814, column 2, last paragraph -----	1-17

2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2012/070747

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2011050953 A2	05-05-2011	CN 102665906 A	12-09-2012
		DE 102009051462 A1	09-06-2011
		EP 2493616 A2	05-09-2012
		WO 2011050953 A2	05-05-2011