



(51) International Patent Classification:

B01J 23/889 (2006.01) **B01D 53/00** (2006.01)
B01J 35/04 (2006.01) **B01J 23/00** (2006.01)

(21) International Application Number:

PCT/US2010/031036

(22) International Filing Date:

14 April 2010 (14.04.2010)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

12/427,375 21 April 2009 (21.04.2009) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))

Published:

— with international search report (Art. 21(3))

[Continued on next page]

(54) Title: COPPER AND MANGANESE CONTAINING BASE METAL CATALYSTS FOR THE OXIDATION OF CARBON MONOXIDE AND VOLATILE ORGANIC COMPOUNDS

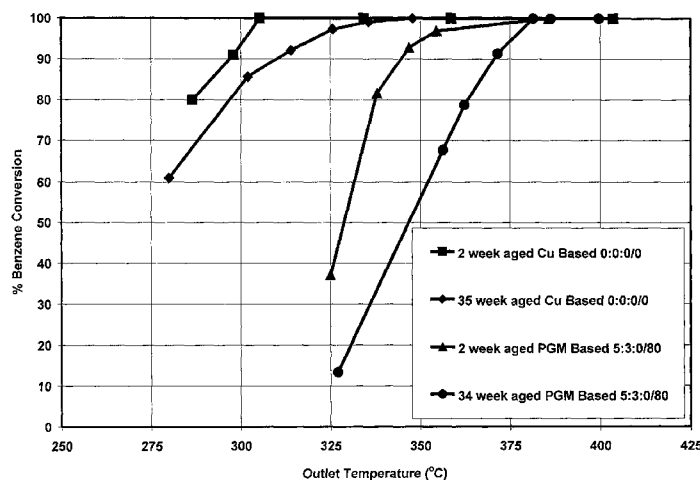


Figure 1b

(57) Abstract: A method for oxidizing carbon monoxide (CO) and volatile organic compounds (VOCs) comprises contacting a gas containing water vapor and said CO and VOCs with a catalyst composition comprising at least one base metal promoter and at least one base metal catalyst supported on an oxide support material comprising one or more of alumina, silica, zirconia, ceria, and titania, wherein the VOCs comprise one or more of methyl acetate, methane, methyl bromide, benzene, methanol, methyl ethyl ketone, butane, and butene.



— *before the expiration of the time limit for amending the
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amendments (Rule 48.2(h))

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COPPER AND MANGANESE CONTAINING BASE METAL CATALYSTS FOR THE OXIDATION OF CARBON MONOXIDE AND VOLATILE ORGANIC COMPOUNDS

FIELD OF THE INVENTION

This invention relates to a method and catalyst composition for treating emissions from industrial and commercial processes.

BACKGROUND OF THE INVENTION

5 Catalytic oxidation is widely used to control carbon monoxide (CO) and volatile organic compound (VOC) emissions from industrial processes. Most of the catalysts are supported noble metals because of their high catalytic activity, good thermal stability, and excellent resistance to chemical poisoning. For applications that require a large volume of catalysts, the use of noble metal oxidation catalysts requires a large
10 amount of capital investment for noble metals. For example, a typical unit for catalytic oxidation of the tail-gas in purified terephthalic acid (PTA) process needs 300 ft³ of noble metal catalysts at a loading of 50g/ft³ platinum (Pt) and 30 g/ft³ palladium (Pd), which would require about 482 oz. of Pt and 289 oz. of Pd. Therefore, there is a strong desire to develop alternative catalysts that have activity and durability at least comparable to the
15 noble metal catalysts.

SUMMARY OF THE INVENTION

According to one embodiment of the present invention, a method for oxidizing carbon monoxide (CO) and volatile organic compounds (VOCs) comprises contacting a gas containing water vapor and said CO and VOCs with a catalyst
20 composition comprising at least one base metal promoter and at least one base metal catalyst supported on an oxide support material comprising one or more of alumina, silica, zirconia, ceria, and titania. The VOCs comprise one or more of methyl acetate, methane, methyl bromide, benzene, methanol, methyl ethyl ketone, butane, and butene.

According to another embodiment of the present invention, a method for
25 oxidizing carbon monoxide (CO) and volatile organic compounds (VOCs) comprises the step of contacting a gas containing water vapor and the CO and VOCs with a catalyst composition consisting essentially of at least one base metal promoter and at least one base metal catalyst supported on an oxide support material comprising one or more of alumina, silica, zirconia, ceria, and titania. The VOCs comprise one or more of methyl
30 acetate, methane, methyl bromide, benzene, methanol, methyl ethyl ketone, butane, and butene.

According to another embodiment of the present invention, a catalyst composition for the oxidation of carbon monoxide (CO) and volatile organic compounds

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(VOC) comprises at least one base metal promoter and at least one base metal catalyst supported on an oxide support material comprising one or more of alumina, silica, zirconia, ceria, and titania.

5 According to another embodiment of the present invention, a catalyst composition for the oxidation of carbon monoxide (CO) and volatile organic compounds (VOC) consists essentially of at least one base metal promoter and at least one base metal catalyst supported on an oxide support material comprising one or more of alumina, silica, zirconia, ceria, and titania.

BRIEF DESCRIPTION OF THE DRAWINGS

10 The invention may be understood from the following detailed description when read in connection with the accompanying drawing. Included in the drawing are the following figures:

Figure 1a is a graph illustrating the percentage of methyl bromide conversion for outlet temperatures and conditions simulating a PTA production process tail-gas for a copper-based catalyst according to an embodiment of the present invention as compared to a platinum group metal based catalyst;

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Figure 1b is a graph illustrating the percentage of benzene conversion for outlet temperatures and conditions simulating a PTA production process tail-gas for a copper-based catalyst according to an embodiment of the present invention as compared to a platinum group metal based catalyst;

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Figure 2a is a graph illustrating the percentage of methyl bromide conversion for temperatures and conditions simulating a PTA production process tail-gas for support materials according to different embodiments of the present invention;

Figure 2b is a graph illustrating the percentage of benzene conversion for temperatures and conditions simulating a PTA production process tail-gas for support materials according to different embodiments of the present invention;

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Figure 2c is a graph illustrating the percentage of carbon monoxide conversion for temperatures and conditions simulating a PTA production process tail-gas for support materials according to different embodiments of the present invention;

Figure 3 is a graph illustrating the percentage of methanol conversion for temperatures for a copper-based catalyst according to an embodiment of the present invention versus a platinum group metal based catalyst;

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Figure 4 is a graph illustrating the percentage of methyl ethyl ketone conversion for temperatures and conditions for a copper-based catalyst according to an embodiment of the present invention versus a platinum group metal based catalyst;

5 Figure 5 is a graph illustrating the percentage of butane conversion for a copper-based catalyst according to an embodiment of the present invention versus a platinum group metal based catalyst;

Figure 6 is a graph illustrating the percentage of butene conversion for a copper-based catalyst according to an embodiment of the present invention versus a platinum group metal based catalyst;

10 Figure 7a is a graph illustrating the percentage of methyl bromide conversion for embodiments of the catalyst composition comprising copper, iron, cobalt, and nickel, respectively, as a base metal catalyst; and

Figure 7b is a graph illustrating the percentage of benzene conversion for embodiments of the catalyst composition comprising copper, iron, cobalt, and nickel, respectively, as a base metal catalyst.

DETAILED DESCRIPTION OF THE INVENTION

Aspects of the present invention include methods for oxidizing and catalyst compositions for the oxidation of carbon monoxide (CO) and volatile organic compounds (VOC). According to one embodiment, a method for oxidizing carbon monoxide (CO) and volatile organic compounds (VOCs) comprises contacting a gas containing water vapor and said CO and VOCs with a catalyst composition comprising at least one base metal promoter and at least one base metal catalyst supported on an oxide support material comprising one or more of alumina, silica, zirconia, ceria, and titania, wherein the VOCs comprise one or more of methyl acetate, methane, methyl bromide, benzene, methanol, methyl ethyl ketone, butane, and butene. According to another embodiment, a method for oxidizing carbon monoxide (CO) and volatile organic compounds (VOCs) comprises contacting a gas containing water vapor, CO, and VOCs with a catalyst composition consisting essentially of at least one base metal catalyst supported on an oxide support material comprising one or more of alumina, silica, zirconia, ceria, and titania, wherein the VOCs comprise one or more of methyl acetate, methane, methyl bromide, benzene, methanol, methyl ethyl ketone, butane, and butene.

Catalytic oxidation is widely used to control VOC and CO emissions from industrial and commercial processes. A method for oxidizing carbon monoxide (CO) and volatile organic compounds (VOCs) utilizes a catalyst in contact with a gas containing at least water vapor, CO, and VOCs. The gas may include VOCs such as saturated and

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unsaturated hydrocarbons, aromatic hydrocarbons, polyhalogenated derivatives thereof, such as halocarbons, dioxins, and hydrocarbons containing one or more sulfur, oxygen, nitrogen, phosphorous, or bromine atoms. The gas may be emitted from an industrial or commercial process. According to one embodiment, the gas may be the tail-gas of a process for producing purified terephthalic acid (PTA).

In a commercial process for producing PTA, terephthalic acid may be produced by oxidation of p-xylene by oxygen using acetic acid as a solvent. This may occur in the presence of a catalyst such as cobalt-manganese using a bromide promoter. The product may be purified by hydrogenation while in a water solution and may then be cooled. The tail-gas in a purified terephthalic acid (PTA) process may comprise oxygen, nitrogen, nitrogen oxides, methyl bromide, benzene, methane, carbon monoxide, methyl acetate, and water. Specifically, a typical PTA process may include 30 parts per million (ppm) methyl bromide, 10 ppm benzene, 100 ppm methane, 1000 ppm carbon monoxide, 500 ppm methyl acetate, 1.5 mol % water, 4 mol % oxygen, and the balance nitrogen. In addition to the constituents listed above, a catalyst according to an embodiment of the present invention may also oxidize and convert other volatile organic compounds such as methyl ethyl ketone, methanol, butane, or butene.

PTA processes may have about 2 mol % steam/water. The catalyst and support must be stable and able effectively to function in an environment with moisture. Certain catalysts and supports, such as zeolites, are known to degrade under hydrothermal conditions, especially over a period of time. Catalyst compositions of the present invention, however, are able to withstand and work effectively in a gas containing water vapor, for example 1.5 mol % to 5 mol % moisture at a temperature of greater than about 400 °C, or alternatively, about 200 °C to about 400 °C, about 200 °C to about 325 °C, about 200 °C to about 300 °C, about 200 °C to about 250 °C, or alternatively less than about 325 °C, less than about 300 °C, or less than about 250 °C.

When the gas, such as a tail-gas from PTA, containing water vapor, CO, and VOCs, is contacted with a catalyst composition according to embodiments of the present invention, the carbon monoxide (CO) and volatile organic compounds (VOCs) are oxidized. The process effluent may be preheated and passed through a catalyst bed in the presence of excess oxygen and the polluting components in the stream are oxidized to carbon dioxide (CO₂), water (H₂O) and hydrogen bromide. Hydrogen bromide from downstream of the catalyst can be easily removed from the effluent by passing the gas through a caustic scrubber, thus removing the pollutants from effluent before emitting the exhaust to the atmosphere. Embodiments of the present invention have been shown to convert methyl bromide, benzene, and carbon monoxide at least as effectively

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as and even more effectively than comparable platinum group metal catalysts, as shown, for example, in Figures 1a and 1b.

When the gas contains other VOCs, such as methanol, methyl ethyl ketone, butane, or butene, a base metal catalyst according to embodiments of the present invention were also able to achieve comparable conversions as the platinum group metal reference catalyst as long as the catalyst bed temperature reached a certain level, as shown, for example, in Figures 3-6.

The catalyst composition comprises at least one base metal catalyst. The at least one base metal catalyst may be selected from copper (Cu), iron (Fe), cobalt (Co), nickel (Ni), and chromium (Cr). In an exemplary embodiment of the present invention, the at least one base metal catalyst is copper. The discovery of the at least one base metal catalyst supported on the supports (described herein below) and promoted with at least one base metal promoter, such as manganese, eliminates the need for noble metals. The base metal catalyst may be added in the form of a nitrate or an acetate. In particular, the copper, for example, in the form of copper nitrate, may be impregnated on a support or coated on a pellet or monolith. Catalysts of the present invention demonstrate superior activity (e.g., they are highly active catalysts) and durability as compared to current commercial noble metal catalysts. For PTA tail-gas emission control, these catalysts are able to convert CO and VOCs at lower temperatures better than PGM catalysts at comparable temperatures. These catalysts also exhibit superior durability and longevity.

The catalyst composition comprises at least one base metal promoter. As used herein, "promoter" or "promoted" are understood to mean a substance that when added into a catalyst, increases the activity of the catalyst. The at least one base metal catalyst promoter may be selected from neodymium (Nd), barium (Ba), cerium (Ce), lanthanum (La), praseodymium (Pr), magnesium (Mg), calcium (Ca), manganese (Mn), zinc (Zn), niobium (Nb), zirconium (Zr), molybdenum (Mo), tin (Sn), tantalum (Ta), or strontium (Sr). In one illustrative embodiment, the at least one base metal catalyst promoter is Mn. The at least one base metal catalyst promoter may be added, for example, in the form of a nitrate in solution or an acetate. For example, when using Mn, the Mn may be added in the form of Mn nitrate. The at least one base metal catalyst promoter and at least one base metal catalyst, e.g., copper, may be impregnated from an aqueous solution onto the oxide support material(s), may be added into a washcoat comprising the oxide support material(s), or may be impregnated into a support previously coated with the washcoat.

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In an exemplary embodiment, copper is the at least one base metal catalyst, and manganese is the at least one base metal promoter. Without wishing to be bound to a particular theory, it is believed that by using the combination of Cu and Mn as the active catalytic components supported on the at least one oxide support material, the Cu and Mn provide increased activity of the catalyst, and Mn may further improve the durability of the catalyst. Additionally and significantly, the Mn appears to provide improved catalyst activity at reduced temperatures. Referencing Figures 1a and 1b, the Cu:Mn catalyst shows excellent VOC conversion at reduced temperatures, e.g., at less than 325°C.

The at least one base metal promoter and the at least one base metal catalyst are supported on an oxide support material. The oxide support material may comprise one or more of alumina, silica, zirconia, ceria, and titania. The oxide support materials may be alumina (Al_2O_3), silica (SiO_2), zirconia (ZrO_2), ceria (CeO_2), and titania (TiO_2), or mixtures of these or mixtures of these with other oxide materials such as perovskites, nickel oxide (NiO), manganese dioxide (MnO_2), praseodymium (III) oxide (Pr_2O_3). Thus, the oxide support material may include composite oxides or mixed oxides of two or more thereof (such as CeZrO_2 mixed oxides, TiZrO_2 mixed oxides, TiSiO_2 mixed oxides, and TiAlO_x oxides where x is dependent on the ratio of TiO_2 to Al_2O_3). The oxide support material may not only serve as a support function, but may also serve a binder function. For example, alumina may act as both a support and a binder in an alumina and CeZrO_2 mixed oxide. The oxide support material may be slurried, or if more than one, the oxide support materials may be slurried together with water to form a washcoat.

The oxide support material may also be stabilized. Stabilizers may be selected from zirconium (Zr), lanthanum (La), aluminum (Al), yttrium (Y), praseodymium (Pr), neodymium (Nd), an oxide thereof, a composite oxide or mixed oxide of any two or more thereof, or at least one alkaline earth metal, e.g., barium (Ba). If each oxide support material is stabilized, the stabilizers may be the same or different. In one embodiment, the oxide support material is Al_2O_3 and CeO_2 . Where the oxide support material is Al_2O_3 , it may be alpha-, gamma-, beta-, delta-, or theta- Al_2O_3 , for example. According to one embodiment, the oxide support material is La-stabilized Al_2O_3 and Zr-stabilized CeO_2 . In another embodiment, the support material comprises 20 mole% La-stabilized Al_2O_3 and 80 mole% Zr-stabilized CeO_2 . According to another embodiment, the support material comprises Ce and Zr present in about a 1:1 mole ratio. For example, in a mixed Zr-stabilized CeO_2 , there would be about 50% Ce and about 50% Zr. More particularly, the support material may comprise Ce and Zr in exactly a 1:1 mole ratio.

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In preparing a catalyst composition comprising at least one base metal promoter and at least one base metal catalyst supported on an oxide support material, the following method may be used. A washcoat may be prepared. An oxide support material support may or may not be milled. If milled, the oxide support material(s) may be milled to a particle size of less than about 20 μm or more particularly in a range of less than 15 μm . The oxide support material(s) may be formed into a slurry using water. The washcoat may be applied to a substrate, for example, in multiple passes or coats. The support may then be impregnated with an aqueous solution of at least one base metal catalyst, for example, copper, and at least one base metal promoter, for example, manganese. The aqueous solution may include copper nitrate and manganese nitrate. Alternatively, a salt, such as a manganese salt or copper salt, may be added directly to the washcoat before application.

One advantageous aspect of the present invention is that the catalyst can function effectively in the absence of precious metals and in certain embodiments may function even more effectively than conventional catalysts containing precious metals. Accordingly, the catalyst composition may be free of platinum group metals (PGMs). For example, the Cu-based catalysts in embodiments of the present invention showed surprisingly effective conversion of CO and VOCs without using any platinum group metals. In fact, in certain embodiments, the Cu-based catalysts had better activity and better durability than the PGM catalysts. Referring now to Figures 1a and 1b, the copper based catalysts have been shown to demonstrate superior activity in comparison to the commercial platinum/palladium catalyst. This reduction in the amount of precious metal in the catalyst should result in significant costs savings in producing the catalyst compositions.

According to another embodiment, a catalyst composition for the oxidation of carbon monoxide (CO) and volatile organic compounds (VOC) comprises at least one base metal promoter and at least one base metal catalyst supported on an oxide support material comprising one or more of alumina, silica, zirconia, ceria, and titania. According to another embodiment, a catalyst composition for the oxidation of carbon monoxide (CO) and volatile organic compounds (VOC) consists essentially of at least one base metal promoter and at least one base metal catalyst supported on an oxide support material comprising one or more of alumina, silica, zirconia, ceria, and titania. "Consisting essentially of" is meant to exclude certain other unclaimed substituents such as platinum group metals.

The catalyst composition may be supported on a substantially inert substrate material, as generally known in the art. The substrate may be of any generally suitable form. For example, the substrate may comprise a flow through monolith, such

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as a ceramic or honeycomb structure, or the substrate may be in the form of foams, or the substrate may be in the form of pellets, fluidized bed particulates, or may comprise particles such as spheres or short extruded segments. The catalyst may be coated onto substrates or the catalysts may be extruded to form self-supported pellets or beads. As is known in the art, a catalyst, for example, a pellet catalyst may be replenished and replaced as necessary and as used.

The present invention provides a catalyst composition for the oxidation of, for example, CO, hydrocarbon, halocarbon, and VOC emissions often emitted from a variety of industrial and commercial processes. The catalyst may be placed in an appropriate oxidation device in which temperatures and flow rates may be controlled. As an effluent stream containing, for example, water, CO, and VOCs come into contact with the catalyst, the components of the effluent are generally converted to CO₂, H₂O, and for halocarbons, haloacid or halogen gas.

It is understood that the catalyst compositions may be utilized over a wide range of temperatures typically encountered in the exhaust from industrial, commercial or energy-generating processes. The catalyst, oxide support materials, and support should be stable over this wide range of temperature and specifically at high gas temperatures. As discussed above, the composition must also be stable and able to effectively function in a gas containing water vapor. Catalyst compositions of the present invention are able to withstand and work effectively in these environments, e.g., as typically encountered in a PTA production process tail-gas.

Compositions according to embodiments of the present invention have also been shown to be extremely durable even after weeks of aging. Aging may include, for example, prolonged exposures to high temperatures, moisture, and exposure to VOCs. A representative aging environment may include a temperature of about 500 °C with about 1.5 mol% moisture content and 100 ppm of methyl bromide. The catalyst may be aged from 2 weeks to upwards of 35 weeks. Referring again to Figures 1a and 1b, it is evident that the Cu-based catalysts in embodiments of the present invention were more active than the comparable PGM based catalysts even after significant aging.

EXAMPLES

Although the invention is illustrated and described herein with reference to specific embodiments, the invention is not intended to be limited to the details shown. Rather, various modifications may be made in the details within the scope and range of equivalents of the claims and without departing from the invention.

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EXAMPLE 1

An oxide, alumina, was milled to a nominal particle size of less than 15 microns to form a slurry. The slurry was washcoated onto a ceramic monolithic substrate with 400 cells per square inch to achieve a loading of 2.75 grams per cubic inch of the substrate. The block was dried at 60°C and fired at 500°C. Subsequently,
5 the block was impregnated with a mixture of aqueous solution of Cu nitrate and Mn nitrate. The target loadings were 0.22 grams of CuO and 0.45 grams of MnO per cubic inch of the substrate. The block was dried at 60°C and fired at 500°C for 2 hours.

EXAMPLE 2

10 A La-stabilized alumina and a CeZrO₂ mixed oxide were milled separately to a nominal particle size of <15 microns to form slurries. These two slurries were mixed together to form a washcoat which contained 20 mol % La-stabilized alumina and 80 mol % CeZrO₂ mixed oxide. The washcoat was coated onto a ceramic monolithic substrate with 400 cells per square inch to achieve a loading of 2.75 grams per cubic
15 inch of the substrate. After dried and fired, the block was impregnated with Cu and Mn following the procedures listed above in Example 1.

EXAMPLE 3

This example was the same as Example 2, except that a TiZrO₂ mixed oxide was used to replace the CeZrO₂ mixed oxide.

EXAMPLE 4

20 This example was the same as Example 2, except that a TiSiO₂ mixed oxide was used to replace the CeZrO₂ mixed oxide.

EXAMPLE 5

25 This example was the same as Example 2, except that a TiAlO_x mixed oxide was used to replace the CeZrO₂ mixed oxide.

EXAMPLE 6

In this embodiment, a first oxide, La-stabilized alumina, was milled to a nominal particle size of <15 microns. A second oxide, CeZrO₂ mixed oxide, was separately milled to a nominal particle size of <15 microns. The separately-milled oxides
30 were blended and slurried. Mn acetate crystals were added and mixed until they were completely dissolved to form a uniform washcoat. The final washcoat contained 17 mol % La-stabilized alumina, 69 mol % CeZrO₂ mixed oxide, and 14 mol % MnO. The washcoat was applied to monolithic substrates with 400 cells per square inch to achieve a loading of 3.20 grams per cubic inch of the substrate. The block was dried at 60°C

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and fired at 500°C. Subsequently, the block was impregnated with an aqueous solution of Cu nitrate to achieve a Cu loading of 0.22 gram of CuO per cubic inch of the substrate. The block was dried at 60°C and fired at 500°C for 2 hours.

EXAMPLE 7

5 In this embodiment, a first oxide, La-stabilized alumina, was milled to a nominal particle size of <15 microns. A second oxide, CeZrO₂ mixed oxide, was separately milled to a nominal particle size of <15 microns. The separately-milled oxides were blended and slurried. Mn acetate crystals were added and mixed until they were completely dissolved to form a uniform slurry. Subsequently, Cu acetate crystals were
10 added to the above slurry and mixed until they were completely dissolved to form a uniform washcoat. The final washcoat contained 16 mol % La-stabilized alumina, 64 mol % CeZrO₂ mixed oxide, 13 mol % MnO, and 7 mol % CuO. The washcoat was applied to monolithic substrates with 400 cells per square inch to achieve a loading of 3.42 grams per cubic inch of the substrate. The block was dried at 60°C and fired at 500°C for 2
15 hours.

EXAMPLE 8

Referring now to Figures 1a and 1b, a Cu-based catalyst was prepared containing Cu supported on Al₂O₃ and CeZrO₂ oxides promoted with Mn, similarly to Example 2 or Example 6. The composition contained no platinum group metals. A
20 commercial Pt50Pd30 catalyst (Pt 50 g/ft³ and Pd 30 g/ft³) was used as a comparative example (50:30:0/80). The ratios are for Pt:Pd:Rh, and the value after the ratio is the total PGM loading in g ft⁻³.

Figures 1a and 1b illustrate the percentage of methyl bromide conversion and benzene conversion, respectively, for outlet temperatures and conditions simulating
25 a PTA production process tail-gas for the copper-based catalyst as compared to the platinum group metal based catalyst.

The testing conditions simulated the conditions in a PTA production process tail-gas where the gas hourly space velocity (GHSV) equaled 25,000 h⁻¹, the pressure drop equaled 150 psig, and the gas mixture comprised 30 ppm methyl bromide,
30 10 ppm benzene, 100 ppm methane, 1000 ppm CO, 500 ppm methyl acetate, 1.5 mol % H₂O, 4.0 mol % O₂, and N₂ as the balance. The aging conditions were at 550°C with 1.5 mol % water, 100 ppm methyl bromide, and air as the balance for 2 weeks, 34 weeks, and 35 weeks, respectively, as indicated on Figures 1a and 1b.

As clearly shown in Figures 1a and 1b, the Cu-based catalyst showed
35 superior activity to the commercial Pt50Pd30 catalyst for both newer catalysts (aged 2

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weeks) and after a long period of aging (aged 34 or 35 weeks). Accordingly, the compositions appear to be extremely durable and maintain their activity even after weeks of aging.

EXAMPLE 9

Referring now to Figures 2a, 2b, and 2c, a Cu-based catalyst was prepared containing Cu supported on Al_2O_3 alone or with other identified oxides, and promoted with Mn. These Cu-based catalysts contained no platinum group metals. Figures 2a, 2b, and 2c illustrate the percentage of methyl bromide conversion, benzene conversion, and CO conversion, respectively, for temperatures and conditions simulating a PTA production process tail-gas for the different support materials. The support materials included (1) Al_2O_3 only; (2) 20 mol % Al_2O_3 + 80 mol % CeZrO_2 mixed oxide; (3) 20 mol % Al_2O_3 + 80 mol % TiZrO_2 mixed oxide; (4) 20 mol % Al_2O_3 + 80 mol % TiSiO_2 mixed oxide; and (5) 20 mol % Al_2O_3 + 80 mol % TiAlO_x mixed oxide.

The testing conditions simulated the conditions in a PTA production process tail-gas where GHSV equaled $25,000 \text{ h}^{-1}$, the pressure drop equaled 150 psig, and the gas mixture comprised 30 ppm methyl bromide, 10 ppm benzene, 100 ppm methane, 1000 ppm CO, 500 ppm methyl acetate, 1.5 mol % H_2O , 4.0 mol % O_2 , and N_2 as the balance. The aging conditions were at 550°C with 1.5% water, 100 ppm methyl bromide, and air as the balance for 2 weeks.

As can be clearly seen in Figures 2a, 2b, and 2c, all identified oxides showed good catalytic activity of Cu:Mn supported on the oxides. Accordingly, Cu:Mn supported on oxide support materials are effective over a wide range of temperatures. It is also evident that the catalytic activity of Cu:Mn supported on the Al_2O_3 + CeZrO_2 support was the most active catalyst.

EXAMPLE 10

Referring now to Figure 3, a Cu-based catalyst was prepared containing Cu supported on Al_2O_3 and CeZrO_2 oxides promoted with Mn. The Cu-based catalyst contained no platinum group metals. A commercial platinum-based catalyst was used as a comparative example. Figure 3 illustrates the percentage of methanol conversion as a function of the outlet temperatures for the copper-based catalyst as compared to a platinum group metal based catalyst.

In Figure 3, the testing conditions included a GHSV equal to $50,000 \text{ h}^{-1}$ and the gas mixture comprised 1000 ppm methanol, 1000 ppm CO, 5 mol % H_2O , 15 mol % O_2 , and N_2 as the balance. As clearly shown in Figure 3, when the temperature reaches 300°C , the Cu:Mn catalyst can achieve 100% methanol conversion.

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EXAMPLE 11

Referring now to Figure 4, a Cu-based catalyst was prepared containing Cu supported on Al_2O_3 and CeZrO_2 oxides promoted with Mn. The Cu-based catalyst contained no platinum group metals. A commercial platinum-based catalyst was used as a comparative example. Figure 4 illustrate the percentage of methyl ethyl ketone (MEK) conversion as a function of the outlet temperatures for the copper-based catalyst as compared to a platinum group metal based catalyst.

In Figure 4, the testing conditions included a GHSV equal to $50,000 \text{ h}^{-1}$ and the gas mixture comprised 250 ppm methyl ethyl ketone, 1000 ppm CO, 5 mol % H_2O , 15 mol % O_2 , and N_2 as the balance. As can be seen in Figure 4, when the temperature reaches 300°C , the Cu:Mn catalyst is comparable to the platinum-based reference catalyst because both achieved about 100% MEK conversion. Accordingly, the Cu-based catalysts of the present invention showed surprisingly effective conversion of MEK without using any platinum group metals.

EXAMPLE 12

Referring now to Figure 5, a Cu-based catalyst was prepared containing Cu supported on Al_2O_3 and CeZrO_2 oxides promoted with Mn. The Cu-based catalyst contained no platinum group metals. A commercial platinum-based catalyst was used as a comparative example. Figure 5 illustrates the percentage of butane conversion for the copper-based catalyst as compared to a platinum group metal based catalyst.

In Figure 5, the testing conditions included a GHSV equal to $50,000 \text{ h}^{-1}$ and the gas mixture comprised 250 ppm butane, 1000 ppm CO, 5 mol % H_2O , 15 mol % O_2 , and N_2 as the balance. As shown in Figure 5, the Cu:Mn catalyst performed in a comparable manner to the platinum based catalyst. Accordingly, the at least one base metal catalyst, e.g., the Cu-based catalysts, of the present invention showed effective conversion of butane without using any platinum group metals.

EXAMPLE 13

Referring now to Figure 6, a Cu-based catalyst was prepared containing Cu supported on Al_2O_3 and CeZrO_2 oxides promoted with Mn. The Cu-based catalyst contained no platinum group metals. A commercial platinum-based catalyst was used as a comparative example. Figure 6 illustrates the percentage of butene conversion for the copper-based catalyst as compared to a platinum group metal based catalyst.

In Figure 6, the testing conditions included a GHSV equal to $50,000 \text{ h}^{-1}$ and the gas mixture comprised 250 ppm butene, 1000 ppm CO, 5 mol % H_2O , 15 mol % O_2 , and N_2 as the balance. As can be seen in Figure 6, the Cu:Mn catalyst did not

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perform as effectively as the platinum based catalyst, but it did maintain good activity in converting the butene at higher temperatures, especially above 300 °C.

EXAMPLE 14

This example was the same as Example 2, except that iron nitrate, cobalt nitrate, or nickel nitrate were used to replace copper nitrate in each case. In particular, a La-stabilized alumina and a CeZrO₂ mixed oxide were milled separately to a nominal particle size of <15 microns to form slurries. These two slurries were mixed together to form a washcoat which contained 20 mol % La-stabilized alumina and 80 mol % CeZrO₂ mixed oxide. The washcoat was coated onto a ceramic monolithic substrate with 400 cells per square inch to achieve a loading of 2.75 grams per cubic inch of the substrate. After the block was dried and fired, the block was impregnated with a mixture of aqueous solution of Cu nitrate (or Fe nitrate, Co nitrate, or Ni nitrate is substituted, respectively) and Mn nitrate following the procedures listed above in Example 1.

Referring now to Figures 7a and 7b, Figure 7a illustrates the percentage of methyl bromide conversion for catalysts with the base metal promoter and the base metal catalyst of copper, iron, cobalt, or nickel, respectively. Figure 7B illustrates the percentage of benzene conversion for catalysts with the base metal promoter and the base metal catalyst of copper, iron, cobalt, or nickel, respectively. While it is evident that the copper-based catalyst demonstrated the best activity in converting the methyl bromide and benzene, the iron, cobalt, and nickel based catalysts also maintain good activity in converting methyl bromide and benzene.

While preferred embodiments of the invention have been shown and described herein, it will be understood that such embodiments are provided by way of example only. Numerous variations, changes and substitutions will occur to those skilled in the art without departing from the spirit of the invention. Accordingly, it is intended that the appended claims cover all such variations as fall within the spirit and scope of the invention.

CLAIMS

1. A method for oxidizing carbon monoxide (CO) and volatile organic compounds (VOCs) comprising the step of:

 contacting a gas containing water vapor and said CO and VOCs with a catalyst composition comprising at least one base metal promoter and at least one base metal catalyst supported on an oxide support material comprising one or more of alumina, silica, zirconia, ceria, and titania, wherein said VOCs comprise one or more of methyl acetate, methane, methyl bromide, benzene, methanol, methyl ethyl ketone, butane, and butene.
2. The method of claim 1 wherein said water vapor is present in said gas in an amount of 1.5 mole percent to 5 mole percent.
3. The method of claim 1 wherein said contacting occurs at a temperature of less than 325 °C.
4. The method of claim 1 wherein said contacting occurs at a temperature of less than 300 °C.
5. The method of claim 1 wherein said contacting occurs at a temperature of less than 250 °C.
6. The method of claim 1, wherein said gas is a tail-gas of a process for producing purified terephthalic acid.
7. A catalyst composition for the oxidation of carbon monoxide (CO) and volatile organic compounds (VOC), said composition comprising at least one base metal promoter and at least one base metal catalyst supported on an oxide support material comprising one or more of alumina, silica, zirconia, ceria, and titania.
8. The catalyst of claim 7 wherein the at least one base metal catalyst is selected from the group consisting of copper (Cu), iron (Fe), cobalt (Co), nickel (Ni), and chromium (Cr).
9. The catalyst of claim 7 wherein the at least one base metal catalyst promoter is selected from the group consisting of neodymium (Nd), barium (Ba), cerium (Ce), lanthanum (La), praseodymium (Pr), magnesium (Mg), calcium (Ca), manganese (Mn), zinc (Zn), niobium (Nb), zirconium (Zr), molybdenum (Mo), tin (Sn), tantalum (Ta), and strontium (Sr).
10. The catalyst of claim 7 wherein said catalyst composition is free of platinum group metals (PGM).

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11. The catalyst of claim 7 wherein the at least one base metal catalyst is copper and wherein the at least one base metal catalyst promoter is Mn.
12. The catalyst of claim 7 wherein said oxide support material is lanthanum (La) stabilized Al_2O_3 .
13. The method of claim 7, wherein said oxide support material is ceria and said ceria is Zr-stabilized CeO_2 .
14. The method of claim 13, wherein said oxide support material comprises Ce and Zr present in a 1:1 mole ratio.

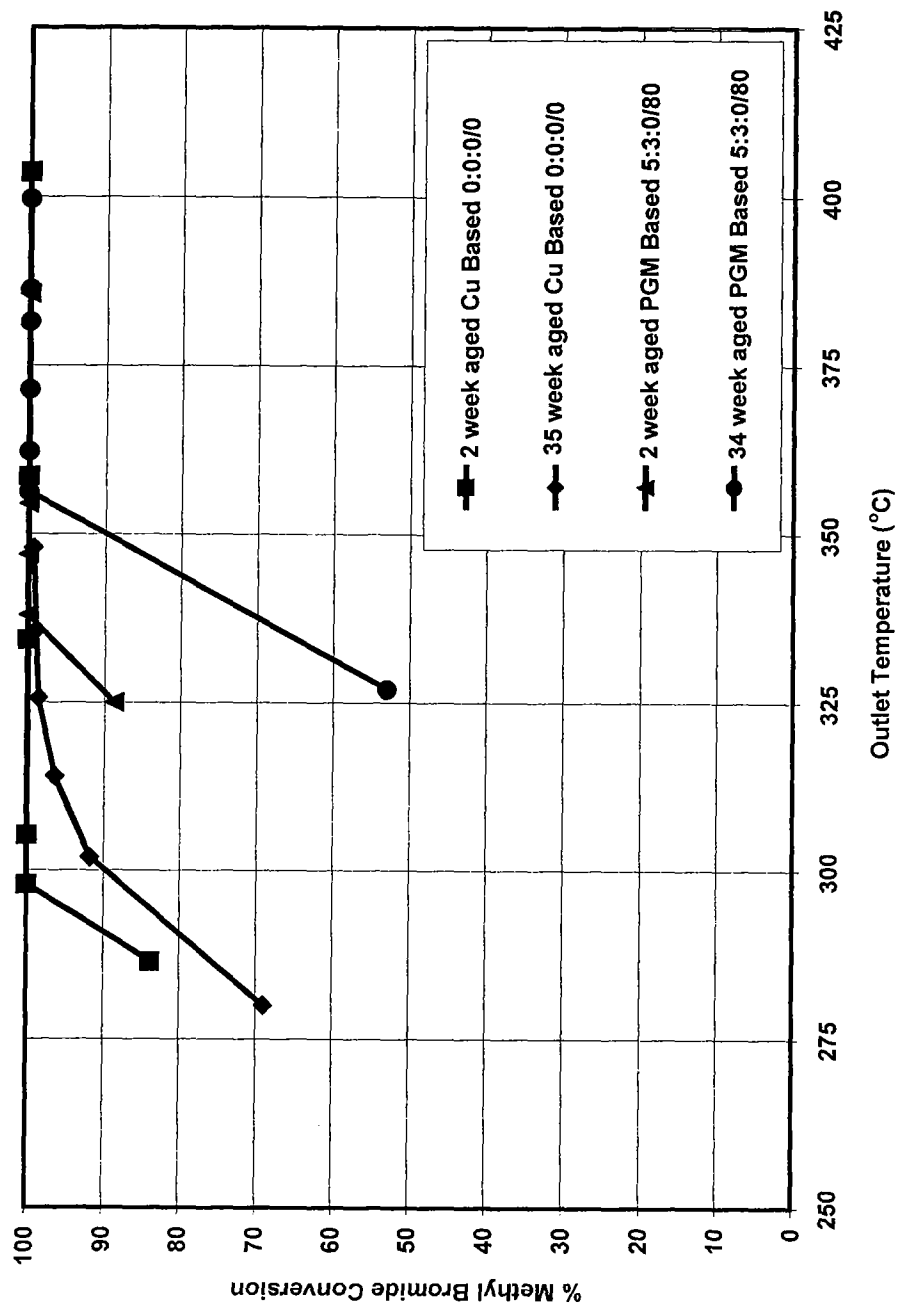


Figure 1a

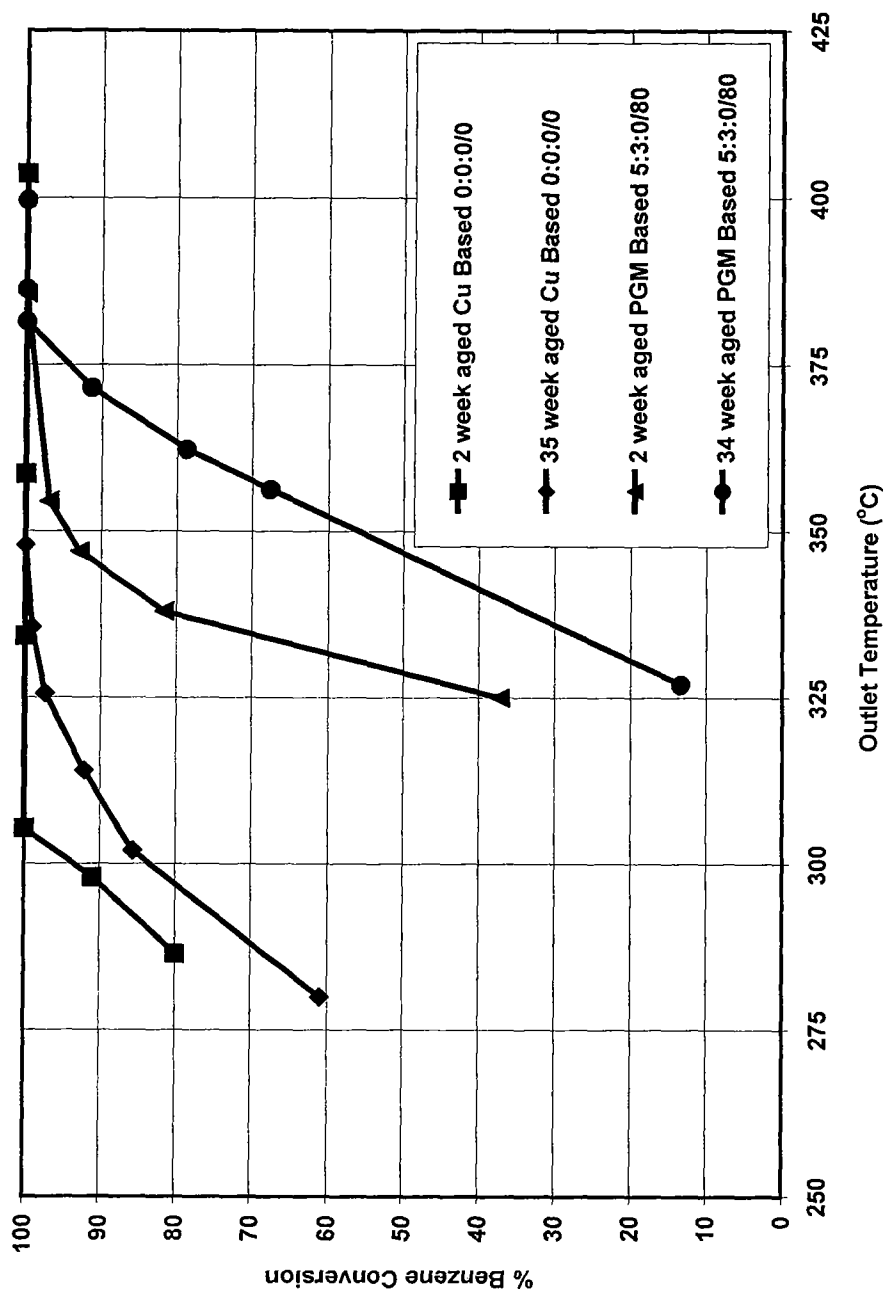


Figure 1b

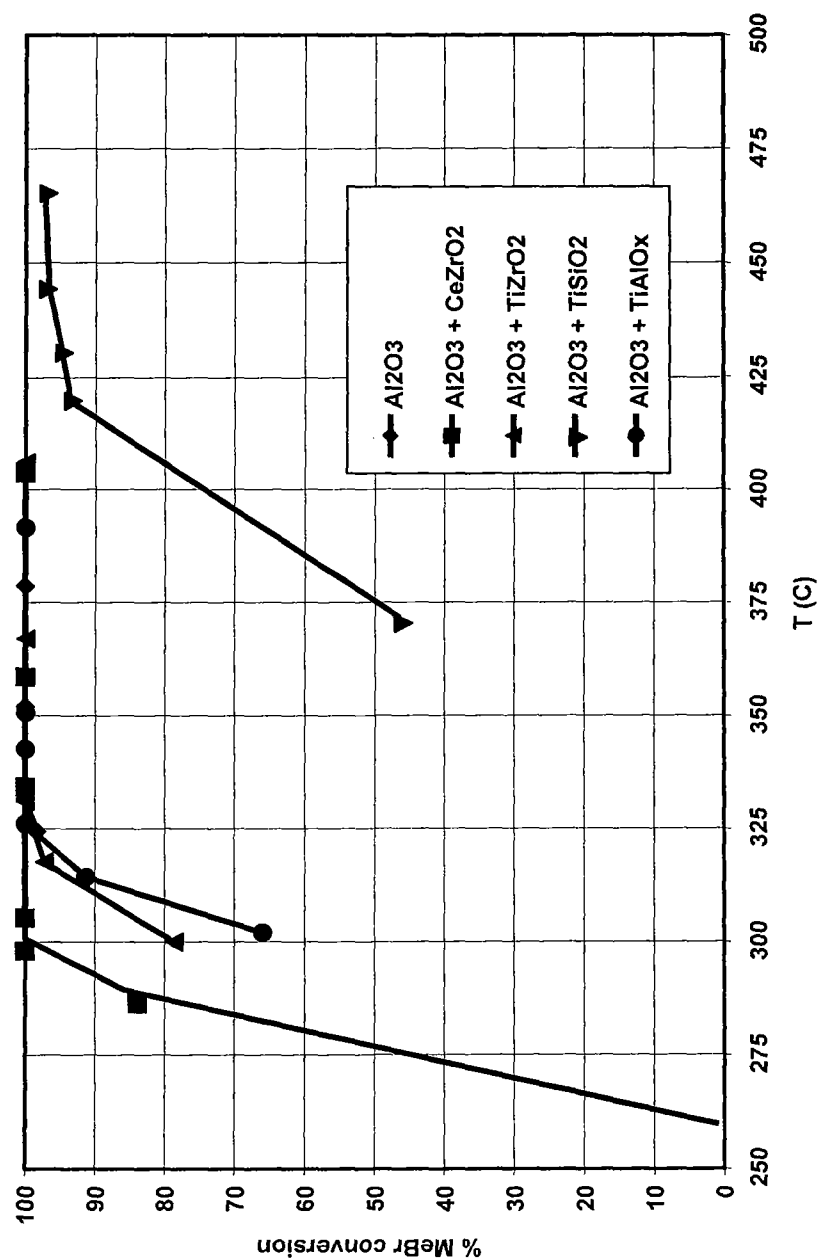


Figure 2a

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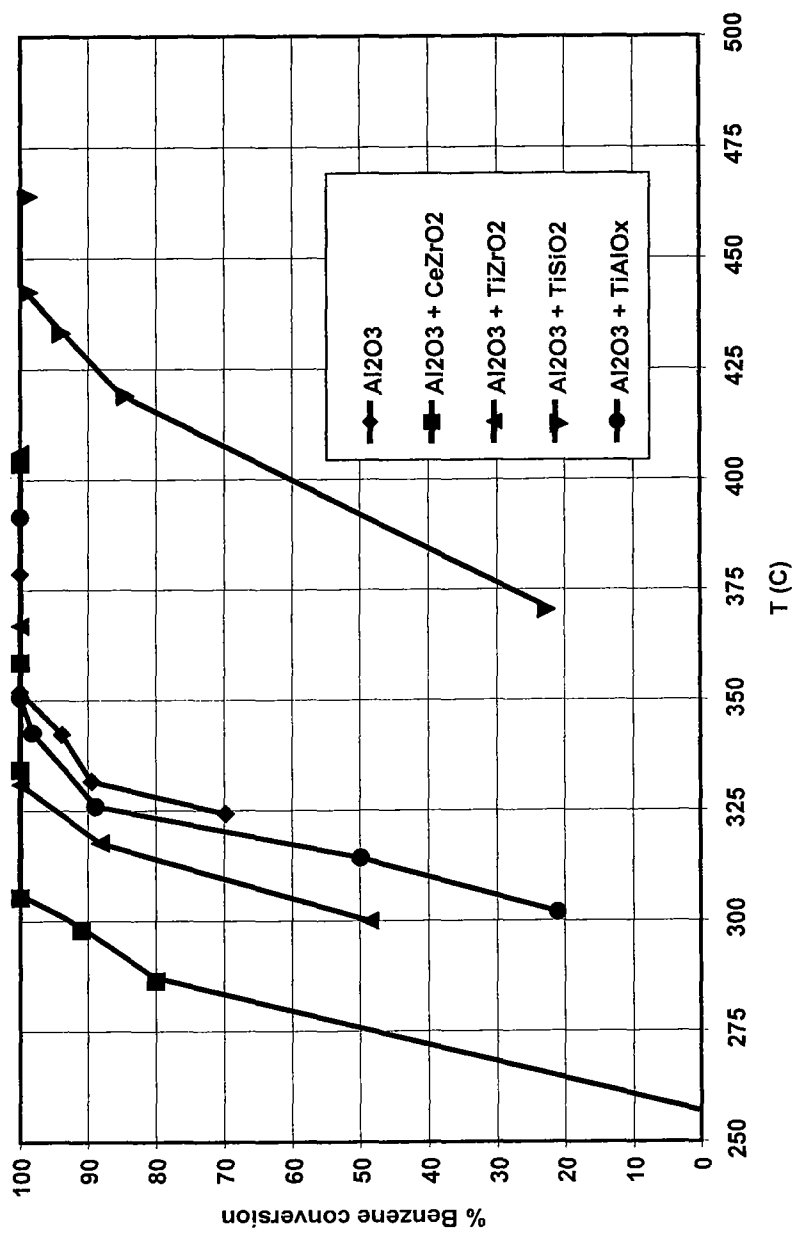


Figure 2b

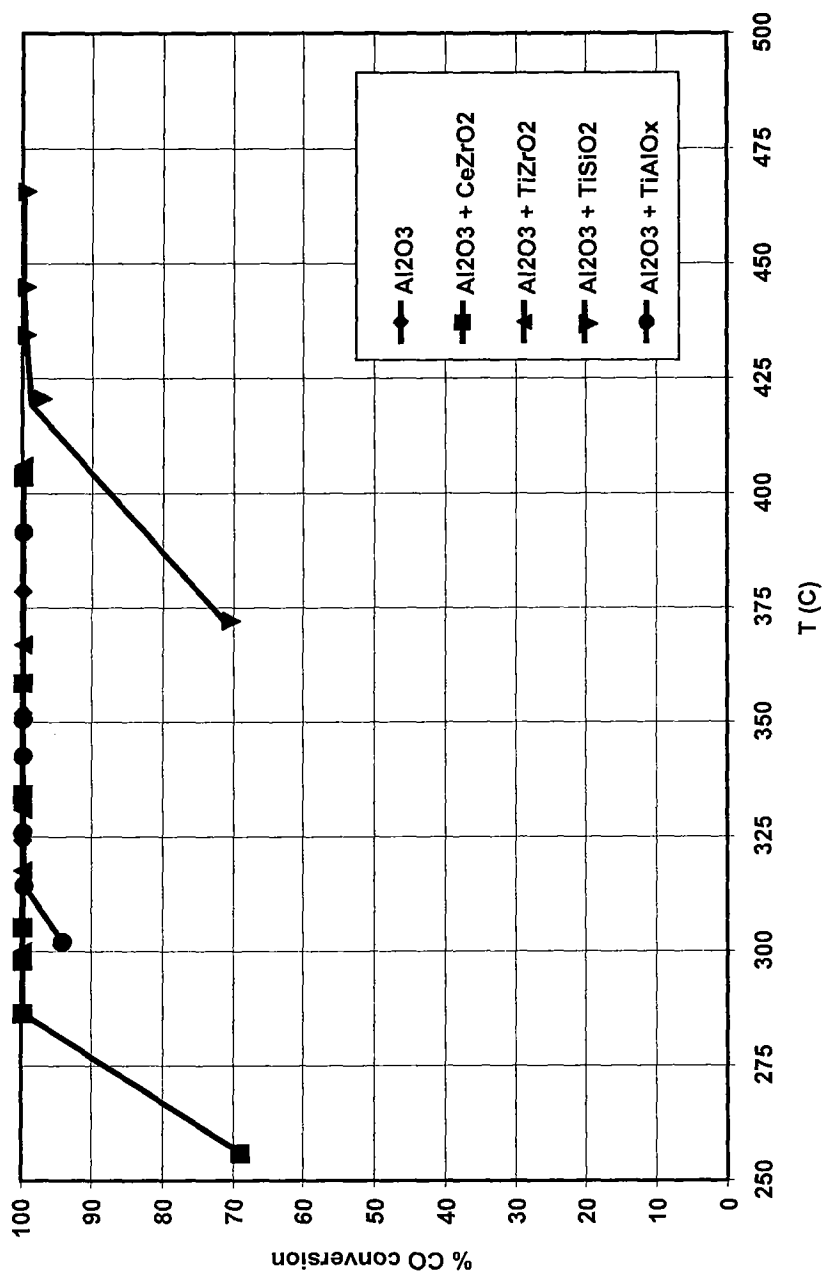


Figure 2c

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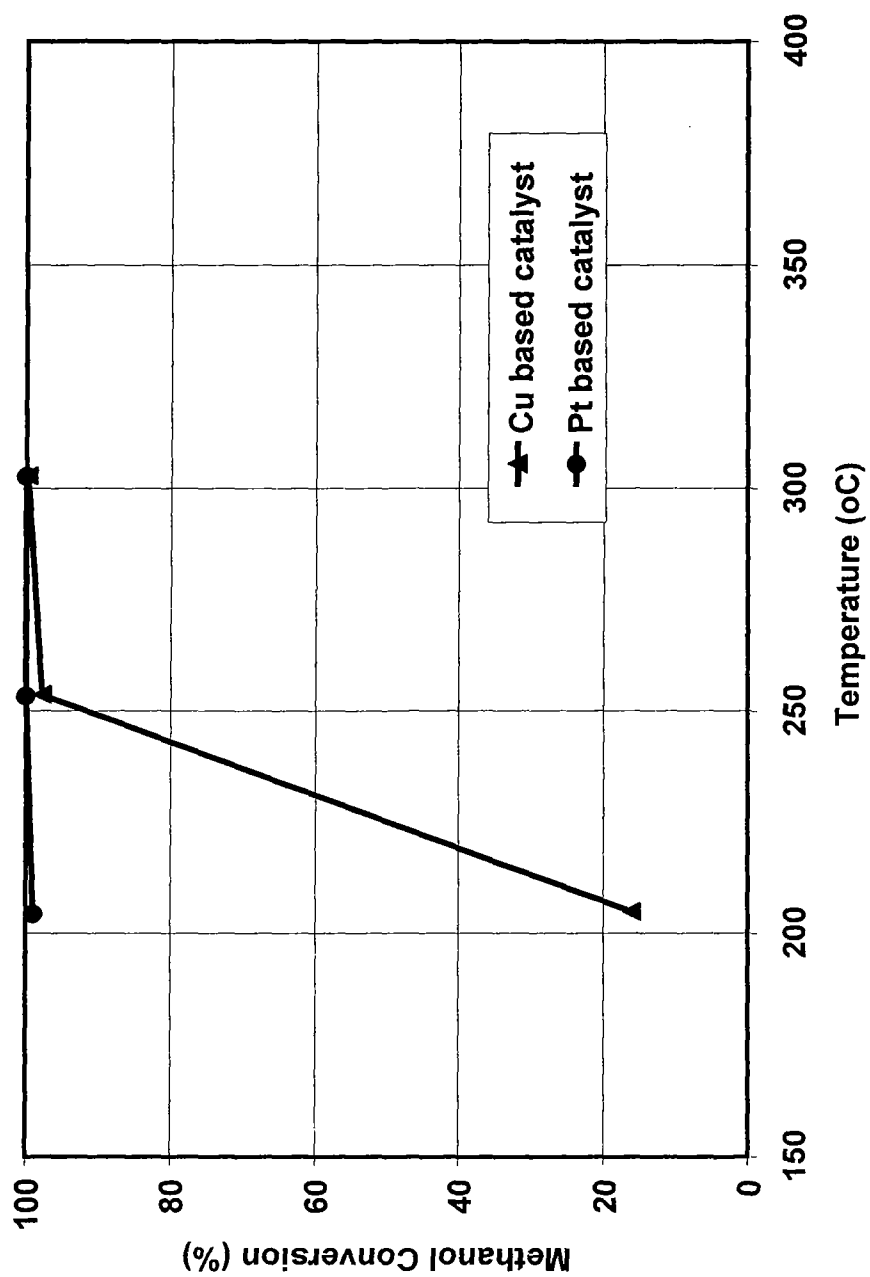


Figure 3

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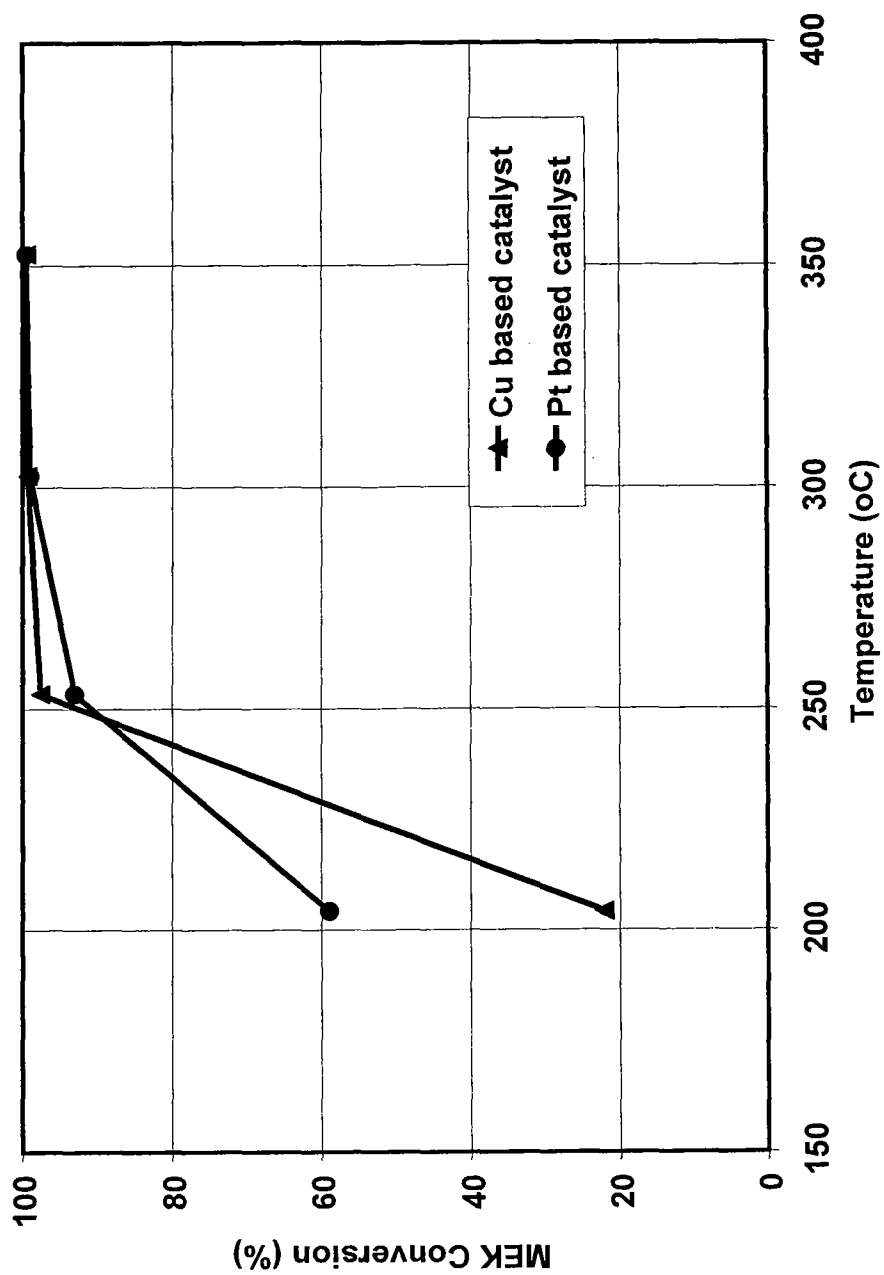


Figure 4

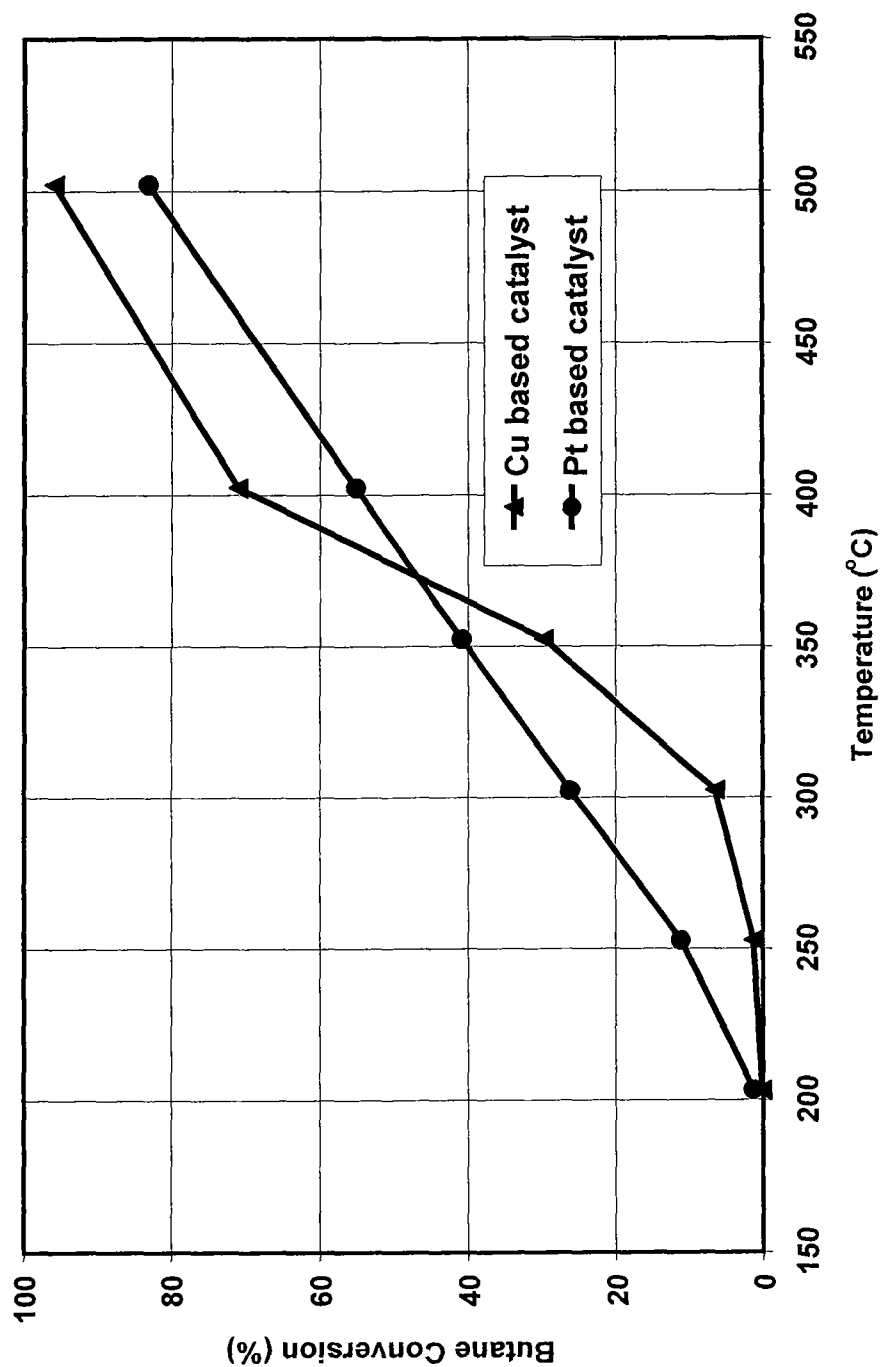


Figure 5

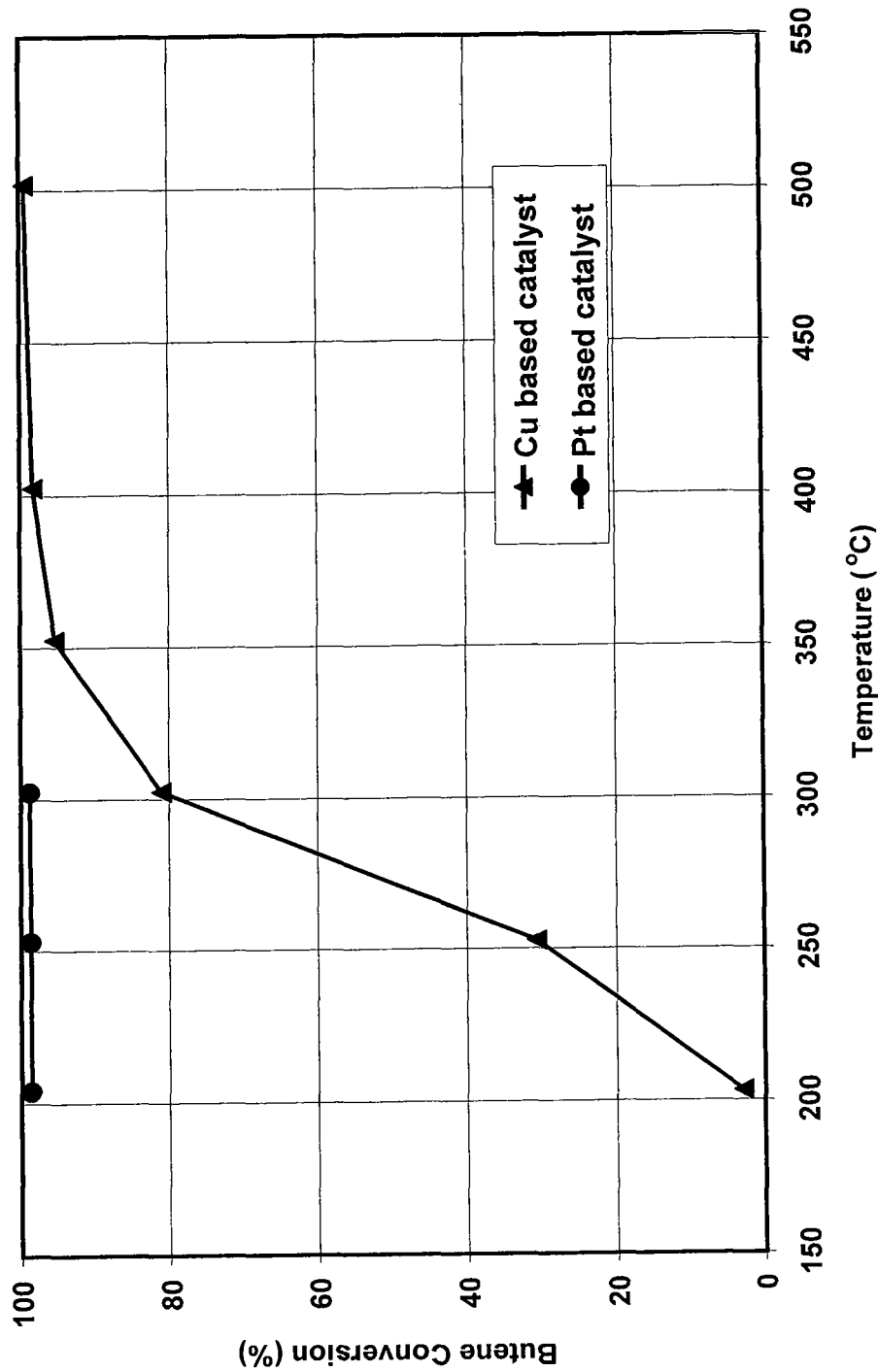


Figure 6

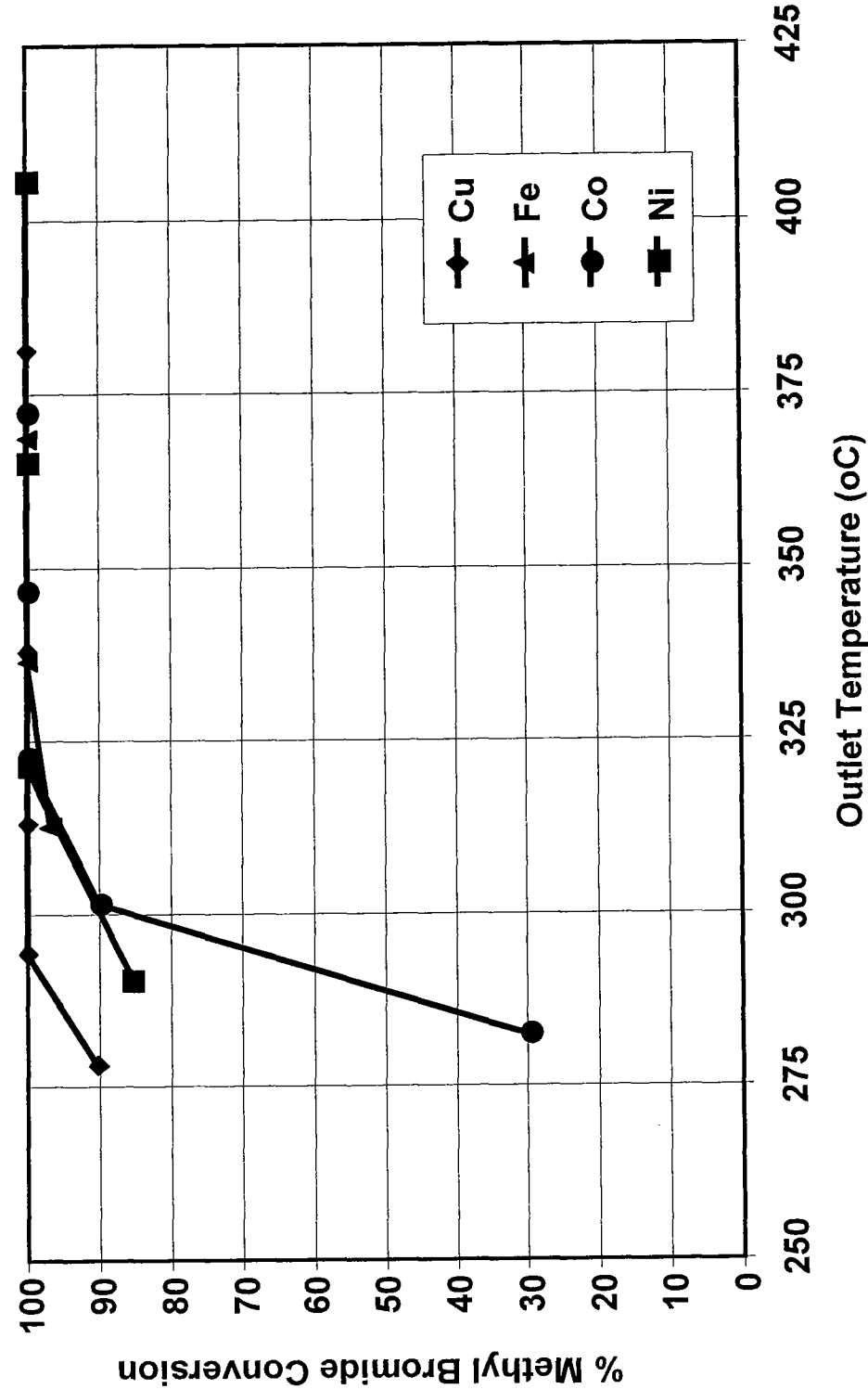


Figure 7a

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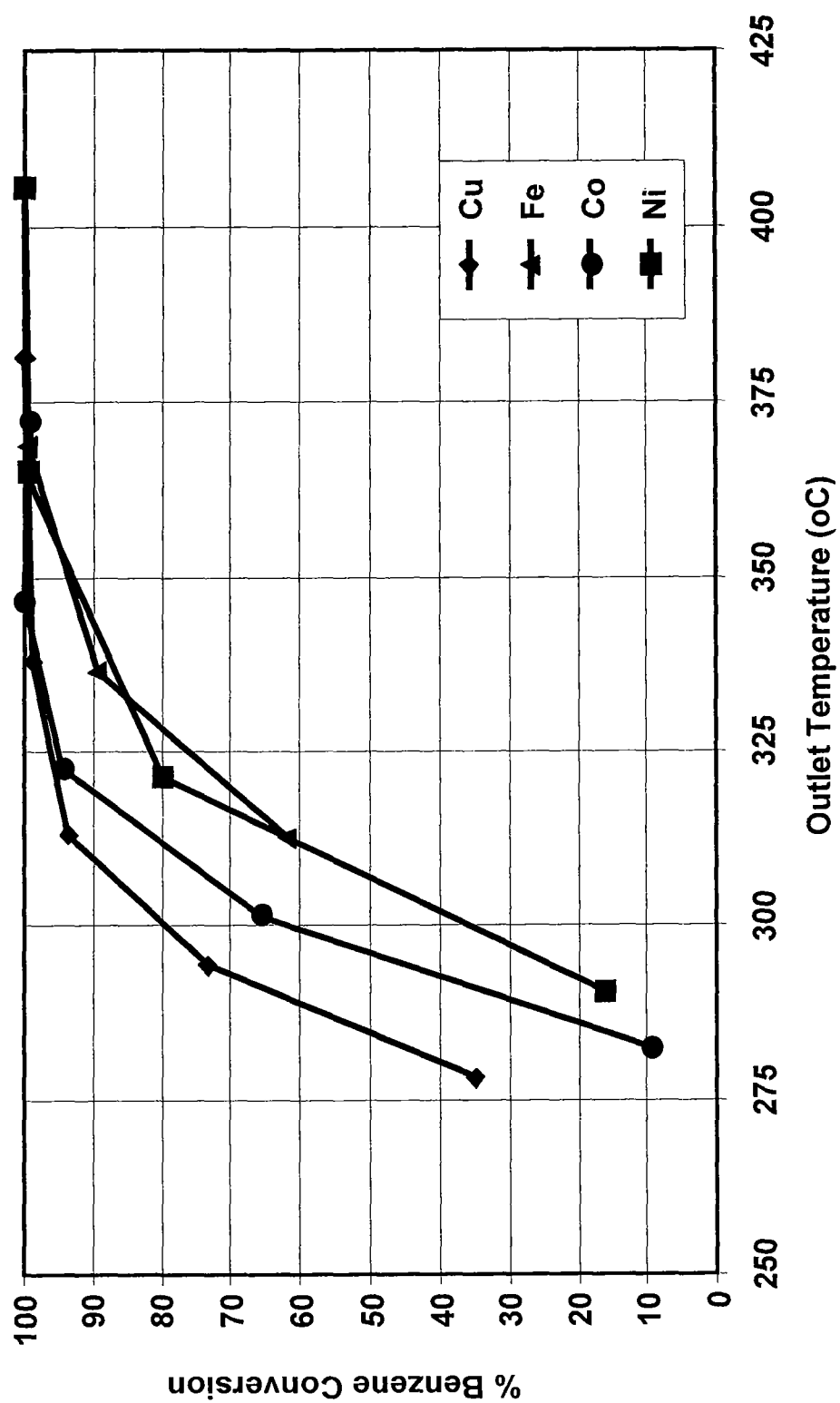


Figure 7b

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/031036

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J23/889 B01J35/04 B01D53/00 B01J23/00
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 B01D

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2008/112871 A1 (OBAYASHI YOSHIKI [JP] ET AL) 15 May 2008 (2008-05-15) the whole document	1-14
X	WO 01/45833 A1 (ELTRON RES INC [US]) 28 June 2001 (2001-06-28) page 21, paragraph 4 - page 44, paragraph 4; claims; examples	1-14
X	WO 03/101612 A2 (JOHNSON MATTHEY PLC [GB]; AIELLO RITA [US]; ANDERSEN PAUL JOSEPH [US]) 11 December 2003 (2003-12-11) page 6 - page 9; claims; examples	1-14
A	DE 37 40 091 A1 (HAUFE PAUL J M [DE]) 15 June 1989 (1989-06-15) the whole document	1-14



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

21 September 2010

Date of mailing of the international search report

06/10/2010

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2010/031036

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