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(54) Title: CATALYSTS FOR HYDROGENATION REACTIONS, PREPARATION METHODS AND USES THEREOF

(57) Abstract: Catalysts for hydrogenation reactions especially acetic ester hydrogenation reactions are disclosed. The catalysts use copper or its oxides or a mixture thereof as an active ingredient and SiO₂ as a carrier, and further include some suitable metal oxides as a promoter. The catalysts have high activity and stability.



CATALYSTS FOR HYDROGENATION REACTIONS, PREPARATION METHODS AND USES THEREOF

FIELD OF THE INVENTION

5 The present application relates to the field of chemical catalysts, in particular, catalysts for hydrogenation reactions.

BACKGROUND OF THE INVENTION

10 Ethanol is widely used as a raw material for making acetic acid, beverages, flavors, dyes, fuels, etc. It is also an excellent solvent and disinfectant. The application of ethanol is becoming broader as an important raw material for the production of chemicals and clean fuels.

15 Conventional industrial production methods of ethanol can be divided into two categories: fermentation and chemical synthesis. The fermentation method has its shortcomings such as low conversion efficiency, high cost as well as competing for food with people. Chemical synthesis of ethanol uses ethylene, a derivative product of petroleum, as a raw material. The equipment for ethanol production by chemical synthesis is required to be resistant to acid and rigorous conditions and therefore is expensive. In addition, this method depends highly on oil resources, and its
20 production cost will increase sharply in response to increasing oil prices. Meanwhile, with the development of the ethanol industry and increasing demand, the problem of raw material and resource shortage will become more prominent. Therefore, it is important to develop methods of preparing ethanol based on non-food and non-oil resources, such as to moderate the production cost.

25 Recently, production of ethanol from synthesis gas has drawn lots of attention since synthesis gas can be obtained from coal, natural gas, biomass and even waste. This can potentially overcome limitation of the raw materials such as oil and food

resources. At present, production of ethanol by hydrogenation of acetic esters which are derived from synthesis gas has gained more industrial interest. The technology for acetic ester production is mature and the price of raw material is low, which makes it possible to scale-up the ethanol production for industrial purposes.

5 The non-precious metal catalysts for producing ethanol by hydrogenation of acetic ester are mainly copper-based catalysts. However, catalytic stability is critical for copper-based catalysts because the copper particles intend to aggregate and sinter at high temperature and may thus lose catalytic activity. Therefore, a critical issue for ethanol production by hydrogenation of acetic ester is to develop copper-based
10 catalysts with high activity and stability.

SUMMARY OF THE INVENTION

The present application relates to catalysts for a hydrogenation reaction and methods for making or using such catalysts.

15 In one aspect, the present application provides a catalyst which comprises metallic copper (Cu) or copper oxide or a mixture thereof, silica and an electron donating oxide, wherein the mass percentage of copper (Cu) element in the catalyst is 10-70%, the mass percentage of silica in the catalyst is 25-89.9%, and the mass percentage of the metal element of the electron donating oxide in the catalyst is
20 0.1%-5%.

In some embodiments, the hydrogenation reaction is an ester hydrogenation reaction. In some embodiments, the ester hydrogenation reaction is an acetate ester hydrogenation reaction.

In some embodiments, the silica is hydrophilic silica. In some embodiments, the
25 hydrophilic silica has less than 50% of its surface hydroxyl group substituted by hydrophobic groups, and still maintains hydrophilic character. In some embodiments, the silica is acidic silica. In some embodiments, the pH value of 4%

aqueous solution of the silica is lower than 6.5. In some embodiments, the specific surface area (BET) of the silica is 50-800 m²/g.

In some embodiments, the electron donating oxide comprises an N-type semi-conductive oxide. In some embodiments, the N-type semi-conductive oxide is an N-type semi-conductive metal oxide. In some embodiments, the N-type semi-conductive metal oxide is ZnO, CdO, TiO₂, CeO₂ or a mixture thereof. In some embodiments, the N-type semi-conductive metal oxide is ZnO. In some embodiments, the mass percentage of the metal element of the electron donating oxide in the catalyst is 0.1-5%.

In another aspect, the present application provides a method for preparing a catalyst, which method comprises: a) mixing Cu containing salt, metal salt and aqueous ammonia solution, wherein the metal salt can be transformed into electron donating oxide; b) adding silica to the solution of step a); c) removing ammonia; d) calcining and grinding the resulting product from step c).

In some embodiments, the method further comprises sieving the product of step d) through a mesh screen. In some embodiments, the method further comprises reducing the product of step d) in the presence of hydrogen or other reducing agent.

In another aspect, the present application provides the uses of the catalysts in hydrogenation reactions.

In another aspect, the present application provides a method of ethanol production by hydrogenation of acetic ester, which comprises: a) contacting acetic ester and hydrogen with a catalyst of the present application; b) carrying out a hydrogenation reaction of the acetic ester and the hydrogen.

DETAILED DESCRIPTION OF THE INVENTION

One aspect of the present application relates to a catalyst for a hydrogenation reaction. The catalyst comprises metallic copper (Cu) or copper oxide or a mixture

thereof, silica and electron donating oxide, wherein the mass percentage of copper (Cu) element in the catalyst is 10-70%, the mass percentage of silica in the catalyst is 25-89.9%, and the mass percentage of the metal element of the electron donating oxide in the catalyst is 0.1%-5%.

5 The term “catalyst” as used herein means a substance that can initiate or increase the rate of a chemical reaction of one or more reactants while not being consumed by the reaction. In some embodiments, the catalyst includes metallic copper (Cu) or copper oxide or the mixture thereof as an active ingredient for catalyzing a hydrogenation reaction. In some embodiments, the copper oxide included in the
10 catalyst is Cu_2O . In some embodiments, the catalyst uses Cu/Cu^+ as main active ingredients.

 The copper (Cu) element in the catalyst of the present application can be contained in the metallic copper or in the copper oxide. If the catalyst of the present application contains a mixture of metallic copper and copper oxide, then the copper
15 element is contained in both the metallic copper and the copper oxide. In some embodiments, the mass percentage of the copper (Cu) element in the catalyst of the present application is 10-70%, or 10-60%, or 10-50%, or 10-40%, or 10-30%, or 10-20%, or 20-70%, or 30-70%, or 40-70%, or 50-70%, or 60-70%. In some
20 embodiments, the mass percentage of the copper (Cu) element in the catalyst of the present application is at least 10%, or at least 15%, or at least 20%, or at least 25%, or at least 30%, or at least 35%, or at least 40%, or at least 45%, or at least 50%. In
 some embodiments, the mass percentage of the copper (Cu) element in the catalyst of present application is no more than 70%, or no more than 65%, or no more than 60%, or no more than 55%, or no more than 50%.

25 In some embodiments, the catalyst further includes electron donating oxides as a promoter which can provide electrons to the active ingredient of the catalyst to facilitate the hydrogenation reaction. The term “electron donating oxide” as used herein means an oxide that can provide electrons to the metal copper or copper oxide of the catalyst in the presence of hydrogen or other reducing agent under the reaction

condition of hydrogenation reaction. In some embodiments, the electron donating oxide comprises an N-type semi-conductive oxide that can provide electrons to the metal copper or copper oxide of the catalyst in the presence of hydrogen or other reducing agent under the reaction condition of hydrogenation reaction. In some
5 embodiments, the electron donating oxide is an N-type semi-conductive oxide or a mixture of two or more N-type semi-conductive oxides. In some embodiments, the N-type semi-conductive oxide is an N-type semi-conductive metal oxide. In some embodiments, the N-type semi-conductive metal oxide is ZnO, CdO, TiO₂, CeO₂ or a mixture thereof. In some embodiments, the N-type semi-conductive metal oxide is
10 ZnO. In some embodiments, the N-type semi-conductive metal oxide can facilitate the formation of the oxidation-reduction cycle of the copper and copper oxide (e.g. Cu⁺/Cu⁰). In some embodiments, the mass percentage of the metal element of the electron donating oxide in the catalyst of the present application is 0.1-5%, or 0.2-3%, or 0.2-1.5%, or 0.5-1%, or 0.5-2%, or 1.5-3%, or 1.5-2.5%. In some embodiments,
15 the mass percentage of the metal element of the electron donating oxide in the catalyst of the present application is at least 0.1%, or at least 0.2%, or at least 0.3%, or at least 0.4%, or at least 0.5%, or at least 0.6%, or at least 0.7%, or at least 0.8%, or at least 0.9%, or at least 1%, or at least 1.5%, or at least 2%, or at least 2.5%. In some embodiments, the mass percentage of the metal element of the electron donating oxide
20 in the catalyst of the present application is no more than 5%, or no more than 4.5%, or no more than 4%, or no more than 3.5%, or no more than 3%, or no more than 2.5%, or no more than 2%. In some embodiments, the electron donating oxide is ZnO, the metal element of the electron donating oxide is Zn, wherein the mass percentage of the Zn element in the catalyst is 0.1-5%, or 0.2-3%, or 0.2-1.5%, or 0.5-1%, or 0.5-2%,
25 or 1.5-3%, or 1.5-2.5%, or wherein the mass percentage of the Zn element in the catalyst is at least 2%, or wherein the mass percentage of the Zn element in the catalyst is at least 0.5%.

In some embodiments, the catalyst of the present application includes silica as a carrier for holding and supporting the active ingredient and the promoter of the

catalyst. The term “silica” as used herein, is a substance that consists of silicon (Si) and oxygen (O) atoms. In some embodiments, the catalyst of the present application contains silica in the form of solid particle or sol or aerosol or other suitable forms. In some embodiments, the silica of the present application contains SiO₂. In some
 5 embodiments, the mass percentage of the silica in the catalyst of the present application is 25-89.9%, or 25-85%, or 25-80%, or 25-75%, or 25-70%, or 25-65%, or 25-60%, or 25-55%, or 25-50%,. In some embodiments, the mass percentage of the silica in the catalyst of the present application is at least 25%, or at least 30%, or at least 35%, or at least 40%, or at least 45%, or at least 50%, or at least 55%, or at least
 10 60%, or at least 65%, or at least 70%, or at least 75%, or at least 80%. In some embodiments, the mass percentage of the silica in the catalyst of the present application is no more than 85%, or no more than 80%, or no more than 75%, or no more than 70%, or no more than 65%, or no more than 60%, or no more than 55%.

In some embodiments, the catalyst of the present application may further include
 15 one or more other materials that are not silica as carriers to hold and support the active ingredient and the promoter of the catalyst. Examples of such other materials are pure silica mesoporous molecular sieves SBA-15, MCM-41, et al.

The mass percentage of each component of the catalyst is calculated as follows:

$$\begin{aligned}\text{Cu\%} &= W_{\text{Cu}}/(W_{\text{Cu}}+W_{\text{X}}+W_{\text{silica}})*100\%, \\ \text{X\%} &= W_{\text{X}}/(W_{\text{Cu}}+W_{\text{X}}+W_{\text{silica}})*100\%, \\ \text{Silica\%} &= W_{\text{silica}}/(W_{\text{Cu}}+W_{\text{X}}+W_{\text{silica}})*100\%,\end{aligned}$$

Wherein Cu% refers to the mass percentage of the copper (Cu) element in the catalyst, X% refers to the mass percentage of the metal element of the electron donating oxides in the catalyst, Silica% refers to the mass percentage of the silica in
 25 the catalyst, W_{Cu} refers to the total mass of the copper (Cu) element of the metallic Cu or copper oxide or a mixture thereof in the catalyst, W_X refers to the total mass of the metal element of the electron donating oxides in the catalyst, W_{silica} refers to the total mass of silica in the catalyst.

The term "hydrogenation reaction" as used herein means any reaction in which hydrogen or an isotope of hydrogen (e.g. deuterium) or a hydrogen transfer agent (e.g. formic acid) is an active reactant and hydrogen is added to a substrate as another reactant of the reaction. Such reactions include hydrogenolysis, saturation reactions, reductive alkylation/amination and also hydroformylation. The substrate or the reactant to be hydrogenated is typically, but not exclusively, selected from: ketone, aldehyde, hydroxy acid, ester, alkene, alkyne, lactone, anhydride, cyclic anhydride, amide, lactam, Schiff's base, alcohol, nitro, hydroxylamine, nitrile, oxime, imine, azine, hydrazone, azide, cyanate, isocyanate, thiocyanate, isothiocyanate, diazonium, azo, nitroso, phenol, ether, furan, epoxide, hydroperoxide, ozonide, peroxide, arene, unsaturated heterocyclic, acetal and ketal. In some embodiments, the hydrogenation reaction is an ester hydrogenation reaction. In some embodiments, the hydrogenation reaction is a ketone hydrogenation reaction. In some embodiments, the hydrogenation reaction is an aldehyde hydrogenation reaction. In some embodiments, the hydrogenation reaction is a hydroxy acid hydrogenation reaction. In some embodiments, the ester hydrogenation reaction is an acetic ester hydrogenation reaction. In some embodiments, the acetic ester hydrogenation reaction is an ethyl acetate hydrogenation reaction. In some embodiments, the acetic ester hydrogenation reaction is a methyl acetate hydrogenation reaction. In some embodiments, the acetic ester hydrogenation reaction is a butyl acetate hydrogenation reaction. In some embodiments, the ester hydrogenation reaction is an aliphatic ester hydrogenation reaction. In some embodiments, the aliphatic ester is an aliphatic ester with 1-6 carbon atoms.

In one aspect, the present application provides the uses of the catalysts in hydrogenation reactions. In some embodiments, the use of the catalyst of present application is the use thereof in acetic ester hydrogenation reactions. In some embodiments, the acetic ester hydrogenation reaction is conducted at the temperature of 200-240°C, or 210-230°C, or 215-225°C. In some embodiments, the acetic ester hydrogenation reaction is conducted at the temperature of 220°C. In some

embodiments, the acetic ester hydrogenation reaction is conducted at the pressure of 0.5-7 MPa, or 0.5-2 MPa, or 1-4 MPa, or 1.5-2.5 MPa. In some embodiments, the acetic ester hydrogenation reaction is conducted at the pressure of 2.0 MPa. In some embodiments, the molar ratio between hydrogen and acetic ester of the acetic ester
5 hydrogenation reaction is 5:1-100:1, or 10:1-100:1, or 30:1-80:1, or 30:1-50:1, or 50:1-80:1. In some embodiments, the conversion rate of the acetic ester hydrogenation reaction is no less than 70%, or no less than 75%, or no less than 80%, or no less than 85%, or no less than 90%. In some embodiments, the main product selectivity of the acetic ester hydrogenation reaction is no less than 90%, or no less
10 than 95%, or no less than 98%.

In some embodiments, the catalyst of the present application contains silica with a specific surface area (BET) of 50-800 m²/g. The term "specific surface area (BET)" as used herein is calculated with reference to the nitrogen desorption isotherm (assuming cylindrical pores) by the B.E.T. technique as described by S. Brunauer, P.
15 Emmett, and E. Teller in the Journal of American Chemical Society, 60, pp 209-319 (1939). In some embodiments, the silica of the present application has a specific surface area (BET) of 100-800 m²/g, or 200-800 m²/g, or 300-800 m²/g, or 400-800 m²/g, or 500-800 m²/g, or 600-800 m²/g, or 700-800 m²/g. In some embodiments, the silica of the present application has a specific surface area (BET) of 100-200 m²/g.
20 or 100-300 m²/g. or 100-400 m²/g, or 100-500 m²/g, or 100-600 m²/g, or 100-700 m²/g. In some embodiments, the silica of the present application has a specific surface area (BET) of at least 100 m²/g, or at least 200 m²/g, or at least 300 m²/g, or at least 400 m²/g, or at least 500 m²/g, or at least 600 m²/g, or at least 700 m²/g. In some embodiments, the silica of the present application has a specific surface area
25 (BET) of no more than 800 m²/g, or no more than 700 m²/g, or no more than 600 m²/g, or no more than 500 m²/g, or no more than 400 m²/g.

In some embodiments, the silica of the present application is hydrophilic silica. In some embodiments, the hydrophilic silica of the present application has none of its surface hydroxyl group substituted by hydrophobic groups. In some embodiments,

the hydrophilic silica of the present application has some of its surface hydroxyl group substituted by hydrophobic groups but still maintains its hydrophilic characteristics. In some embodiments, the hydrophilic silica has less than 5%, or less than 10%, or less than 20%, or less than 30%, or less than 40%, or less than 50%, or less than 60%,
 5 or less than 70% of its surface hydroxyl group substituted by hydrophobic groups. The number of silica surface hydroxyl groups can be determined by the titrimetric method. In brief, the titrimetric method includes the following steps: firstly, measure 2.0 g of dry silica and soak it in 25 mL of ethanol, followed by adding 75 mL of 20% NaCl solution, mix well; secondly, adjust the solution to a pH of 4.0 by adding 0.1
 10 mol/L HCl solution; finally adjust the solution to a pH 9.0 by adding 0.1 mol/L NaOH solution, waiting until the pH remains stable for at least 3 minutes. The number of surface hydroxyl groups of silica is then represented by the volume of NaOH used to adjust 2.0 g of silica from pH 4.0 to pH 9.0. The BET surface area of the silica is defined as S (m^2/g), the volume of NaOH used is defined as V (mL), and the
 15 calculation formula of the number of surface hydroxyl groups of silica ($/\text{nm}^2$) is as follows:

$$\text{Number of surface hydroxyl groups of Silica } (/ \text{nm}^2) = 6.02 \times 10^{23} \times V/2 \times 10^{-4} \times S \times 10^{-18}$$

The surface hydroxyl group substitution of silica can be calculated by dividing
 20 the result of the number of surface hydroxyl groups of standard silica (silica with no substitution of hydroxyl groups by hydrophobic groups) minus the number of surface hydroxyl groups of treated silica by the number of surface hydroxyl groups of the standard silica. Any silica whose surface is treated with silylating agents, for example halogenated silanes such as alkylchlorosilanes, siloxanes, in particular
 25 dimethylsiloxanes such as hexamethyldisiloxane, or silazanes, will have its surface hydroxyl groups substituted by hydrophobic groups.

In some embodiments, the silica of the present application is acidic silica wherein a 4% aqueous solution of the silica has a pH value below 7.0. The pH value of silica can be determined by thoroughly mixing 4 grams of dry silica with 100 milliliters of

distilled water and then measure the pH of the solution. In some embodiments, the 4% aqueous solution of the silica has a pH value of lower than 6.5, or lower than 6.0, or lower than 5.0, or lower than 4.0, or lower than 3.0, or lower than 2.0, or lower than 1.0. In some embodiments, the 4% aqueous solution of the silica has a pH value of 2.0-6.0. In some embodiments, the 4% aqueous solution of the silica has a pH value of 3.0-5.0.

In some embodiments, the catalyst is reduced before use e.g. by the conventional method of heating prepared catalyst in the presence of a reducing agent such as hydrogen, carbon monoxide, or any other suitable reducing agent. In some embodiments, the catalyst is reduced by heating it in the presence of hydrogen and/or carbon monoxide.

The reactivity of a catalyst can be tested by any known method in the field. In some embodiments, the following schemes are used to test the reactivity of a catalyst. The test on the catalyst for producing ethanol by hydrogenation of acetic ester was carried out in a continuous flow fixed-bed reactor, wherein the weight of the catalyst loaded was 1.0 g. Pure hydrogen was used to reduce the catalyst under atmospheric pressure at 350°C at a gas speed of 100 mL/min, wherein the temperature was raised from room temperature to 350°C at the rate of 1~2°C /min and maintained for 3 hrs. After the temperature was lowered to the reaction temperature at the rate of 2°C /min, the raw materials were introduced to start the reaction. The reaction products were analyzed by gas chromatography, wherein the chromatography column was 30m FFAP-type polar capillary column, and hydrogen flame ionization detector (FID) was used to detect the raw materials and reaction products.

The calculation formula of the acetic ester (A) conversion rate (X_A) and product selectivity (S_M) is as follows:

$$X_A = \frac{\text{Quantity of Converted A}}{\text{Quantity of Fed A}} \times 100\%$$

$$S_M = \frac{\text{Quantity of Produced M}}{\text{Quantity of Converted A}} \times 100\%$$

The quantity of A or M was calculated based on carbon moles included in A or M. The “M” in the formula above refers to the reaction product, which can be main product ethanol, or side-products ethane, diethyl ether, acetaldehyde, methanol, etc.

In some embodiments, the catalyst of the present application can achieve a
5 conversion rate of no less than 95% in a hydrogenation reaction. In some
embodiments, the catalyst of the present application can achieve a conversion rate of
no less than 90%, or no less than 85%, or no less than 80%, or no less than 75%, in a
hydrogenation reaction.

In some embodiments, the catalyst of the present application can achieve a
10 product selectivity of no less than 95% in a hydrogenation reaction. In some
embodiments, the catalyst of the present application can achieve a product selectivity
of no less than 90%, or no less than 85%, or no less than 80%, or no less than 75%, in
a hydrogenation reaction.

In one aspect, the present application provides a catalyst containing copper and
15 copper oxide as active ingredients and an N-type semi-conductive metal oxide as
promoter (e.g. ZnO or CeO₂), wherein the promoter can facilitate the formation of the
oxidation-reduction cycle (Cu^+/Cu^0 , $\text{Zn}^{2+}/\text{Zn}^{(2-\delta)+}$ or $\text{Ce}^{4+}/\text{Ce}^{(4-\delta)+}$) in the atmosphere of
feed gas (ester/hydrogen) as well as improve and maintain the ratio of Cu^+/Cu^0 in the
copper-based catalyst so as to improve the activity and stability of the catalyst in the
20 acetic ester hydrogenation reaction.

EXAMPLES

The invention will be further illustrated by the following non-limiting examples. These Examples are set forth to aid in the understanding of the invention but are not
25 intended to, and should not be construed to limit its scope in any way. The
Examples do not include detailed descriptions of conventional methods that would be
well known to those of ordinary skill in the art (chemical synthesis techniques, etc.). Unless indicated otherwise, percentages are mass percentages; parts are parts by

weight, molecular weight is average molecular weight, temperature is indicated in Celsius, and pressure is at or near atmospheric.

Example 1 Preparation of Catalysts

Catalyst A

5 36.3 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was weighed to prepare 500 mL $\text{Cu}(\text{NO}_3)_2$ solution with a concentration of 0.3 mol/L. 157 mL $\text{Cu}(\text{NO}_3)_2$ solution was loaded into a 250 mL beaker. Then 18 mL ammonia aqueous solution (25 wt%) was added to the $\text{Cu}(\text{NO}_3)_2$ solution drop by drop to make the pH value of the final solution about 9-10. 12 g SiO_2 (4% aqueous solution with pH 4.9) was added to the copper ammonia
10 solution under stirring. The beaker was put in a 35°C water bath to let the solution age for 4 hrs, and then the temperature was raised to 90°C and maintained at such temperature for 2.5 hrs to evaporate the ammonia. The resulting precipitate was filtered and washed until the pH value of the filtrate reached about 7, and then the filtered cake was moved to a crucible, dried in the oven at 120 °C for 12 hrs, and
15 calcined for 4 hrs at a temperature of 450°C. The resulting material was crushed and then sieved through a 20-40 mesh screen. The obtained catalyst was denoted as Catalyst A. Catalyst A contains a mixture of copper, copper oxides such as Cu_2O , and SiO_2 .

The mass percentage of each component of catalyst A is calculated as follows:

$$20 \quad \text{Cu}\% = W_{\text{Cu}} / (W_{\text{Cu}} + W_{\text{SiO}_2}) * 100\%$$

$$\text{SiO}_2\% = W_{\text{SiO}_2} / (W_{\text{Cu}} + W_{\text{SiO}_2}) * 100\%$$

Nominal mass percentage:

Molecular Weight of Cu = 64, Molecular Weight of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ = 242,

$$W_{\text{Cu}} = 36.3 \text{ g} * (64 / 242) * (157 \text{ mL} / 500 \text{ mL}) \approx 3 \text{ g},$$

$$25 \quad W_{\text{SiO}_2} = 12 \text{ g},$$

$$\text{Cu}\% = 3 \text{ g} / (3 \text{ g} + 12 \text{ g}) * 100\% = 20\%,$$

$$\text{SiO}_2\% = 12 \text{ g} / (3 \text{ g} + 12 \text{ g}) * 100\% = 80\%.$$

The calculated nominal mass percentage is: Cu%=20%, SiO₂%=80%. The nominal mass percentage of each component is approximately equal to the mass percentage calculated based on ICP-MS (inductively coupled plasma mass spectrometry) measurements.

Catalyst A'

The preparation steps were the same as Catalyst A except that SiO₂ with less hydroxyl groups (4% aqueous solution of the SiO₂ has pH 7) was used to replace the SiO₂ in Catalyst A. Catalyst A' containing a mixture of copper, copper oxides (such as Cu₂O), and SiO₂ was obtained.

Catalyst B

The preparation steps were the same as Catalyst A except that 0.34 g Zn(NO₃)₂·6H₂O was added to the Cu(NO₃)₂ solution before the addition of ammonia aqueous solution. Catalyst B (Cu%=20%, Zn%=0.5%, SiO₂%=79.5%) containing a mixture of copper, copper oxides (such as Cu₂O), ZnO and SiO₂ was obtained.

The mass percentage of each component of catalyst B is calculated as follows:

$$\text{Cu}\% = W_{\text{Cu}} / (W_{\text{Cu}} + W_{\text{Zn}} + W_{\text{SiO}_2}) * 100\%$$

$$\text{Zn}\% = W_{\text{Zn}} / (W_{\text{Cu}} + W_{\text{Zn}} + W_{\text{SiO}_2}) * 100\%$$

$$\text{SiO}_2\% = W_{\text{SiO}_2} / (W_{\text{Cu}} + W_{\text{Zn}} + W_{\text{SiO}_2}) * 100\%$$

Nominal mass percentage:

Molecular Weight of Cu = 64, Molecular Weight of Cu(NO₃)₂·3H₂O = 242,

Molecular Weight of Zn = 65, Molecular Weight of Zn(NO₃)₂·6H₂O = 297,

$$W_{\text{Cu}} = 36.3 \text{ g} * (64 / 242) * (157 \text{ mL} / 500 \text{ mL}) \approx 3 \text{ g},$$

$$W_{Zn} = 0.34 \text{ g} * (65 / 297) \approx 0.074 \text{ g},$$

$$W_{SiO_2} = 12 \text{ g},$$

$$Cu\% = 3 \text{ g} / (3 \text{ g} + 0.074 \text{ g} + 12 \text{ g}) * 100\% = 20\%,$$

$$Zn\% = 0.074 \text{ g} / (3 \text{ g} + 0.074 \text{ g} + 12 \text{ g}) * 100\% = 0.5\%,$$

$$5 \quad SiO_2\% = 12 \text{ g} / (3 \text{ g} + 0.074 \text{ g} + 12 \text{ g}) * 100\% = 79.5\%.$$

The calculated nominal mass percentage is Cu%=20%, Zn%=0.5%, SiO₂%=79.5%. The nominal mass percentage of each component is approximately equal to the weight percentage calculated based on ICP-MS measurements.

10 Catalyst B'

The preparation steps were the same as Catalyst A except that 0.37 g Ni(NO₃)₂·6H₂O was added to the Cu(NO₃)₂ solution before the addition of ammonia aqueous solution. Catalyst B' containing a mixture of copper, copper oxides such as Cu₂O, NiO and SiO₂ was obtained.

15 The mass percentage of each component of catalyst B' is calculated as follows:

$$Cu\% = W_{Cu} / (W_{Cu} + W_{Ni} + W_{SiO_2}) * 100\%$$

$$Ni\% = W_{Ni} / (W_{Cu} + W_{Ni} + W_{SiO_2}) * 100\%$$

$$SiO_2\% = W_{SiO_2} / (W_{Cu} + W_{Ni} + W_{SiO_2}) * 100\%$$

Nominal mass percentage:

20 Molecular Weight of Cu = 64, Molecular Weight of Cu(NO₃)₂·3H₂O = 242,
Molecular Weight of Ni = 59, Molecular Weight of Ni(NO₃)₂·6H₂O = 291,

$$W_{Cu} = 36.3 \text{ g} * (64 / 242) * (157 \text{ mL} / 500 \text{ mL}) \approx 3 \text{ g},$$

$$W_{Ni} = 0.37 \text{ g} * (59 / 291) \approx 0.075 \text{ g},$$

$$W_{SiO_2} = 12 \text{ g},$$

$$\text{Cu}\% = 3 \text{ g} / (3 \text{ g} + 0.075 \text{ g} + 12 \text{ g}) * 100\% = 20\%,$$

$$\text{Ni}\% = 0.075 \text{ g} / (3 \text{ g} + 0.075 \text{ g} + 12 \text{ g}) * 100\% = 0.5\%,$$

$$\text{SiO}_2\% = 12 \text{ g} / (3 \text{ g} + 0.075 \text{ g} + 12 \text{ g}) * 100\% = 79.5\%.$$

The calculated nominal mass percentage is Cu%=20%, Ni%=0.5%,
 5 SiO₂%=79.5%. The nominal mass percentage of each component is approximately equal to the mass percentage calculated based on ICP-MS measurements.

Catalyst C

The preparation steps were the same as Catalyst A except that 0.23 g
 10 Ce(NO₃)₃·6H₂O was added to the Cu(NO₃)₂ solution before the addition of ammonia aqueous solution. Catalyst C containing a mixture of copper, copper oxides such as Cu₂O, CeO₂ and SiO₂ was obtained.

The mass percentage of each component of catalyst C is calculated as follows:

$$\text{Cu}\% = W_{\text{Cu}} / (W_{\text{Cu}} + W_{\text{Ce}} + W_{\text{SiO}_2}) * 100\%$$

$$15 \quad \text{Ce}\% = W_{\text{Ce}} / (W_{\text{Cu}} + W_{\text{Ce}} + W_{\text{SiO}_2}) * 100\%$$

$$\text{SiO}_2\% = W_{\text{SiO}_2} / (W_{\text{Cu}} + W_{\text{Ce}} + W_{\text{SiO}_2}) * 100\%$$

Nominal mass percentage:

Molecular Weight of Cu = 64, Molecular Weight of Cu(NO₃)₂·3H₂O = 242,

Molecular Weight of Ce = 140, Molecular Weight of Ce(NO₃)₃·6H₂O = 434,

$$20 \quad W_{\text{Cu}} = 36.3 \text{ g} * (64 / 242) * (157 \text{ mL} / 500 \text{ mL}) \approx 3 \text{ g},$$

$$W_{\text{Ce}} = 0.23 \text{ g} * (140 / 434) \approx 0.074 \text{ g},$$

$$W_{\text{SiO}_2} = 12 \text{ g},$$

$$\text{Cu}\% = 3 \text{ g} / (3 \text{ g} + 0.074 \text{ g} + 12 \text{ g}) * 100\% = 20\%,$$

$$\text{Ce}\% = 0.074 \text{ g} / (3 \text{ g} + 0.074 \text{ g} + 12 \text{ g}) * 100\% = 0.5\%,$$

$$\text{SiO}_2\% = 12 \text{ g} / (3 \text{ g} + 0.074 \text{ g} + 12 \text{ g}) * 100\% = 79.5\%.$$

The calculated nominal mass percentage is $\text{Cu}\%=20\%$, $\text{Ce}\%=0.5\%$, $\text{SiO}_2\%=79.5\%$. The nominal mass percentage of each component is approximately equal to the mass percentage calculated based on ICP-MS measurements.

5

Catalyst C'

The preparation steps were the same as Catalyst A except that 0.37 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added to the $\text{Cu}(\text{NO}_3)_2$ solution before the addition of ammonia aqueous solution. Catalyst C' containing a mixture of copper, copper oxides such as Cu_2O , CoO and SiO_2 was obtained.

10

The mass percentage of each component of catalyst C' is calculated as follows:

$$\text{Cu}\% = W_{\text{Cu}} / (W_{\text{Cu}} + W_{\text{Co}} + W_{\text{SiO}_2}) * 100\%$$

$$\text{Co}\% = W_{\text{Co}} / (W_{\text{Cu}} + W_{\text{Co}} + W_{\text{SiO}_2}) * 100\%$$

$$\text{SiO}_2\% = W_{\text{SiO}_2} / (W_{\text{Cu}} + W_{\text{Co}} + W_{\text{SiO}_2}) * 100\%$$

15 Nominal mass percentage:

Molecular Weight of Cu = 64, Molecular Weight of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ = 242,

Molecular Weight of Co = 59, Molecular Weight of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ = 291,

$$W_{\text{Cu}} = 36.3 \text{ g} * (64 / 242) * (157 \text{ mL} / 500 \text{ mL}) \approx 3 \text{ g},$$

$$W_{\text{Co}} = 0.37 \text{ g} * (59 / 291) \approx 0.075 \text{ g},$$

20 $W_{\text{SiO}_2} = 12 \text{ g},$

$$\text{Cu}\% = 3 \text{ g} / (3 \text{ g} + 0.075 \text{ g} + 12 \text{ g}) * 100\% = 20\%,$$

$$\text{Co}\% = 0.075 \text{ g} / (3 \text{ g} + 0.075 \text{ g} + 12 \text{ g}) * 100\% = 0.5\%,$$

$$\text{SiO}_2\% = 12 \text{ g} / (3 \text{ g} + 0.075 \text{ g} + 12 \text{ g}) * 100\% = 79.5\%.$$

The calculated nominal mass percentage is Cu% =20%, Co%=0.5%, SiO₂%=79.5%. The nominal mass percentage of each component is approximately equal to the mass percentage calculated based on ICP-MS measurements.

5 Catalyst D

The preparation steps were the same as Catalyst A, wherein 1.34 g Zn(NO₃)₂·6H₂O was added to the Cu(NO₃)₂ solution before the addition of ammonia aqueous solution. Catalyst D containing a mixture of copper, copper oxides such as Cu₂O, ZnO and SiO₂ was obtained.

10 The mass percentage of each component of catalyst D is calculated as follows:

$$\text{Cu}\% = W_{\text{Cu}} / (W_{\text{Cu}} + W_{\text{Zn}} + W_{\text{SiO}_2}) * 100\%$$

$$\text{Zn}\% = W_{\text{Zn}} / (W_{\text{Cu}} + W_{\text{Zn}} + W_{\text{SiO}_2}) * 100\%$$

$$\text{SiO}_2\% = W_{\text{SiO}_2} / (W_{\text{Cu}} + W_{\text{Zn}} + W_{\text{SiO}_2}) * 100\%$$

Nominal mass percentage:

15 Molecular Weight of Cu = 64, Molecular Weight of Cu(NO₃)₂·3H₂O = 242,
Molecular Weight of Zn = 65, Molecular Weight of Zn(NO₃)₂·6H₂O = 297,

$$W_{\text{Cu}} = 36.3 \text{ g} * (64 / 242) * (157 \text{ mL} / 500 \text{ mL}) \approx 3 \text{ g},$$

$$W_{\text{Zn}} = 1.34 \text{ g} * (65 / 297) \approx 0.29 \text{ g},$$

$$W_{\text{SiO}_2} = 12 \text{ g},$$

20 Cu% = 3 g / (3 g + 0.29 g + 12 g) * 100% = 20%,

$$\text{Zn}\% = 0.29 \text{ g} / (3 \text{ g} + 0.29 \text{ g} + 12 \text{ g}) * 100\% = 2.0\%,$$

$$\text{SiO}_2\% = 12 \text{ g} / (3 \text{ g} + 0.329 \text{ g} + 12 \text{ g}) * 100\% = 78.0\%.$$

The calculated nominal mass percentage is Cu%=20%, Zn%=2.0%, SiO₂%=78.0%. The nominal mass percentage of each component is approximately equal to the weight percentage calculated based on ICP-MS measurements.

Table 1: Summary of Catalyst compositions

Catalyst	Cu (%)	SiO ₂ (%)	N-type metal oxide (%)	P-type metal oxide (%)
A	20	80 (acidic)	--	--
A'	20	80 (non-acidic)	--	--
B	20	79.5 (acidic)	0.5(ZnO)	--
B'	20	79.5 (acidic)	--	0.5(NiO)
C	20	79.5 (acidic)	0.5(CeO ₂)	--
C'	20	79.5 (acidic)	--	0.5(CoO)
D	20	78 (acidic)	2.0(ZnO)	--

5

Example2: Catalytic characteristics of catalysts for ethyl acetate (EA) hydrogenation

The catalytic characteristics of the catalysts A and A' for the hydrogenation of ethyl acetate is listed in Table 2. The reaction was carried out at the conditions of 220°C, 2 MPa, H₂/EA ratio=80:1 and at a feeding speed LHSV_{EA} = 0.36 mL/(g cat· h) (LHSV_{EA} is the liquid hourly space velocity of ethyl acetate); data were collected at 2 hrs after each reaction conducted.

Table 2: Catalytic characteristics of catalysts for hydrogenation of ethyl acetate

Catalyst	Conversion Ratio (%)	Product Selectivity (%)
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	EA	Ethane	Diethyl ether	Aldehyde	Ethanol
A	92.3	0.9	0.2	1.9	96.9
A'	36.7	13.8	10.9	1.3	74.0

It can be seen from Table 2 that catalysts with two types of SiO₂ carrier showed different catalytic characteristics for the hydrogenation of ethyl acetate. The characterization revealed that the SiO₂ support with better activity has the following characteristics: (i) its suspension solution is acidic; (ii) it has better hydrophilic properties. This indicates that the hydrophilic acidic SiO₂ is suitable for the hydrogenation of ethyl acetate.

The catalytic characteristics of catalysts A-D and catalysts B'-C' in hydrogenation of ethyl acetate is listed in Table 3. The reaction was carried out at the conditions of 220°C, 1 MPa, H₂/EA ratio=30:1 and LHSV_{EA} =0.36 mL/(g cat· h) ; data were collected at 2 hrs after each reaction conducted.

Table 3: The catalytic characteristics of the catalysts for hydrogenation of ethyl acetate

Catalyst	Conversion Ratio (%) EA	Product Selectivity (%)			
		Ethane	Diethyl ether	Aldehyde	Ethanol
A	71.6	1.1	0.1	0.6	98.3
B	78.6	1.0	0.1	0.8	98.2
C	73.4	1.0	0.1	0.8	98.2
D	80.0	1.9	0.2	0.6	97.3
B'	57.7	2.6	0.2	0.6	96.5
C'	41.2	2.6	0.1	0.6	96.7

It can be seen from Table 3 that the activity of the catalyst with N-type semi-conductor oxide (Catalysts B, C, D) is better than that of the catalyst without electron donating oxide (Catalyst A), while the activity of the catalyst with P-type semi-conductor oxide (Catalysts B', C') is significantly worse than that of the catalyst without electron donating oxide (Catalyst A), which indicates that N-type semi-conductor oxide is more suitable than P-type semi-conductor oxide to be the promoter of the catalyst for the hydrogenation of ethyl acetate. When the mass percentage of Zn element of ZnO added in the catalyst is 2% (Catalyst D), the EA conversion is up to 80% and the selectivity to the target product (ethanol) is also up to 97.3%, which are both much higher when comparing to the EA conversion ratio and the ethanol selectivity in the Catalysts with NiO (Catalyst B', 57.7% and 96.5%, respectively) and CoO (Catalyst C', 41.2% and 96.7%, respectively).

Example 3: Stability of catalyst for ethyl acetate hydrogenation

The stability of the catalysts was tested for ethanol production by ethyl acetate hydrogenation reaction under the following conditions: firstly, a 370 hrs test was carried out under the conditions of 220°C, 1 MPa, H₂/EA ratio = 50:1 and LHSV_{EA}=1.08 mL/(g cat·h). Then the temperature was decreased to room temperature at the rate of 2°C /min and hydrogen was introduced to protect the catalysts for 130 hrs. After that, the test was reinitialized under the reaction conditions of 220°C, 1 MPa, H₂/EA ratio=10:1 and LHSV_{EA}= 4.98 mL/(g cat·h). The reaction was kept for 300 hrs. The partial results of the stability test are shown in Table 4, wherein samples were taken from the reaction at different time points and the ethyl acetate conversion rate and ethanol product selectivity of the reaction at each such time point were determined. The time points listed in Table 4 are the lapsed time from the beginning of the whole reaction process.

Table 4: Stability Test of Different Catalysts

Time	Catalyst A	Catalyst B	Catalyst C	Catalyst D	Catalyst B'
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(hrs)	Conv. (EA%)	Selec. (EtOH%)	Conv. (EA%)	Selec. (EtOH%)	Conv. (EA%)	Selec. (EtOH%)	Conv. (EA%)	Selec. (EtOH %)	Conv. (EA%)	Selec. (EtOH%)
48	78.4	99.1	80.5	99.2	80.5	99.0	91.2	98.9	67.4	99.0
360	83.0	99.2	85.3	99.3	83.2	99.1	95.7	99.0	69.3	99.0
390	77.7	99.2	81.2	99.2	79.0	99.1	93.7	99.0	65.5	99.1
484	73.7	99.2	78.1	99.3	76.3	99.1	94.5	99.1	61.9	99.0
533	25.7	99.3	30.0	99.4	27.4	99.2	57.4	99.2	19.6	99.1
795	19.8	99.1	24.0	99.3	21.9	99.2	60.4	99.2	15.9	98.9

It can be seen from Table 4 that ZnO or CeO₂ can significantly improve the activity and stability of the catalyst while NiO significantly reduced the activity of the catalyst. The catalyst D with ZnO (Zn%=2%) showed 95.7% conversion of ethyl acetate and 99% selectivity to ethanol after a 360 hrs reaction.

5

Example 4: Catalytic characteristics of catalysts for ethyl acetate hydrogenation under different reaction condition

Table 5 shows the catalytic characteristics of the catalyst A for the hydrogenation of ethyl acetate at 2 hrs after each reaction was conducted under different conditions.

10 Table 5: The catalytic characteristics of the copper-based catalyst under different conditions

Temp. (°C)	Pressure (MPa)	H ₂ /EA (mol/mol)	Conversion Ratio (%)	Selectivity (%)			
				Ethane	Diethyl ether	Aldehyde	Ethanol
200	2.0	80:1	28.44	0.27	0.35	2.20	97.18

220	0.1	80:1	46.40	1.35	0.17	3.39	95.26
220	0.5	80:1	87.33	1.07	0.10	1.83	97.00
220	1.0	80:1	96.20	1.20	0.05	1.24	97.51
220	2.0	10:1	45.23	1.70	0.25	0.83	97.22
220	2.0	30:1	89.30	1.03	0.08	0.63	98.26
220	2.0	50:1	97.44	1.11	0.04	0.58	98.28
220	2.0	80:1	98.96	1.37	0.03	1.36	97.24
240	2.0	80:1	98.61	3.41	0.12	1.85	94.63

Loading weight of catalyst A: 1 g, material LHSV_{EA}: 0.36 mL/(g cat·h)

Table 5 shows that, the reaction condition obviously affect the catalytic characteristics of Catalyst A. The increase of reaction temperature promoted EA conversion, with no apparent effects on ethanol selectivity. At 220°C, ethanol selectivity reached up to above 98%. When increasing temperature beyond that, the change in EA conversion was not apparent but the selectivity slightly decreased. High reaction pressure was beneficial to EA conversion. EA conversion increased from 46% to 87% as the pressure rose from 0.1 MPa to 0.5 MPa. A gradual increase of EA conversion rate to 98% was observed when the pressure was raised from 0.5 MPa to 2.0 MPa, while the ethanol selectivity was not apparently affected. The increase of H₂/EA ratio lifted the EA conversion but the effect of H₂/EA ratio on ethanol selectivity was not apparent.

Example 5: Catalytic characteristics of catalysts for methyl acetate (MA) hydrogenation

The catalytic characteristics of the catalysts A/B/B'/D for the hydrogenation of methyl acetate is listed in Table 6. The reaction was carried out at conditions of 220°C, 5

MPa, H_2/MA ratio=10:1 and $LHSV_{MA}=2.1$ mL/(g cat· h); data were collected at 2 hrs after each reaction conducted.

Table 6: The catalytic characteristics of the catalysts for hydrogenation of MA

Catalyst	Conversion Ratio (%) MA	Selectivity (%)			
		Ethyl acetate	Methanol	Others	Ethanol
A	94.86	4.36	31.40	2.67	61.57
B	97.03	1.36	31.46	2.47	64.71
D	98.20	1.45	30.88	3.98	63.69
B'	74.85	19.62	29.47	6.87	44.05

Note: theoretical value of ethanol selectivity in MA hydrogenation is 66.67%.

- 5 It can be seen from Table 6 that the conversion of MA and the selectivity of ethanol with N-type semi-conductor oxide is better than that of the catalyst without electron donating oxide, while the conversion of MA and the selectivity of ethanol with P-type semi-conductor oxide is significantly worse than that of the catalyst without electron donating oxide, which indicates that N-type semi-conductor oxide is more suitable than P-type semi-conductor oxide to be the promoter of the catalyst for the hydrogenation of methyl acetate.
- 10

Equivalents

- Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents of the specific embodiments of the invention described herein. Such equivalents are intended to be encompassed by the appended claims.
- 15

Entire contents of all non-patent documents, patent applications and patents cited throughout this application are incorporated by reference herein in their entirety.

As used herein, the singular forms “a”, “an” and “the” are intended to include the plural forms as well, unless the context clearly indicates otherwise. It will be further understood that the terms “comprises”, “comprising”, “includes” and/or “including,” if used herein, specify the presence of stated features, integers, steps, operations, 5 elements and/or components, but do not preclude the presence or addition of one or more other features, integers, steps, operations, elements, components and/or groups thereof.

The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise 10 specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as “40 mm” is intended to mean “about 40 mm.”

Every document cited herein, including any cross referenced or related patent or application is hereby incorporated herein by reference in its entirety unless expressly 15 excluded or otherwise limited. The citation of any document is not an admission that it is prior art with respect to any invention disclosed or claimed herein or that it alone, or in any combination with any other reference or references, teaches, suggests or discloses any such invention. Further, to the extent that any meaning or definition of a term in this document conflicts with any meaning or definition of the same term in a 20 document incorporated by reference, the meaning or definition assigned to that term in this document shall govern.

While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the 25 invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope and spirit of this invention.

CLAIMS

We claim:

1. A catalyst for hydrogenation reaction, which comprises metallic copper (Cu) or copper oxide or a mixture thereof, silica and electron donating oxide, wherein the mass percentage of copper (Cu) element in the catalyst is 10-70%, the mass percentage of silica in the catalyst is 25-89.9%, and the mass percentage of the metal element of the electron donating oxide in the catalyst is 0.1%-5%.
2. The catalyst of claim 1, wherein the hydrogenation reaction is an ethyl acetate hydrogenation reaction or a methyl acetate hydrogenation reaction.
3. The catalyst of claim 1, wherein the silica is a hydrophilic silica having less than 50%, or less than 40%, or less than 30% of its surface hydroxyl group substituted by hydrophobic groups.
4. The catalyst of claim 1, wherein the silica is an acidic silica, or wherein the pH value of a 4% aqueous solution of the silica is lower than 6.5, or is between 2.0-6.0, or between 3.0-5.0.
5. The catalyst of claim 1, wherein the electron donating oxide is an N-type semi-conductive metal oxide.
6. The catalyst of claim 5, wherein the N-type semi-conductive metal oxide is ZnO, CdO, TiO₂, CeO₂ or a mixture thereof.
7. The catalyst of claim 1, wherein the mass percentage of the metal element of the electron donating oxide in the catalyst is 0.1-5%, or 0.2-3%, or 0.2-1.5%, or 0.5-1%, or 0.5-2%, or 1.5-3%, or 1.5-2.5%.
8. A method for preparing a catalyst of any one of claims 1-7, which comprises:
 - a) mixing Cu containing salt, metal salt and aqueous ammonia solution, wherein the metal salt can be made into the electron donating oxide;
 - b) adding silica into the solution of (a) ;
 - c) removing ammonia;
 - d) calcining and grinding the resulting product from step c).

9. Use of the catalyst of any of claims 1-7 in a hydrogenation reaction.
10. The use of claim 9, wherein the hydrogenation reaction is an acetic ester hydrogenation reaction.
11. The use of claim 10, wherein the acetic ester hydrogenation reaction is conducted at a temperature of 200-240 °C, or 210-230 °C.
12. The use of claim 10, wherein the acetic ester hydrogenation reaction is conducted at a pressure of 0.5-7 MPa, or 0.5-2 MPa, or 1-4 MPa.
13. The use of claim 10, wherein the acetic ester hydrogenation reaction is conducted at the mole ratio between hydrogen and acetic ester of 10:1-100:1, or 5:1-100:1, or 30:1-80:1, or 30:1-50:1, or 50:1-80 :1.
14. The use of claim 10, wherein the conversion rate of the acetic ester hydrogenation reaction is no less than 70%, or no less than 75%, or no less than 80%, or no less than 85%, or no less than 90%.
15. The use of claim 10, wherein the product selectivity of the acetic ester hydrogenation reaction is no less than 90%, or no less than 95%, or no less than 98%.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2014/083009

A. CLASSIFICATION OF SUBJECT MATTER

B01J 23/83(2006.01)i

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)

B01J23/-

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)

CNPAT,CNKI, WPI, EPODOC,CA; dalian institute of chemical physics, ma xiaogang, ge qingjie, catalyst, hydrogenation, copper, silica, electron donating oxide, zinc

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 102962071 A (JIANGSU SOPO GROUP CO. LTD. ET AL.) 13 March 2013 (2013-03-13) description, paragraphs [0006]-[0010], [0023]-[0025], [0057]	1-15
E	CN 104174407 A (CAS DALIAN CHEM. & PHYSICAL INST.) 03 December 2014 (2014-12-03) description, paragraphs [0011]-[0026], [0038]-[00846]	1-9
A	CN 103333059 A (BEIJING DONGFANG HONGSHENG NEW ENERGY ET AL.) 02 October 2013 (2013-10-02) description, paragraphs [0015]-[0027]	1-15
A	US 2010197486 A1 (CELANESE INT. CORP.) 05 August 2010 (2010-08-05) description, paragraphs [0009]-[0017]	1-15
A	US 2005051463 A1 (HEVRON U.S.A. INC.) 10 March 2005 (2005-03-10) description, paragraphs [0007]-[0011]	1-15

☐ Further documents are listed in the continuation of Box C.☒ 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

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“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

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Date of the actual completion of the international search

01 April 2015

Date of mailing of the international search report

28 April 2015

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2014/083009

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
CN	102962071	A	13 March 2013	None			
CN	104174407	A	03 December 2014	None			
CN	103333059	A	02 October 2013	EP	2810930	A1	10 December 2014
				CN	103333059	B	17 September 2014
				US	2014364653	A1	11 December 2014
US	2010197486	A1	05 August 2010	None			
US	2005051463	A1	10 March 2005	None			