METHOD OF PREPARING A COPPER-BASED CATALYST FOR CARBON DIOXIDE HYDROGENATION

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority of Singapore application no. 10202400777S filed on 19 March 2024, the contents of it being hereby incorporated by reference in its entirety for all purposes.

TECHNICAL FIELD

[0002] The present disclosure generally relates to a method of preparing a copper-based catalyst. In particular, the present disclosure relates to a method of preparing a copper-based catalyst comprising ternary metal oxides for carbon dioxide hydrogenation.

BACKGROUND

[0003] Methanol production from carbon dioxide has gained significant attention due to its potential to reduce carbon dioxide emissions while providing a sustainable synthesis route for methanol in the chemical industry. Currently, conventional catalysts such as $Cu/ZnO/Al_2O_3$ and $Cu/ZnO/ZrO_2$ dominate this field. However, these established catalysts face limitations in catalytic activity, selectivity, and stability, largely attributed to the concurrent reverse water-gas shift (RWGS) reaction and active phase sintering. Overcoming these challenges requires a fresh perspective, one that involves crafting Cu-Zn-Zr oxide catalysts.

[0004] The use of Cu-Zn-Zr oxide catalysts in carbon dioxide hydrogenation is known and despite the extensive coverage of these catalysts in the literature, achieving highly dispersed copper with a uniform nanoparticle size and abundant Cu-Zn or Zn-Zr interfaces remains a challenge. Moreover, existing reports on core-shell structured catalysts often focus on structure control by utilizing low copper loading (less than 15 wt.%) or applying precursors such as metal-organic frameworks (MOFs). There is a huge gap in the application of these catalysts due to low efficiency and high costs.

[0005] Another significant challenge is maintaining the original metal interfaces of the catalyst, as the Cu-Zn or Zn-Zr interfaces are crucial for the activation of carbon dioxide and the selectivity of methanol.

[0006] It is therefore desirable to provide a method for preparing a catalyst for the carbon dioxide hydrogenation that seeks to address at least one of the problems described hereinabove, or at least to provide an alternative solution.

SUMMARY

[0007] In accordance with a first aspect of the present disclosure, a method of preparing a copper-based catalyst is provided. The method comprises mixing a colloidal solution containing a hydroxycarbonate precursor comprising copper (Cu), zinc (Zn) and zirconium (Zr) cations, with a tetraethyl orthosilicate (TEOS) and ethanol mixed solution to obtain a solution; adjusting pH of the solution; isolating a solid phase from the solution; drying the solid phase; and calcining the solid phase to obtain a silicon dioxide (SiO_2)-encapsulated copper-based catalyst consisting of Cu-Zn-Zr ternary metal oxide nanoparticles encapsulated in silicon dioxide (SiO_2), represented by Cu-Zn-ZrO_x@SiO_2.

[0008] In some embodiments, the method further comprises preparing the hydroxycarbonate precursor. The step of preparing the hydroxycarbonate precursor comprises mixing a mixed salt solution containing metal cations consisting of copper (II) ions, zinc (II) ions and zirconium (IV) ions with a precipitating agent under room temperature to form a precipitate; aging the precipitate for a duration; separating the precipitate to obtain a slurry; and drying the slurry to obtain the hydroxycarbonate precursor comprising copper (Cu), zinc (Zn) and zirconium (Zr) cations.

[0009] In accordance with a second aspect of the present disclosure, a copper-based catalyst is provided. The copper-based catalyst comprises Cu-Zn-Zr ternary metal oxide nanoparticles encapsulated in silicon dioxide (SiO_2), forming a uniform core-shell nanostructure, represented by Cu-Zn-ZrO_x@SiO_2.

[0010] In some embodiments, the copper-based catalyst is configured for use in carbon dioxide hydrogenation to convert carbon dioxide into methanol.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] Various embodiments of the present disclosure are described hereinbelow in the detailed description with reference to the following drawings:

FIG. 1A shows a TEM image of a freshly prepared Cu-Zn-Zr ternary metal oxide synthesized in accordance with an embodiment of the method of the present disclosure.

FIG. 1B shows a TEM image of a freshly prepared SiO_2-encapsulated Cu-Zn-Zr ternary metal oxides synthesized in accordance with an embodiment of the method of the present disclosure.

FIG. 2 shows an SEM image of the freshly prepared SiO_2-encapsulated Cu-Zn-Zr ternary metal oxides of FIG. 1B.

FIG. 3 shows the XRD patterns of the synthesized Cu-Zn-ZnO_x catalysts with and without SiO_2 shell. (a) shows the pattern of Cu-Zn-ZrO_x (CZZ) prepared using the co-precipitate method in accordance with an embodiment of the present disclosure, (b) shows the pattern of Cu-Zn-ZrO_x@SiO_2 (CZZ@30 SiO_2) core shell catalyst prepared via a two-step method without surfactant, and (c) shows the pattern of Cu-Zn-ZrO_x@SiO_2-R (CZZ@30 SiO_2-R) obtained using Stöber method with cetyltrimethylammonium bromide (CTAB) as the surfactant.

FIG. 4 shows the XRD patterns of the Cu-Zn-ZnO_x catalysts with and without SiO_2 shell at different calcination temperature. (a) shows the pattern of Cu-Zn-ZrO_x calcined at 300°C, (b) shows the pattern of Cu-Zn-ZrO_x@SiO_2 core shell catalyst calcined at 400°C, and (c) shows the pattern of Cu-Zn-ZrO_x calcined at 400°C.

FIG. 5 is a graph showing the catalytic hydrogenation of carbon dioxide over Cu-Zn-ZrO_x oxide catalyst.

DESCRIPTION

[0012] The following description sets forth exemplary methods, parameters, and the like. The embodiments are described in sufficient detail to enable those skilled in the art to practise the invention. Other embodiments may be utilized, and structural and logical changes may be made without departing from the scope of the invention. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

[0013] Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments. Features that are described in the context of an embodiment may correspondingly be applicable to the other embodiments, even if not explicitly described in these other embodiments. Furthermore, additions and/or combinations and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

[0014] In the context of various embodiments, the articles "a", "an" and "the" as used with regard to a feature or element include a reference to one or more of the features or elements.

[0015] In the context of various embodiments, the term "about" or "approximately" as applied to a numeric value encompasses the exact value and a reasonable variance, e.g. within 10% of the specified value.

[0016] As used herein, the term "and/or" includes any and all combinations of one or more of the associated listed items.

[0017] By "comprising" it is meant including, but not limited to, whatever follows the word "comprising". Thus, use of the term "comprising" indicates that the listed elements are required or mandatory, but that other elements are optional and may or may not be present.

[0018] By "consisting of" is meant including, and limited to, whatever follows the phrase "consisting of". Thus, the phrase "consisting of" indicates that the listed elements are required or mandatory, and that no other elements may be present.

[0019] The present disclosure relates to a method of preparing a copper-based catalyst comprising ternary metal oxides. The method involves a two-step process comprising preparing a hydroxycarbonate precursor comprising ternary metal oxides using a modified co-precipitation method, redispersing the hydroxycarbonate precursor and applying a silicon dioxide (SiO_2) layer using a modified sol-gel method to obtain a silicon dioxide (SiO_2)-encapsulated ternary metal oxide catalyst. The SiO_2-encapsulated ternary metal oxide catalyst exhibits exceptional efficacy as a catalyst in carbon dioxide hydrogenation reactions.

[0020] According to a first aspect, the method comprises mixing a colloidal solution containing a hydroxycarbonate precursor comprising copper (Cu), zinc (Zn) and zirconium (Zr) cations, with a tetraethyl orthosilicate (TEOS) and ethanol mixed solution to obtain a solution; adjusting pH of the solution; isolating a solid phase from the solution; drying the solid phase; and calcining the solid phase to obtain a silicon dioxide (SiO_2)-encapsulated copper-based catalyst consisting of Cu-Zn-Zr ternary metal oxide nanoparticles encapsulated in silicon dioxide (SiO_2), represented by Cu-Zn-ZrO_x@SiO_2.

[0021] A silicon dioxide (SiO_2) layer is formed via the hydrolysis of TEOS when the TEOS and the ethanol mixed solution are mixed with the colloidal solution containing the hydroxycarbonate precursor, and this layer encapsulates the hydroxycarbonate precursor that forms the core material of the SiO_2-encapsulated copper-based catalyst.

[0022] The hydroxycarbonate precursor can be mixed with the TEOS and ethanol mixed solution using any suitable method. In some embodiments, the TEOS and ethanol mixed solution is rapidly added to the colloidal solution of hydroxycarbonate precursor while stirring at room temperature. The stirring speed may range from 400 to 600 rpm; however, one skilled in the art will appreciate that other stirring speeds may be employed to ensure complete mixing and reaction. In some embodiments, the stirring speed may be set to 400 rpm, 500 rpm or 600 rpm.

[0023] In various embodiments, the pH of the solution is adjusted to 12. Any suitable pH adjustment agent may be used, including but not limited to sodium hydroxide, potassium hydroxide, calcium hydroxide or ammonium hydroxide.

[0024] After adjusting the pH of the solution, the solution is continuously stirred at room temperature to ensure complete reaction and encapsulation of the hydroxycarbonate precursor by silicon dioxide. The solution is then subjected to a separation procedure to isolate a solid phase from the solution. Any suitable method can be used to isolate the solid phase. Such methods include, but are not limited to, filtration, centrifugation, decantation or evaporation. In some embodiments, the solid phase is isolated by centrifugation.

[0025] The solid phase isolated from the solution is then dried before calcination. Any suitable method can be used for drying the solid phase, including, but not limited to, oven drying, vacuum drying, or a combination thereof. In some embodiments, the solid phase is oven dried at an elevated temperature. The elevated temperature may range from 60°C to 80°C, and in some embodiments, at 60°C. The drying process may take place for a few hours to overnight, depending on the moisture content of the solid phase upon separation from the solution.

[0026] The dried solid phase then undergoes calcination. In some embodiments, this step involves calcining the solid phase at a temperature ranging from 300°C to 400°C, in some embodiments, at 400°C for about 3 hours, and at temperature ramp rate of 5°C min^{-1}. The test results reported in the Example 3 show that the crystalline size of the Cu-Zn-ZrO_x@SiO_2 catalyst remained unchanged even when calcined at 400°C. This indicates that the SiO_2 shell effectively preserves metal dispersion, preventing excessive crystalline growth during the calcination and reaction processes. This preservation benefits and enhances catalyst performance in the carbon dioxide hydrogenation process.

[0027] Prior to mixing the hydroxycarbonate precursor with the TEOS and ethanol mixed solution, the hydroxycarbonate precursor is redispersed in a solvent to form the colloidal solution. The solvent can be deionized water or any other suitable solvent. When the colloidal

solution of the hydroxycarbonate precursor comes into contact with the TEOS and ethanol mixed solution, which serves as the source of silicon, the hydroxycarbonate precursor forms the core material that is encapsulated by silicon dioxide.

[0028] In various embodiments, the TEOS and ethanol present in the mixed solution are in a molar ratio of 1:52.

[0029] The method of the present disclosure may further include preparing the hydroxycarbonate precursor via the modified co-precipitation method at room temperature, with a constant pH. The hydroxycarbonate precursor is prepared by mixing a mixed salt solution containing metal cations consisting of copper (II) ions, zinc (II) ions and zirconium (IV) ions with a precipitating agent under room temperature to form a precipitate. This is followed by aging the precipitate for a duration; separating the precipitate to obtain a slurry; and drying the slurry to obtain the hydroxycarbonate precursor comprising copper (Cu), zinc (Zn) and zirconium (Zr) cations. The hydroxycarbonate precursor obtained by the method is a Cu-Zn-Zr hydroxycarbonate precursor, represented by [(Cu-Zn-Zr)CO_3 (Cu-Zn-Zr)$(OH)_2$].

[0030] In some embodiments, the mixed salt solution comprises copper (II) nitrate trihydrate ($Cu(NO_3)_2$ $2.5H_2O$), zinc nitrate hexahydrate ($Zn(NO_3)_2$ $6H_2O$), and zirconium nitrate hexahydrate ($ZrO(NO_3)_2$ $6H_2O$). The concentration of the metallic cations in the mixed salt solution can be controlled by varying the amounts of the compounds to be added to the deionized water. In some embodiments, the concentration of the metallic cations is maintained at 0.2M.

[0031] In some embodiments, sodium carbonate (Na_2CO_3) is added as the precipitating agent. One skilled in the art will appreciate that other precipitating agents may be used without departing from the scope of the present disclosure. In some embodiments, the concentration of the precipitating agent is maintained at the same concentration as the metallic cations. This is to ensure complete precipitation of all the metallic cations. In some embodiments, the concentration of the precipitating agent is maintained at 0.2 M.

[0032] In some embodiments, the precipitate is aged with stirring. The aging may take place over a duration of 3 to 5 hours, in some embodiments, about 3 hours.

[0033] In some embodiments, the step of drying the slurry includes drying the slurry at an elevated temperature. The elevated temperature may range from 60°C to 80°C, and in some embodiments, at 60°C. Any suitable method can be used for drying the slurry including, but not limited to, oven drying, vacuum drying, or a combination thereof. The drying may take place for a few hours to overnight.

[0034] According to a second aspect of the present disclosure, a copper-based catalyst is provided. The copper-based catalyst comprises Cu-Zn-Zr ternary metal oxide nanoparticles encapsulated in silicon dioxide (SiO_2), forming a uniform core-shell nanostructure, represented by Cu-Zn-ZrO_x@SiO_2.

[0035] In some embodiments, the core-shell nanostructure has an average diameter ranging from 40 to 60 nm.

[0036] In various embodiments, the Cu-Zn-Zr ternary metal oxide is in a molar ratio of 1:x:1, where x represents different values of the molar ratio, ranging from 0 to 4.

[0037] The method and the copper-based catalyst of the present disclosure offers several advantages. By carefully controlling the catalyst's composition and structure through modified co-precipitation techniques, the method achieves a highly homogeneous dispersion of Cu-Zn-Zr ternary metal oxides, at approximately 4 nm in size. This high degree of dispersion results in an abundance of Cu/Zn/Zr interfaces, which greatly enhance catalytic activity.

[0038] Furthermore, the implementation of the modified sol-gel technique creates a unique core-shell structure, which not only improves copper (Cu) dispersion but also effectively inhibits crystalline growth during calcination and reaction. This intricate design leads to a substantial increase in metal surface area, particularly at the active copper (Cu) and Cu-Zn-Zr interfaces, which is crucial for optimizing selectivity in the catalytic process.

[0039] The method of the present disclosure is also less complex. As detailed in the Examples section, the method does not involve the use of harmful or toxic chemicals, and the method effectively preserves all the Cu-Zn/Zr and Zn-Zr interfaces after coating with the silicon dioxide (SiO_2) shell. This preservation of interfaces is expected to enhance the catalyst's performance.

[0040] The method is scalable. The scalability of preparing the copper-based catalyst and the synthesizing the Cu-Zn-Zr ternary metal oxides is notable, allowing for the preparation of larger batches of catalyst, making it highly suitable for industrial applications. Results from the Examples demonstrate that the highly efficient Cu-Zn-Zr metal oxides serve as the core material, integrated within a core-shell structure, and this configuration provides distinctive catalytic sites while mitigating active phase sintering during the carbon dioxide hydrogenation to methanol process. The strategic creation and preservation of pivotal Cu-Zn and Zn-Zr interfaces play a vital role in carbon dioxide activation and subsequently influence the selectivity of methanol production. This design also enhances the even dispersion of metal constituents within the catalyst, ensuring heightened stability throughout the entire reaction process.

[0041] By adopting the core-shell structure, the yield of methanol is significantly boosted. This unique structure facilitates carbon dioxide activation, resulting in higher reaction rates and improved overall efficiency. This aspect makes the method of the present disclosure economically viable and environmentally friendly route for sustainable methanol synthesis.

[0042] Overall, the use of the catalyst can distinctly elevate both the performance and stability of methanol production from carbon dioxide. Compared to existing technologies, the distinct synthesis and core-shell structure of the SiO_2-encapsulated copper-based catalyst contribute to superior performance, positioning it as an exceptional choice for carbon dioxide catalysis and paving the way for advancements in sustainable energy solutions.

[0043] To facilitate a better understanding of the present disclosure, the following examples of specific embodiments are given. In no way should the following examples be read to limit or define the entire scope of the disclosure. One skilled in the art will recognize that the examples set out below are not an exhaustive list of the embodiments of this disclosure.

EXAMPLES

Example 1

[0044] Synthesis of Cu-Zn-Zr Hydroxycarbonate Precursor

[0045] Cu-Zn-Zr hydroxycarbonate precursor was prepared using a modified co-precipitation method at room temperature, with a constant pH.

[0046] Firstly, $Cu(NO_3)_2$ $2.5H_2O$, $Zn(NO_3)_2$ $6H_2O$, and $ZrO(NO_3)_2$ $6H_2O$ salts, where the molar ratio of Cu^{2+}: Zn^{2+}: Zr^{4+} is 1:x:1 (with x ranging between 0 to 4), were dissolved in 200 mL of deionized water to control the concentration of metallic cations at 0.2 M. The resulting solution was stirred for 30 minutes at room temperature to form a homogenous mixed salt solution. Simultaneously, sodium carbonate (Na_2CO_3) was dissolved in deionized water as the precipitating agent, and its concentration was maintained at 0.2 M. The same carbonate and metal molar ratio were chosen to ensure complete precipitation of all the metallic cations. Both solutions were then added dropwise into 200 mL of deionized water (mother liquor) with vigorous stirring, to adjust the pH value to around 6.1 (6.1 ± 0.2) at room temperature. After the reaction, the precipitate was aged with stirring for 3 hours, followed by centrifugation and several washes with deionized water to ensure complete removal of sodium ions (Na^+). The obtained slurry was dried at 60°C overnight, resulting in the Cu-Zn-Zr hydroxycarbonate precursor, denoted as (Cu-Zn-Zr)CO_3 (Cu-Zn-Zr)$(OH)_2$.

Example 2

[0047] Synthesis of SiO_2-encapsulated Cu-Zn-Zr ternary metal oxides (Cu-Zn-ZrO_x@SiO_2)

[0048] The Cu-Zn-ZrO_x@SiO_2 was obtained via a one-pot hydrolysis method.

[0049] Firstly, the dried Cu-Zn-Zr hydroxycarbonate precursor obtained in Example 1 was redissolved in 100 mL of deionized water and homogenized for 20 minutes to achieve a highly dispersed solution. Following this, an as-prepared TEOS and ethanol mixed solution was rapidly added to the precursor solution with stirring at 500 rpm, and a 0.1 M sodium hydroxide (NaOH) solution was slowly dropped (0.5 mL min^{-1}) into the mixture to adjust the pH to 12. The solution was continuously stirred at 500 rpm for 12 hours at room temperature. Finally, the raw material was collected by centrifugation and washed three times with water. The product was then dried at 60°C overnight. Subsequently, the obtained solid was calcined at 400°C for 3 hours, at a temperature ramp of 5°C min^{-1}.

Example 3

[0050] Catalyst Characterization

[0051] The transmission electron microscopy (TEM) images presented in FIG. **1A** and **1B** reveal the morphology of the freshly synthesized Cu-Zn-Zr ternary metal oxides and the SiO_2-encapsulated Cu-Zn-Zr ternary metal oxide (Cu-Zn-ZrO_X@SiO_2) nanoparticles. Significantly, the Cu-Zn-ZrO_x nanoparticles displayed a remarkably even dispersion, with copper (Cu) nanoparticles measuring 4 nm in size, and a wealth of interfaces was evident as per the TEM analysis. The image on the right, i.e. FIG. **1B** clearly indicates that each Cu-Zn-ZrO_x nanoparticle was well encased within the a silicon dioxide (SiO_2) shell, forming a uniform core-shell nanostructure. Moreover, the Cu-Zn-ZrO_x nanoparticles were separated by a thinner silicon dioxide wall, further enhancing the distinct core-shell configuration. The size distribution analysis of the encapsulated Cu-Zn-ZrO_x nanoparticles demonstrates a relatively narrow range, with an average size of less than 4 nm. These results illustrate the significant effect of the SiO_2 shell in limiting the growth of Cu-Zn-ZrO_x particles during the calcination process. This aspect is particularly crucial in obtaining highly dispersed metallic Cu after reduction. The protective SiO_2 shell not only maintains the uniformity of the core-shell structure but also prevents the agglomeration and growth of the Cu-Zn-ZrO_x nanoparticles during the

high-temperature reduction process. These factors are crucial for optimizing the catalytic performance of the material.

[0052] The morphologies of the freshly synthesized Cu-Zn-ZrO_x@SiO_2 nanoparticles were characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

[0053] FIG. **2** is a SEM image of the freshly synthesized Cu-Zn-ZrO_x@SiO_2 nanoparticles. The SEM image reveals that the nanoparticles possess a highly dispersed spherical shape with an average diameter of 50 nm. Importantly, there was no evidence of aggregation of the Cu-Zn-Zr oxides or secondary nucleation of SiO_2 nanoparticles observed in the SEM image. Moreover, the SiO_2 layer was found to be homogeneously covering the Cu-Zn-ZrO_x nanoparticles, indicating a uniform and well-defined coating. These results demonstrate the successful synthesis and effective encapsulation of the Cu-Zn-ZrO_x nanoparticles within the SiO_2 layer, leading to well-defined and isolated spherical structures.

[0054] The XRD patterns displayed in FIG. **3** offer valuable insights into the crystal structures and phases of the prepared Cu-Zn-ZrO_x@SiO_2 core-shell catalyst. For comparison, the XRD patterns of a Cu-Zn-ZrO_x without SiO_2 shell (CZZ) catalyst, and a Cu-Zn-ZrO_x@SiO_2-R (CZZ@30 SiO_2-R) catalyst prepared via the Stöber method (as detailed in the reference, *Advanced Function Materials*, 2021, 31, 2102896-2102912), were also included. Interestingly, it is evident from the XRD patterns that the structure of the Cu-Zn-ZrO_x@SiO_2 core-shell catalyst remains almost unchanged after the coating with the SiO_2 shell. This demonstrates that the original Cu-Zn and Zn-Zr phases were fully preserved in the core-shell catalyst, indicating the successful formation of the core-shell nanostructure. When compared with the counterparts prepared via the Stöber method, there were nearly no diffraction peaks corresponding to ZnO and ZrO_2 observed in the XRD pattern of the Cu-Zn-ZrO_x@SiO_2 core-shell catalyst. This observation highlights the unique advantages of the innovative two-step method employed in the present disclosure. Overall, the XRD analysis confirms that the core-

shell catalyst retains the original crystal structures of Cu-Zn and Zn-Zr, indicating that the SiO_2 shell effectively encapsulates the Cu-Zn-ZrO_x nanoparticles while preserving their core properties. Furthermore, the absence of ZrO_2 peaks demonstrates the superiority of the two-step method over the Stöber method in achieving improved catalyst characteristics for potential catalytic applications.

[0055] FIG. **4** presents the XRD patterns of the Cu-Zn-ZnO_x catalysts calcined under different temperatures, along with the Cu-Zn-ZrO_x@SiO_2 core-shell catalyst calcined at 400°C. Increasing calcination temperature (300°C to 400°C) narrows diffraction peaks of Cu, Zn, and Zr oxides, indicating larger crystalline size in Cu-Zn-ZnO_x catalysts. In contrast, Cu-Zn-ZrO_x@SiO_2 core-shell catalyst maintains unchanged crystalline size after 400°C calcination, unlike Cu-Zn-ZnO_x catalyst. This shows that SiO_2 shell effectively preserves metal dispersion and prevents excessive metal particle growth.

Example 4

[0056] Carbon Dioxide Hydrogenation Catalytic Testing

[0057] The catalytic behaviour of Cu-Zn-ZrO_x was tested in carbon dioxide hydrogenation under 250°C, GHSV of 20,000 mL $gcat^{-1}$ h^{-1}, and a pressure of 9.9 MPa in a fixed bed reactor. The catalyst (400 mg, 100 to 200 μm) was mixed with silicon carbide (SiC) particles and placed in the reactor between quartz wool layers. Subsequently, the hydrogenation reaction was executed at 250°C using a pre-mixed H_2/CO_2 gas (in a 3:1 ratio) at a pressure of 9.9 MPa. As illustrated in FIG. **5**, the Cu-Zn-ZrO_x catalysts achieved a space time yield (STY) surpassing 1.2 g $gcat^{-1}h^{-1}$, maintaining this level for over 1000 hours, showcasing an impressive combination of ultra-high activity and stability.

[0058] Additionally, Cu-Zn-ZrO_x@SiO_2 was evaluated in carbon dioxide hydrogenation under 280°C, GHSV of 15,000 mL $gcat^{-1}$ h^{-1}, and a pressure of 6.5 MPa in a fixed bed reactor. The catalyst (400 mg, 100 to 200 μm) was mixed with SiC particles and placed in the reactor

between quartz wool layers. Before the reaction, the catalyst was in-situ reduced at 300°C under a flow of hydrogen for 2 hours. Then, the hydrogenation reaction was conducted at 280°C with a premixed H_2/CO_2 gas (3:1 ratio) at 6.5 MPa.

[0059] The Cu-Zn-ZrOx@SiO_2 catalyst demonstrated excellent performance in carbon dioxide hydrogenation. It achieved a carbon dioxide conversion of 25.3% with 60% methanol selectivity and an impressive Methanol STY of 0.6 g g_{cat}^{-1} h^{-1} (Table 1). Notably, the Methanol STY was three times higher than similar state-of-the-art catalysts, which can be attributed to the catalyst's abundant Cu-Zn/Zn-Zr interfaces and highly dispersed metallic Cu after reduction.

[0060] **Table 1:** Comparison of the core-shell catalyst of the present disclosure with other state-of-the-art core-shell catalysts

Catalyst	**Temp. (°C)**	**Pressure (bar)**	**GHSV (10^3 h^{-1})**	**X_{CO2} (%)**	**S_{MeOH} (%)**	**STY_{MeOH} (g g_{cat}^{-1} h^{-1})**	**Ref.**
Cu-Zn-ZrO_x (CZZ)	250	100	20	32.3	73.7	1.31	present work
MCZZ (16)	220	9.7	10	9.7	91.4	0.5	1
CuO-ZnO-ZrO_2	250	60	25	19.6	50	0.72	2
(Cu-Zn-ZrO_x @SiO_2)	280	64	15	25.3	59.9	0.60	present work
Cu/ZnO@m-SiO_2	280	30	20	9.8	78.1	0.44	3
Cu/ZnO@UiO-bpy	250	40	18	3.3	100	0.026	4
CuIn@SiO_2	280	30	7.5	12.5	78.2	0.22	5
Cu-SiO_2p	225	50	6	3.5	77	0.12	6
Cu@ZrO_2/MOF	260	30	15.6	12	40	0.16	7

[0061] Although embodiments of the invention have been shown and described, the invention is not limited to the described embodiments. Instead, it would be appreciated by those skilled in the art that various modifications and variations can be made to the embodiments of the invention without departing from the scope of the invention, the scoop of which is set forth in the following claims.

Claims

1. A method of preparing a copper-based catalyst, the method comprising:

mixing a colloidal solution containing a hydroxycarbonate precursor comprising copper (Cu), zinc (Zn) and zirconium (Zr) cations, with a tetraethyl orthosilicate (TEOS) and ethanol mixed solution to obtain a solution;

adjusting pH of the solution;

isolating a solid phase from the solution;

drying the solid phase; and

calcining the solid phase to obtain a silicon dioxide (SiO_2)-encapsulated copper-based catalyst consisting of Cu-Zn-Zr ternary metal oxide nanoparticles encapsulated in silicon dioxide (SiO_2), represented by Cu-Zn-ZrO_x@SiO_2.

2. The method of claim 1, wherein the step of calcining includes calcining the precipitate at 400°C for about 3 hours, with a temperature ramp rate of 5°C min^{-1}.

3. The method of claim 1, wherein the pH of the solution is adjusted to 12.

4. The method of claim 1, further comprising:

preparing the hydroxycarbonate precursor, wherein the step of preparing the hydroxycarbonate precursor comprises:

mixing a mixed salt solution containing metal cations consisting of copper (II) ions, zinc (II) ions and zirconium (IV) ions with a precipitating agent under room temperature to form a precipitate;

aging the precipitate for a duration;

separating the precipitate to obtain a slurry; and

drying the slurry to obtain the hydroxycarbonate precursor comprising copper (Cu), zinc (Zn) and zirconium (Zr) cations.

5. The method of claim 4, further comprising:

redispersing the hydroxycarbonate precursor in a solvent to form the colloidal solution prior to mixing the hydroxycarbonate precursor with the tetraethyl orthosilicate (TEOS) and ethanol mixed solution.

6. The method of claim 4, wherein the hydroxycarbonate precursor is a Cu-Zn-Zr hydroxycarbonate precursor, represented by $[Cu\text{-}Zn\text{-}Zr)CO_3\ (Cu\text{-}Zn\text{-}Zr)(OH)_2]$.

7. The method of claim 4, wherein the mixed salt solution comprises copper(II) nitrate trihydrate ($Cu(NO_3)_2\ 2.5H_2O$), zinc nitrate hexahydrate ($Zn(NO_3)_2\ 6H_2O$), and zirconium nitrate hexahydrate ($ZrO(NO_3)_2\ 6H_2O$).

8. The method of claim 4, wherein the slurry is dried at 60°C.

9. The method of claim 4, wherein the concentration of metal cations in the mixed salt solution is maintained at 0.2M.

10. The method of claim 9, wherein the concentration of the precipitating agent is maintained at the same concentration as the metal cations.

11. A copper-based catalyst comprising Cu-Zn-Zr ternary metal oxide nanoparticles encapsulated in silicon dioxide (SiO_2), forming a uniform core-shell nanostructure, represented by $Cu\text{-}Zn\text{-}ZrO_x@SiO_2$.

12. The copper-based catalyst of claim 11, wherein the core-shell nanostructure has an average diameter ranging from 40 to 60 nm.

13. The copper-based catalyst of claim 11, wherein the copper-based catalyst is configured for use in carbon dioxide hydrogenation to convert carbon dioxide into methanol.