Preparation of bimetal Cu–Co nanoparticles supported on meso–macroporous SiO_2 and their application to higher alcohols synthesis from syngas

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A B S T R A C T

Meso–macroporous SiO_2 supported $LaCo_{0.7}Cu_{0.3}O_3$ were prepared by impregnation method and used as catalysts for higher alcohols synthesis (HAS) from syngas. These catalysts were characterized by using BET, H_2-TPR, XRD, SEM, TEM and XPS techniques. By reducing the catalysts, bimetallic nanoparticles with core–shell structure supported on SiO_2–La_2O_3 were made, and the structure of the nano bimetal could be adjusted via controlling the reduction conditions. The supported bimetal with cobalt as the core and copper as the shell favored the alcohols synthesis, while the bimetal with copper as the core and cobalt as the shell generated more hydrocarbons. The thus prepared bimetal catalysts exhibited very good catalytic performance for HAS from syngas.

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1. Introduction

Due to the increasing oil price and decreasing fossil resources [1,2], higher alcohols synthesis (HAS) from coal or biomass via syngas has arisen widespread concern, owing to the potential application of higher alcohols as oxygenates fuels, fuel additives and other intermediates for chemical feed stocks [3]. However, it is difficult to commercialize this process on account of the low activity, selectivity or poor stability of the catalysts developed till now.

The catalysts reported for HAS mainly include the modified methanol catalysts, the modified Fisher–Tropsch catalysts, the Mo-based catalysts and the Rh-based catalysts. Although supported Rh catalysts show very good activity and high selectivity to ethanol [4–6], the price has limited their extensive application. Alkali-modified Mo-based catalysts are attractive due to their excellent resistance to sulfur poisoning, however the catalysts must be utilized at a strict radio of $H_2/CO = 1:1$, high temperature and pressure [7,8]. As for the modified methanol catalysts, methanol is the major product [9–12].

With higher activity, excellent selectivity to higher alcohols at milder reaction conditions, modified Fisher–Tropsch catalysts,

typically Cu–Co and Cu–Fe, become the most attractive catalysts for HAS. For Cu–Co based catalysts, copper can activate CO non-dissociatively and subsequently generate alcohols, while Co enables the dissociative CO adsorption and C—C chain growth [13,14]. Hence, the synergistic effect and the surface distribution of the two active components have significant influence on the catalytic performance for the synthesis of alcohols [13]. $CuCoO_2$ [15] and $CuCo_2O_4$ [13,16–18], in which Cu and Co should be uniformly distributed at the atomic level, are regarded as the most effective precursors and those can be transformed to Cu–Co alloy after reduction. Nevertheless, CuO and Co_3O_4 could hardly be avoided during the formation of $CuCoO_2$ and $CuCo_2O_4$, which would be reduced to metal copper and metal cobalt in the reaction process and generate methanol and hydrocarbons, respectively.

In $LaCo_{1-x}Cu_xO_3$, a perovskite-type oxide (PTO), both copper and cobalt ions are located in the well-defined perovskite structure and the mutual interaction between these elements can be obtained. $LaCo_{1-x}Cu_xO_3$ can be converted to Cu–Co/La_2O_3 which is the highly dispersed bimetallic Cu–Co nanoparticles supported on La_2O_3 after pretreatment under hydrogen [19–24]. However, due to the limited content and the low specific surface area of the La_2O_3 from $LaCo_{1-x}Cu_xO_3$, the La_2O_3 cannot load so many Cu–Co nanoparticles [20]. In our previous study [23], $LaFeO_3$ was introduced to improve the dispersion of Cu–Co nanoparticles. After reduction, Co_3O_4/$LaFe_{0.7}Cu_{0.3}O_3$ transferred

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into Co–Cu/La$_2$O$_3$–LaFeO$_3$ and the catalyst was highly active and selective for HAS. However, the support of LaFeO$_3$ is not stable enough in the reaction atmosphere of the syngas, besides of that the support of La$_2$O$_3$–LaFeO$_3$ was derived from the perovskite oxide, so the amount and the specific surface area of the support are still limited.

Recently, studies on mesoporous and macroporous materials have been focus of widespread research for use in the fields of catalysis [25–27]. To the best of our knowledge, only two reports on meso–macroporous catalyst for HAS can be found. The multifunctional silica–silica bimodal pore support was prepared by incipient-wetness impregnation of commercially silica gel with silica sol and firstly applied to HAS by Ding et al. [27]. The catalyst of Cu–Fe supported on the bimodal pore support exhibited good catalytic activity and high selectivity to C$_{2+}$OH, due to the well dispersion of active metal sites and high diffusion efficiency of products inside the bimodal pore structures. Lu et al. [28] developed a series of unsupported three-dimensionally ordered macroporous Cu–Fe catalysts by using a glyoxylate route colloidal crystal template method, the catalysts showed high activity and selectivity to C$_{2+}$OH. They owned the excellent catalytic performance to the unique ordered porous structure of the catalysts, the uniformly distributed active components and the synergetic effect between Cu and χ-Fe$_5$C$_2$.

In this work, a series of LaCo$_{0.7}$Cu$_{0.3}$O$_3$/meso–macroporous SiO$_2$ catalysts were prepared, in which both the ions of copper and cobalt were located in perovskite structures and could be highly dispersed at atomic level, resultantly, the formation of bimetallic Cu–Co with copper and cobalt in interaction should be favored in the reduction process. Meanwhile, after reduction of LaCo$_{0.7}$Cu$_{0.3}$O$_3$, the formation of La$_2$O$_3$ could also act as a promoter to HAS. By the way, the meso–macroporous SiO$_2$ was used as the support to load the bimetal nanoparticles, and the porosity of the support favors the diffusion of the reactants and the reacted products.

2. Experimental

2.1. Catalyst preparation

2.1.1. Material

Analytical grade chemicals including La(NO$_3$)$_3$·6H$_2$O, Co(NO$_3$)$_2$·6H$_2$O, Cu(NO$_3$)$_2$·3H$_2$O, citrate acid, styrene, and glycol were purchased from Tianjin Guangfu Technology Development Co. Ltd and used without further purification.

2.1.2. Preparation of meso–macroporous SiO$_2$

The PS (polymerized styrene) foams were prepared by polymerization of styrene in highly concentrated water-in-oil emulsion, which was stated in detail in our previous work [29]. The meso–macroporous SiO$_2$ were prepared by sequential impregnation of PS template with silica gel as stated in [26]. This impregnation process was repeated for 7 times until the weight of the sample did not change. The impregnated samples were dried at 60 °C for 24 h and then calcined in N$_2$ at 600 °C for 4 h to remove the P123 (Aldrich, EO$_{20}$PO$_{70}$EO$_{20}$, M_a = 5800) and PS template, thus the meso–macroporous SiO$_2$ was obtained.

2.1.3. Preparation of LaCo$_{0.7}$Cu$_{0.3}$O$_3$/meso–macroporous SiO$_2$ catalysts

The LaCo$_{0.7}$Cu$_{0.3}$O$_3$/meso–macroporous SiO$_2$ catalysts were prepared according to incipient wetness impregnation method. Lanthanum nitrates, cobalt nitrates and copper nitrates with a La/Co/Cu molar ratio of 1:0.7:0.3 were dissolved in deionized water. Then, citrate acid with the molar amount of 1.2 times of the total cations and the glycol with a molar amount of 20% of the citrate acid were added into the above solution. The meso–macroporous

SiO$_2$ support was soaked into the solution for 24 h. The impregnated samples were dried at 120 °C for 24 h, and then calcined at 300 °C and 600 °C for 2 and 5 h in air, respectively, with a heating rate of 2 °C min^{-1}. For the catalysts with the higher loadings (30% and 40%) of LaCo$_{0.7}$Cu$_{0.3}$O$_3$, the impregnation process was repeated once more. After the first impregnation, the sample was dried at 120 °C for 24 h, and then calcined at 300 °C for 2 h. The thus prepared catalysts were named as y%LaCo$_{0.7}$Cu$_{0.3}$O$_3$/SiO$_2$, in which y% stands for the mass fraction of LaCo$_{0.7}$Cu$_{0.3}$O$_3$ in the calcined catalysts of LaCo$_{0.7}$Cu$_{0.3}$O$_3$/meso–macroporous SiO$_2$.

For comparison, 20%LaCoO$_3$/SiO$_2$ was prepared similarly.

Before reaction, the catalyst was heated to 600 °C in N$_2$ with a heating rate of 10 °C min^{-1} and then switched to H$_2$ atmosphere and maintained in H$_2$ at 600 °C for 3 h, the thus reduced samples were labeled as y%Cu–Co/La$_2$O$_3$–SiO$_2$ (N). A sample of 20%LaCo$_{0.7}$Cu$_{0.3}$O$_3$/SiO$_2$ was heated to 600 °C in H$_2$ at a rate of 10 °C min^{-1} and maintained in H$_2$ at 600 °C for 3 h was labeled as 20% Cu–Co/La$_2$O$_3$–SiO$_2$ (H).

2.2. Catalyst characterization

X-ray diffraction (XRD) measurements were recorded on a Bruker D8-Focus X-ray diffractometer with Ni-filtered Cu Kα radiation (λ = 0.15406 nm) at room temperature. The spectra were collected between 10° and 80° (2θ degree) at a scanning speed of 5°/min.

Nitrogen adsorption and desorption isotherms were performed on a Trwastar 3000 micromeritics apparatus at −196 °C. The specific surface areas were calculated based on the BET method and the pore size distributions were confirmed from the adsorption branch of the isotherms using the BJH model. All samples were outgassed under vacuum at 300 °C for 4 h prior to analysis.

Scanning electron microscopy (SEM) characterizations were performed on a Hitachi S-4800 field-emission scanning electron microscope to observe the macroporous structures of the samples, which were treated with Au sputtered first.

Transmission electron microscopy (TEM) pictures and high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) line scans were obtained on a JEOL JEM-2100F microscope field-emission transmission electron microscope. Samples were finely ground to fine particles in an agate mortar, and then dispersed into ethanol ultrasonically. Finally the well-dispersed samples were deposited onto a Mo gird covered by holey carbon film.

Temperature programmed reduction (TPR) experiments were carried out in a quartz tube reactor. In each run, 50 mg of the catalyst was loaded into a quartz tube reactor, purged for 30 min with 5% H$_2$/Ar to remove the air in the reactor, and then heated to 800 °C from room temperature with a rate of 10 °C min^{-1} in the presence of 5% H$_2$/Ar with a flow of 30 mL min^{-1}. TCD was used as the detector.

X-ray photoelectron spectroscopy (XPS) of the reduced samples were performed using Al Kα (hν = 1253.6 eV) radiation with PHI-1600 photoelectron spectrometer. The spectra were obtained at an X-ray power of 250 W and an energy step of 0.1 eV. Before test, all the samples were vacuumized at room temperature and sealed to prevent oxidation. The residual pressure in the analysis chamber was approximately 2 × 10^{-10} Torr during the analysis. The C1s peak (284.6 eV) was used to correct all XPS spectra.

2.3. Catalytic performance test for CO hydrogenation

Catalytic performance tests were evaluated in a stainless-steel fixed-bed continuous-flow reactor and gas chromatograph (GC) combination system. In each run, 800 mg catalyst was loaded into the reactor and then reduced at 600 °C for 3 h in the presence of H$_2$ with a flow rate of 30 mL min^{-1}. After reduction, the reactor