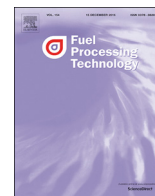




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Research article

A new catalyst of Co/La₂O₃-doped La₄Ga₂O₉ for direct ethanol synthesis from syngas

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ABSTRACT

The catalyst for direct ethanol synthesis (DES) from syngas was investigated in this work, which is Co/La₂O₃-doped La₄Ga₂O₉. The catalyst was prepared by using LaCo_{1-x}Ga_xO₃ with perovskite phase as the precursor to intensify the interaction in the elements of Co, La and Ga. The catalysts were characterized by using XRD, H₂-TPR, TEM, EDS, XPS, BET, ICP and TG techniques. This catalyst showed high selectivity to ethanol and excellent stability including excellent resistance to sintering and carbon deposition. It seems that the ethanol is generated in the interface between metallic Co and La₄Ga₂O₉, and in the interface cobalt would be positively charged due to the interaction between Co nanoparticles and La₄Ga₂O₉. The results and the related discussions indicate that Co/La₂O₃-doped La₄Ga₂O₉ catalyst is a promising catalyst for DES from syngas.

Graphical abstracts.

1. Introduction

Ethanol has been widely used as a potential alternative synthetic fuel additive blended with gasoline and as a renewable fuel component for transportation sectors [1]. It can also be served as feedstock and intermediates for the synthesis of a variety of commodity and products in the chemicals and polymer industries [2, 3]. At present, ethanol is produced mainly from biomass conversion via biological fermentation process through a sugar platform, which is restricted by the limited grains. Syngas is produced in large-scale in the industry from natural gas reforming and coal or biomass gasification, therefore, direct synthesis ethanol from syngas is an expected process [4, 5].

A wide range of homogeneous and heterogeneous catalysts have been investigated for the direct ethanol synthesis (DES) from syngas. Catalysts for DES in the homogeneous process include Co, Ru or Rh metal complexes, which directly produce ethanol and C₂₊ oxygenates from syngas [6, 7]. Certain oxy-solvents, iodide or ionic liquids have been used as the promoters. The homogeneous catalytic processes are relatively more selective to ethanol. However, the high price of the catalyst, high operating pressure and the tedious procedures involved in catalyst separation and recycling make these processes unattractive for commercial applications [3, 7].

The heterogeneous catalysts employed for DES from syngas are developed from higher alcohols synthesis (HAS) with catalyst acted as the technical focus. The reported catalysts can be classified into four categories. Noble metals, such as Rh, Ru, and Re based catalysts, show high selectivity to ethanol while suffering high price and sintering [3, 8]; Methanol synthesis catalysts modified with alkali promoters generate mainly methanol [4, 9]; Mo-based catalysts are resistant to sulfur poisoning while the reaction conditions are very strict [10]; and the modified Fischer-Tropsch catalysts, include Cu-Ni, Cu-Fe and Cu-Co based catalysts. Cu-Ni based catalysts exhibited high activity while methanol and methane are the main products. Cu-Fe based catalysts are active for water gas shift reaction (WGS), generating too much CO₂. Cu-Co based catalysts suffer from phase separation and sintering, leading to the poor stability [11–15].

For modified Fischer-Tropsch catalysts, the synergy between the active sites is critical. Taking Cu-Co based catalysts as the example, CO is adsorbed associatively form on the sites of copper atoms, while on Co sites, CO is adsorbed in dissociative state and is hydrogenated, and ethanol is formed by coupling the two kinds of the adsorbed CO under the synergy between the active sites of Cu and Co. [4, 5] Otherwise, mono Cu and Co would generate methanol and methane, respectively. Thus, the preparation of supported Cu-Co alloy nanoparticles (NPs) is

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critical [16, 17]. The generally used preparation methods for supported bimetallic nanocatalysts include impregnation and precipitation methods [18, 19], which lead to a non-homogeneous distribution of the two kinds of metallic species, resulting in the existence of the mono metal NPs. [20, 21] It is an effective way for preparing bimetallic nanocatalysts by using complex metal oxides as the precursors, such as hydroxalite, spinel and perovskite-type oxides (PTOs). In a complex metal oxide, the metal ions are uniformly mixed at the atomic level, favoring the formation of alloy NPs.

In our previous works [14, 22, 23], $\text{LaCo}_{1-x}\text{Cu}_x\text{O}_3$ perovskite phase was highly dispersed on ZrO_2 , then Cu-Co alloy NPs supported on La_2O_3 -doped ZrO_2 could be obtained by reducing $\text{LaCo}_{1-x}\text{Cu}_x\text{O}_3/\text{ZrO}_2$. In $\text{LaCo}_{1-x}\text{Cu}_x\text{O}_3$, copper and cobalt ions are confined in a PTO crystallite and mixed uniformly at the atomic level, therefore, the atoms of Cu and Co resulted from reducing $\text{LaCo}_{1-x}\text{Cu}_x\text{O}_3$ would tend to interact to form Cu–Co alloy NPs and the resulted catalyst showed good catalytic performance for HAS [24]. PTOs is generally noted as ABO_3 , which are well-known as catalysts for oxidation or reduction reactions [25, 26]. A large number of natural and synthetic compounds have the perovskite structure in which the A and B sites can be partially substituted by a broad range of metal cations in different oxidation states [27].

Recently, He et al. [28, 29] reported that CoGa based catalyst supported on alumina derived from layered double hydroxides is highly selective for HAS. They claimed that Ga donate electrons to neighboring Co sites, being responsible for CO dissociative adsorption and the Co were responsible for linearly nondissociative CO adsorption, boosting the CO insertion step to afford alcohol products.

The synergy between Co and Ga requires each other close contact, hence, $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ should be a promising precursor for preparing the catalyst. $\text{LaCo}_{0.65}\text{Ga}_{0.35}\text{O}_3$ was converted to $\text{Co}/\text{La}_4\text{Ga}_2\text{O}_9$ doped with La_2O_3 , which also showed high selectivity to ethanol and excellent stability for DES from $\text{CO} + \text{H}_2$.

2. Experimental

2.1. Materials

Analytical grade chemicals of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, citric acid and glycol were purchased from Aladdin and used without further purification. Analytical grade chemicals of $\text{Ga}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was purchased from Beijing HWRK Chem. Deionized water was used in all the experimental processes.

2.2. Preparation of catalysts

A series of $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ ($x = 0, 0.2, 0.3, 0.35, 0.4, 0.5$ and 1) were prepared according to the citrate complexing method [30]. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ga}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in deionized water at molar ratio of $\text{La}:\text{Co}:\text{Ga} = 1:(1-x):x$ in which citric acid in 120% molar of the total cations and glycol in 20% molar amount of the citrate acid were added. The resultant solution was dried at 80 °C in a beaker. The resulted sample was dried at 120 °C for 12 h and subsequently calcined at 450 and 700 °C for 3 and 5 h at a heating rate of 2 °C min^{-1} , respectively. For comparison, $\text{Co}_3\text{O}_4\text{-Ga}_2\text{O}_3$ was prepared similarly with Co/Ga molar ratio of 65/35.

2.3. Catalyst characterization

The phase structure analyses of the catalysts were determined by the X-Ray Diffraction (XRD) technique which was recorded on an X'Pert Pro instrument, a $\text{Co K}\alpha$ radiation source was used with an accelerating voltage of 40 kV and an electric current of 40 mA. The spectrum was collected at scanning speed of 5 ° min^{-1} .

Temperature programmed reduction (TPR) tests were carried out on a fixed-bed microreactor in order to study the reducibility of the metal

ions in the catalysts. In each run, 50 mg of the catalyst was loaded into a quartz tube reactor and pretreated with 5% H_2/Ar to remove the air in the reactor at room temperature. Then, the catalyst was heated from room temperature to 900 °C at a heating rate of 10 °C min^{-1} in the presence of 5% H_2/Ar flow at a flow rate of 50 mL min^{-1} . Besides, gas produced after TPR tests such as H_2O , CO_2 and nitrogen oxide will be removed by alkali-lime and silicone.

Transmission electron microscopy (TEM) images and high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) line scans for the determination of metal composition and elemental mapping was 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 Cu grid covered by holey carbon film.

X-ray photoelectron spectroscopy (XPS) tests were performed using $\text{Al K}\alpha$ ($h\nu = 1253.6$ eV) radiation on ESCALAB 250Xi photoelectron spectrometer. The binding energy (BE) of C 1s (284.8 eV) was used to correct all XPS spectra.

Specific surface areas of the catalysts were evaluated by N_2 adsorption according to the BET method on a Trwastar 3000 micromeritics apparatus. All samples were pretreated in vacuum at 300 °C for 4 h before experiments.

Thermogravimetric analysis (TG) was operated on a DTG-50/50H thermogravimetric analyzer to obtain the amount of coke and heavy hydrocarbon deposited on the used catalyst. During the tests, the sample was heated from 20 to 900 °C at a ramping rate of 10 °C min^{-1} in the air.

The content of elements in the fresh catalyst was determined by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700 ×).

2.4. Catalyst testing

The DES tests were carried out in a stainless-steel continuous fixed-bed flow microreactor and gas chromatograph (GC) combination system. 0.6 g of the catalyst with 40–60 mesh grain size was used in each run. All catalysts were reduced at 570, 790, 800, 815, 830 and 880 °C (this is the temperatures for complete reduction of cobalt ions to the corresponding catalyst) for $x = 0, 0.2, 0.3, 0.35, 0.4$ and 0.5 for 3 h at a heating rate of 5 °C min^{-1} with H_2 flow rate of 50 mL min^{-1} , respectively. Subsequently, the reactor was cooled to room temperature, and the pressure was increased to 3 MPa by feeding the syngas mixture of $\text{H}_2/\text{CO}/\text{N}_2 = 8/4/1$ in molar from the pressurized manifold, where N_2 was used as the internal standard gas for analyzing the composition of the off-gas. The gas hourly space velocity (GHSV) was set at 3900 $\text{mL (g}_{\text{cat}} \text{h)}^{-1}$. At each reaction temperature, the reaction was maintained for 12 h to reach the steady state, then data of catalytic performance began to collect.

A gas chromatograph with two packed columns was used to analyze the products. CO , H_2 , CH_4 , CO_2 and N_2 among the gas products were separated online using a TDX-01 packed column (2 m) connected to the TCD detector. Hydrocarbons and the condensed liquid products were analyzed off-line using a Porapak Q column (3 m) connected to FID detector. In all measurements, the carbon balance and mass balance were between 95% and 105%. CO conversion (X_{CO}), the product selectivity (S_i) and the mass fraction of a certain alcohol in the total alcohols (W_i) were calculated according to the following equations:

$$X_{\text{CO}} = \frac{\text{CO}_{\text{in}} - \text{CO}_{\text{out}}}{\text{CO}_{\text{in}}} \times 100\%$$

$$S_i = \frac{nC_i}{\sum nC_i} \times 100\%$$

$$W_i = \frac{m_i}{\sum m_i} \times 100\%$$

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