



Short communication

Hydrogenation of CO₂ to dimethyl ether on La-, Ce-modified Cu-Fe/HZSM-5 catalysts

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ABSTRACT

Cu–Fe–La/HZSM-5 and Cu–Fe–Ce/HZSM-5 bifunctional catalysts were prepared and applied for the direct synthesis of dimethyl ether (DME) from CO₂ and H₂. The catalysts were characterized by X-ray diffraction (XRD), N₂ adsorption–desorption, H₂-temperature programmed reduction (H₂-TPR), and X-ray photoelectron spectroscopy (XPS). The results showed that La and Ce significantly decreased the outer-shell electron density of Cu and improved the reduction ability of the Cu–Fe catalyst in comparison to the Cu–Fe–Zr catalyst, which may increase the selectivity for DME. The Cu–Fe–Ce catalyst had a greater specific surface area than the Cu–Fe–La catalyst. This promoted CuO dispersion and decreased CuO crystallite size, which increased both the DME selectivity and the CO₂ conversion. The catalysts were stable for 15 h.

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1. Introduction

With the economic development and the expansion of industrialization, the combustion of coal, gasoline, natural gas, and other hydrocarbons increases the CO₂ content in the atmosphere every year, causing the earth's temperature to rise [1]. However, CO₂ is also a potential carbon resource. To utilize CO₂ and solve the environmental problems caused by CO₂, the key issue is to develop technologies to capture, store and use CO₂ [2,3]. One way to do this is to effectively translate CO₂ into hydrocarbon fuels by, for example, CO₂ hydrogenation to dimethyl ether (DME) [4].

Presently, there are two main processes for synthesizing DME — a two-step process and a one-step process — using CO₂ and H₂ as the raw materials. The one-step process combines methanol synthesis and methanol dehydration catalysts in the same reactor to directly synthesize DME from CO₂ and H₂. This method has received considerable attention, as it is thermodynamically and economically more advantageous than the traditional two-step process. However, the one-step process still remains in the laboratory exploration stage. The catalysts used in the one-step process to synthesize DME include Cu-based catalysts such as CuO–TiO₂–ZrO₂/HZSM-5 [5], Cu–ZnO/Al₂O₃ [6], CuO–ZnO–

Al₂O₃/HZSM-5 [7,8], CuO–ZnO–Al₂O₃–ZrO₂/HZSM-5 [9], and Cu–ZnO–ZrO₂/HZSM-5 [10], along with non-Cu-based catalysts including Pd–Pd₂Ga [11,12]. Due to the stability of CO₂, its activation is a bottleneck problem that is difficult to solve, and the CO₂ hydrogenation reaction is conducted at 4–8 MPa and 250–350 °C, leading to the deactivation of the catalyst. Even when used Cu–Fe–Zr/HZSM-5 was used as catalyst [13,14], which decreased the pressure and temperature to 3–4 MPa and 220–260 °C, respectively, the conversion of CO₂ was still only 25%–30% and the selectivity of DME was only 40%–50% [13,15], limiting the industrial application of this method.

La and Ce have been added to catalysts to promote the dispersion of metal, decrease the reduction temperature and the crystallite size, and improve the thermal stability of the catalyst [16–18]. Based on a previous Cu–Fe–Zr catalyst [13,14], the Cu–Fe–La, and Cu–Fe–Ce catalysts were synthesized in this work using a homogeneous precipitation method. The catalysts were then characterized by X-ray diffractometer (XRD), N₂ adsorption–desorption, H₂-temperature programmed reduction (H₂-TPR), and X-ray photoelectron spectrometer (XPS), and applied in the hydrogenation of CO₂ to DME.

2. Experimental

2.1. Preparation of catalyst

The precursor of the methanol synthesis catalyst was prepared by homogeneous precipitation. Cu(NO₃)₂·3H₂O and Fe(NO₃)₃·9H₂O were weighed according to the Cu/Fe molar ratio of 3:2. Likewise,

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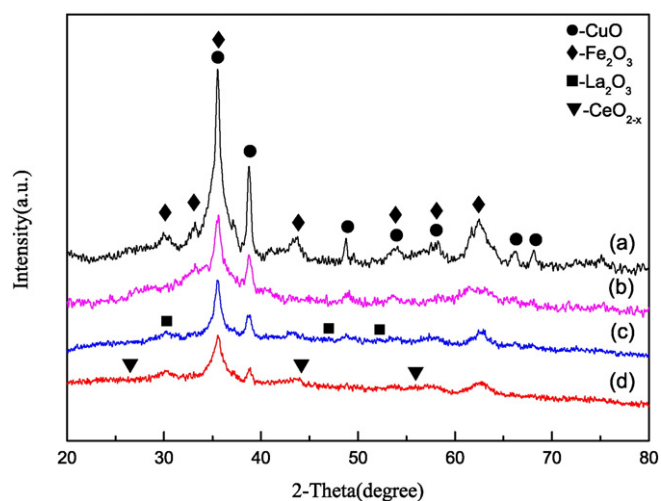


Fig. 1. XRD patterns of Cu-Fe (a), Cu-Fe-Zr (b), Cu-Fe-La (c) and Cu-Fe-Ce (d) calcined at 400 °C without H₂ reduction.

Zr(NO₃)₄·5H₂O, La(NO₃)₃·6H₂O, and Ce(NO₃)₃·6H₂O were weighed based on the corresponding ZrO₂, La₂O₃, and CeO₂ contents of 1.0 wt% in the ternary metal oxides. After mixed oxide Cu-Fe-Ce, Cu-Fe-La and Cu-Fe-Zr (i.e., the methanol dehydration components) were prepared via homogeneous precipitation, they were mechanically mixed with HZSM-5 (Shanghai Novel Chemical Technology Co., Ltd.) with a silica–alumina ratio of 300:1 in a 1:1 mass ratio. The details of the preparation method are given in the supporting information.

2.2. Characterization of the catalyst

XRD, XPS, N₂ adsorption–desorption and H₂-TPR were used to characterize the catalysts following previously reported procedures [13].

2.3. Catalytic hydrogenation of CO₂ to DME

The reaction process for DME synthesis from CO₂ and H₂ can be found in the literature [13]. The feed gas was a mixture of H₂ and CO₂ gas (4:1 mol ratio) after reduction, and the catalytic hydrogenation of CO₂ to DME was performed at 260 °C and 3.0 MPa with a gaseous hourly space velocity (GHSV) of 1500 mL·g_{cat}⁻¹·h⁻¹. The details of the catalytic hydrogenation of CO₂ to DME are found in the literature [13].

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the XRD patterns of the Cu-Fe, Cu-Fe-Zr, Cu-Fe-La and Cu-Fe-Ce catalysts calcined at 400 °C without H₂ reduction.

The characteristic peaks of monoclinic CuO (JCPDS No. 48-1548) at $2\theta = 35.49^\circ$, 38.69° , and 58.26° and of cubic crystalline Fe₂O₃ (JCPDS No. 39-1346) at $2\theta = 30.24^\circ$, 35.63° , and 62.93° are found in the XRD patterns of Cu-Fe-La and Cu-Fe-Ce. Compared with Cu-Fe and Cu-Fe-Zr, the diffraction peaks of CuO and Fe₂O₃ in the Cu-Fe-La and Cu-Fe-Ce patterns are broadened, and the peak intensities are weakened, indicating that the crystallite size of CuO is smaller. Smaller crystallites correspond to better copper dispersion. The crystallite sizes of CuO (111) in the Cu-Fe-La and Cu-Fe-Ce catalysts were calculated using the Sherrer equation and determined to be 19.1 and 17.6 nm, respectively. However, the crystallite sizes in the Cu-Fe and Cu-Fe-Zr catalysts are 22.5 and 19.3 nm, respectively, indicating that the modification of La₂O₃ and CeO₂ decreased the crystallite size of CuO and promoted the dispersion of CuO [19]. The crystallite size of the Cu-Fe-Ce catalyst is clearly the smallest among the catalysts. The diffraction peaks at $2\theta = 29.9^\circ$, 46.1° , and 52.1° were attributed to the La₂O₃ phase (JCPDS No. 05-0602). Peaks corresponding to CeO_{2-x} at $2\theta = 26.3^\circ$, 43.9° and 55.7° (JCPDS No. 49-1415) were found. These results suggested that some of the smaller-sized Cu²⁺ ions (ionic radius of 0.79 Å compared to 0.92 Å for Ce⁴⁺) entered the CeO₂ lattice to form a Ce_{1-x}Cu_xO_{2-x} solid solution [20].

3.2. Nitrogen adsorption/desorption of catalysts

Fig. 2 shows the N₂ adsorption–desorption isotherms and pore size distribution profiles of the Cu-Fe, Cu-Fe-Zr, Cu-Fe-La, and Cu-Fe-Ce catalysts calcined at 400 °C without H₂ reduction.

Based on the IUPAC classification, the N₂ adsorption–desorption isotherms of the Cu-Fe-La and Cu-Fe-Ce catalysts (Fig. 2A) belonged to IV-type isotherms. In the low- and medium-pressure region ($P/P_0 = 0.0$ – 0.8), the amount of adsorbed N₂ gently increased, indicating that the adsorption of N₂ on the internal surfaces of catalyst pores shifted from monolayer to multilayer. In the high-pressure region ($P/P_0 = 0.8$ – 1.0), an H3-type hysteresis loop was generated by capillary condensation, suggesting that the Cu-Fe-La and Cu-Fe-Ce catalysts were mesostructured materials [21]. The pore size distribution profiles (Fig. 2B) indicate that the majority of mesopores had diameters of approximately 3 nm. The specific surface areas of the Cu-Fe, Cu-Fe-Zr, Cu-Fe-La, and Cu-Fe-Ce catalysts were calculated using the Brunauer–Emmett–Teller (BET) equation according to the N₂

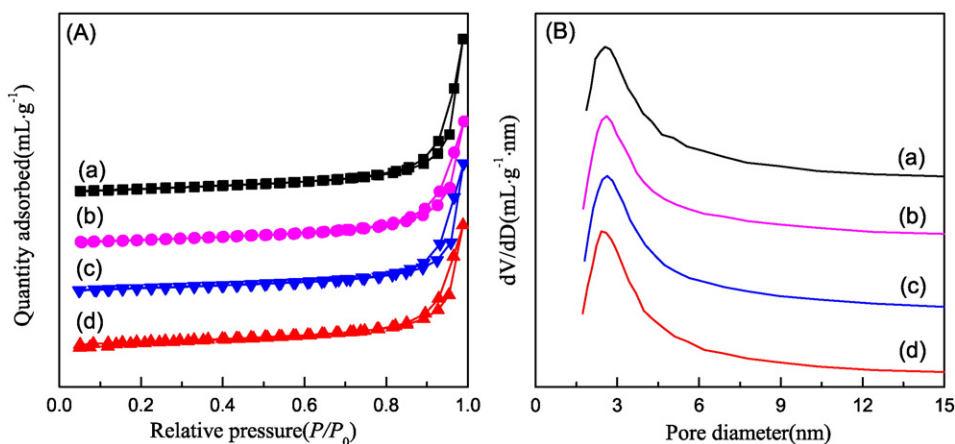


Fig. 2. Nitrogen adsorption/desorption isotherms (A) and pore size distribution profiles (B) of Cu-Fe (a), Cu-Fe-Zr (b), Cu-Fe-La (c) and Cu-Fe-Ce (d) catalysts calcined at 400 °C without H₂ reduction.

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