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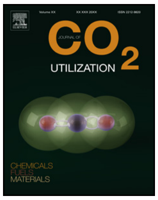

Synthesis of dimethyl carbonate from methanol and CO_2 over Fe–Zr mixed oxides

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ABSTRACT

A series of Fe–Zr mixed oxides with different Fe content were prepared and used for direct synthesis of dimethyl carbonate (DMC) from CO_2 and methanol. The best catalytic performance was achieved over the $Fe_{0.7}Zr_{0.3}O_y$ catalyst, with DMC yield of 0.44 $mmol\cdot gcat^{-1}$ and DMC selectivity of 100% under the reaction conditions of 110 °C and 12 MPa. Characterization results of N_2 physisorption, XRD, XPS, TPR and NH_3/CO_2-TPD indicated that the Fe–Zr mixed oxides with coexistence structure of hexagonal Fe_2O_3 and cubic Fe_2O_3 favored the formation of moderately acidic and basic sites, which then improved the activation of CO_2 and methanol. The DMC yield was shown to be linearly related to the amount of moderately acidic and basic sites.

1. Introduction

Dimethyl carbonate (DMC) could be used as green and alternative chemical for corrosive and toxic reagents such as dimethyl sulfate and phosgene in methylation or carbonylation processes [1,2]. Compared with traditional synthetic methods [3–10], the direct synthesis of dimethyl carbonate from CO_2 and methanol was an economic and environmental route [11,12], which not only could avoid using of toxic substances such as CO and phosgene, but also solved the problem of CO_2 mitigation and excess capacity of methanol. However, due to the limit of thermodynamic equilibrium, DMC yield was still very low. Therefore, the development of high activity and high stability catalyst was demanded.

At present, metal tetra-alkoxides, metal oxides, metal acetates, alkali compound, supported metal catalysts *etc.* were used. Metal tetra-alkoxides [13–17] were considered to be the most active catalysts, among which organotin tetra-alkoxides were widely studied. However, these homogeneous catalysts were difficult to recycling due to the decomposition in the present of H_2O that lead to deactivation. Recently, alkali compound such as potassium carbonate were used in which corrosive and expensive methylation agent such as methyl iodide need to be added to the reaction system [18–20]. Supported metal catalysts such as Cu–Ni [21–25] or Cu–Fe [26,27] were also investigated which exhibited better catalytic performance in fixed bed reactor. Modified metal oxides, especially zirconia-based [28,29], cerium-based [30–33], vanadium-based catalysts [34] had also shown good catalytic activity due to both the acid and base sites on the catalyst surface. Among them, the amphoteric oxide, ZrO_2 with vicinal acid-basic active sites showed better catalytic performance in the direct synthesis of DMC. Tomishige [35,36] had found that the catalytic activity of ZrO_2 could be improved after modification of H_3PO_4. Jiang [37,38] had reported that $H_3PW_{12}O_{40}$ modified ZrO_2 had better catalytic activity than ZrO_2. Tomishige [39,40] had also prepared the CeO_2–ZrO_2 solid solution with better activity under high calcination temperature.

Iron (III) oxide with acidic and basic sites was low cost, eco-friendly and thus widely investigated in many heterogeneous reactions, such as isomerizations, Friedel-Crafts reactions, *etc.* [41–43], methanol gas-sensing test [44]. Because acid-base bifunctional catalysts were efficient for the direct synthesis of DMC from methanol and CO_2 [28,45,46], and few works about the Fe–Zr mixed oxides as catalyst for the reaction were reported. In the present paper, we proposed to modify ZrO_2 with Fe to improve the acidity and basicity on the catalyst surface and tried to clarify the relationship between the surface structure, acid-base property and the catalytic performance.

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2. Experimental

2.1. Catalyst preparation

Fe-Zr mixed oxides (Fe $_xZr_{1-x}O_y$) with different Fe content (x = 0.3, 0.5, 0.7, 0.9) were prepared by sol-gel process using Fe$(NO_3)_3 \cdot 9H_2O$ and $Zr(NO_3)_4 \cdot 5H_2O$ as precursors. Typically, ethanol solution (200 mL, 0.2 mol L^{-1}) with different $Fe(NO_3)_3 \cdot 9H_2O$ and Zr$(NO_3)_4 \cdot 4H_2O$ molar ratio was dropped into a 400 mL beaker. A solution of citric acid in ethanol (0.2 mol L^{-1}, 100 mL) was then slowly added with stirring. After continuous stirring for further 24 h at room temperature, the mixed solution was evaporated at 80 °C overnight to form the sponge yellow gel. Then, the gel was dried at 80 °C for 24 h and milled followed by calcination at 500 °C in air for 4 h. The catalysts with different molar ratio of Fe_2O_3:ZrO_2 was denoted as Fe $_xZr_{1-x}O_y$ (x = 0.3, 0.5, 0.7, 0.9).

2.2. Catalyst characterization

The specific surface area of the catalysts were determined by N_2 adsorption-desorption at liquid nitrogen temperature −196 °C using a Micromeritics Tristar II (3020) apparatus. The specific surface areas were calculated according to the Brunauer-Emmett-Teller (BET) equation and the pore volume were calculated from the desorption branch of the isotherm using the Barrett, Joyner and Halenda (BJH) equation.

The X-ray diffraction (XRD) patterns of catalysts were measured on a Bruker D8 Advance (Germany) diffractometer equipped with a Cu Kα. The scattering intensities were measured over an angular range of 10–80° at a scanning speed of 5°/min.

The X-ray photoelectron spectroscopy (XPS) spectra were obtained using a Thermo ESCALAB 250 spectrometer equipped with Al Ka radiation (h ν = 1486.6 eV) under an ultrahigh vacuum. The values of binding energy (eV) were taken relatively to that of C ls electrons of hydrocarbons on the sample surface (produced by adventitious carbon), which was accepted to be equal to 284.8 eV.

The reducibility of the catalysts were studied by H_2-temperature-programmed reduction (H_2-TPR). 50 mg of freshly calcined catalysts was placed on the middle of glass wool in a quartz tube. Then the TPR experiments were carried out in 5% H_2/N_2 at flow rate of 50 mL min^{-1}. The temperature of the reactor was increased from room temperature to the final temperature of 1000 °C with a ramping rate of 10 °C/min. Effluent gas was purified by silica gel desiccant and 5A molecular sieve. The hydrogen consumed during TPR was monitored continuously by a thermal conductivity detector (TCD).

Temperature programmed desorption of NH_3 (NH_3-TPD) was carried out on the GAM 200 Mass Spectrometer for the measurement of the acidity of the catalysts. Each sample (0.1 g) was placed in the quartz reactor and pretreated in an Ar flow (25 mL min^{-1}) at 500 °C for 1 h. The adsorption of NH_3 was performed at 40 °C with pure NH_3 (50 mL min^{-1}) for 30 min, followed by an Ar purge for 1 h to remove the physisorbed NH_3. The desorption process was performed at a heating rate of 10 °C·min^{-1} from 40 °C to 500 °C and the evolved NH_3 was monitored with a thermal conductivity detector.

Temperature programmed desorption of CO_2 (CO_2-TPD) was carried out on the Micromeritics Auto Chem II Chemisorption Analyzer for the measurement of the basicity of the catalysts. The operational process and condition were same with NH_3-TPD.

2.3. Catalytic evaluation of catalysts

Direct synthesis of DMC from methanol and carbon dioxide was carried out in a 50 mL stainless-steel autoclave equipped with a magnetic stirrer. Typically, methanol (12 g) and catalyst (1.0 g) were charged into the reactor. Then CO_2 was introduced into the reactor with an initial pressure of 5.0 MPa at room temperature. The reactor was then heated to 110 °C and stirred constantly for 4 h. After the reaction, the reactor was cooled to room temperature and depressurized. In order to quantitatively analyze composition of the mixture, n-butyl alcohol was added as an internal standard substance. The products were analyzed by a gas chromatograph (FID-GC920) equipped with a capillary column (DB-210, 25 m × 0.22 mm).

3. Results and discussion

3.1. Textural and structural properties of the prepared samples

Crystal structures of Fe-Zr mixed oxides were investigated by XRD and the spectra were shown in Fig. 1. For pure ZrO_2, the diffraction peaks at 2θ of 24.4° (011), 28.2° (−111), 31.5° (111), 40.7° (−112) and 45.5° (−202) could be assigned to the monoclinic phase of ZrO_2 (JCPDS 37-1484) while the characteristic peaks at 2θ of 30.2° (011), 35.2° (110), 50.3° (112), 60.7° (121), 62.9° (202) and 74.5° (220) could be ascribed to the tetragonal phase of ZrO_2 (JCPDS 50-1089). Pure Fe_2O_3 exhibited a hexagonal phase (JCPDS 33-0664) at 2θ of 24.1° (012), 33.1° (104), 35.6° (110), 40.8° (113), 49.4° (024), 54.1° (116), 62.4° (214) and 63.9° (300).

After addition of Fe ($Fe_{0.3}Zr_{0.7}O_y$), the phase of zirconia disappeared and only a very broad peak attributed to amorphous α-Fe_2O_3 was observed. It was inferred that iron-zirconium solid solution might be formed because the surface Fe/Zr ratio was closed to the bulk Fe/Zr ratio (Table 2) [47]. While for $Fe_{0.5}Zr_{0.5}O_y$ and $Fe_{0.7}Zr_{0.3}O_y$, cubic phase (2θ of 30.1° (220), 43.1° (400), 56.9° (511), 62.6° (440)) of Fe_2O_3 was observed which suggested that some Zr^{4+} ions had incorporated into the Fe_2O_3 lattice and lead to the crystal phase transformation of some Fe_2O_3 from hexagonal to cubic phase [48]. At high Fe content ($Fe_{0.9}Zr_{0.1}O_y$), the crystal structure was in hexagonal phase of Fe_2O_3, which was similar to that of the pure Fe_2O_3.

The textures of the catalysts were listed in Table 1. The specific surface area of the Fe-Zr solid solutions increased significantly from 20 $m^2 g^{-1}$ to 87 $m^2 g^{-1}$ upon increasing of the Fe content, suggesting that the introduction of Fe was beneficial to the increase of the surface area to some extend. High surface area might cause the exposure of more active sites and thus lead to a higher catalytic activity. It could also be seen that the pore volumes increased from 0.034 $cm^3 g^{-1}$ to 0.088 $cm^3 g^{-1}$ with the introduction of Fe and the

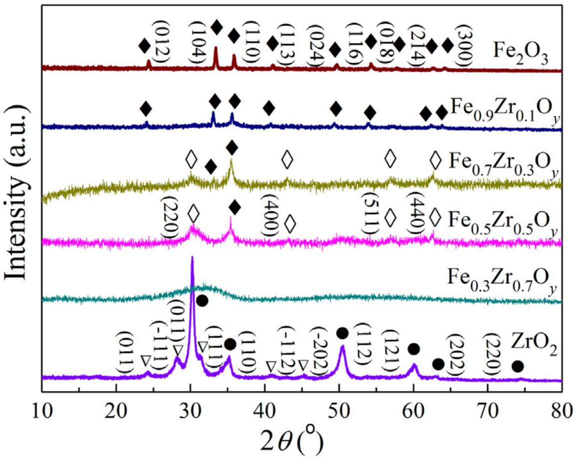

Fig. 1. XRD patterns of the Fe-Zr solid solutions: (◆) hexagonal Fe_2O_3, (◇) cubic Fe_2O_3, (●) tetragonal ZrO_2, (▽) monoclinic ZrO_2.