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$(Al_{1-x}Cr_x)_4B_6O_{15}$ $(0.08 \le x \le 0.14)$: Metal borates catalyze the dehydration of methanol into dimethyl ether

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ABSTRACT

PKU-5 ($Al_4B_6O_{15}$) is potentially a solid acid catalyst, and it possesses an interesting open-framework composed of [AlO_6] and [B_2O_5] groups. PKU-5 shows a high thermal stability, while no physical and chemical properties were investigated thus far, because of the difficulty in its synthesis. Cr-stabilized PKU-5 with the formula $(Al_{1-x}Cr_x)_4B_6O_{15}$ $(0.08 \le x \le 0.14)$ can be easily prepared by annealing Cr-doped PKU-1 precursors. XRD and TEM experiments demonstrate Cr^{3+} has been successively incorporated into the framework of PKU-5. NH_3-TPD measurements indicate that the partial substitution of Al^{3+} by Cr^{3+} leads to a small change of acid sites in total amounts and distributions. Cr-PKU-5 shows a good catalytic activity for methanol dehydration from 300 to 450 °C. Other operation conditions, such as the Cr^{3+} content, space velocity of methanol were also discussed in detail to evaluate its catalytic performance.

1. Introduction

Recently dimethyl ether (DME) has received global attentions as a potential and green fuel for diesel engines due to the shortage of the petroleum supply in the near future [1]. It can be used as the aerosol propellant, replacing chlorofluorocarbons in the fine chemicals industry [2,3], and also as an important intermediate for making other high value-added chemicals, such as lower olefins, methyl acetate and dimethyl sulphate [4].

There are two major methods to produce DME: an indirect synthesis from methanol dehydration over solid acid catalysts, or a direct synthesis from syngas over bifunctional catalysts. For the latter method, methanol is produced as an intermediate and consumed in dehydration reaction, so methanol does not appear in the final step [5–10]. Unfortunately the optimum catalytic reaction temperatures for the two consecutive reactions are different, thus it is difficult to operate the process in a way to ensure both high activity and selectivity in a single reactor. Both these two processes involve methanol dehydration over a solid acid catalyst, thus far, many dehydration catalysts have been investigated extensively [11–23], such as molecular sieves, γ-alumina, aluminum phosphates, and many of them have shown higher performance in methanol dehydration.

Generally speaking, catalysts with weak acidity require a high operation temperature to achieve a required efficiency. However, this will lead to a low selectivity of DME due to non-catalytic side reactions. Solid catalysts with strong acidity could be effective at relatively low temperatures, but the catalysts are quite susceptible to adsorb water or basic molecules and therefore promote side reactions, such as a deep dehydration into unsaturated hydrocarbons. Therefore, people are seeking catalysts with appropriate acidity.

Alumina (γ-Al_2O_3) shows moderate acidities, and has been considered as a good catalyst for methanol dehydration to DME. However, alumina will deactivate rapidly in the presence of water [24]. Other catalysts with stronger acidic sites, like zeolites [25–27] and zeolite-related materials [28–31] could have higher activities than γ-Al_2O_3, but unfortunately the deactivation problem would be more significant due to the production of hydrocarbons (HC). So, our idea is to develop a new Al-based catalyst. For example, we speculate that the incorporation of boron into alumina may create more acid centers and adjust the acidic property.

During the last decades, a series of open-framework aluminoborates with related structural features have been discovered, denoted as PKU-1, PKU-2, and PKU-5 [32–34]. As shown in Fig. 1, their backbones are all consisted of edge-sharing octahedra [AlO_6], and borates groups, in the forms of [BO_3], [B_2O_5] or [B_3O_7]

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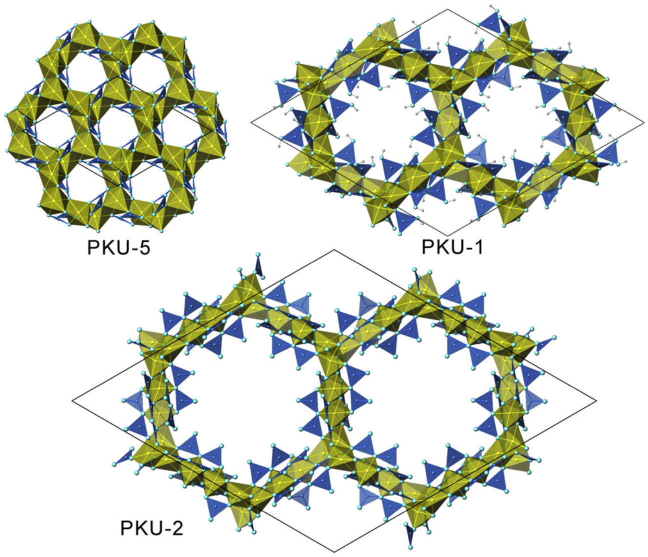

Fig. 1. Projections of the PKU-*n* frameworks along the *c*-axis. AlO_6 and BO_3 are expressed as yellow octahedra and blue triangles. Disengaged water molecules inside channels are omitted for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

fragments, decorate to the $[AlO_6]$ framework and behave as charge neutralizers by sharing vertex oxygen atoms. These aluminoborates are octahedron-based microporous materials and can potentially work as molecular sieves with specific acid sites. We are particularly interested with PKU-5 ($Al_4B_6O_{15}$), because it is a dehydrated borate and possesses the highest hydrothermal stability and probably adequate acidity, satisfying the basic requirements to catalyze the dehydration of methanol. PKU-5 crystallizes in the space group *R*3 with the lattice parameters $a = 11.434$, $c = 6.483$ Å [34]. Each $[AlO_6]$ octahedron shares three edges with the neighboring octahedra forming ten-membered ring channels. The nitrogen adsorption experiment (BET) indicates that the free space of PKU-5 is about 48 m^2/g. In addition, $[B_2O_5]$ groups in PKU-5 can probably behave as the acid centers for methanol dehydration.

Aluminoborate PKU-5 ($Al_4B_6O_{15}$) can be hydrothermally prepared at 350 °C [34]. Alternatively, the PKU-5 structure can be stabilized with rational Cr-substitutions, forming $(Al_{1-x}Cr_x)_4B_6O_{15}$ by annealing Cr-substituted PKU-1 precursors ($(Al_{1-x}Cr_x)_3B_6O_{11}(OH)_5 \cdot nH_2O$). [35] Here, the existence of Cr^{3+} in the parent PKU-1 is necessary for its temperature-induced transition into PKU-5. Therefore, we applied a two-step process to prepare PKU-5 samples with different Cr contents and investigate their potentials as acid catalysts for methanol dehydration. To the best of our knowledge, it is the first case to use aluminoborate to catalyze methanol dehydration.

2. Experimental

2.1. Catalyst preparation

The PKU-5 ($(Al_{1-x}Cr_x)_4B_6O_{15}$, $0.08 \le x \le 0.14$) catalysts with different Cr^{3+}-contents were prepared via a two-step reaction procedure. First, Cr-substituted PKU-1 with the formula $(Cr_xAl_{1-x})_3B_6O_{11}(OH)_5 \cdot nH_2O$ were prepared by boric acid flux method as reported in literature [32]. For a typical reaction, H_3BO_3 (100 mmol), $Al(NO_3)_3$ (3.68 mmol) and $Cr(NO_3)_3$ (0.32 mmol) were ground and loaded into a 100 ml Teflon autoclave, then the autoclave was sealed and heated at 240 °C for 5 days. After cooling to room temperature, the resultant solid was washed with warm water (70 °C) until the residual boric acid was completely removed. The as-synthesized Cr-PKU-1 samples were denoted as PKU-1a, PKU-1b, PKU-1c and PKU-1d, according to the increase *x*. All of the Cr-PKU-1 samples were heated in a muffle furnace at temperature 700 °C for 12 h and decomposed into a mixture of corresponding Cr-PKU-5 and residual B_2O_3. The final obtained samples were water-washed and labeled as PKU-5a, PKU-5b, PKU-5c and PKU-5d. Further heating Cr-PKU-5 at temperature of 950 °C, Cr-PKU-5 will finally transform into $(Al_{1-x}Cr_x)_4B_2O_9$ (denoted as Cr-$Al_4B_2O_9$).

2.2. Catalyst characterizations

Powder X-ray diffraction data were collected on a PANalytical X'pert powder diffractometer equipped with a PIXcel 1D detector and Cu Kα radiation ($\lambda = 1.5406$ Å). The operation voltage and current are 40 kV and 40 mA, respectively. Le Bail refinements were applied to obtain the cell parameters using TOPAS software package [36]. Transmission electron microscopy (TEM) were performed on a JEM-2100F electron microscope (accelerating voltage of 200 kV) equipped with Energy Dispersive X-ray (EDX) detector. The sample was ultrasonically dispersed in ethanol, and then the suspension was deposited on a microgrid coated with a holey carbon film. The specific surface area was determined by BET method with nitrogen adsorption at 77 K using a Quantachrome Quadrasorb SI analyzer. Prior to the measurements, the samples were degassed at 300 °C for 5 h. The acidity was measured with temperature-programmed desorption of NH_3 molecules (NH_3-TPD) using a Quantachrome ChemBET Pulsar with a thermal conductivity detector (TCD). A given amount of the sample was pretreated in a flowing helium at 400 °C for 1 h, cooled to 100 °C, and then exposed to 5% NH_3/He mixer gas (50 ml/min) for 30 min. After saturation, the sample was flushed in a He flow for 30 min to remove NH_3 molecules which are loosely bound on the sample. The reactor temperature was programmed at a ramp rate of 15 °C/min from 100 °C to 700 °C.

X-ray photoelectron spectra (XPS) were acquired with UK Kratos Axis Ultra spectrometer with Al Kα X-ray source operated at 15 kV and 15 mA. Kinetic energies of photoelectrons were measured using a hemispherical electron analyzer working at the constant pass energy (40 eV). The pressure in the chamber was less than 5.0×10^{-9} Torr. The powder samples were pressed into stainless steel holders and then mounted on a support rod placed in the pretreatment chamber. The XPS data were taken in increments of 0.1 eV with dwell times of 500 ms. Electron binding energies were calibrated against the C 1s emission at $E_b = 284.6$ eV to correct the contact potential differences between the sample and the spectrometer.

2.3. Catalyst evaluation

The catalytic performance for methanol dehydration was evaluated on a micro-reactor system. Prior to activity measurements, the calcined samples were finely ground in an agate mortar, pelletized, crushed, and sieved to 40–60 mesh size. 0.3 g catalyst was placed in the middle of a stainless steel tubular reactor, and pre-treated at 400 °C in a N_2 flow of 40 ml/min for 5 h. As the reactor temperature was cooled to 200 °C, methanol was fed by a micro-liquid pump with the weight hourly space velocity (WHSV) of methanol varying from 0.79 to 7.92. An online gas chromatograph (Techcomp GC 7800) equipped with a TCD detector and a Porapak Q column (60–80 mesh, $\phi 3 \times 3000$ mm) was connected to analyze the components in the effluent with a sampling frequency of 1 h^{-1}. Some operation conditions, the characteristics of the laboratory-scale apparatus and the catalyst used in this study were summarized in Table 1.