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Effects of Cs-substitution and partial reduction on catalytic performance of Keggin-type phosphomolybdic polyoxometalates for selective oxidation of isobutane☆

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ABSTRACT

The catalytic performance of Cs-substituted phosphomolybdic salts was studied for selective oxidation of isobutane. The results of activity tests revealed that 360 °C was the optimal reaction temperature. It was demonstrated that oxidizing sites not only took dominating part in the activation of isobutane, but also influenced the product distribution. Besides, appropriate Cs addition led to moderate acidity of catalysts, favoring the selectivity to desired products. Furthermore, to obtain partially reduced catalysts, different calcination atmospheres were investigated and certain proportion of Mo^{5+} produced during calcination was crucial for the redox reaction. The catalyst calcined in N_2 showed the highest yield of MAA (7.0%). Fe-substitution enhanced the activity of catalysts by rapid reoxidation of Mo^{5+}.

1. Introduction

Methacrylic acid (MAA) is an important chemical intermediate to produce methyl methacrylate (MMA), which can be used as a monomer for the production of acrylic plastics, such as polymethyl methacrylate [1,2]. Because of its good transparency and weather resistance, the global demand for polymers of MMA is increasing rapidly [3]. New applications like high-performance flat panel displays for polyacrylates are fueling MMA demand as well. The conventional MMA process is acetone-cyanohydrin (ACH) route, which is most widely commercialized in Europe and North America [4]. But the utilization of highly toxic reactant HCN and disposal of large quantities of ammonium bisulfate waste are two main problems [2]. So since 1980s, the oxidation of isobutene or t-butanol appears to be another alternative route for MMA production. However, the technology in Asian is confined by the acquisition of raw materials and complexity of the two-stage process via the formation of methacrolein (MAL) [5]. The utilization of isobutane which comes from abundant C4 resources in petrochemical industry is gaining more attention recently. Thus the direct synthesis of MAA by the oxidation of isobutane seems particularly promising because of its simplicity of the one-stage process and low environmental impact, as well as the abundant available raw material [6].

Polyoxometalates (POMs) are a group of compounds which contain metal-oxo anionic clusters. The composition and properties of POMs can be tuned by introducing different metals which act as counter-cations and partial substituted cations in polyanions [7–9]. Therefore, POMs are extensively used in both homogeneous and heterogeneous catalysis [10,11]. Keggin-type POMs with both variable acidity and redox properties are potentially useful for reactions of making oxygenated compounds from hydrocarbons [5,8]. During the reactions, it is reported that the acidity plays an important role in activating C–H bonds, and the redox properties are responsible for oxygen insertion reactions to generate oxidized products [4]. Up to now, many attempts have been made to optimize the composition of POM catalyst for the selective oxidation of isobutane to MAA. The optimal catalyst is considered to be Keggin-type molybdophosphoric salts modified by alkali and transition metal ions, aiming at the improvement of its stability and reactivity. The substitution of protons by potassium or cesium and transition metal ions (e.g. Ni^{2+}, Cu^{2+}, Te^{4+}) in both counter-cations and the Keggin anions (V to Mo, As to P, etc.) is mostly reported [9,12–14]. In addition, some other studies of POM catalysts supported on different carriers, SiO_2 [15], Sb_2O_3 [16] and other POMs [17], indicated that a better dispersion of active components could be obtained.

Although much progress has been made since the employment of POMs for isobutane oxidation to MAA, there are still some limitations for their future industrial applications. POMs can be qualified for reactions that happen at relatively low temperatures, while it seems to be a difficult task for them to withstand the high temperatures for the activation of alkanes. The introduction of certain elements, such as V,

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As, Sb and Te [9,13,16], leads to a significant enhancement of both catalysts thermal stability and the yields of desired products. However, it obviously goes against the aim of green chemistry when using the toxic chemicals, and the economy of processes should be taken into account as well. In addition, the mechanism of the reaction is not clear yet [4].

In this work, the role of Cs in Fe-substituted phosphomolybdic cesium salt for isobutane oxidation was studied in detail, and the catalytic performance of partially reduced catalysts prepared by calcination was investigated for the first time. A range of environmentally benign Fe-substituted POM catalysts with different Cs contents was prepared to identify the effects of Cs on the catalytic activity and selectivity to desired products. Besides, the acidity was investigated for the effects on activation of isobutane and catalytic performance over Cs-substituted catalysts. In addition, partially reduced catalysts were prepared by calcination method and first used in oxidation of isobutane. The catalysts were calcined under different atmospheres before reaction, in order to study the generation of active sites and their stability. The study of catalyst acidity and nature of active sites provided a better design of catalysts and deeper insight into the reaction mechanism.

2. Experimental

2.1. Catalyst preparation

The Fe-substituted phosphomolybdic cesium salt was synthesized by conventional co-precipitation method, using ammonia as a precipitation agent. The prescribed amounts of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Sinopharm Group), $Fe(NO_3)_3\cdot 9H_2O$ (Sinopharm Group) and Cs_2CO_3 (Wuhan Baijierui Chem.) were dissolved in deionized water in sequence. After the addition of 85% H_3PO_4 into the resulting suspension, the Keggin-type POM was formed with the employment of ammonia to control pH at an appropriate value. The precipitate was vigorously stirred and evaporated at 80 °C until dryness. Then the catalyst was dried at 140 °C overnight and calcined in air at 380 °C for 2 h if necessary. In the salts $(NH_4)_xCs_yFe_{0.2}PMo_{12}O_{40}$, x and y were the amount of NH_4^+ and Cs^+ ions, respectively. Hereinafter the salts would be denoted in the abbreviated form as $Cs_yFe_{0.2}$, $y = 0$, 0.6, 1.2, 1.8, 2.2.

2.2. Catalyst characterization

Infrared spectra (FT-IR) were recorded on a Nicolet NEXUS 670 equipped with an MCT detector. The samples were ground with KBr and pressed into KBr wafers to subtract the corresponding background reference. The acidity measurements were also performed by FT-IR after pyridine adsorption. All spectra were recorded from 400 to 4000 cm^{-1} and each spectrum involved the accumulation of 64 scans at a resolution of 4 cm^{-1}.

Powder X-ray diffraction (XRD) was examined using X'pert PRO MPD diffractometer with Cu-$K\alpha$ radiation at 40 kV and 40 mA, scanning from 5° to 75° with a speed of 10 °/min.

Thermogravimetry (TG-DTA) was carried out on DTU-2A differential thermogravimetric analyzer to study structural changes of catalysts during calcination in air. The samples were heated in alumina crucibles from room temperature to 800 °C at a rate of 10 °C/min.

X-ray fluorescence (XRF) chemical analysis was performed at room temperature on an AXIOS-Petro apparatus.

The specific surface areas and pore volumes of the catalysts were measured with a Quadrasorb SI instrument by N_2 adsorption–desorption method at 77 K. To ensure complete removal of the adsorbed moisture, all samples were degassed at 300 °C for 4 h prior to the measurement.

Table 1. Chemical analysis and texture properties of the catalysts after calcination at 380 °C.

Catalyst	Atomic ratio			BET surface area (m^2/g)	Pore volume (cm^3/g)
	12Cs/Mo	12Fe/Mo	12P/Mo		
$Cs_0Fe_{0.2}$	–	0.22	1.3	4	0.024
$Cs_{0.6}Fe_{0.2}$	0.6	0.22	1.3	5	0.033
$Cs_{1.0}Fe_{0.2}$	1.0	0.23	1.3	6	0.046
$Cs_{1.2}Fe_{0.2}$	1.2	0.23	1.2	6	0.053
$Cs_{1.8}Fe_{0.2}$	1.7	0.20	1.2	13	0.072
$Cs_{2.2}Fe_{0.2}$	2.1	0.20	1.2	19	0.120

The redox behavior of catalysts was determined by temperature-programmed reduction of hydrogen (H_2-TPR), with 10% H_2/N_2 (30 mL/min) in the temperature range of 80–400 °C.

X-ray photoelectron spectroscopy (XPS) measurements were conducted on an ESCALab 250 apparatus equipped with monochromatic Al$K\alpha$ radiation, operating at 300 W. The vacuum in the analysis chamber was stabilized at 3×10^{-7} Pa. Binding energies were calibrated using C 1 *s* peak at 284.6 eV.

2.3. Catalytic test

The selective oxidation of isobutane was conducted in a conventional fixed-bed reactor under atmospheric pressure. The reaction temperature was 360 °C, to obtain a better product distribution and maintain intact Keggin structure after reaction. The catalytic bed made of 1.5 g of catalyst (particles ranging from 125 to 250 μm in size) was sandwiched between two identical pure silicon oxide layers. During the reaction, the reactants were fed by a mass flow controller with the following composition: isobutane 33%, O_2 18%, and N_2 balance. The residence time was equal to 1.7 s, which was shorter than most of that reported in previously published articles. The outlet gases were analyzed by a Bruker 450 gas chromatograph equipped with three detectors, two TCD detectors to analyze H_2 and CO_2, CO, O_2, N_2, and an FID detector to determine the content of hydrocarbons. Other products were absorbed in water and analyzed on an Agilent 6820 gas chromatograph equipped with an HP-INNOWAX capillary column and an FID detector. The conversion and the selectivity were determined for a time on stream of 3–5 h of reaction, when nearly steady-state conditions were obtained. The carbon balance was in the range of 90%–100%.

Isobutane conversion, product yield and selectivity are defined as follows:

$$\text{Isobutane conversion (mol\%)} = \left(1 - \frac{\text{mole of isobutane in the product}}{\text{mole of isobutane in the feed}}\right) \times 100$$

$$\text{Product yield (mol\%)} = \frac{\text{Mole of carbon in product } i \text{ in the product}}{\text{Mole of carbon in isobutane in the feed}} \times 100$$

$$\text{Product selectivity (mol\%)} = \frac{\text{Product yield}}{\text{Isobutane conversion}} \times 100$$

3. Results and discussion

3.1. Catalyst characterization

The chemical compositions and texture properties of the prepared catalysts are listed in Table 1. The results of chemical analysis were in good agreement with the theoretical stoichiometries, and the obvious increase of the surface area of catalysts was also observed with Cs addition.