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Catalytic dehydration of glycerol to acrolein over HPW supported on Cs^+ modified SBA-15

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ABSTRACT

The sustainable production of acrolein from glycerol dehydration is a competitive alternative to the propylene-based technology. A new catalyst, $H_3PW_{12}O_{40}$ supported on Cs^+ modified SBA-15 (HPW/Cs-SBA), was prepared and tested for glycerol dehydration. The catalysts were characterized using N_2 adsorption–desorption, X-ray diffraction, Fourier-transform infrared spectroscopy, NH_3 temperature-programmed desorption, and thermogravimetric analysis. The dispersion of Keggin anion on the support was improved by grafting Cs^+ onto the silica surface followed by partial neutralization of $H_3PW_{12}O_{40}$ (HPW) with Cs^+ to form $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW). Good activity and selectivity for dehydration of glycerol to acrolein were obtained by converting the strong acid sites of HPW to selective medium acid sites. The best catalyst, with 50% of HPW loading (denoted as 50HPW/Cs-SBA), had the largest fraction of medium acid sites (71%) and gave 85% of acrolein yield at 300 °C with co-feeding of O_2. The stability of 50HPW/Cs-SBA was significantly improved, with acrolein yield retained above 85% after 150 h of reaction. In addition, this catalyst had a good thermal stability at coke burning temperature of 500 °C. The yield of acrolein was correlated with the fraction of medium acid sites on the catalysts.

1. Introduction

Acrolein is used in the production of acrylic acid and its esters. The current technology for producing acrolein is based on the selective oxidation of propylene over complex multi-component $BiMoO_x$-based catalysts [1]. However, this technology will become less competitive as crude oil price increases. In recent years, the selective dehydration of glycerol has been studied as an alternative technology for producing acrolein from biomass-derived molecules. With the fast development of the biodiesel industry, the price of glycerol has decreased from 800 to 300 $/t. This makes the sustainable production of acrolein from glycerol competitive with the technology based on propylene [2].

In recent years, some researchers studied the dehydration of glycerol to acrolein over bulk and supported acidic catalysts [3], in particular with heteropoly acids (HPAs) as active compounds [2]. HPAs have attracted attentions due to their high activity and selectivity on the Keggin structures [4]. The HPA catalysts can be classify into bulk HPA and supported HPA types. For the glycerol dehydration reaction, the main drawbacks of bulk HPAs are their strong acid sites and limited thermal stability. The strong acid sites always cause coke formation during the glycerol dehydration reaction, so the catalyst regeneration is needed [5,6]. However, the Keggin-type HPW, HSiW, HPMo and HSiMo decompose at 465, 445, 375 and 350 °C, respectively [2,7]. The decomposition at the regeneration temperature leads to dramatic loss in the catalyst acidity and activity. Therefore, for many catalytic applications, the HPA compound is dispersed on a high surface area support to tune the acid strength and improve the thermal stability. For the supported HPAs, silica is often used as the suitable support because it weakly interacts with HPA and the Keggin structure is well preserved [7]. Using the HPW/SBA-15 catalyst, acrolein selectivity of 75% has been achieved [8]. However, the weak interaction between HPW and silica support results in a relatively poor dispersion, high acid strength and low thermal stability of HPW. The catalyst deactivates quickly due to coke formation on the strong acid sites. Another way to improve the HPW property is to partially neutralize HPW with alkali metals. For example, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW) has been shown to give a better performance for dehydration of glycerol to acrolein than HPW, but its stability is still unsatisfactory due to coke formation on the remained strong acid sites [9].

In this work, we demonstrated a method to realize high dispersion of HPW on silica. It combined both the beneficial effect of the alkaline cation neutralization and the dispersion of HPA on a high surface area support [10,11]. The support used was SBA-15, which has a high surface area (600–1000 $m^2\,g^{-1}$) and uniform tubular channels with large tunable pore diameters of 5–30 nm to accommodate the HPW Keggin structure [12–14]. The HPW precursor was supported on SBA-15 pretreated with Cs^+. This Cs^+ modification of SBA-15 enhanced the dispersion and catalytic performance of

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HPW [14–16]. Cs^+ was chosen since it has been reported to be able to increase the selectivity to acrolein in the glycerol dehydration reaction [9]. The obtained HPW/Cs-SBA catalyst was highly active and selective for dehydration of glycerol to acrolein. The catalyst had good thermal stability at coke burning temperature of 500 °C. It was also found that the yield of acrolein was closely correlated to the fraction of medium acid sites of the catalysts.

2. Experimental

2.1. Catalyst preparation

The HPW/Cs-SBA catalyst was prepared using the two-step vacuum impregnation method reported by Soled et al. and used by others [10,17]. The support SBA-15 was provided by Nanjing XFNANO Materials Tech Co., Ltd. In the first step, SBA-15 (0.5 g) was pumped to a vacuum of 10^{-4} Torr with a rotary mechanical pump to remove water molecules, nitrogen and other contaminations from the pores of SBA-15. An aqueous solution of Cs_2CO_3 (Alfa Aesar) was introduced under vacuum according to the HPW loading at Cs^+/HPW molar ratio of 2.5. Then the system was allowed to return to atmosphere pressure, and HPW was impregnated into the channels of SBA-15 by capillary force overnight at room temperature. Then the impregnated support was dried at 100 °C in air, followed by calcination at 500 °C for 3 h. In the second step, HPW was impregnated using $H_3PW_{12}O_{40}{\cdot}nH_2O$ (Alfa Aesar) aqueous solution in a similar way to form $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW). According to the HPW loading (w in wt%), the final catalyst samples were denoted as *w*HPW/Cs-SBA.

The HPW/SBA-15 catalyst was prepared by vacuum impregnation of HPW using the similar procedure but without Cs^+ modification [8,18]. The final catalyst samples were denoted as *w*HPW/SBA.

For comparison, the bulk CsPW was also prepared from aqueous solutions of Cs_2CO_3 and $H_3PW_{12}O_{40}{\cdot}nH_2O$ with a method reported in the literature [9,18]. To do this, an appropriate amount of Cs_2CO_3 aqueous solution was added dropwise to an aqueous solution of HPW at room temperature with vigorous stirring. The Cs content, x in $Cs_xH_{3-x}PW_{12}O_{40}$, was determined by the amount of added Cs_2CO_3 solution. The fine particles obtained were heated in air by increasing the temperature to 300 °C at a heating rate of 5 °C/min, calcined at 300 °C for 4 h, and then cooled to room temperature at 5 °C/min.

2.2. Catalyst characterization

The BET surface areas of the catalyst samples were calculated from nitrogen adsorption–desorption isotherms measured at −196 °C using a physical adsorption apparatus (Quandasorb-SI-4, Quantachrome).

The XRD analysis was performed on an automated powder X-ray diffractometer (40 kV, 40 mA, Bruke D8 Advance) using a Cu Kα radiation source and a nickel filter in the 2θ range of 1°–90°. The samples were dried under vacuum at 200 °C for 5 h before measurement. In order to test the catalyst thermal stability, the catalysts after calcination at 500 °C in air were also analyzed for comparison.

NH_3-TPD was carried out using an automated adsorption system (ChemBET Pulsar TPR/TPD, Quantachrome) with an online thermal conductivity detector (TCD). A sample of 100 mg was placed in a quartz tubular reactor and pretreated at 150 °C with a N2 flow of 30 mL/min for 1 h, and then cooled to 100 °C. NH_3 was introduced at a flow rate of 30 mL/min for 0.5 h at 100 °C, and then the sample was purged in a N2 stream until a constant TCD level was obtained. The reactor temperature was programmed at a rate of 5 °C/min to 700 °C and the desorbed NH_3 was detected online by TCD.

The coke amount on the spent catalysts was measured using thermogravimetric (TG) analysis (NETZSCH STA 409PC) at a heating rate of 20 °C/min under 50 mL/min O_2.

2.3. Catalytic reaction

The experiments of glycerol dehydration were carried out at 300 °C under atmospheric pressure in a fixed bed reactor (10 mm i.d.) using 0.5 g of catalyst. The reactor tube was placed in an electrical furnace with an inner diameter that matched the outer diameter of the reactor tube to optimize heat transfer and have a long zone of uniform temperature. The particle sizes of the catalysts were in the range of 325–500 μm. In addition to the supported catalysts, bulk CsHPW and bare SBA-15 with the same particle size were also tested for comparison. The catalyst was diluted with inert quartz particles to avoid hot spots. A HPLC pump (Series 2,001-5 mL/min, SS, S. G. Seal Self Flush, Pulse Damper) was used to feed an aqueous solution of 20 wt% glycerol into the reactor. Dry nitrogen (15 mL/min) was used as carrier. Oxygen (3 mL/min) was added when studying the effect of oxygen co-feeding. The flow rates were controlled by mass flow controllers. The measured axial profile of the catalyst bed temperature confirmed that the reaction was carried out under isothermal conditions. All reactants and products in the tubings were heated to at least 200 °C to avoid undesired condensation.

For most reaction experiments, the weight hourly space velocity (WHSV) in terms of glycerol was 0.72 h^{-1}, which was relatively high compared with the values (0.2–0.6 h^{-1}) for other HPAs catalysts reported in the literature [2,19,20]. The use of a high WHSV was favorable to study the catalyst stability. The feed was first evaporated by a heated bed of quartz beads before it entered the catalyst bed. The reaction products and unconverted glycerol were collected in a cold trap (−5 °C) at the reactor outlet. The mass balance for each trap was determined to confirm proper operation of the setup. The collected liquids were analyzed offline by gas chromatograph (GC 7900, Techcomp Ltd.) equipped with a FID detector and a TM-SuperWax column (60 m × 0.25 mm × 0.25 μm, Techcomp Ltd.). The reaction was conducted for 20 h in most cases. The condensed products during the first two hours of reaction were not used because they did not satisfy the mass balance. The glycerol conversion and product selectivity were calculated based on the number of carbon atoms as follows:

$$\text{Glycerol conversion} = \frac{\text{moles of reacted glycerol}}{\text{moles of glycerol in the feed}} \times 100\%$$

$$\text{Product selectivity} = \frac{\text{moles of carbon in a defined product}}{\text{moles of carbon in reacted glycerol}} \times 100\%$$

$$\text{Product yield} = \text{Glycerol conversion} \times \text{Product selectivity}$$

The glycerol molecule has a primary and a secondary hydroxyl groups, thus it has two reaction pathways of dehydration. Over the catalysts used in this work, acrolein was the main product. Trace amounts of CO_x, methane, ethane, ethylene, propane and propylene were also detected, but with a total selectivity of less than 5%. Due to the low amount of hydrocarbon and CO_x in the gas phase, only the liquid products were measured.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. BET surface area

The physical properties of the catalysts are listed in Table 1. The BET surface area, pore volume and pore diameter of the supported