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Article

Highly selective and stable CsPW/Nb₂O₅ catalysts for dehydration of glycerol to acrolein

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ABSTRACT

Acrolein production by gas-phase dehydration of glycerol at 300 °C, catalyzed by a Cs⁺-substituted Keggin-type phosphotungstate, Cs_{2.5}H_{0.5}PW₁₂O₄₀ (CsPW), supported on Nb₂O₅ was investigated. The catalysts were characterized using N₂ adsorption-desorption, X-ray diffraction, Fourier-transform infrared and Raman spectroscopies, and NH₃ temperature-programmed desorption. It was demonstrated that Lewis acid sites were responsible for byproduct formation, and that Brønsted acid sites of medium strength were the active sites for acrolein production by glycerol dehydration. The acidity of the supported CsPW was affected by the calcination temperature and CsPW loading. The CsPW was well dispersed on Nb₂O₅ at loadings ≤ 20 wt%, and the strong acid sites of bulk CsPW were converted to selective medium acid sites. The CsPW catalyst with 20% of CsPW loading calcined at 500 °C gave 96% of glycerol conversion and 80% of acrolein selectivity, and there was no significant deactivation in 10 h. The catalyst with a 20% decrease in activity was regenerated by simple coke burning with air at 500 °C.

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1. Introduction

Acrolein is used in the production of acrylic acid and its esters, which are used as an aquatic herbicide and algicide in irrigation canals, as a microbicide in oil wells, liquid hydrocarbon fuels, cooling water towers, and water treatment ponds, and as a slimicide in the manufacture of paper. The current technology for producing acrolein is based on the selective oxidation of propylene over complex multi-component Bi-MoO_x-based catalysts. However, this technology will become less competitive as crude oil prices increase. In recent years, the selective dehydration of glycerol has been studied as an alternative technology for producing acrolein from biomass-derived molecules. Its feedstock, glycerol, is a byproduct of biodiesel production, and 0.1 t of glycerol are produced per 1

t of biodiesel [1–3]. With the fast development of the biodiesel industry, the price of glycerol has decreased from 800 to 300 \$/t [4,5]. This makes the sustainable production of acrolein from glycerol competitive with the technology based on propylene.

Different catalysts have been developed and studied for the dehydration of glycerol to acrolein. Chai et al. [6–9] classified the solid catalysts into four groups according to their acidities. Group 1 includes the basic catalysts, with Hammett acidities *H*₀ higher than +7, such as CeO₂ and MgO, which have very low selectivities for acrolein. Group 2 includes catalysts with *H*₀ between –3 and +7, such as SiO₂, ZrO₂ [10], Ta₂O₅ [11], and supported nickel sulfate [12]. Group 3 includes catalysts with *H*₀ between –8 and –3, such as H₃PW₁₂O₄₀/α-Al₂O₃ [6], H₄SiW₁₂O₄₀ supported on activated carbon [13], Nb₂O₅ calcined

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at 400 °C [7], Al_2O_3 [14], and WO_3/ZrO_2 [15]; these are the most effective catalysts, with high selectivities of 60% to 70% for acrolein. Group 4 includes strong acid catalysts with H_0 less than -8 , such as H β zeolite [16], sulfonated Zr [17], and alumina-silicate [18]; these suffer from fast deactivation as a result of coking. Among these catalysts, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPW) has high activity and selectivity but poor stability. Chai et al. [9] optimized the catalytic performance by HPW loading on ZrO_2 , but the stability of the catalyst was still unsatisfactory. In addition, the regeneration of HPW by combustion of coke is difficult because of its relatively low thermal stability [19]. In comparison, $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (CsPW) has a much better thermal stability, and a recent study showed that it has high activity and selectivity for dehydration of glycerol to acrolein, with 100% initial conversion of glycerol and 98% selectivity for acrolein [19]. Unfortunately, this catalyst also has poor stability, with the glycerol conversion decreasing to 40% after 6 h as a result of coke formation on its strong acid sites [20]. Haider et al. [21] developed Cs- and Rb-exchanged silicotungstic acids supported on Al_2O_3 as catalysts for glycerol dehydration to acrolein. Although the acrolein yield was improved, the catalyst was deactivated at a glycerol feed of 20 wt%.

The catalytic performance of supported HPW or CsPW catalysts depend significantly on the support (ZrO_2 , SiO_2 , and SBA-15) [22,23]. It is therefore valuable to investigate other support materials to further improve the selectivity and stability of the CsPW supported catalysts for glycerol dehydration. Among the metal oxides, Nb_2O_5 is attractive as it is a water-tolerant solid acid catalyst for various reactions involving water, such as esterification, hydrolysis, dehydration, and hydration [24–26]. Moreover, the surface area, pore diameter, acidity, and other properties of Nb_2O_5 are tunable by changing the calcination temperature [27]. Lauriol-Garbey et al. [25] and Massa et al. [26] investigated several ZrNbO catalysts for glycerol dehydration to study the correlation between acid-base properties and catalytic properties. Omata et al. [28] synthesized complex metal oxides of W and Nb with a layered structure, via a hydrothermal method, to improve the acrolein yield.

In this work, CsPW/ Nb_2O_5 catalysts were synthesized and studied in the dehydration of glycerol to acrolein, to improve the catalyst selectivity and stability. The catalyst samples were denoted by $w\text{CsPW-Nb}T$, where w is the weight fraction of CsPW and T is the calcination temperature. The CsPW used in this work was $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ because it has been reported to be the most active among the acidic Cs salts due to the largest amount of surface acid sites. The effects of CsPW loading ($w = 5\text{--}60$ wt%) and calcination temperature ($T = 400\text{--}700$ °C) were studied to optimize the catalytic properties and performance. The mechanism of the improved selectivity and stability of the CsPW after loading on Nb_2O_5 is discussed based on the catalyst characterization and reaction evaluation results.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of CsPW

CsPW was prepared using the procedure described by Pizzio et al. [29]. An appropriate amount of Cs_2CO_3 aqueous solution (0.10 mol/L, 99.99%, Alfa Aesar, MA, USA) was added dropwise using a syringe pump at a constant rate of 1.0 mL/min to an aqueous solution of HPW (0.08 mol/L, 20 mL, 99.99% Alfa Aesar, MA, USA) at room temperature with vigorous stirring. The Cs content, x in $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$, was determined by the amount of added Cs_2CO_3 solution. At the beginning of the addition of Cs_2CO_3 , fine precipitates were formed, resulting in a milky solution. After aging at room temperature overnight, the water was removed from the solution by slow evaporation at 50 °C. The fine particles obtained were heated in air by increasing the temperature to 300 °C at a heating rate of 5 °C/min, calcining at 300 °C for 4 h, and then cooling to room temperature.

2.1.2. Preparation of Nb_2O_5

To prepare Nb_2O_5 , an aqueous solution of ammonium oxalato-niobate (0.4 g/mL), $\text{Nb}(\text{NH}_4)(\text{C}_2\text{O}_4)_2\text{NbO} \cdot n\text{H}_2\text{O}$ (99.99%, Aldrich, MO, USA), was added to ethylene glycol to give a volume ratio of 1:2 [30,31]. The pH of the solution was controlled to be 8–9 by adding 28% NH_3 aqueous solution. The solution was kept in a water bath, heated to 65 °C with stirring, and maintained at this temperature until no more precipitate formed. After precipitation, the solution was cooled to room temperature, and the solid was separated by centrifugation and washed three times with deionized water. The solid obtained was dried at 80 °C in a vacuum, and calcined in air at a particular temperature (400, 500, 600, and 700 °C) for 2 h, at a heating rate of 5 °C/min, and then cooled to room temperature. These obtained Nb_2O_5 samples were used as catalysts for comparison with the supported $w\text{CsPW-Nb}T$ catalysts.

2.1.3. Preparation of $w\text{CsPW-Nb}T$

For the preparation of $w\text{CsPW-Nb}T$, the Nb_2O_5 support was prepared first using the same procedure as described in Section 2.1.2 but without calcination. Cs_2CO_3 and HPW were then introduced into the Nb_2O_5 by a vacuum-assisted impregnation method [32–34]. The Nb_2O_5 precipitates were separated and dried, and then pretreated under a vacuum of better than 0.1 Pa to remove impurities and air trapped in the porous structure. The obtained Nb_2O_5 was not calcined before impregnation with Cs_2CO_3 and HPW. A desired amount of Cs_2CO_3 was added to deionized water, and a Cs_2CO_3 solution (0.10 mol/L) was added to the Nb_2O_5 powder under vacuum. The vacuum was then turned off and the system was kept overnight at atmospheric pressure and room temperature to let Cs_2CO_3 penetrate into the micro- and mesopores of the Nb_2O_5 by capillary force. Excess water was removed using a rotary evaporator at 40 °C, and the obtained sample was dried at 100 °C in air for 2 h. HPW was then impregnated into the prepared $\text{Cs}_2\text{CO}_3/\text{Nb}_2\text{O}_5$ using the same procedure except that a HPW solution (0.08 mol/L) was used. The powder obtained was heated in flowing air to a particular temperature (400, 500, 600, and 700 °C at 5 °C/min), calcined for 4 h, and then cooled to room temperature. Based on the CsPW loading (w in wt%) and thermal treatment temperature (T in °C), the final catalyst samples were denoted by

wCsPW-NbT ($w = 5\text{--}60$, $T = 400\text{--}700$). The samples were stored in vials in a desiccator until used.

2.2. Characterization

The surface areas of the catalyst samples were calculated from N_2 adsorption-desorption isotherms measured at $-196\text{ }^\circ\text{C}$ using a physical adsorption apparatus (Quandasorb-SI-4, Quantachrome). The samples were dried under vacuum at $200\text{ }^\circ\text{C}$ for 5 h before the measurements. X-ray diffraction (XRD) was performed with an automated powder X-ray diffractometer (40 kV, 40 mA, Bruker D8 Advance) using a $\text{Cu K}\alpha$ radiation source and a Ni filter in the 2θ range $1^\circ\text{--}90^\circ$.

The Keggin anion density, expressed as the number of Keggin anions per square nanometer of the sample surface (CsPW nm^{-2}), was determined from the actual CsPW loading and sample surface area, using the following equation [9]:

$$\text{Keggin anion density (CsPW nm}^{-2}\text{)} = \frac{[\text{CsPW loadings (wt\%)} \div 100 \times (6.02 \times 10^5)]}{[\text{BET surface area of catalyst (m}^2\text{ g}^{-1}\text{)} \times \text{relative molecular mass of CsPW}]}$$

Ammonia temperature-programmed desorption (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 (100 mg) was placed in a quartz tubular reactor and pretreated at $150\text{ }^\circ\text{C}$ with a N_2 flow of 30 mL/min for 1 h, and then cooled to $100\text{ }^\circ\text{C}$. Ammonia was introduced at a flow rate of 30 mL/min for 0.5 h at $100\text{ }^\circ\text{C}$, and then the sample was purged in a N_2 stream until a constant TCD level was obtained. The reactor temperature was programmed at a rate of $5\text{ }^\circ\text{C/min}$ to $700\text{ }^\circ\text{C}$ and desorbed NH_3 was detected online by the TCD.

Laser Raman spectra were recorded in the range $200\text{--}2000\text{ cm}^{-1}$ using a microscopic confocal Raman spectrometer (Renishaw RM2000) working at a laser wavelength of 514 nm^{-1} . Fourier-transform infrared (FT-IR) spectra of fresh and spent catalysts were obtained with an FT-IR spectrometer (Nicolet NEXUS670) using powder catalyst mixed with KBr.

The coke amount on the spent catalysts was determined using thermogravimetric (TG) analysis (NETZSCH STA 409PC) at a heating rate of $20\text{ }^\circ\text{C/min}$ under an O_2 flow of 50 mL/min.

2.3. Catalytic reaction

The experiments on glycerol dehydration were carried out at $300\text{ }^\circ\text{C}$ at atmospheric pressure in a fixed-bed reactor (inner diameter 10 mm) 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 give a long uniform-temperature zone. The catalyst particle sizes were in the range $325\text{--}500\text{ }\mu\text{m}$. In addition to the supported catalysts, bulk CsPW and an Nb_2O_5 support with the same particle sizes were also tested for comparison. The catalysts were diluted with inert quartz particles to avoid hot spots. A high-performance liquid chromatography pump (Series 2001, 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 N_2 (15 mL/min) mixed with O_2 (3 mL/min) was used as the carrier, and the flow rates were controlled by mass flow controllers. Measurement of the axial temperature profile in the catalyst bed confirmed that the reaction was carried out under isothermal conditions. All reactants and products in the tubing were heated to at least $200\text{ }^\circ\text{C}$ to avoid undesired condensation.

The catalytic performance was evaluated at a gas hourly space velocity (GHSV) of 97.4 h^{-1} in terms of glycerol. The use of this relatively high glycerol GHSV for the reaction helped our understanding of the catalyst stability. The feed was evaporated using a heated bed of quartz beads before it entered the catalyst bed. The reaction products and unconverted glycerol were collected in a cold trap ($-5\text{ }^\circ\text{C}$) at the reactor outlet. The mass balance for each trap was determined to check proper operation of the setup. The liquids collected were analyzed offline using a gas chromatograph (GC 7900, Techcomp Ltd.) equipped with a flame ionization detector and a TM-SuperWax column ($60\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$, Techcomp Ltd). The reaction was conducted for 12 h in most cases. The condensed products during the first 2 h 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.

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

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

Glycerol has primary and secondary hydroxyl groups and has two main reaction pathways for dehydration. With the heteropoly acid catalysts, acrolein was the main product, followed by acetol. In consecutive reactions, it was mostly $\text{C}_1\text{--}\text{C}_3$ oxygenates (allyl alcohol, acetaldehyde, propionaldehyde, acetic acid, propionic acid, and acrylic acid) that were produced, together with some unidentified products. Trace amounts of hydrocarbons, including methane, ethane, ethylene, propane, and propylene, and CO_x , were also detected, but with a total selectivity of less than 5%. Because of the low amount of hydrocarbons and CO_x in the gas phase, only the liquid products were measured.

3. Results and discussion

3.1. Effect of calcination temperature and CsPW loading on catalyst properties

3.1.1. BET surface area and Keggin anion density

The BET surface area and Keggin anion density on the surfaces of the CsPW-NbT samples are listed in Table 1. It can be seen that the surface area of Nb_2O_5 significantly decreased from 105 to $16\text{ m}^2/\text{g}$ with increasing calcination temperature from 400 to $700\text{ }^\circ\text{C}$. All the CsPW-Nb samples had higher surface areas than their Nb_2O_5 counterparts. For example, the surface area of Nb600 was $36\text{ m}^2/\text{g}$, whereas it was $45\text{ m}^2/\text{g}$ for 20CsPW-Nb600. The reason is that the large Cs ions increased the interstitial volumes between Keggin units and created new

Table 1

BET surface areas and reaction results for catalysts.

Sample	BET surface area (m ² /g)	Keggin anion density (CsPW nm ⁻²)	Glycerol conversion ^a (%)	Acrolein selectivity ^a (%)	Coke amount ^b (wt%)
Nb400	105	—	88 (100)	50 (39)	9.2
Nb500	59	—	92 (100)	47 (30)	5.8
Nb600	36	—	76 (89)	33 (30)	0.9
Nb700	16	—	32 (40)	28 (22)	0.6
CsPW	141	—	41 (100)	51 (94)	8.9
20CsPW-Nb400	108	0.39	85 (94)	64 (66)	5.2
20CsPW-Nb500	66	0.66	96 (98)	80 (75)	2.6
20CsPW-Nb600	45	0.96	91 (92)	60 (65)	2.3
20CsPW-Nb700	20	2.21	83 (85)	61 (61)	1.5
5CsPW-Nb500	63	0.17	92 (98)	62 (72)	3.4
40CsPW-Nb500	62	1.46	82 (97)	63 (80)	3.6
60CsPW-Nb500	68	1.93	75 (99)	52 (89)	6.1

Reaction conditions: 300 °C, catalyst powder (325–500 μm) 0.5 g, gas flow rate (N₂:O₂ = 5:1) 18 mL/min, glycerol aqueous solution (20 wt%) 0.6 mL/h (0.24 h⁻¹ glycerol WHSV), 10–11 h.

^a Values in brackets refer to glycerol conversion and acrolein selectivity at TOS of 2 h.

^b Coke amounts in used catalysts after reaction for 11 h measured with thermal analysis.

pores, therefore the surface lost by plugging was compensated for. This impact of Cs ions on porosity has also been reported for Cs-exchanged silicotungstic acid on silica and aluminosilicate supports [35].

For the same calcination temperature, the surface area did not change much with the CsPW loading. When the CsPW loading increased from 5% to 20%, the surface areas of the samples calcined at 500 °C slightly increased from 63 to 66 m²/g. Further increases in the CsPW loading to 40% resulted in a very similar surface area (62 m²/g for 40CsPW-Nb500).

The Keggin anion density of the CsPW-Nb catalysts calculated from the surface areas changed with the calcination temperature and CsPW loading. At the same CsPW loading (20 wt%), the samples calcined at lower temperatures always showed higher surface areas, and consequently lower Keggin anion densities. As expected, the Keggin anion density generally increased with increasing CsPW loading of the samples. The 60CsPW-Nb500 catalyst had a Keggin anion density of 1.93 CsPW/nm², which was higher than that of its 5/20/40CsPW-Nb500 counterparts with the same calcination temperatures. Assuming a cross-section of 1.44 nm² for the CsPW Keggin unit [34], the average numbers of layers calculated for the 5, 20, 40, and 60CsPW-Nb500 catalysts were 0.26, 0.92, 2.11, and 2.77, respectively.

3.1.2. XRD results

The effects of calcination temperature and CsPW loading on the XRD patterns of Nb₂O₅ and the wCsPW-NbT catalysts are shown in Fig. 1. Clear diffraction peaks at $2\theta = 22.6^\circ$, 28.4° , 36.7° , and 46.2° from pseudo-hexagonal Nb₂O₅ crystals (TT phase) were observed for the Nb₂O₅ samples calcined at 400, 500, and 600 °C. The peak at $2\theta = 28.4^\circ$ was split into two peaks when the calcination temperature was increased to 700 °C. This indicated the transformation of the pseudo-hexagonal TT phase to the orthorhombic T phase of Nb₂O₅ during calcination at 700 °C [9,24]. The pseudo-hexagonal TT phase has a lower crystallinity and can be considered to be a modification of the orthorhombic T phase. These observations were consistent with earlier results [7,36].

The effect of CsPW loading (5–60 wt%) on the XRD patterns of the CsPW-Nb500 samples is shown in Fig. 1(8) and (10)–(12). On increasing the CsPW loading from 5 to 60 wt%, the intensities of the diffraction peaks associated with the Keggin structure increased. For 5CsPW-Nb500 and 20CsPW-NbT, no peaks assignable to CsPW were detected, demonstrating that the CsPW species were well dispersed on the Nb₂O₅ support. The 40CsPW-Nb500 and 60CsPW-Nb500 catalysts gave peaks at $2\theta = 10.2^\circ$, 20.6° , 25.3° , 29.4° , and 34.6° , which are attributed to Keggin CsPW.

3.1.3. Catalyst acidity

The NH₃-TPD results (Fig. 2) showed the effect of the calcination temperature and CsPW loading on the acidity of CsPW-Nb samples. The desorption temperature of NH₃ was

Fig. 1. XRD patterns of Nb₂O₅, CsPW, and CsPW-Nb catalysts with different calcination temperatures and CsPW loadings. (1) Nb700; (2) Nb600; (3) Nb500; (4) Nb400; (5) CsPW; (6) 20CsPW-Nb700; (7) 20CsPW-Nb600; (8) 20CsPW-Nb500; (9) 20CsPW-Nb400; (10) 5CsPW-Nb500; (11) 40CsPW-Nb500; (12) 60CsPW-Nb500.

Fig. 2. NH_3 -TPD profiles of Nb_2O_5 , CsPW, and CsPW-Nb catalysts. (1) Nb700; (2) Nb600; (3) Nb500; (4) Nb400; (5) CsPW; (6) 20CsPW-Nb700; (7) 20CsPW-Nb600; (8) 20CsPW-Nb500; (9) 20CsPW-Nb400; (10) 5CsPW-Nb500; (11) 40CsPW-Nb500; (12) 60CsPW-Nb500.

used to classify the acid sites into weak (150–300 °C), medium (300–500 °C), and strong (500–700 °C) sites [37]. Figure 2 shows the TPD profiles of 20CsPW-NbT and Nb_2O_5 calcined at 400–700 °C. All the NH_3 -TPD profiles displayed one or more wide peaks from 100 °C to approximately 600 °C, showing a broad distribution of weak acid sites on Nb_2O_5 and medium acid sites on 20CsPW-NbT. The acid strengths of the Nb_2O_5 samples in Fig. 2(1)–(4) were similar to those for Nb_2O_5 calcined at comparable temperatures obtained by Tang et al. [36]. Compared with Nb_2O_5 , a larger amount of acid sites was observed on 20CsPW-NbT. A comparison of 20CsPW-Nb500 and 20CsPW-Nb400 in Fig. 2(8) and (9) shows that the increase in the calcination temperature increased the fraction of medium acid sites. When the calcination temperature was further increased, the total amount of acid sites decreased on 20CsPW-Nb600/700. The weak acid sites of 20CsPW-Nb700 (Fig. 2(6)) were attributed to supported WO_3 , resulting from CsPW decomposition at high calcination temperature; similar desorption peaks were observed over WO_3/ZrO_2 and WO_3/TiO_2 by Ulgen et al. [15,38].

The NH_3 -TPD profiles of CsPW-Nb500 catalysts with different CsPW loadings are shown in Fig. 2(10)–(12). The results showed that the amount of acid sites on CsPW-Nb500 increased with increasing CsPW loading, and the 40/60CsPW-Nb500 catalysts showed a strong acid peak at 600 °C.

3.1.4. Raman results

Figure 3 shows the effect of calcination temperature on the Raman spectra of the 20CsPW-NbT catalysts. The CsPW sample showed Raman bands at 216, 233, and 1010 cm^{-1} . These peaks are assigned to the Keggin structure of the $\text{PW}_{12}\text{O}_{40}^{3-}$ anion [22,39]. The band at 216 cm^{-1} is attributed to $\nu_s(\text{W}-\text{O}_\mu)$ (O_μ is

Fig. 3. Raman spectra of CsPW and 20CsPW-NbT catalysts with different calcination temperatures. (1) CsPW; (2) 20CsPW-Nb700; (3) 20CsPW-Nb600; (4) 20CsPW-Nb500; 20CsPW-Nb400.

bridging oxygen or μ -oxo) [40]. Band at 1010 cm^{-1} is characteristic of phosphotungstate with a Keggin structure attributed to $\text{W}=\text{O}_t$ (O_t is terminal oxygen) in the Keggin anions of CsPW. This band shifted to 996 cm^{-1} for 20CsPW-NbT as a result of bond weakening after loading on the Nb_2O_5 support, as discussed by Chai et al. [9].

Raman bands associated with WO_3 species were not detected for the samples calcined at 400–500 °C, indicating that the 20CsPW-Nb400/500 catalysts retained the Keggin structure of phosphotungstate. However, the other samples calcined at higher temperature (especially 700 °C) showed a band for WO_3 at 847 cm^{-1} [41], indicating that CsPW partly decomposed to WO_3 , which agrees well with the NH_3 -TPD result. It has been reported that the decomposition temperature of CsPW is 600 °C [23].

3.2. Glycerol dehydration on CsPW-Nb

Table 1 lists the results of glycerol dehydration at time on stream (TOS) of 10–11 h over CsPW-Nb, Nb_2O_5 , and CsPW. The product distribution over all the catalysts did not change much during the reaction after the initial period, i.e., TOS < 2–3 h. The types of byproducts from all the catalysts were similar. Acetol, allyl alcohol, and acetaldehyde from glycerol dehydration and subsequent decarboxylation were the main byproducts [42–44]. The dehydration of glycerol over all the CsPW-Nb catalysts showed an induction period before reaching a steady selectivity for acrolein.

After reaction for 11 h, the CsPW catalyst had 8.9 wt% coke and the glycerol conversion decreased from 100% to 41% because of its strong acid sites. Supporting CsPW on Nb_2O_5 significantly increased the glycerol conversion and acrolein selectivity and decreased coke deposition. The best catalyst, 20CsPW-Nb500, gave 96% glycerol conversion and 80% selectivity for acrolein at 10 h with only 2.6 wt% coke. Improved catalytic performance was achieved by tuning the acidity. The strong acid sites on CsPW were converted to selective medium ones [45]. As shown in Fig. 2, 20CsPW-NbT mainly showed desorption peak at 400–500 °C for medium acid sites, compared with

CsPW and Nb₂O₅.

3.3. Effect of catalyst preparation parameters on catalytic performance

3.3.1. Effect of calcination temperature

The conversions and selectivities at TOS = 10–11 h over Nb₂O₅ and 20CsPW-NbT with different calcination temperatures are shown in Fig. 4. The 20CsPW-NbT catalysts gave much higher glycerol conversions and selectivities for acrolein than the bare Nb₂O₅ catalyst did for all calcination temperatures. The 20CsPW-Nb400 gave the maximum glycerol conversion (100% at TOS = 2–3 h) and 66% acrolein selectivity. However, it was the catalyst 20CsPW-Nb500 that showed the highest selectivity for acrolein (80% at TOS = 10–11 h). Increasing the catalyst calcination temperature to 600 °C decreased the acrolein selectivity to 60%–65%, with a small decrease in glycerol conversion to 91%–93%. A further increase in the catalyst calcination temperature to 700 °C decreased the glycerol conversion by 13% and the acrolein selectivity by 15%–19% relative to its 20CsPW-Nb500 counterpart; this was the result of decomposition of CsPW to WO₃ in Fig. 3(2) and a decrease in the number of medium acid sites in Fig. 2(6). For the Nb₂O₅ catalysts, Nb400 and Nb500 were better than Nb600 and Nb700 in terms of activity. Deactivation was observed for all the Nb₂O₅ catalysts, and Nb700 showed only 32% conversion after 10–11 h.

The catalytic performance of Nb₂O₅ was significantly affected by the calcination temperature, which changed the surface acidity and crystallization of Nb₂O₅. The splitting of the peak at $2\theta = 28.4^\circ$ in Fig. 1 indicated a transformation of the pseudo-hexagonal TT phase to the orthorhombic T phase of Nb₂O₅.

Fig. 4. Effects of CsPW modification and calcination temperature of 20CsPW-NbT catalyst on glycerol conversion (a) and acrolein selectivity (b) at TOS = 10–11 h.

during calcination at 700 °C [24]. Furthermore, an increase in the calcination temperature resulted in a decrease in the amount of acid sites on Nb₂O₅, as shown in Fig. 2, probably by transformation of Nb₂O₅ crystallites. The CsPW-Nb catalysts showed better thermal stabilities than their Nb₂O₅ counterparts. Loading on Nb₂O₅ helped to retain the CsPW Keggin structure and medium acid sites until it was partially decomposed to WO₃ at 700 °C. The CsPW-Nb catalyst can therefore be regenerated by a simple treatment at a relatively high temperature, e.g., 500 °C, if necessary.

3.3.2. Effect of CsPW loading

The active component loading is an important factor in catalytic performance [13,35,37,44]. Figure 5 shows the effect of CsPW loading on the catalytic performance of CsPW-Nb500. In the first 2–3 h, all the tested catalysts had high catalytic activities, with glycerol conversion close to 100% (Table 1) and the selectivity for acrolein in the first 2–3 h increased from 30% to 89% when the CsPW loading was increased from 0% to 60%, and pure CsPW showed 94% acrolein selectivity. The 20CsPW-Nb500 catalyst exhibited the highest catalytic performance for a long run time. The yield of acrolein over 20CsPW-Nb500 increased to 76.8% (96% glycerol conversion and 80% acrolein selectivity), and there was no significant deactivation within 10 h. The catalytic performance became worse, and more coke deposition was found after reaction for 10 h when the CsPW loading was above 40%. Significant deactivation was observed at TOS = 10–11 h over 40CsPW-Nb500 and 60CsPW-Nb500 (Fig. 5) and pure CsPW (Table 1), resulting in 10%–60% decreases in glycerol conversion and 20%–40% decreases in selectivity for acrolein, depending on the CsPW loading. At the same time, the coke amount increased from 3.4 wt% on 5CsPW-Nb500 to 6.1 wt% on 60CsPW-Nb500.

Layer thickening or aggregation of CsPW increased with increasing CsPW loading. The theoretical numbers of layers for the 5, 20, 40, and 60CsPW-Nb500 catalysts were 0.26, 0.92, 2.11, and 2.77, respectively. This suggested that the best catalyst, 20CsPW-Nb500, had approximately a monolayer of CsPW. The bulk CsPW peaks appeared in the XRD pattern of 40CsPW-Nb500, and their intensities increased for 60CsPW-Nb500 because of the multiplicity of the CsPW layers or aggregation of

Fig. 5. Effect of CsPW loading in wCsPW-Nb500 catalysts on glycerol conversion and acrolein selectivity at TOS = 10–11 h.

CsPW into a bulk form. The catalyst has to be loaded with an appropriate loading to give an approximate monolayer of supported CsPW to achieve high selectivity for acrolein. When the CsPW loading resulted in more than one layer, only the bottom layer of CsPW interacted directly with the support surface, whereas the other layers of CsPW on top had similar properties to those of unsupported CsPW and had strong acidity as shown by the NH_3 -TPD results. This explanation was consistent with the results of Okuhara et al. [23], who calculated the Keggin anion density and reported that CsPW with more than two layers on the surface exhibited the intrinsic acidity of the bulk phase and poor catalytic performance for methanol carbonylation.

When there were multiple layers of CsPW on the support surface, the selectivity for acrolein decreased with increasing CsPW loading. This was attributed to the increases in side reactions and coke formation. The product was probably strongly adsorbed on the strong acid sites of the bulk CsPW, and oligomerization to form a coke precursor would occur, as shown in Fig. 6 similar phenomenon was reported in the synthesis of 5,8-dimethyl- α -tetralone from *p*-xylene with γ -butyrolactone [35].

3.4. Catalyst thermal stability and regeneration

Although the 20CsPW-Nb500 catalyst was stable for at least 10 h of reaction, a 20% decrease in activity was observed after 120 h. A regeneration step was therefore still necessary, and it was important to determine whether the thermal stability of the catalyst was high enough for regeneration by burning off the coke formed on the catalyst. After 120 h, the reaction flow was switched to an air flow of 70 mL/min, and the reactor temperature was increased to 500 °C and maintained for 3 h to regenerate the catalyst. The catalyst was then cooled to the

Fig. 6. Comparison of reaction routes for 20CsPW-Nb500 (a) and 60CsPW-Nb500 (b).

Fig. 7. Evolution of glycerol conversion (1) and acrolein selectivity (2) as a function of time at 300 °C before and after in situ regeneration at 500 °C for 3 h.

reaction temperature, and the reactant flow was reintroduced into the reactor. The glycerol conversions and acrolein selectivities before and after regeneration are shown in Fig. 7. It can be seen that the catalytic activity was completely recovered by the heat treatment, and there was a similar initial period of selectivity increase and a similar deactivation behavior. This result suggested that coke formation was the main reason for catalyst deactivation during the dehydration of glycerol.

The FT-IR spectra of the fresh and regenerated 20CsPW-Nb500 catalysts are shown in Fig. 8. For 20CsPW-Nb500, the main bands at 1090, 992, 890, and 801 cm^{-1} appeared. The band at 992 cm^{-1} was assigned to the $\text{W}=\text{O}$ group interacting with Cs^+ and H_3O^+ ions, that at 890 cm^{-1} to the $\nu(\text{W}-\text{O}_c-\text{W})$ mode, and that at 801 cm^{-1} to $\nu(\text{W}-\text{O}_b-\text{W})$ [20,29,39]. The latter two bands are characteristic of phosphotungstate with the Keggin structure. The very similar FT-IR spectra of the fresh and regenerated catalysts showed that the structure of the regenerated catalyst was the same as that of the fresh one. This result further confirmed that the 20CsPW-Nb500 catalyst had high stability and could be regenerated.

Fig. 8. FT-IR spectra of fresh (1) and regenerated (2) 20CsPW-Nb500 catalysts.

Graphical Abstract

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Highly selective and stable CsPW/Nb₂O₅ catalysts for dehydration of glycerol to acrolein

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A new catalyst, Cs_{2.5}H_{0.5}PW₁₂O₄₀/Nb₂O₅, was prepared for the selective dehydration of glycerol to acrolein. The best catalyst, with 20 wt% Cs_{2.5}H_{0.5}PW₁₂O₄₀ loading and a calcination temperature of 500 °C, gave a 76% yield of acrolein and showed no significant deactivation within 10 h.

4. Conclusions

Cs_{2.5}H_{0.5}PW₁₂O₄₀ (CsPW) supported on Nb₂O₅ was an effective catalyst for the gas-phase dehydration of glycerol to acrolein. The CsPW-Nb catalyst achieved improved selectivity and stability compared with pure Nb₂O₅ and CsPW. Loading on Nb₂O₅ converted the strong acid sites of bulk CsPW to medium acid sites, which were effective catalytic sites for selective dehydration of glycerol to acrolein. The 20CsPW-Nb500 catalyst prepared with a calcination temperature of 500 °C and CsPW loading of 20 wt% was the best catalyst and gave a high acrolein selectivity of 80% and a glycerol conversion of 96%. The effects of calcination temperature and CsPW loading were discussed based on the characterization results and reaction data. In addition, Nb₂O₅ helped to retain the CsPW Keggin structure and medium acid sites at high temperatures. The CsPW/Nb₂O₅ catalysts can therefore be regenerated by simple coke burning with air at 500 °C.

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References

- [1] Xia S X, Zheng L P, Nie R F, Chen P, Lou H, Hou Z Y. *Chin J Catal* (夏水鑫, 郑丽萍, 聂仁峰, 陈平, 楼辉, 侯昭胤. 催化学报), 2013, 34: 986
- [2] Hu J Y, Liu X Y, Wang B, Pei Y, Qiao M H, Fan K N. *Chin J Catal* (胡基业, 刘晓钰, 王彬, 裴燕, 乔明华, 范康年. 催化学报), 2012, 33: 1266
- [3] Hu J Y, Liu X Y, Fan Y Q, Xie S H, Pei Y, Qiao M H, Fan K N, Zhang X X, Zong B N. *Chin J Catal* (胡基业, 刘晓钰, 范义秋, 谢颂海, 裴燕, 乔明华, 范康年, 张晓昕, 宗保宁. 催化学报), 2013, 34: 1020
- [4] Katryniok B, Paul S, Belliere-Baca V, Rey P, Dumeignil F. *Green Chem*, 2010, 12: 2079
- [5] Ma J P, Yu W Q, Wang M, Jia X Q, Lu F, Xu J. *Chin J Catal* (马继平, 于维强, 王敏, 贾秀全, 路芳, 徐杰. 催化学报), 2013, 34: 492
- [6] Chai S H, Wang H P, Liang Y, Xu B Q. *Green Chem*, 2007, 9: 1130
- [7] Chai S H, Wang H P, Liang Y, Xu B Q. *J Catal*, 2007, 250: 342
- [8] Chai S H, Wang H P, Liang Y, Xu B Q. *Green Chemistry*, 2008, 10: 1087
- [9] Chai S H, Wang H P, Liang Y, Xu B Q. *Appl Catal A*, 2009, 353: 213
- [10] Shiju N R, Brown D R, Wilson K, Rothenberg G. *Top Catal*, 2010, 53: 1217
- [11] Tao L Z, Yan B, Liang Y, Xu B Q. *Green Chem*, 2013, 15: 696
- [12] Gu Y L, Liu S Z, Li C Y, Cui Q K. *J Catal*, 2013, 301: 93
- [13] Ning L L, Ding Y J, Chen W M, Gong L F, Lin R H, Lü Y, Xin Q. *Chin J Catal* (宁丽丽, 丁云杰, 陈维苗, 龚磊峰, 林荣和, 吕元, 辛勤. 催化学报), 2008, 29: 212
- [14] Yang L, Joo J B, Kim Y J, Oh S, Kim N D, Yi J. *Korean J Chem Eng*, 2008, 25: 1014
- [15] Ulgen A, Hoelderich W. *Catal Lett*, 2009, 131: 122
- [16] Kim Y T, Jung K D, Park E D. *Appl Catal A*, 2011, 393: 275
- [17] Cavani F, Guidetti S, Marinelli L, Piccinini M, Ghedini E, Signoretto M. *Appl Catal B*, 2010, 100: 197
- [18] Kim Y T, Jung K D, Park E D. *Appl Catal B*, 2011, 107: 177
- [19] Alhanash A, Kozhevnikova E F, Kozhevnikov I V. *Appl Catal A*, 2010, 378: 11
- [20] Misono M. *Chem Commun*, 2001: 1141
- [21] Haider M H, Dummer N F, Zhang D, Miedziak P, Davies T E, Taylor S H, Willock D J, Knight D W, Chadwick D, Hutchings G J. *J Catal*, 2012, 286: 206
- [22] Gao R H, Chen H, Le Y Y, Dai W L, Fan K N. *Appl Catal A*, 2009, 352: 61
- [23] Okuhara T, Watanabe H, Nishimura T, Inumaru K, Misono M. *Chem Mater*, 2000, 12: 2230
- [24] Tanabe K, Okazaki S. *Appl Catal A*, 1995, 133: 191
- [25] Lauriol-Garbay P, Postole G, Lorient S, Auroux A, Belliere-Baca V, Rey P, Millet J M M. *Appl Catal B*, 2011, 106: 94
- [26] Massa M, Andersson A, Finocchio E, Busca G, Lenrick F, Wallenberg L R. *J Catal*, 2013, 297: 93
- [27] Nowak I, Ziolk M. *Chem Rev*, 1999: 3603
- [28] Omata K, Izumi S, Murayama T, Ueda W. *Catal Today*, 2013, 201: 7
- [29] Pizzio L R, Cáceres C V, Blanco M N. *Appl Catal A*, 1998, 167: 283
- [30] Jehng J M, Wachs I E. *ACS Symposium Series*, 1995, 133: 191
- [31] Ristic M, Popovic S, Music S. *Mater Lett*, 2004, 58: 2658
- [32] Lu S F, Wang D L, Jiang S P, Xiang Y, Lu J L, Zeng J. *Adv Mater*, 2010, 22: 971
- [33] Izumi Y, Ono M, Kitagawa M, Yoshida M, Urabe K. *Microporous Mater*, 1995, 5: 255
- [34] Alsalm A M, Wiper P V, Khimyak Y Z, Kozhevnikova E F, Kozhevnikov I V. *J Catal*, 2010, 276: 181
- [35] Kamiya Y, Okuhara T, Misono M, Miyaji A, Tsuji K, Nakajo T. *Catal Surv from Asia*, 2008, 12: 101
- [36] Tang Z C, Yu D H, Sun P, Li H, Huang H. *Bull Korean Chem Soc*, 2010, 31: 3679
- [37] Shen L Q, Feng Y H, Yin H B, Wang A L, Yu L B, Jiang T S, Shen Y T,

- Wu Z A. *J Ind Eng Chem*, 2011, 17: 484
- [38] Ulgen A, Hoelderich W F. *Appl Catal A*, 2011, 400: 34
- [39] Devassy B M, Halligudi S B. *J Mol Cat A*, 2006, 253: 8
- [40] Thouvenot R, Fournier M, Franck R, Rocchiccioli-Deltcheff C. *Inorg Chem*, 1984, 23: 598
- [41] Martin C, Solana G, Malet P, Rives V. *Catal Today*, 2003, 78: 365
- [42] Atia H, Armbruster U, Martin A. *Appl Catal A*, 2011, 393: 331
- [43] de Oliveira A S, Vasconcelos S J S, de Sousa J R, de Sousa F F, Filho J M, Oliveira A C. *Chem Eng J*, 2011, 168: 765
- [44] Lauriol-Garbey P, Millet J M M, Lorient S, Belliere-Baca V, Rey P. *J Catal*, 2011, 281: 3612
- [45] Gu Y L, Liu S Z, Li C Y, Cui Q K. *J Catal*, 2013, 301: 93

高选择性和稳定性的CsPW/Nb₂O₅催化剂用于甘油脱水制备丙烯醛

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摘要: 以磷钨酸铯盐Cs_{2.5}H_{0.5}PW₁₂O₄₀(CsPW)为活性组分, 负载到Nb₂O₅载体上, 并用于甘油脱水制备丙烯醛的反应中. 通过调节焙烧温度(400–700 °C)以及活性组分负载量(5–60 wt%), 对催化剂酸性进行调节. CsPW负载量为20 wt%, 500 °C焙烧的CsPW/Nb₂O₅催化剂性能最佳, 甘油转化率为96%, 丙烯醛选择性为80%, 反应10 h内没有失活现象, 并且该催化剂具有良好的热稳定性, 可通过烧炭进行再生.

关键词: 甘油脱水; 丙烯醛; 五氧化二铌; 磷钨酸铯盐

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