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Catalytic amination of glycerol with dimethylamine over different type ofheteropolyacid/Zr-MCM-41 catalysts



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ABSTRACT

The effect of different type of heteropolyacid/Zr-MCM-41 catalysts on the catalytic amination of glycerol with dimethylamine to produce Dimethylamino-3-propanal was researched. Under the premise of their respective optimum loading amount, the specific surface area, pore volume and pore size of the H₆P₂W₁₈O₆₂/Zr-MCM-41(Cat-2) were higher than those of the H₃PW₁₂O₄₀/Zr-MCM-41(Cat-1). Cat-1 exhibited more total acidity than that of Cat-2, which resulted in the higher glycerol conversion of Cat-1 at the beginning of the reaction, but the coke deposited on Cat-1 was more than that of Cat-2. The amount of Brønsted acid sites and ratio of B/(B + L) on Cat-2 were higher than that of Cat-1. Therefore, the catalytic stability, selectivity and yield of Dimethylamino-3propanal of Cat-2 were higher than those of Cat-1, which proved that the Brønsted acid sites are good for the catalytic amination of glycerol with dimethylamine to produce Dimethylamino-3-propanal. The leaching ratio of Cat-2 is slightly more than that of Cat-1, because H₆P₂W₁₈O₆₂ is more hydrophilic than H₃PW₁₂O₄₀. However, the stability of Cat-2 is higher than that of Cat-1, therefore, the main reason for deactivation of catalyst is the formation of carbon deposit during this reaction. And the reaction pathway of catalytic amination of glycerol with dimethylamine was proposed. Furthermore, the reaction temperature, GHSV and the molar ratio of dimethylamine/glycerol were optimized on Cat-2 catalyst. Under the optimum reaction conditions: 300 °C, $H_6P_2W_{18}O_{62}$ loading of 20 wt%, GHSV of 3 h⁻¹, glycerol aqueous concentration of 10 wt%, dimethylamine aqueous concentration of 30 wt%, molar ratio of dimethylamine/glycerol of 2.5, the glycerol conversion, selectivity and yield of Dimethylamino-3-propanal were 95.6%, 80.8% and 77.2%, respectively.

Introduction

Biodiesel is a very significant renewable energy source, which has received increasing attention for the replacement of fossil resources. With the rapid development of biodiesel, a huge quantity of byproduct glycerol is generated. Generally, 10 wt% of glycerol can be generated during the production of biodiesel. Therefore, it is urgent to transform glycerol into valuable chemicals. So many relevant researches have been done, such as dehydration of glycerol to acrolein [1,2], reforming of glycerol to hydrogen [3], hydrogenation of glycerol to 1,2-propanediol [4], oxidation of glycerol to glyceric acid [5], esterification of glycerol to monoacylglycerol [6], and catalytic amination of glycerol to Dimethylamino-2-propanone [7], and so on. In our work, we plan to produce Dimethylamino-3-propanal by catalytic amination of glycerol with dimethylamine. Dimethylamino-3-propanal is a very important amine chemical product, which can be used as surfactants, pharmaceuticals, pesticides, fuel additives, and so on. However, as far as we know, there are few reports about the catalytic amination of glycerol. Safariamin et al. [7] researched the direct amination of glycerol over heteropolyacid-based catalysts. They prepared the $Cs_{2.5}H_{0.5}PMo_{12}O_{40}/$ SiO₂ catalysts with different loadings. The highest yield of Dimethylamino-2-propanone (33%) was observed over the $Cs_{2.5}H_{0.5}PMo_{12}O_{40}/$ SiO₂ catalysts with loading of 50 wt%. However, the specific surface area, pore volume, average pore radius and NH_3 uptake of the catalyst were very low. Therefore, the glycerol conversion and Dimethylamino-2-propanone selectivity were very low, and there is no Dimethylamino-3-propanal produced during the process. The catalytic performance would be further improved.

Heteropolyacid with stable Keggin structure $(H_3PW_{12}O_{40})$ is a strong Brønsted acid and extensively studied in many acid-catalyzed

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reactions [8]. However, little attention has been given to another heteropolyacid with Wells-Dawson structure (H₆P₂W₁₈O₆₂). According to the electrostatic theory, Wells-Dawson type H₆P₂W₁₈O₆₂ possesses stronger Brønsted acid sites compared to the Keggin type H₃PW₁₂O₄₀ [9]. Briand et al. [10] previously gave a detailed introduction about its catalytic properties and applications. The Wells-Dawson type heteropolyacids have super-acidity and excellent stability in the solid phase and in solution [11]. Various acid catalytic reactions are all effective with an appropriate Wells-Dawson type heteropolyacid catalyst, such as esterification [12], synthesis of coumarins [13], synthesis of flavones [14], oxidation of 1,4-dihydropyridine [15], and oxidation of cyclooctene and cyclohexene with hydrogen peroxide [16].

Considering the low surface area of pure bulk heteropolyacid, several acidic or neutral supports including alumina, active carbon, silica, titanium and zirconia have been employed for heteropolyacid [17], which can increase abundant acid sites. Mesoporous material MCM-41 is a versatile support due to its large surface area, large pore size, and high thermal stability [18,19]. However, there is very weak acidity on the pure MCM-41 support, and it is well-known that pure MCM-41 silica is Lewis solid without Brønsted acid sites [20-22]. To improve the acidity of pure silica MCM-41, adding elements into its framework is essential. For example, García-Sancho et al. [23] studied a family of zirconium doped mesoporous silica catalysts in the dehydration of glycerol. The results suggested that Zr doped mesoporous silica catalysts markedly created the Brønsted acid sites on the MCM-41 and the catalysts showed high catalytic performance.

In our work, we research the catalytic amination of glycerol with dimethylamine over different type of heteropolyacid supported on Zr-MCM-41 catalysts, and compare the catalytic amination performance of $H_3PW_{12}O_{40}/Zr$ -MCM-41 (Cat-1) and $H_6P_2W_{18}O_{62}/Zr$ -MCM-41(Cat-2). Furthermore, the reaction pathway is also proposed by analysing the results of products distribution and characterization.

Experimental

Catalyst preparation

The MCM-41support was prepared according to our recent report [24]. Firstly, 1.8 g of cetyltrimethylammonium bromide (CTAB) was dissolved in 20 ml of distilled water under stirring. After this, 15 ml of aqueous ammonium was added to the above solution, followed by the addition of 5.3 g of tetraethylorthosilicate (TEOS) dropwise while stirring. The resultant solution was stirred at room temperature for 2 h, and then transferred into a Teflon-lined stainless-steel autoclave, heated under 100 °C for 52 h, and the solution was kept under static conditions in the autoclave. The solid product was filtered, washed with deionized water. The white solid obtained was dried at 100 °C for 12 h. Finally, the MCM-41 material was obtained by calcining at 550 °C for 3 h in air.

The Zr-MCM-41 sample was prepared according to the literature [23,24]. TEOS was used as Si precursor and zirconium-n-propoxide (70% in propanol) as Zr source, together with CTAB as synthesis template. The preparation procedure of a Zr-MCM-41 sample with a molar ratio of Si/Zr = 15 was as follows: firstly, two solutions were prepared: the first solution was prepared by adding 3.0 ml of zirconium-n-propoxide (70% in propanol) and 22.8 ml of TEOS while stirring; the second solution was made by adding 12.2 g of CTAB into 110 ml water under stirring, followed by the addition of 110 ml of aqueous NH₃ (28 wt%). Then, the first solution was added into the second solution dropwise. The resultant solution was vigorously stirred for about 2 h, until a gel was formed. The resultant gel was transferred into a Teflon-lined stainless-steel autoclave without stirring and heated at 100 °C for 50 h. After cooling to room temperature, the solid product was filtered and washed with deionized water. The white solid obtained was dried in air at 80 °C for 12 h. Finally, the sample was calcined at 550 °C for 3 h in air.

Molecular Catalysis 457 (2018) 51-58

Wells-Dawson type H₆P₂W₁₈O₆₂ was prepared according to the literatures with some modifications [25,26]. 15 g of Na₂WO₄·2H₂O was dissolved in 35 ml of hot water under stirring, afterward 12.5 ml of an aqueous solution of H₃PO₄(85%) was added while vigorous stirring. After 30 min, the resultant solution was sealed in a Teflon-lined autoclave and heated at 140 °C for 6 h, and the resultant solution was kept under static conditions in the Teflon-lined autoclave. Then, the autoclave was cooled to room temperature. 15 ml of concentrated HCl (37%) was added to the above solution. After this, it was extracted with the same volume of diethyl ether. The yellow powder was obtained by evaporating ether, and then dried at 120 °C for 8 h.

The H₃PW₁₂O₄₀/Zr-MCM-41 (Cat-1) and H₆P₂W₁₈O₆₂/Zr-MCM-41 (Cat-2) catalysts were synthesized both using wet impregnation method. 1 g of MCM-41 was dispersed in 20 ml of deionized water under constant stirring. Then, a calculated amount of H₃PW₁₂O₄₀ or H₆P₂W₁₈O₆₂ was added with vigorous stirring. The suspension was stirred for 4h at room temperature, and then evaporated to dryness. The resulting solid was dried in an oven at 120 °C for 8 h and then calcined in air at 300 °C for 3 h. Finally, the Cat-1 and Cat-2 catalysts with different heteropolyacid loading amounts (2, 4, 8, 12, 16, 20, 24, 28, 30, 32, 36 and 40 wt%) were obtained.

Catalyst characterization

X-ray powder diffraction (XRD) analysis was recorded on a Shimadzu XRD-6000 using Cu K α radiation ($\lambda = 1.5405$ Å) with the second monochromator at 45 kV and 40 mA with a scanning speed of 2° in 2θ /min. FTIR spectra of the samples were performed on a Nexus 670 IR spectrometer in the range of $4000-400 \text{ cm}^{-1}$ at a resolution of 4 cm⁻¹. Each spectrum was average over 128 scans. The specific surface area, pore size and pore volume of the samples were obtained by nitrogen adsorption-desorption isotherm using a Micromeritics ASAP 2020 instrument. The specific surface area was calculated by the BET method. The total pore volume was determined by N2 adsorption at a relative pressure of 0.99, and the pore diameter was obtained from the desorption isotherm by the BJH method. Ammonia temperature-programmed desorption (NH3-TPD) profiles were obtained by Builder PCA-1200, and the amount of acid sites was calculated by quantifying the desorbed NH₃ from NH₃-TPD. Infrared spectroscopy (FT-IR) after pyridine adsorption experiments were performed using a Shimadzu FTIR-8700 spectrometer. The amount of Brønsted and Lewis acid sites determined from the intensities of the IR bands at 1540 and 1445 cm⁻¹ for adsorbed pyridine using Emeis' method [27]. The equations are as follows:

C(pyridine on B sites) = $1.88 \text{ IA(B) } \text{R}^2/\text{W};$

 $C(pyridine on L sites) = 1.42 IA(L) R^2/W;$

C = concentration (mmol/g catalyst);

IA(B, L) = integrated absorbance of B or L band (cm⁻¹);

- R = radius of catalyst disk (cm);
- W = weight of disk (mg).

The contact angles of water in air on the catalysts were measured using a Krüss DSA100 instrument. Before measurement, the powder sample was compressed into a disk with a thickness of approximately 1 mm (ca. 2 MPa). A drop of water(1 µL) was injected on the sample disk. The appearance of the water drop was recorded at ca. 0.1 s with a digital camera. The contact angle was determined by a photogoniometric method. W elemental content analysis was analyzed by means of inductively coupled plasma (ICP). The carbon content in the spent catalysts was analyzed for elemental analysis by using a CHNS analyzer (Vario EL III).

The Keggin type H₃PW₁₂O₄₀ was obtained from Sigma-Aldrich.

Catalytic reaction

The catalytic activity was evaluated at atmospheric pressure in a vertical fixed-bed reactor (50 cm length, 8 mm i.d.) using 0.5 g of catalyst. The catalyst was ground and sieved to sizes between 20 and 40 mesh and placed in the middle part of the reactor, with quartz particles packed at both ends. The reaction temperature was monitored by a thermocouple which was placed near the catalyst bed. Before reaction, the samples were pretreated at 120 °C under nitrogen flow (40 mL/min) for about 1 h to remove adsorbed water. The 10 wt% glycerol aqueous solution and 30 wt% dimethylamine (DMA) aqueous solution were firstly introduced into a vaporizer by two HPLC pumps at a certain proportion. Then the mixture was introduced from the top of the reactor at a certain flow rate under nitrogen atmosphere. The reaction carried out under a given temperature. A small part of the reaction products were used for On-line Analysis, and the left products were collected in a conical flask cooled in a water-ice mixture.

The products were analyzed by a SP 6890 gas chromatograph (GC) equipped with a flame ionization detector (FID) and HP-INNOWAX capillary column(60 m \times 0.32 mm \times 0.25 µm) using methanol as internal standard. And the chromatograph is equipped with an on-line analysis device, which can prevent the product from being oxidized by air. 0.5 ml samples are injected hourly into the chromatograph. The column oven was maintained at 40 °C for 2 min. The column was operated from 40 to 100 °C with a ramping rate of 20 °C/min, and kept at 100 °C for 2 min. And then the column was operated from 100 to 180 °C with a ramping rate of 20 °C/min, and kept at 180 °C for 2 min. Finally, the column was operated from 180 to 280 °C with a ramping rate of 20 °C/min, and then kept at 280 °C for 2 min. Glycerol conversion and product selectivity were quantified as follows:

Glycerol conversion (%) = (Moles of glycerol reacted/Moles of glycerol in the feed) $\times ~100$

Product selectivity (%) = (Moles of carbon in a product formed/Moles of carbon in glycerol consumed) \times 100

Results and discussion

Catalyst characterization

Fig. 1 presents the FT-IR spectra of the Zr-MCM-41, $H_3PW_{12}O_{40}$, Cat-1, $H_6P_2W_{18}O_{62}$ and Cat-2. On the Zr-MCM-41, the band around 1300–1000 cm⁻¹ is attributed to an asymmetric stretching mode of Si–O–Si. Moreover, the bands at 791 and 450 cm⁻¹ are ascribed to the symmetric stretching vibration and bending vibration of the rocking mode of Si–O–Si, respectively. The band at 960 cm⁻¹ is due to the



symmetric stretching vibration of Si-OH [28]. The Keggin type $H_3PW_{12}O_{40}$ shows several strong bands at 1080 cm⁻¹ (P–O), 985 cm⁻¹ (W=O), 889cm⁻¹, 804 cm⁻¹ (W-O-W), and one weak band at 523 cm⁻¹ (W–O–P) [29–34]. For the Cat-1, the characteristic bands of the Keggin ion are observed clearly, indicating the presence of H₃PW₁₂O₄₀ on the support. However, addition of H₃PW₁₂O₄₀ on Zr-MCM-41 reduces the intensity of these characteristic vibration bands and some of these bands overlap with that of the Zr-MCM-41 support. Four characterization bands of Wells-Dawson type anion at 1091, 963, 914, 782 cm⁻¹, which can be assigned to P–O, W=O, W–O_b–W, and W-O_c-W vibrations respectively [35]. For the Cat-2 catalyst, the corresponding characterization bands of Wells-Dawson anion are obviously noticed, suggesting that H₆P₂W₁₈O₆₂ is incorporated in the mesoporous molecular sieves. However, a decrease of the intensity of these characteristic vibration bands is found. In addition, some of these bands overlap with that of the Zr-MCM-41.

Fig. 2(A) displays the low-angle XRD patterns of the samples. The patterns consist of a very strong peak along with two weak peaks for all samples, which accord with a well ordered hexagonal mesoporous structure [36,37]. However, it is observed that when an amount of zirconium and heteropolyacid is incorporated into the Si-MCM-41 framework, intensities of the XRD peaks gradually become weaker. This suggests that the mesoporous structure of MCM-41 supports remains almost unchanged but the long-range order is decreased noticeably. According to the high-angle XRD patterns of the materials (Fig. 2(B)), for H₃PW₁₂O₄₀, many intense diffraction peaks particularly at about 20, 26.7 and 29.6° are clearly found between $2\theta = 10$ and 90°. For H₆P₂W₁₈O₆₂, several intense diffraction peaks especially at about 18.4, 24.6 and 27.2° are observed. Compared to bulk heteropolyacid, the supported catalysts show only a broad peak in the range of $2\theta = 15-40^{\circ}$ corresponding to the formation of an amorphous phase, indicating that heteropolyacid is finely dispersed on Zr-MCM-41.

The results of nitrogen adsorption-desorption of MCM-41, Zr-MCM-41, Cat-1 and Cat-2 samples are shown in Table 1. The surface area of MCM-41 is $1013 \text{ m}^2/\text{g}$. After addition of zirconium, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$, the surface area of these samples decreases continuously to 843 (for Zr-MCM-41), 710 (for Cat-1) and 745 m^2/g (for Cat-2). Compared with the MCM-41, the specific surface area, pore volume and pore size with zirconium and heteropolyacid loading catalysts are significantly decreased, indicating that the zirconium and heteropolyacid are either deposited on the external surface, or being introduced in the porosity, filling the pores of the mesoporous MCM-41 support. However, the catalysts still retain uniform mesoporous systems, which are well in accordance with the XRD results.

The temperature-programmed desorption profiles were collected using NH₃ as a probe molecule, and we deconvoluted the NH₃-TPD spectra of catalysts, as shown in Fig. 3. The amount of acid sites are summarized in Table 1. It is generally accepted that the acid strength depends on the ammonia desorption temperature: weak (100-200 °C), medium (200-400 °C) and strong (> 400 °C) [38]. It is obvious that MCM-41 has almost no TPD signal, which is in agreement with the results reported by the research team led by Zheng [30,39-42] and Sancho et al. [43], indicating the pure MCM-41 did not have obvious acidity. On the other hand, Zr-MCM-41 exhibits two peaks of NH₃-TPD at 190 °C and 230 °C, which are attributed to the weak and medium acid site, respectively. When the H₃PW₁₂O₄₀ and H₆P₂W₁₈O₆₂ are supported on the Zr-MCM-41, both of NH₃-TPD temperatures shift right, indicating that the strength of weak and medium acid sites are enhanced. The amount of weak, medium acid sites and total acidities of the catalysts are in an order of Cat-1 > Cat-2 > Zr-MCM-41. Both of NH₃-TPD temperatures of Cat-1 are higher than those of Cat-2, indicating that the acid strength of Cat-1 is stronger than that of Cat-2.

Fig. 4 exhibits the FTIR spectra of pyridine adsorption of the samples. Cat-1, Cat-2 and Zr-MCM-41 catalysts contain Brønsted and Lewis acid sites, as indicated by the adsorption peaks at about 1538 cm^{-1} and 1445 cm^{-1} , respectively [44]. Furthermore, the peak at about



Fig. 2. (A) Low-angle XRD diffraction patterns of MCM-41, Zr-MCM-41, Cat-1 and Cat-2; (B) High-angle XRD diffraction patterns of $H_3PW_{12}O_{40}$, $H_6P_2W_{18}O_{62}$, Cat-1 and Cat-2. Cat-1: $H_3PW_{12}O_{40}$ loading of 30 wt%, Cat-2: $H_6P_2W_{18}O_{62}$ loading of 20 wt%.

1490 cm⁻¹ is attributed to both Brønsted and Lewis acid sites. The concentration of Brønsted and Lewis acid sites are reported in Table 1.

There is only Lewis acid site detected on the MCM-41. It is wellknown that pure MCM-41 silica is Lewis solid without Brønsted acid sites [20-22], and the acidity is very weak, it is almost impossible to detect the NH₃-TPD peak on the MCM-41. The Brønsted acid sites in Zr-MCM-41 catalyst detected are due to the presence of atoms of Zr replaced the Si ones [45]. The generation of these Brønsted acid sites is associated with the changes in electron density on Si, due to charge imbalance or difference of electronegativity, resulting from introduction of Zr atom in the vicinity of the Si-OH, weakens the Si-OH bond [43,46]. It can be seen from Table 1 that the loading of heteropolyacid results in a noticeable increase in the Brønsted and Lewis acid sites on Cat-1 and Cat-2, and the amount of Lewis acid sites on the Cat-1 is higher than that of the Cat-2, while the amount of Brønsted acid sites on Cat-2 is higher than that of the Cat-1. According to relevant reference [47,48], the Brønsted acid sites were increased due to the presence of small clusters of heteropolyacid, which is a kind of natural protonic acid, and the Lewis acid sites could be due to the interaction between heteropolyacid with Zr-MCM-41 support, which creates the ionic group of $[Zr-MCM-41 - OH_2^+]$. The possible interaction is shown as follows:

 $\begin{aligned} & \text{Zr-MCM-41} - \text{OH} \ + \ \text{H}_3\text{PW}_{12}\text{O}_{40}/\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62} \rightarrow [\text{Zr-MCM-41} - \text{OH}_2^+] \\ & [\text{H}_2\text{PW}_{12}\text{O}_{40}^-/\text{H}_5\text{P}_2\text{W}_{18}\text{O}_{62}^-] \end{aligned}$

Catalytic amination performance

Fig. 5 exhibits the catalytic behavior of Cat-1 with different $H_3PW_{12}O_{40}$ loadings and Cat-2 with different $H_6P_2W_{18}O_{62}$ loadings. The glycerol conversion gradually increase as adding the $H_3PW_{12}O_{40}$ loading from 2 wt% to 30 wt% on Cat-1. Then, the conversion begin to decrease with increasing of $H_3PW_{12}O_{40}$ loadings after 30 wt%. As increasing the loading of $H_3PW_{12}O_{40}$ phase, the acidity of Cat-1 gradually increases, therefore, the glycerol conversion becomes higher and higher. When the $H_3PW_{12}O_{40}$ loading is more than 30 wt%, excess



Fig. 3. NH₃-TPD spectra of MCM-41, Zr-MCM-41, Cat-1 and Cat-2 catalysts. Cat-1: $H_3PW_{12}O_{40}$ loading of 30 wt%, Cat-2: $H_6P_2W_{18}O_{62}$ loading of 20 wt%.



Fig. 4. Pyridine-adsorption FT-IR spectra of MCM-41, Zr-MCM-41, Cat-1 and Cat-2. Cat-1: $H_3PW_{12}O_{40}$ loading of 30 wt%, Cat-2: $H_6P_2W_{18}O_{62}$ loading of 20 wt%.

Table 1

Physicochemical properties and acidities of MCM-41, Zr-MCM-41, Cat-1 (H₃PW₁₂O₄₀ loading of 30 wt%) and Cat-2 (H₆P₂W₁₈O₆₂ loading of 20 wt%) catalysts.

Catalyst	Surface area (m²/g)	Pore volume (cm ³ /g)	Pore size (nm)	Acidity (mmol NH ₃ /gcat)		Brønsted acidity (µmol/gcat)	Lewis acidity (µmol/gcat)	B/(L + B)	
				Weak	Medium	Strong			
MCM-41 Zr-MCM-41 Cat-1 Cat-2	1013 843 710 745	0.82 0.68 0.51 0.59	3.06 2.86 2.54 2.77	 0.14 0.38 0.18	 0.13 0.41 0.20	 		97.69 94.87 143.75 128.37	 0.53 0.62 0.66



Fig. 5. Effect of amount of $H_3PW_{12}O_{40}$ and $H_6P_2W_{18}O_{62}$ loading on the catalytic performance. Reaction conditions: 300 °C, GHSV of 3 h⁻¹, reaction time 2 h, glycerol aqueous concentration of 10 wt%, DMA aqueous concentration of 30 wt%, molar ratio of DMA/glycerol of 2.5.

 $\rm H_3PW_{12}O_{40}$ phase would agglomerate or superpose in the mesoporous channels, which would result in the decrease of the surface area, pore volume and pore size, and hyperacidity would cause the formation of coke. Therefore, the catalytic performance begins to become weaker and weaker. In our work, we chose the $\rm H_3PW_{12}O_{40}$ loading of 30 wt% on Cat-1. According to the same reason, we chose the $\rm H_6P_2W_{18}O_{62}$ loading of 20 wt% on Cat-2.

The catalytic performance of MCM-41, Zr-MCM-41, Cat-1 and Cat-2 catalysts are shown in Table 2. We can see that the glycerol conversion, D-3 and D-2 selectivity on the Zr-MCM-41 are higher than those of MCM-41, because there is very weak acidity on the MCM-41. At the beginning of the reaction, the order of the glycerol conversion is MCM-41 < Zr-MCM-41 < Cat-2 < Cat-1, it's the same as the order of total amount of acidity on these catalysts. And the order of the D-3 selectivity is MCM-41 < Zr-MCM-41 < Cat-1 < Cat-2, it's the same as the order of amount of Brønsted acid sites on these catalysts (in Table 1). Therefore, we conclude that more amount of acidity is good for the glycerol conversion and the Brønsted acid site is good for formation of D-3.

The catalytic amination performance comparison between Cat-1 and Cat-2 was shown in Fig. 6, and the coke amounts of the catalyst used after 10 h and the W elemental content of the fresh catalyst and catalyst used after 10 h were shown in Table 3. We can see that the glycerol conversion on Cat-1 is higher than that of Cat-2 before 5 h reaction time. However, the glycerol conversion on Cat-2 is higher than that of Cat-2 is higher than that of Cat-1 after 5 h reaction time. During 10 h reaction time, the

 Table 2
 Glycerol conversion and product distribution results over different catalysts.

		Selectivity (%)					
Catalyst	^a C _{gly} (%)	^b D-3	^c D-2	^d HA	^e Ac	^f AD	^g FD
MCM-41	40.3	6.5	5.7	18.3	45.3	15.5	8.7
	(31.5)	(4.7)	(9.1)	(20.5)	(41.6)	(17.3)	(6.8)
Zr-MCM-41	65.8	39.2	34.3	7.8	5.7	8.3	2.2
	(48.7)	(35.9)	(38.9)	(8.1)	(3.4)	(11.7)	(2.0)
Cat-1	98.8	61.5	32.6	2.1	1.7	1.3	0.8
	(67.4)	(59.8)	(34.6)	(2.8)	(0.3)	(2.3)	(0.2)
Cat-2	95.2	80.8	11.4	1.6	3.1	1.8	1.3
	(72.5)	(79.4)	(12.9)	(2.8)	(1.0)	(3.6)	(0.3)

Reaction conditions: 300 °C, GHSV of 3 h⁻¹, reaction time 2 h, H₃PW₁₂O₄₀ loading of 30 wt% (Cat-1), H₆P₂W₁₈O₆₂ loading of 20 wt% (Cat-2), glycerol aqueous concentration of 10 wt%, DMA aqueous concentration of 30 wt%, molar ratio of DMA/glycerol of 2.5. ^aConversion of glycerol; ^bDimethylamino-3-propanal; ^cDimethylamino-2-propanone; ^dHydroxyacetone; ^eAcrolein; ^fAcetaldehyde; ^gFormaldehyde. In brackets, conversion and selectivity after 10 h on stream.



Fig. 6. The catalytic amination performance of Cat-1 and Cat-2 catalysts. Reaction conditions: 300 °C, GHSV of $3 h^{-1}$, $H_3 P W_{12} O_{40}$ loading of 30 wt% (Cat-1), $H_6 P_2 W_{18} O_{62}$ loading of 20 wt% (Cat-2), glycerol aqueous concentration of 10 wt%, DMA aqueous concentration of 30 wt%, molar ratio of DMA/glycerol of 2.5.

Table 3

The leaching ratio and coke over Cat-1 ($H_3PW_{12}O_{40}$ loading of 30 wt%) and Cat-2 ($H_6P_2W_{18}O_{62}$ loading of 20 wt%) catalysts.

Catalysts	W (wt%)	Leaching ratio (%)	Coke (wt%)
Cat-1(fresh)	23.0	-	-
Cat-1 (used)	21.6	6.1	3.2
Cat-2(fresh)	15.2	-	-
Cat-2(used)	14.1	7.3	1.7

glycerol conversion decreased from 98.8% to 67.4% on the Cat-1, however, the glycerol conversion decreased from 95.2% to 72.5% on the Cat-2. The stability of Cat-2 is obviously higher than that of Cat-1. The reason may be that the total amount of acidity on Cat-1 is more than that of Cat-2, which is good for improving the glycerol conversion. However, more acidity results in producing more amount of coke on Cat-1 at the same time. In Table 1, the surface area, pore volume and pore size of the Cat-2 catalyst are larger than those of Cat-1, which would reduce the constraints to the mass transfer and usually improve the performance by facilitating both the access of the reactants to the active sites and the diffusion of reaction products. However, the active sites and pore are easy to be covered by the coke on the Cat-1 catalyst. Therefore, the glycerol conversion on Cat-1 is higher than that of Cat-2 at the beginning of reaction. As the reaction time increasing, the deactivation of Cat-1 is more serious than that of Cat-2. In Table 3, the leaching ratio of W over the used Cat-2 (7.3%) is slightly more than that of Cat-1(6.1%), which may be attributed to that $H_6P_2W_{18}O_{62}$ is more hydrophilic than H₃PW₁₂O₄₀. However, the stability of Cat-2 is higher than that of Cat-1, therefore, the main reason for deactivation of catalyst is the formation of carbon deposit during this reaction.

The hydrophilic/hydrophobic properties of the Cat-1 and Cat-2 catalysts were characterized by the water contact angles measurements. The results were shown in Fig. 7. The contact angle of $H_6P_2W_{18}O_{62}/Zr$ -MCM-41 (23°) is less than that of $H_3PW_{12}O_{40}/Zr$ -MCM-41 (44°), indicating that $H_6P_2W_{18}O_{62}/MCM$ -41 is more hydrophilic than $H_3PW_{12}O_{40}/MCM$ -41.

All kinds of products were shown in Table 4. We can see that the selectivity of Dimethylamino-3-propanal, acrolein, acetaldehyde and formaldehyde on the Cat-2 are higher than those of Cat-1, however, the selectivity of Dimethylamino-2-propanone and hydroxyacetone on the Cat-1 are higher than those of Cat-2 at the same reaction time. According to the results of pyridine-FTIR in Table 1, the Cat-2 exhibits more Brønsted and less Lewis acid sites than those of Cat-1, and the ratio of B/(L + B) on Cat-2 is higher than that of Cat-1. Therefore, we conclude that the Brønsted acid sites are helpful to produce



Dimethylamino-3-propanal, and the Lewis acid sites easily lead to the formation of Dimethylamino-2-propanone. And as the reaction time increasing, the selectivity of Dimethylamino-3-propanal, acrolein and formaldehyde becomes lower and lower on the same catalyst, however, the selectivity of Dimethylamino-2-propanone, hydroxyacetone and acetaldehyde becomes higher and higher. We suggest the reason may be that the Brønsted acid sites are easier to be covered by the coke than the Lewis acid sites.

Reaction pathway of catalytic amination

Based on the above results, the reaction pathway of catalytic amination of glycerol with dimethylamine (DMA) is proposed in Fig. 8. There are two dehydration routes on different types of acid sites. On the Brønsted acid sites, the protonated glycerol is dehydrated to produce 3hydroxypropanal, which can easily convert to acrolein [49,50]. The produced acrolein furtherly reacts with DMA to produce Dimethylamino-3-propanal. The unstable 3-hydroxypropanal can be decomposed to formaldehyde and acetaldehyde, and it also can react directly with DMA to produce Dimethylamino-3-propanal. On the Lewis acid sites, hydroxyacetone is formed through dehydration and deprotonation of the protonated intermediate. Further, methylglyoxal is produced by dehydrogenation of hydroxyacetone. However, the methylglyoxal is unstable, which can be decarbonylated to acetaldehyde [51], and it also can react directly with DMA to produce Dimethylamino-2-propanone. And the acid catalyzed C-C bond cleavage of hydroxyacetone to acetaldehyde and formaldehyde maybe happened at the same time. The 3-hydroxypropanal, acrolein and hydroxyacetone can be converted into the coke under the strong acidic condition [52].

Table 4

The product distribution results over Cat-1 and Cat-2.

Fig. 7. Contact angles of water on (a) Cat-1 and (b) Cat-2. $H_3PW_{12}O_{40}$ loading of 30 wt% (Cat-1), $H_6P_2W_{18}O_{62}$ loading of 20 wt% (Cat-2)



According to the results of Dimethylamino-3-propanal yield in Fig. 6, we know that the catalytic amination performance of Cat-2 is superior to that of Cat-1, so we have investigated the effects of reaction temperature, molar ratio of glycerol/DMA and GHSV of gas mixture on the catalytic amination performance of Cat-2.

Effect of reaction temperature

The effect of reaction temperature on the catalytic amination performance of Cat-2 is shown in Fig. 9. The high reaction temperature is helpful to improve the glycerol conversion, because the catalytic amination of glycerol is a kind of endothermic reaction. Therefore, the glycerol conversion is gradually improved as increasing the reaction temperature. After 300 °C, the trend of increasing conversion slows down as increasing the reaction temperature, and the D-3 selectivity begins to become lower and lower because of the coke and other byproducts formation under higher temperature. Finally, the yield of D-3 begins to decrease after 300 °C reaction temperature.

Effect of GHSV

The effect of GHSV on the catalytic amination performance of Cat-2 is shown in Fig. 10. From the results, it can be clearly seen that the GHSV has a significant impact on the catalytic amination performance. As increasing of GHSV from 1 to $10 h^{-1}$, the glycerol conversion gradually decreases, and the D-3 selectivity gradually increases, simultaneously. We infer the reason maybe that the higher space velocity shortens the residence time for glycerol with the catalysts, and the residence time for by-products of acetaldehyde and formaldehyde with acid sites on the catalyst is also shortened. Therefore, the probability of the coke produced from the acetaldehyde, formaldehyde, 3-hydroxypropanal and acrolein under the strong acidic condition would be

Catalysts	Reaction time (h)	Selectivity (%)						
		Dimethylamino- – 3-propanal	Dimethylamino- – 2-propanone	Hydroxyacetone	Acrolein	Acetaldehyde	Formaldehyde	
Cat-1	1	61.5	32.6	2.1	1.7	1.3	0.8	
	2	61.5	32.8	2.2	1.5	1.4	0.6	
	3	61.3	32.8	2.4	1.4	1.5	0.6	
	4	61.2	33.0	2.4	1.3	1.6	0.5	
	5	61.2	33.1	2.6	1.1	1.6	0.4	
	6	61.1	33.3	2.7	0.7	1.8	0.4	
	7	61.1	33.5	2.7	0.5	1.9	0.3	
	8	60.6	33.8	2.8	0.5	2.0	0.3	
	9	60.2	34.2	2.7	0.4	2.2	0.3	
	10	59.8	34.6	2.8	0.3	2.3	0.2	
Cat-2	1	80.8	11.4	1.6	3.1	1.8	1.3	
	2	80.7	11.6	1.7	2.9	2.0	1.1	
	3	80.5	11.6	1.9	2.6	2.4	1.0	
	4	80.4	11.8	2.0	2.3	2.5	1.0	
	5	80.3	11.8	2.2	2.1	2.8	0.8	
	6	80.3	12.1	2.3	1.8	2.9	0.6	
	7	80.1	12.4	2.4	1.5	3.1	0.5	
	8	79.9	12.6	2.6	1.3	3.1	0.5	
	9	79.6	12.8	2.7	1.0	3.5	0.4	
	10	79.4	12.9	2.8	1.0	3.6	0.3	

Reaction conditions: 300 °C, GHSV of 3 h⁻¹, H₃PW₁₂O₄₀ loading of 30 wt% (Cat-1), H₆P₂W₁₈O₆₂ loading of 20 wt% (Cat-2), glycerol aqueous concentration of 10 wt %, DMA aqueous concentration of 30 wt%, molar ratio of DMA/glycerol of 2.5.



Fig. 8. Proposed reaction pathway of catalytic amination of glycerol with dimethylamine.



Fig. 9. Effect of reaction temperature on the catalytic amination performance of Cat-2. Reaction conditions: reaction time 2 h, $H_6P_2W_{18}O_{62}$ loading of 20 wt%, GHSV of 3 h⁻¹, glycerol aqueous concentration of 10 wt%, DMA aqueous concentration of 30 wt%, molar ratio of DMA/glycerol of 2.5.

reduced obviously, and the probability of D-3 formation is increased at the same time. The highest yield of D-3 was appeared at the GHSV of $3 h^{-1}$.

Effect of molar ratio of DMA/glycerol

The effect of molar ratio of DMA/glycerol on the catalytic amination performance of Cat-2 is shown in Fig. 11. As the molar ratio of DMA/ glycerol increasing, the glycerol conversion gradually increased until the molar ratio is 2.5, then the glycerol conversion gradually decreased. The reason is that an appropriate amount of DMA is good for reaction with acrolein, 3-hydroxypropanal or hydroxyacetone, which promotes the reaction of glycerol conversion. However, the excessive amount of DMA may cause that the acid sites on the Cat-2 were covered by DMA, and it is difficult for the access of the glycerol to the acid sites, which results in decreasing the glycerol conversion. The D-3 selectivity gradually increased with increasing of the molar ratio of DMA/glycerol,



Fig. 10. Effect of GHSV on the catalytic amination performance of Cat-2. Reaction conditions: 300 °C, reaction time 2 h, $H_6P_2W_{18}O_{62}$ loading of 20 wt%, glycerol aqueous concentration of 10 wt%, DMA aqueous concentration of 30 wt%, molar ratio of DMA/glycerol of 2.5.

and the highest yield of D-3 was appeared at the 2.5 M ratio of DMA/ glycerol.

Conclusions

In this work, the performance of Cat-1 was compared with that of Cat-2 during the catalytic amination of glycerol with dimethylamine to produce Dimethylamino-3-propanal. Firstly, the optimum loading amount of two kinds catalysts were obtained under the same reaction conditions. Under the premise of the optimum loading, the specific surface area, pore volume and pore size of the Cat-2 were higher than those of the Cat-1. Cat-1 exhibited more total acidity than that of Cat-2, but the amount of Brønsted acid sites and ratio of B/(B + L) on Cat-2 were higher than that of Cat-1. The amount of coke on Cat-2 was lower than that of Cat-1. Therefore, the catalytic stability, selectivity and yield of Dimethylamino-3-propanal of Cat-2 were higher than those of Cat-1, which proved that the Brønsted acid sites are good for the catalytic



Fig. 11. Effect of molar ratio of DMA/glycerol on the catalytic amination performance of Cat-2. Reaction conditions: 300 °C, reaction time 2 h, $H_6P_2W_{18}O_{62}$ loading of 20 wt%, GHSV of 3 h⁻¹, glycerol aqueous concentration of 10 wt%, DMA aqueous concentration of 30 wt%.

amination of glycerol with dimethylamine to produce Dimethylamino-3-propanal. According the product distribution results, the reaction pathway of catalytic amination of glycerol with dimethylamine was proposed. Furthermore, the reaction temperature, GHSV and the molar ratio of DMA/glycerol were optimized on Cat-2 catalyst.

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