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# CeO<sub>2</sub> promoting allyl alcohol synthesis from glycerol direct conversion over MoFe/CeO<sub>2</sub> oxide catalysts: morphology and particle sizes dependent

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## Abstract

MoFe-N, MoFe/c–CeO<sub>2</sub>, MoFe/p<sub>1</sub>–CeO<sub>2</sub>, and MoFe/p<sub>2</sub>–CeO<sub>2</sub> (where N, c, and p stand for non-supported, nanocube, and nanoparticle) oxide catalysts were designed for gas-glycerol direct catalytic conversion into allyl alcohol. The catalysts also were characterized by XRD, TEM, BET, H<sub>2</sub>-TPR, and NH<sub>3</sub>-TPD. Mo–Fe oxides were highly dispersed on the surface of c-CeO<sub>2</sub> and p-CeO<sub>2</sub> supports, different with the MoFe-N consist of crystalline Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> crystalline phase. The support effect and special natural property of CeO<sub>2</sub> significantly improve the allyl alcohol selectivity from gas-glycerol over MoFe/CeO<sub>2</sub>. The p-CeO<sub>2</sub> with low particle sizes and crystalline degree was superior to high-crystalline nanocube c-CeO<sub>2</sub> to promote its interaction with the MoFe oxide active components, and improve the surface acid site concentration and reducibility of MoFe/CeO<sub>2</sub> as well as catalytic activity and stability for allyl alcohol synthesis from gas-glycerol oversion reached 97.1%, and the selectivity of allyl alcohol, ethanol, propanoic acid, and acrylic acid were 23.3%, 8.6%, 12.6%, and 7.8%, respectively, yielding allyl alcohol of 22.6%.

**Keywords** Mo–Fe oxides  $\cdot$  Allyl alcohol  $\cdot$  Glycerol  $\cdot$  CeO<sub>2</sub> support effect  $\cdot$  Biomass resource

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#### Introduction

Nowadays, depletion of fossil fuel resources and the global warming problem have promoted the development of renewable energies (biomass and solar energy, etc.) all over the world, [1–3]. Typically, biodiesel, as a successful utilization of biomass, has been produced on a large scale during the past decade, and the production has continually increased [4, 5]. The most widely adopted biodiesel production method is transesterification of triglycerides obtained from vegetable oils and animal fats; however, glycerol is produced as a main byproduct at roughly a tenth the mass of the biodiesel [6, 7]. The chemocatalytic technologies to convert glycerol into high-value chemicals receive great attention as an effective way to deal with glycerol, which has created an international research hotspot in recent years [8, 9]. Glycerol comprises a versatile starting material for the preparation of various compounds possessing a C3 backbone, such as 1,2- or 1,3-propanediol, acrolein, dihydroxyacetone, and so on [10].

Inspiringly, a few works have focused on allyl alcohol, which is used as a large-scale industrial chemical intermediate, promoting additions, substitutions, decomposition, oxidation, re-arrangement, and polymerisation reactions based on this commodity to produce resins, paints, coatings, silane coupling agents, and polymer crosslinking agents [11]. The basic motivation is that the current industrial processes of allyl alcohol production are fossil fuel-based routes, involving hydrolysis of allyl chloride (from propylene), Meerwein–Pondorf reduction of acrolein with isopropanol, and hydrolysis of allyl acetate (from propylene reacting with acetic acid) [12, 13]. Synthesis of allyl alcohol from glycerol shows potential significance on energy and environmental aspects.

Recently, reported chemocatalytic conversion of glycerol into allyl alcohol involved two effective ways. One is in the presence of sacrificial additives (extra hydrogen donors), such as formic acid-assisted liquid-glycerol DODH (deoxydehydration), H<sub>2</sub>-sacrificed liquid-glycerol DODH over a heterogeneous ReO<sub>x</sub>-Au/ CeO<sub>2</sub> catalyst, and H<sub>2</sub>-sacrificed gas-glycerol dehydration-hydrogenation over the bifunctional Ag/ZSM-5 catalysts, which, however, showed obvious drawbacks of requiring a special solvent, high pressure, prolonged reaction time, low conversion or low selectivity [14-16]. The other is gas-glycerol direct conversion into allyl alcohol without any hydrogen donors, first reported by Liu et al., that about 24% of allyl alcohol yielded from glycerol (Con. 99%) over the FeO<sub>x</sub> catalysts [17]. Attracted by advantages of low raw-material cost, high-efficiency simple reaction, and mild reaction condition et al., Fe-based oxide catalysts were further developed for gas-glycerol direct conversion into allyl alcohol, such as Fe/Al<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/(Fe<sub>2</sub>O<sub>3</sub>)<sub>0.16</sub>, ZrO<sub>2</sub>-FeO<sub>x</sub>, and H-ZSM5/Fe [18-20]. However, the selectivity of allyl alcohol was 10-15%, which can be obviously improved to above 20% over the catalysts after adding base metals (K, Rb etc.) to reduce surface acidic property, such as ZrO<sub>2</sub>(7%)-FeO<sub>2</sub>/Rb, K/ZrO<sub>2</sub>-FeO<sub>2</sub>, γ-Alumina/Fe/Rb, and H-ZSM5/Fe/Rb [20-22]. The moderate-acid sites and redox sites both are key active centers for this reaction, which are important for preparing new catalysts with high activity, selectivity and stability [17-24].

Following previous studies that bimetal MoFe oxides having higher catalytic performance than single Mo or Fe oxides for gas-glycerol conversion to allyl alcohol and the CeO<sub>2</sub> without high specific surface area and porous structure also showing relatively excellent support effect comparing with alkaline MgO, acidic ZrO<sub>2</sub>, and neutral CNTs,, this work aims to prepared MoFeO,/CeO2 bimetal oxides catalysts with different nano-morphologies and particle sizes for gas-glycerol direct catalytic conversion to allyl alcohol [23, 24]. The catalysts design was inspired by  $CeO_2$  has redox sites and can catalyze the glycerol conversion to produce intermediate-radical hydrogen ([H·]), and finally obtaining methanol, which is different with the SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> supports and may benefit allyl alcohol production [25]. At the same time, physicochemical property and catalytic performance of CeO<sub>2</sub> (or metal/CeO<sub>2</sub> catalysts) are always dependent on the morphology and nanoparticle sizes [26-29]. The prepared MoFe/CeO<sub>2</sub> oxide catalysts are also characterized by using X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET), transmission electron microscopy (TEM), NH<sub>3</sub>-temperature programmed desorption (NH<sub>3</sub>-TPD), and H<sub>2</sub>-temperature programmed reduction (H<sub>2</sub>-TPR) analyses.

#### Experimental

#### **Catalyst preparation**

The nanocube c-CeO<sub>2</sub> was prepared by hydrothermal methods followed the Mai et al.'s recipe [24]. Typically, 1.96 g Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and 16.88 g NaOH was dissolved in 40 mL and 30 mL deionized water, respectively. The NaOH solution was added dropwise into the Ce(NO<sub>3</sub>)<sub>3</sub> solution under stirring at room temperature. The mixed solution was adequately stirred for an additional 30 min at room temperature and then transferred into a 100-mLTeflon bottle. The Teflon bottle was tightly sealed and hydrothermally treated in a stainless-steel autoclave at 180 °C for 24 h. After cooling, the obtained precipitate was collected, washed with distilled water, dried at 100 °C for 24 h, and finally calcined at 500 °C for 4 h in air.

The nanoparticles  $CeO_2$  was prepared by precipitation methods, using dilute ammonia water and NaOH solution (0.5 mol/L) as the precipitates, respectively. 3.0 g Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O were dissolved in 100 mL deionized water. The NaOH solution (0.5 mol/L) was then added dropwise in the Ce(NO<sub>3</sub>)<sub>3</sub> solution under stirring, until the pH of the solution reached 9.0. The obtained precipitate was thoroughly washed with distilled water in ordered to remove the undesired Na<sup>+</sup> ions, and subsequently dried overnight in an oven at 100 °C for 24 h. The dried sample was calcined at 500 °C for 4 h, and the obtained CeO<sub>2</sub> sample is denoted as p<sub>1</sub>-CeO<sub>2</sub>. The sample, prepared by following the same process using the dilute ammonia water as the precipitate, denoted as p<sub>2</sub>-CeO<sub>2</sub>.

MoFe/CeO<sub>2</sub> catalysts were prepared by simple wet impregnation. Briefly, a certain amount of  $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$  and Fe(NO<sub>3</sub>)<sub>2</sub>·9H<sub>2</sub>O  $(n_{Mo}/n_{Fe}=0.3;$  final Mo–Fe oxide loading of 5 wt%) were dissolved in distilled water, followed by adding several drops of HNO<sub>3</sub> (67%). Then, a corresponding amount of CeO<sub>2</sub> (c-CeO<sub>2</sub>, p<sub>1</sub>-CeO<sub>2</sub> or p<sub>2</sub>-CeO<sub>2</sub>) was added to the solution and stirring for 2 h at room

temperature. After staying for 24 h, the solution was spin-flash evaporated at 80 °C until the solvent being completely removed. Through drying overnight, the sample was calcinated at 500 °C for 3 h. Finally, the catalyst was obtained and designated as MoFe/c–CeO<sub>2</sub>, MoFe/p<sub>1</sub>–CeO<sub>2</sub>, and MoFe/p<sub>2</sub>–CeO<sub>2</sub>, respectively. The unsupported MoFe composite oxides catalyst (denoted as MoFe-N) was prepared following the same process without adding CeO<sub>2</sub>.

## **Catalyst characterization**

## **XRD** characterization

X-ray diffraction (XRD) patterns were recorded on a Fangyuan DX-1000 powder X-ray diffractometer (China) with Cu K $\alpha$  radiation at a tube voltage of 40 kV, and the data of  $2\theta$  were collected from 10° to 80° range with 0.02° of the step size at the rate of 5° min<sup>-1</sup>. Low-angle XRD patterns were recorded on a Rigaku D/Max–2500/ PC diffractometer with a rotating anode using Ni filtered Cu–K $\alpha$  (as radiation source ( $\lambda$ =0.15418 nm) radiation at 40 kV of a tube voltage and 200 mA of a tube current. The data were corrected from 0.5° to 5° with 0.02° increment and recording time of 100 s at each increment.

#### **BET characterization**

Adsorption and desorption isotherms were collected on Autosorb-6 at -196 °C. Prior to the measurement, all samples were degassed at 200 °C until a stable vacuum of ca. 5 m Torr was reached. The specific surface area was assessed using the Brunauer–Emmett–Teller (BET) method from adsorption data in a relative pressure range from 0.06 to 0.10.

## **TEM analysis**

Transmission electron microscopy (TEM) was performed using a Tecnai  $G^2$  Spirit microscope operating with an acc3eleration voltage of 120 kV. For the TEM measurement, the samples were prepared by ultrasonication in ethanol, evaporating a drop of the resultant suspension onto a carbon–coated copper grid.

## H<sub>2</sub>-TPR studies

H<sub>2</sub> temperature programmed reduction (H<sub>2</sub>–TPR) was conducted using a conventional apparatus equipped with a TCD detector. 25 mg of sample was placed in a quartz tube (4.0 mm ID), and pretreated at 250 °C for 30 min in a pure N<sub>2</sub> flow of 30 mL min<sup>-1</sup>. After the temperature cooled down, H<sub>2</sub>–TPR was performed by heating the samples at 10 °C min<sup>-1</sup> from 50 to 700 °C in a 5% H<sub>2</sub>–N<sub>2</sub> mixture flowing at 30 ml·min<sup>-1</sup>.

#### NH<sub>3</sub>-TPD studies

NH<sub>3</sub> temperature programmed desorption (NH<sub>3</sub>–TPD) was conducted using a conventional apparatus equipped with a TCD detector. 50 mg of sample was placed in a quartz tube (4.0 mm ID), and pretreated with gas He (30 mL/min) at 300 °C for 1 h; as the temperature cooled down to 50 °C, NH<sub>3</sub> was chemisorbed until equilibrium was reached. Then TPD was performed by heating the samples at 10 °C min<sup>-1</sup> from 50 to 600 °C in gas He flowing at 30 mL min<sup>-1</sup>.

#### **Catalytic activity measurement**

Catalytic tests of all catalysts were carried out in a continuous flow fixed-bed quartz tubular reactor (i.d. 8 mm) under atmospheric pressure. The quartz tube reactor containing 200 mg of catalysts mixed with 200 mg of quartz (both sieved, 380-700 µm) was placed inside a tubular furnace. The carrier gas (N<sub>2</sub>) was passed downward through the reactor containing the catalyst bed, while electronic mass flow controller (D07-7A/ZM, China) was used to control the flow rate at 10 mL min<sup>-1</sup>. After the temperature of the reactor had reached 340 °C, a 35 wt% glycerol aqueous solution was pumped in at a flow rate of 1 mL  $h^{-1}$  using a syringe pump (LSP01-1A, china). The products were collected in every 2 h using ethanol cooled by an ice-water trap, and the obtained product yields showed the average of each 2 h. The collected liquid samples were analyzed with a HP 5890 Series II gas chromatograph equipped with a HP-INNOWAX (19091 N-113, 30 m\*0.32 mm\*0.25 mm) and an FID detector. 1,2-propanediol was selected as the internal standard for the quantification of glycerol and products. In addition, all samples were also checked without standard and no 1,2-propanediol was detected in all cases. The product selectivity was calculated with mol-based method, and the products yields were calculated based on the amount of glycerol fed to the reactor.

## **Results and discussion**

#### **XRD characterization**

Figure 1 presents the XRD patterns of the prepared MoFe-N and MoFe/CeO<sub>2</sub> catalysts, in which, MoFe-N showed a series of typical XRD peaks attributed to  $Fe_2(MoO_4)_3$  (PDF#97-010-0606) and  $Fe_2O_3$  (PDF#00-033-0664). Differently, for MoFe/CeO<sub>2</sub> catalysts, it can be only observed similar prominent XRD peaks occurred at  $2\theta = 28.56^{\circ}$ ,  $33.12^{\circ}$ ,  $47.46^{\circ}$ ,  $56.32^{\circ}$ ,  $59.14^{\circ}$ ,  $69.44^{\circ}$ ,  $76.66^{\circ}$ , and  $79.14^{\circ}$ , which are associated with the fluorite-like CeO<sub>2</sub> crystalline phase [26–30]. The absence of Mo and/or Fe oxide XRD peaks for MoFe/CeO<sub>2</sub> catalysts confirmed that Mo and/or Fe oxides were highly-dispersed on the surface of CeO<sub>2</sub> support or under the detection limit of XRD resulting from the low mass loading of Mo and Fe oxides, which may enhance the interaction between the Mo–Fe oxides and CeO<sub>2</sub>



Fig. 1 The wide-angle XRD patterns of the MoFe-N and MoFe/CeO<sub>2</sub> catalysts

[27–29]. Moreover, it can be observed the CeO<sub>2</sub> XRD peaks of MoFe/ $p_1$ –CeO<sub>2</sub> and MoFe/ $p_2$ –CeO<sub>2</sub> are much lower in intensity than that of the MoFe/c–CeO<sub>2</sub>. The low degree crystalline of p-CeO<sub>2</sub> (supports) usually existed many crystalline defects and exhibit different physico-chemical property comparing well to crystalline c-CeO<sub>2</sub>, so as to affect the surface acidity and reducibility of MoFe/CeO<sub>2</sub> [29, 30].

#### TEM characterization

The morphology and particle sizes of the MoFe oxides supported on the  $CeO_2$  prepared by different methods were examined by TEM, and the micrographs of the obtained nano-oxide samples were shown in Fig. 2.

The MoFe/c–CeO<sub>2</sub>, of which the CeO<sub>2</sub> prepared through hydrothermal methods, exhibited nanocube shapes with uniform particle sizes (about 25 nm) and regular shapes, in accord with the previous literatures [26-30]. In contrast, the CeO<sub>2</sub> prepared by precipitation methods gave the MoFe/p<sub>1</sub>-CeO<sub>2</sub> and MoFe/p<sub>2</sub>-CeO<sub>2</sub> with irregular particle shapes. Differently, the particle sizes  $MoFe/p_1$ -CeO<sub>2</sub> were distributed in the range of 11-23 nm, lager than that of MoFe/p<sub>2</sub>-CeO<sub>2</sub> distributed in diameter range of 7–17 nm, which can be attributed to the different precipitants of NaOH and NH<sub>3</sub>·H<sub>2</sub>O with different OH<sup>-</sup> release rates. The different shapes and particle sizes of CeO<sub>2</sub> well revealed CeO<sub>2</sub> prepared by hydrothermal and precipitation methods having different degree of crystallinity (XRD results in Fig. 1). At the same time, the specific surface areas of the MoFe/c–CeO<sub>2</sub>, MoFe/p<sub>1</sub>–CeO<sub>2</sub> and MoFe/p<sub>2</sub>-CeO<sub>2</sub> were also characterized and calculated through the BET equation (as shown in Table 1), which were 23.2, 20.5, and 41.8 m<sup>2</sup>/g, respectively. The morphology, particle sizes, and specific surface area of the CeO<sub>2</sub>-based catalysts were always key factors affecting adsorption and activation of reactants for gas-solid heterogeneous catalytic reaction [27–30].

CeO<sub>2</sub> promoting allyl alcohol synthesis from glycerol direct...





Fig. 2 The TEM images of the MoFe/c–CeO<sub>2</sub> (a), MoFe/p<sub>1</sub>–CeO<sub>2</sub> (b), and MoFe/p<sub>2</sub>–CeO<sub>2</sub> (c) oxide catalysts

Table 1 The physico-chemical property data of MoFe-N and MoFe/CeO2 catalysts	Sample	$S_{\rm BET}$ (m <sup>2</sup> /g)	Acid site concen- tration (mmol/g)	Acid site density (µmol/ m <sup>2</sup> )
	MoFe-N	6.27	0.134	0.214
	MoFe/c-CeO <sub>2</sub>	23.2	0.148	0.064
	MoFe/p <sub>1</sub> -CeO <sub>2</sub>	20.5	0.234	0.114
	MoFe/p2-CeO2	41.8	0.339	0.081

# H<sub>2</sub>-TPR study

The H<sub>2</sub>-TPR test was conducted on the prepared MoFe-N and MoFe/CeO<sub>2</sub> catalysts, and the H<sub>2</sub>-TPR profiles are shown in Fig. 3. It can be observed from



Fig. 3 The  $H_2$ -TPR spectrum for the prepared CeO<sub>2</sub> catalysts

Fig. 3, that the H<sub>2</sub>-TPR curve of MoFe-N deviated from the baselines (as shown by the arrow) at approximately 470 °C, and formed two multiple H<sub>2</sub> consumption peaks with the lower-temperature one centered at about 550 °C. However, The MoFe/CeO<sub>2</sub> shifted the H<sub>2</sub>-TPR peaks to lower reaction temperatures. The MoFe/C–CeO<sub>2</sub> showed the H<sub>2</sub>-TPR curve with two peaks centered at 508 °C and 637 °C, respectively. The H<sub>2</sub>-TPR curve of MoFe/p<sub>1</sub>–CeO<sub>2</sub> have two H<sub>2</sub> consumption peaks centered at 457 °C and 668 °C, respectively. For MoFe/p<sub>2</sub>–CeO<sub>2</sub>, the H<sub>2</sub> reducing reaction started at 260 °C, and formed an obvious peak centered at about 420 °C in the H<sub>2</sub>-TPR curve.

H<sub>2</sub>-TPR study is an important technology for metal oxides catalysts to infer the dispersion and reducibility of reducible species from the temperatures, intensities and areas of the TPR hydrogen consumption peaks [31, 32]. It should be pointed out that  $Fe_2O_3$  has reduction temperature greater than 400 °C following a two-step reduction process:  $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO$  (lower than 800 °C), and the composite Fe–Mo oxides such as  $Fe_2(MoO_4)_3$  and  $FeMoO_4$  are more stable and difficult to be reduced towards individual Fe oxides [33-36]. Thus, according to the XRD results, the H<sub>2</sub>-TPR peak of MoFe-N at 550 °C is mainly attributed to the reduction of Fe<sub>2</sub>O<sub>3</sub> species [33, 34]. For the MoFe/CeO<sub>2</sub> catalysts, the shift of the  $H_2$ -TPR peaks to low reduction temperatures was benefit from the CeO<sub>2</sub> and Mo-Fe oxides being well dispersed on the surface of  $CeO_2$ . But, it is not easy to clearly attribute the H<sub>2</sub> reduction peaks to the concise metal oxides (CeO<sub>2</sub> or Fe<sub>2</sub>O<sub>3</sub>) because the CeO<sub>2</sub> has a relatively high reduction temperature the same as  $Fe_2O_3$  [29, 30]. For this, the MoFe/p<sub>1</sub>-CeO<sub>2</sub> and MoFe/p2-CeO2 have lower reduction temperatures than MoFe/c-CeO2, which can be ascribed to the p1-CeO2 and p1-CeO2 naturally having lower reduction temperatures than the c-CeO<sub>2</sub> because of the smaller particles and lower crystallinity of p-CeO<sub>2</sub> (confirmed by XRD and TEM). Moreover, the  $p_1$ -CeO<sub>2</sub> and  $p_1$ -CeO<sub>2</sub> with small particles and low crystallinity can also promote the reduction of the surface

loading Fe and Mo oxides, so that the MoFe/ $p_1$ -CeO<sub>2</sub> and MoFe/ $p_2$ -CeO<sub>2</sub> have low reduction temperatures, especially for the MoFe/ $p_2$ -CeO<sub>2</sub> [28–30].

In terms of the reduction temperature results in Fig. 3, the prepared catalysts can be ranked as  $MoFe/p_2-CeO_2 > MoFe/p_1-CeO_2 > MoFe/c-CeO_2 > MoFe-N$ , following the reducibility from high to low. The different reducibility of  $MoFe/CeO_2$  oxide catalysts demonstrated that the catalysts provided redox sites with different catalytic oxidability at a certain reaction temperature for glycerol converting to ethylene glycol radical or glycerol (or intermediate products) being oxidized to  $CO_x$ , which may have obvious effect on the products distribution of the glycerol catalytic conversion [17, 22, 24].

#### NH<sub>3</sub>-TPD

The surface acid sites of catalysts seem to be the initial active centers for the glycerol molecules in gas–solid catalytic conversion reaction [17–22]. To investigate the surface acidity and acid strength, NH<sub>3</sub>-temperature programmed desorption (NH<sub>3</sub>-TPD) experiments were carried out on the MoFe-N and MoFe/CeO<sub>2</sub> catalysts, and the results were shown in Fig. 4. As shown in Fig. 4, the NH<sub>3</sub>-TPD curves of the MoFe-N, deviate from the baseline (as shown by the arrow) at about 83 °C, and formed a prominent NH<sub>3</sub>-TPD peak centered at about 117 °C. The MoFe/CeO<sub>2</sub> catalysts shifted the initial NH<sub>3</sub> desorption temperatures to above 100 °C, with the curves forming multiple NH<sub>3</sub>-TPD peaks in the range of 125–260 °C. The MoFe/  $p_2$ –CeO<sub>2</sub> has NH<sub>3</sub>-TPD peaks with relatively higher desorption temperature than the MoFe/p<sub>1</sub>–CeO<sub>2</sub> and MoFe/c–CeO<sub>2</sub>. The occurrence of clear NH<sub>3</sub>-TPD peaks in the range of 100–300 °C indicates the surface of the MoFe-N and MoFe/CeO<sub>2</sub> catalysts only hold moderate (weak) acidic property, though the acidity of these catalysts having different strength following the order: MoFe/p<sub>2</sub>–CeO<sub>2</sub> > MoFe/



Fig. 4 The NH<sub>3</sub>-TPD curves of the MoFe-N and MoFe/CeO<sub>2</sub> oxide catalysts

 $p_1$ -CeO<sub>2</sub>-MoFe/C-CeO<sub>2</sub> > MoFe-N [21–24]. The acid sites of the MoFe-N were provided by the Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> in terms of the XRD result, while the surface acid sites of the MoFe/CeO<sub>2</sub> catalyst samples also come from additional CeO<sub>2</sub> in addition to the MoFe oxides, because the CeO<sub>2</sub> naturally has weak acidity.

At the same time, the amounts of surface acid sites of the MoFe-N and MoFe/ CeO<sub>2</sub> catalysts can be inferred from the corresponding NH<sub>3</sub>-TPD peak area of the samples [23, 24]. The acid site density and acid site concentration of the samples in terms of the NH<sub>3</sub>-TPD (combining with catalyst mass and specific surface area from BET) results were calculated and showed in Table 1. The corresponding data showed the MoFe-N and MoFe/c-CeO2 have surface acid site concentration of 0.134 mmol/g and 0.148 mmol/g, respectively. For the MoFe/p<sub>1</sub>-CeO<sub>2</sub> and MoFe/p<sub>2</sub>-CeO<sub>2</sub> catalysts, the surface acid site concentration obviously increased to 0.234 mmol/g and 0.339 mmol/g, respectively. Based on this reference data, the catalysts, can be ranked as MoFe/p2-CeO2>MoFe/p1-CeO2-MoFe/c-CeO2>MoFe-N, with the same order as the surface acidic strength of the studying catalyst samples. This phenomenon suggests the CeO<sub>2</sub> supports can enhance the surface acid site concentration and acidic strength of the supported MoFe oxide catalysts to a certain extent, but which was obviously influenced by the crystallinity degree and particle size of CeO<sub>2</sub>. Combining with the XRD, TEM, and BET results, the CeO<sub>2</sub> with lowdegree crystallinity and small particles can be a suitable metal-oxide support to has strong interaction with the surface MoFe oxides and to improve the surface acid site concentration and acidic strength of the MoFe/CeO<sub>2</sub> catalyst system. The distinct surface acid strength and acid site concentration may lead to different catalytic activities of MoFe-N and MoFe/CeO2 catalysts for the gas-glycerol catalytic conversion, because of the surface acid sites are the reactive sites for glycerol conversion, but also can cause coke formation [21, 22, 27].

#### **Catalytic activity**

Table 2 presents the results that the investigated catalytic performance of the MoFe-N and MoFe/CeO<sub>2</sub> catalysts for gas-glycerol direct conversion. As shown in Table 2, the catalytic conversion of glycerol over the MoFe-N, MoFe/c-CeO<sub>2</sub>, MoFe/ p<sub>1</sub>-CeO<sub>2</sub>, and MoFe/p<sub>2</sub>-CeO<sub>2</sub> was 71.3%, 71.7%, 81.0%, and 97.1%, respectively. The selectivity of allyl alcohol over MoFe-N was 14.6%, which increased to above 22% over the MoFe/CeO<sub>2</sub> catalysts. Prominently, the MoFe/ $p_2$ –CeO<sub>2</sub> has the high DODH catalytic activity with the highest allyl alcohol yield of 22.6%. Additionally, the investigated products from glycerol catalytic conversion over the MoFe-N and MoFe/CeO<sub>2</sub> catalysts included propanol, acrolein, ethanol, acetol, acetone, propanoic acid, and acrylic acid, but with low selectivity under 10%. The propanoic acid and acrylic acid selectivity over the MoFe/p<sub>2</sub>–CeO<sub>2</sub> reached 12.6 and 7.8%, respectively, which were obviously higher than that over the other MoFe-based oxides catalysts. The CeO<sub>2</sub> supported MoFe oxides catalysts (MoFe/ $p_2$ –CeO<sub>2</sub>) seems superior to the previously reported ZrO<sub>2</sub>-FeO<sub>x</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/(Fe<sub>2</sub>O<sub>3</sub>)<sub>0.16</sub>,  $\gamma$ -Alumina/Fe/Rb, and H-ZSM-5/Fe/Rb catalysts with allyl alcohol selectivity less than 20% from glycerol direct conversion through gas-solid catalytic reaction [18–22].

Catalysts	Conversion (%)	Products select	ivity (%)							Allyl alco
		Path I: DODH		Path II: De (2, -OH)	hydration	Path III:	Dehydration	(1, –OH)		hol yıeld (%)
		Allyl alcohol	Propanol	Acrolein	Ethanol	Acetol	Acetone	Propanoic acid	Acrylic acid	
MoFe-N	71.3	14.6	3.2	8.8	7.5	4.3	6.7	1.4	3.2	10.4
MoFe/c-CeO <sub>2</sub>	71.7	22.9	2.5	5.9	8.3	3.6	4.5	2.0	3.6	16.4
MoFe/p <sub>1</sub> -CeO <sub>2</sub>	81.0	24.5	2.3	10.2	9.3	4.4	4.5	6.2	5.9	19.9
MoFe/p2-CeO2	97.1	23.3	2.3	6.9	8.6	3.6	4.1	12.6	7.8	22.6

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It can be known from the results in Table 2, the allyl alcohol selectivity increased about 10% over the prepared MoFe/CeO<sub>2</sub> catalysts in comparison to the MoFe-N, suggesting the CeO<sub>2</sub> support can obviously improve the catalytic activity of MoFe bimetal oxides for allyl alcohol synthesis from gas-glycerol. As is known, the ally alcohol produced from glycerol direct conversion needs a co-function of moderate acid centers and non-acid centers (redox centers), through dehydration and followup hydrogen transfer (hydrogen reduction) process [17, 21, 24]. According to the H<sub>2</sub>-TPR results, the MoFe/CeO<sub>2</sub> samples have higher reducibility (oxidability) than the MoFe-N resulting from the increasing specific surface area and strong interaction between MoFe oxides and the CeO<sub>2</sub> support. Importantly, the CeO<sub>2</sub> revealed to have high catalytic performance for carbon-carbon (C-C) bonds of glycerol to produce hydrogen radical and finally obtained methanol [25]. Here, the hydrogen radical was needed for allyl alcohol synthesis, and the hydrogen donor came from the glycerol molecules as the previous verified [17-24]. The enhanced catalytic activity of MoFe/CeO<sub>2</sub> catalysts for allyl alcohol selectivity can be attributed to the enhanced oxidability of MoFe/CeO2 and natural special property of CeO2 facilitating the dehydration and C-C bonds cleavage of glycerol over the MoFe/CeO2 catalysts. In summary, the support effect and special natural property of CeO2 significantly improve the allyl alcohol selectivity of MoFe/CeO2 catalysts from gasglycerol direct conversion.

Based on the glycerol conversion and allyl alcohol yields from high to low, followed the order of  $MoFe/p_2-CeO_2 > MoFe/p_1-CeO_2 > MoFe/c-CeO_2 > MoFe/N$ , that is, the  $CeO_2$  as the support significantly improves the catalytic activity of MoFe bimetal oxides for gas-glycerol direct conversion to allyl alcohol without any extra hydrogen donors. According to the results in Figs. 4 and 5, the glycerol conversion over the MoFe-N and MoFe/CeO<sub>2</sub> keep a positive linear relation with the strength and concentration and surface moderate acid sites (Figs. 4 and 5).



Fig. 5 The relationship of glycerol conversion and allyl alcohol selectivity with the surface acid site concentration of the MoFe-N and MoFe/CeO<sub>2</sub> oxide catalysts

Thus, the increment of the glycerol conversion can be attributed to the increasing surface acid site concentration (surface acid amounts) and surface acidic strength of the MoFe/CeO<sub>2</sub> catalysts, due to the glycerol conversion starting at the activation and dehydration of the hydroxyl groups over the surface acid centers of catalysts [21–24]. Moreover, the results also tell that the morphology, particle sizes and crystalline of CeO<sub>2</sub> have important influence on the catalytic performance, in terms of the XRD and TEM results. The CeO<sub>2</sub> with smaller particle sizes and low crystalline degree was superior to nanocube CeO<sub>2</sub> with high crystalline degree to promote its interaction with the MoFe oxide active components and improve the surface acid site concentration and reducibility of MoFe/CeO<sub>2</sub> (H<sub>2</sub>-TPR and NH<sub>3</sub>-TPD results in Figs. 3 and 4). Thus, the MoFe/p<sub>2</sub>–CeO<sub>2</sub> showed higher catalytic activity than the MoFe/p<sub>1</sub>–CeO<sub>2</sub> and MoFe/c–CeO<sub>2</sub> for allyl alcohol yielding from gas-glycerol conversion. In addition, it need to be explained that the higher propanoic acid and acrylic acid selectivity over the MoFe/p<sub>2</sub>–CeO<sub>2</sub> resulted from its higher oxidability [28–30].

The existence of various byproducts of acrolein, acetol, acetaldehyde, propionaldehyde, and acetone is a typical phenomenon for allyl alcohol synthesis from gas-glycerol direct conversion because the 1,2 or 1,3 dehydration and cleavage of carbon–carbon bonds of glycerol can undergo over the acidic-redox MoFe-based oxide catalysts [21–25]. According to the previous studies, acrolein and acetol were produced from the 1,2 or 1,3 dehydration of glycerol over the acid centers, respectively, and the subsequent reaction of these molecules over the acid and/or redox sites produced acetaldehyde, propionaldehyde, acetone, propanoic acid and acrylic acid [21–24].

#### **Catalytic stability**

Glycerol can easily undergo condensation on the acid oxide catalysts. The products allyl alcohol, acrolein, and acetol are more active than the reactant glycerol over acid catalysts because of the coexistence of carbon-carbon double bonds and carbon-oxygen double bonds or a hydroxyl group in the molecule. These can all form a mass of carbonaceous deposits continuously increase on the catalysts, leading to significant deactivation observed over the reported  $\gamma$ -alumina/Fe and K [5] /ZrO<sub>2</sub>-FeO<sub>x</sub> catalysts with the time-on-stream of 3 h [20-28]. For this, the catalytic stability of the MoFe/p2-CeO2 and MoFe/c-CeO2 catalyst was investigated, and the corresponding results are shown in Fig. 6a and b. As Fig. 6a presented, for MoFe/p2-CeO2, the catalytic conversion of glycerol gradually reduced in average rate of 5%/h in the range of time-on-stream 2-10 h. But, the products including allyl alcohol acrolein, ethanol, acetol, and propionaldehyde keep a good constant electivity in 10 h. For MoFe/c-CeO<sub>2</sub>, the glycerol conversion badly decreased in the investigated reaction time of 8 h, and the allyl alcohol selectivity also obviously decreased. In comparison, the MoFe/p2-CeO2 showed higher catalytic stability than the MoFe/c-CeO2, probably benefiting from the CeO2 with small nano particle sizes and low degree of crystalline improving the carbon resistance of MoFe/p<sub>2</sub>-CeO<sub>2</sub>.



Fig. 6 The glycerol conversion and products distribution as a function of time-on-stream over the MoFe/  $p_2$ -CeO<sub>2</sub> (a) and MoFe/c–CeO<sub>2</sub> (b) catalysts

## Conclusions

Nanocube and nano-particle MoFe/CeO<sub>2</sub> catalysts were successfully prepared through simple wet impregnation methods, using nanocube and nanoparticle CeO<sub>2</sub> as the supports. Different from the MoFe-N (without supports) consisting of crystalline Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> crystalline phase, Mo–Fe oxides were well-dispersed on CeO<sub>2</sub> for the MoFe/CeO<sub>2</sub> (c-CeO<sub>2</sub>, p<sub>1</sub>-CeO<sub>2</sub>, and p<sub>2</sub>-CeO<sub>2</sub>) catalysts. The CeO<sub>2</sub> effectively improve the reducibility and surface moderate acid sites (acidic strength) of MoFe/CeO<sub>2</sub>, and nanoparticle CeO<sub>2</sub> (especially for p<sub>2</sub>-CeO<sub>2</sub>) with low particle sizes and crystalline degree was superior to high-crystalline nanocube c-CeO<sub>2</sub>. The

allyl alcohol selectivity from glycerol direct conversion obviously increased over the MoFe/CeO<sub>2</sub> in comparison with that over the MoFe-N, which benefited from the support effect and special natural property of CeO<sub>2</sub>. The catalysts, based on the catalytic performance for glycerol conversion to allyl alcohol can be ranked as MoFe/p<sub>2</sub>–CeO<sub>2</sub> > MoFe/p<sub>1</sub>–CeO<sub>2</sub> > MoFe/c–CeO<sub>2</sub> > MoFe-N, showing positive relationship with the surface acid concentration and reducibility of catalysts. Over the MoFe/p<sub>2</sub>–CeO<sub>2</sub>, allyl alcohol of 22.6% yielded from the glycerol (conversion of 97.1%), along with acrolein, ethanol, propanoic acid, and acrylic acid produced with the selectivity of 6.9%, 8.6%, 12.6%, and 7.8%, respectively. The MoFe/p<sub>2</sub>–CeO<sub>2</sub> showed better catalytic stability than the MoFe/c–CeO<sub>2</sub>, but the glycerol conversion gradually decreased as the reaction continued.

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