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Lewis acid property and catalytic performance of MoO₃/SiO₂ for propylene epoxidation by CHP: Effects of precipitant pH value and rare earth additive

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ABSTRACT

High dispersed 10% MoO₃/SiO₂ catalysts were prepared by the sol–gel method using a precipitant (ammonium hydroxide) with different pH values, and investigated by XRD, FT-IR spectroscopy of pyridine adsorbed and Raman spectroscopy techniques, and so on. The results show that the catalytic performance of MoO₃/SiO₂ for the epoxidation of propylene with cumene hydroperoxide (CHP) is affected by pH value of precipitant, and MoO₃/SiO₂ prepared with precipitant of pH 9 exhibits the highest yield of propylene oxide (PO). It has been found that the weak Lewis acidic sites on MoO₃/SiO₂ are the active sites of the propylene epoxidation with CHP, total amount of Lewis acid sites on the catalyst surface is related with the CHP conversion, and the weaker Lewis acid sites is in favor of the propylene epoxidation. When the amount of Lewis acid sites on the catalyst surface is more and their acid strength is higher, the CHP degradation and PO acid-catalytic hydrolysis would be speeded up, resulting in a reduction of the PO selectivity. The concentration and strength of the Lewis acid sites on MoO₃/SiO₂ are affected by pH of precipitant, and the catalyst prepared with precipitant of pH 9.0 possesses the most weakly Lewis acidic sites and the highest selectivity to PO (91.5%). Besides, the addition of certain amount of Nd can increase the weakly acidic sites to enhance CHP conversion and reduce the Lewis acidity of the catalyst thus suppress PO hydrolysis.

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1. Introduction

Propylene oxide (PO) is an important chemical intermediate [1]. It is used worldwide to produce versatile products including polyether polyols, propylene glycols and propylene glycol ethers, because it reacts readily with compounds containing active hydrogen atoms, such as alcohols, amines and acids. The Halcon method is one of the main industrial process to manufacture propylene oxide. However in the general Halcon process, the autoxidation of ethylbenzene or isobutene, which is used to generate alkylhydroperoxide as the oxidant of the epoxidation, produces a large

amount of low value by-products. To be more environmentally friendly, many studies have been made regarding the use of H_2O_2 [2,3] or O_2 [4–6] as oxidants, which do not produce any by-product. However, H_2O_2 is an expensive oxidant, and the catalytic epoxidation of propylene with O_2 usually gives poor selectivity for PO, because of the high activity of the allylic C–H in propylene. An alternative route of propylene peroxidation, which does not involve by-product, makes use of cumene hydroperoxide (CHP) as the oxidant [7], in which the cumyl alcohol formed after epoxidation can be recycled back to CHP after hydrogenolysis and oxidation. The reaction route is shown in Eq. (1):



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The main by-products of this route are phenol, acetone, dimethylphenylcarbinol (DMPC, here refers to those produced by

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the decomposition rather than the epoxidation of CHP) and acetophenone due to the decomposition of CHP, as shown in Eqs. (2)-(4):



Meanwhile, the hydrolysis of propylene oxide may also occur as Eq. (5).

$$\wedge$$
 + H₂O \rightarrow \wedge OH OH (5)

The epoxidation of olefins with hydroperoxides can take place effectively over group IVB, VB and VIB metals catalysts. Molvbdenum-based catalysts are one of the most widely used epoxidation catalysts [8]. The molybdenum complexes, ranging from monomeric molybdenum to molybdenum clusters and from (NH₄)₆Mo₇O₂₄·4H₂O to metallic molybdenum, can catalyze the epoxidation of different kinds of alkenes with various peroxides as oxygen donors [9]. To overcome the difficulty in separating and recycling a catalyst from the reaction mixture, in recent years the molybdenum complexes are often heterogenized onto different supports by an immobilized [10,11], impregnation [12], grafting [13] or sol-gel method [14,15]. The supports may be polymers [16], carbon materials [17], silica [18-20] and so on. Among the molybdenum-based catalysts, molybdenum oxide supported on silica has attracted much attention for its high commercialized potential as solid acid catalyst [21]. The studies reported on the MoO₃/SiO₂ catalyst are mainly focused on molybdenum specials, such as Mo or Mo peroxide species [22-24], Mo valence [25,26] and so on. However, the effect of preparation process on the property of acid sites, especially a strength distribution of acid sites on the catalyst surface due to the different interactions between molybdenum and silica were rarely reported. As a solid acid catalyst, MoO₃/SiO₂ has been used wide in nitration [15,27,28], esterification [29], transesterification [30], acetalization [31], partial oxidation [32,33], condensation [34] and double bond migration [35] besides epoxidation of olefins [24]. Therefore, it is necessary to study the influence factors on the acid sites of MoO₃/SiO₂ catalysts during the preparation procedure.

Herein, high dispersed 10% MoO₃/SiO₂ catalysts were prepared by sol–gel method and the epoxidation of propylene with CHP on the MoO₃/SiO₂ catalysts was investigated. The surface Lewis acidity of MoO₃/SiO₂ catalyst and an effect of surface Lewis acidity on its catalytic performance for the epoxidation of propylene with CHP were investigated by changing pH value of precipitant and adding rare earth additives in the preparation process, which were investigated by XRD, pyridine FT-IR and Raman spectroscopies, and so on. The relationship between the catalytic performance for the epoxidation and the characters of acid sites of the MoO₃/SiO₂ catalyst was discussed.

2. Experimental

All chemicals were purchased from commercial sources (Sinopharm Chemical Reagent Co. Ltd., except CHP, which from SINOPEC) and used for the reaction without further purification.

2.1. Catalyst preparation and pretreatment

The 10% MoO_3/SiO_2 catalysts were prepared by a sol-gel method. In a typical preparation, tetraethylorthosilicate (TEOS, 88 mmol) was dissolved in ethanol (20 mL) followed by adding ammonium hydroxide aqueous solution (40 mmol, pH = 8.0–10.5) under mechanical stirring. After stirring at 353 K for 30 min, $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ aqueous solution (0.65 mmol, 40 mL) was added in above synthesis solution. The formed gel was aged at room temperature for 2 days, dried at 383 K for 24 h, and finally calcined at 823 K for 5 h. The modified catalyst samples were similarly prepared while adding the mixed solutions of nitrates (W, Cr, La, Ce and Nd, respectively) and ammonium heptamolybdate.

The MoO₃/SiO₂ catalyst was pretreated by degassing at 773 K under 1.0×10^{-7} Torr for 4 h and then exposing it to 0.2 Torr pyridine for 10 min at room temperature. This catalyst was marked as MoO₃/SiO₂-Py.

3. Propylene epoxidation

A mixture of *tert*-butanol (40 mL), CHP (48%, industrial grade, 20 mL) and the catalyst (200 mg, 0.14 mmol Mo) was placed into an autoclave and 0.6 MPa propylene gas was charged at room temperature. The reaction mixture was heated to 353 K under stirring and kept at 353 K for 4 h. The products were analyzed by a Clarus 500 Gas Chromatograph (PerkinElmer) equipped with a flame ionization detector (FID) and AE.PEG-20 M separation column (30 m × 0.32 mm × 0.33 μ m), and toluene was used as an internal standard. The conversion of CHP was determined by an iodometric titration. The conversion of CHP (X_{CHP}), the selectivity to PO (S_{CHP}) for CHP and the yield of PO (Y_{PO}) are calculated as follows:

$$X_{\text{CHP}}$$
 (%) $\frac{n_{\text{CHP}}^{i} - n_{\text{CHP}}^{i}}{n_{\text{CHP}}^{i}} \times 100\%,$

(2)

(3)

(4)

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The catalytic performances of 10%MoO ₃ /SiO ₂ catalysts for the propylene epoxidat	tion by CHP.
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Catalyst (pH of precipitant)	X _{CHP} (%)	Selectivity (%)					Y _{PO} (%)
		РО	1,2-Propanediol	Acetone	DMPC ^a	Acetophenone	
8.0	83.7	77.7	1.3	9.3	10.6	0.9	65.1
8.5	82.5	84.9	1.0	5.2	8.0	0.8	70.0
9.0	86.5	91.5	0.5	2.8	4.3	0.8	79.1
9.5	84.4	80.9	1.2	7.3	9.7	0.7	68.2
10.0	86.9	85.2	0.7	5.0	8.3	0.7	74.0
10.5	87.0	82.5	1.1	6.4	9.2	0.6	71.8

Reaction conditions: 200 mg catalyst, 20 mL CHP, 40 mL tert-butanol at 353 K for 4 h.

^a The DMPC amount only results from thermal decomposition of CHP and excludes those formed in propylene epoxidation.

$$S_{\text{CHP}}$$
 (%) = $\frac{n_{\text{PO}}}{n_{\text{CHP}}^{i} - n_{\text{CHP}}^{t}} \times 100\%$,

 Y_{CHP} (%) = ($S_{\text{CHP}} \times X_{\text{CHP}}$) × 100%

where n_{CHP}^i and n_{CHP}^t are the initial and final mole number of CHP in the reaction mixture respectively, and n_{PO} is the mole number of PO produced.

3.1. Characterization of catalyst

The powder X-ray diffraction (XRD) patterns of all samples were recorded on a Rigaku D-MAX RB X-ray diffractometer operated at 40 kV and 40 mA with CuK α radiation (λ = 1.541 Å). The nitrogen adsorption at low temperature was performed on a Quantachrome Nova 4200e surface area and pore size analyser using static adsorption procedures, and the surface areas of catalysts were calculated by the BET method. The FT-IR spectra were recorded on a Nicolet NEXUS 670 FT-IR spectrometer, and the sample to be measured was ground with KBr and pressed into thin wafer. Laser Raman spectra (LRS) of samples were collected at ambient condition on an HR LabRaman 800 system equipped with a CCD detector. A laser beam (λ = 514 nm) was used for an excitation.

The FT-IR spectra of pyridine (Py) adsorbed on sample were also recorded on a Nicolet Nexus 670 FT-IR spectrometer. The sample was pressed into 20 mg/cm² self-supporting wafer, and then this wafer was placed in a quartz infrared cell equipped with CaF₂ windows, which contained a heating device. The IR chamber was evacuated to 1.0×10^{-7} Torr at 773 K for 4 h, and then the wafer was cooled down to room temperature and exposed to pyridine of 1.5×10^{-2} Torr for 10 min. The spectra were recorded when the pre-treated sample was desorbed at different temperature. The acid concentration was quantitatively evaluated according to the method of Emeis [36].

4. Results and discussion

4.1. Catalytic performance of MoO₃/SiO₂ for the propylene epoxidation

The catalytic performances of the MoO_3/SiO_2 catalysts prepared with ammonium hydroxide (precipitant) of different pH values were tested for the epoxidation reaction of propylene by cumene hydroperoxide (CHP), and the results are presented in Table 1. It can be seen that the catalyst prepared with ammonium hydroxide of pH 9.0 exhibits the best catalytic performance, and 79.1% PO yield, 91.5% PO selectivity and 87.5% CHP conversion are obtained, respectively.

For the CHP conversions, the MoO_3/SiO_2 catalysts prepared with precipitant of different pH values are very similar to each other, but their selectivity and yield of PO are various. With an increase in pH of the ammonium hydroxide, the prepared MoO_3/SiO_2 catalyst exhibits increasing selectivity and yield of PO. Using the catalyst prepared with ammonium hydroxide of pH 9.0, the highest PO selectivity and PO yield can be obtained. Further increasing pH of precipitant, the PO selectivity and PO yield over the catalyst prepared are decreased on the contrary.

The by-products in the propylene epoxidation with CHP include 1,2-propanediol, acetone, DMPC (dimethylphenylcarbinol, excluding those formed in propylene epoxidation) and acetophenone, in which acetone, DMPC and acetophenone result mainly from decomposition of CHP. As shown in Table 1, the amount of formed 1,2-propanediol is very few, suggesting that the hydrolysis of PO to 1,2-propanediol barely occurs. The catalyzed decomposition of CHP produces acetone and DMPC, and the thermal decomposition of CHP generates acetophenone [37]. It can be noted that the amount of produced acetophenone is very few and almost same for the all catalysts; the amounts of formed acetone and DMPC are different for different catalysts, and for acetone and DMPC resulted from catalyzed decomposition of CHP, their concentrations are very low over the catalyst prepared with ammonium hydroxide of pH 9.0, comparing with other catalysts.

4.2. Characterization of MoO₃/SiO₂ catalysts

The BET surface area of SiO₂ prepared by this sol-gel method is $452 \text{ m}^2/\text{g}$, and the MoO₃/SiO₂ catalysts prepared behave smaller surface area than the pure silica (Table 2), which is due to a deposition of the molybdenum species on the silica surface. Furthermore, the effect of precipitant pH on the surface area of these MoO₃/SiO₂ catalysts is unobvious, and their BET surface areas are ~430 m²/g except the catalyst (pH 10.5) of 408 m²/g, which indicates that the difference of catalytic performance between catalysts is not mainly resulted from the diversity of their surface areas.

As shown in Fig. 1S, the XRD spectra of the MoO_3/SiO_2 catalysts exhibit the characteristic peak of amorphous SiO_2 , and no definite diffraction peaks of molybdenum species can be observed for these $10 \text{ wt\%} MoO_3/SiO_2$ catalysts, indicating good dispersion of molybdenum oxide on SiO_2 support. In contrast, monolayer coverage by impregnation on SiO_2 was not achieved at above 5% molybdenum oxide, due to the low concentration of surface OH group and the low reactivity between adjacent silanol groups to form siloxane bridges [38]. The high dispersion of MoO_3 on SiO_2 in this work has been obtained due to the high concentration of OH group on silicon gel in the sol–gel process.

To further explore the structure of MoO₃ on the SiO₂ surface, the FT-IR spectroscopy was used to test the surface properties of SiO₂, MoO₃ and MoO₃/SiO₂ samples. As shown in Fig. 1, the FT-IR spectra of all MoO₃/SiO₂ samples exhibit the absorption bands at 1300–1020, 800 and 467 cm⁻¹ which are corresponding to asymmetric stretching, symmetric stretching and bending modes of bulk Si–O–Si, respectively [39]. These IR spectra are similar to the IR spectra of SiO₂ (Fig. 1a) and indicate that the MoO₃/SiO₂ samples have the similar surface chemical structures with SiO₂.

Table 2

BET surface areas (S_{BET}) and amounts of Lewis acid sites of MoO₃/SiO₂ catalysts.

Catalyst (pH of precipitant)	$S_{\text{BET}}(m^2/g)$	Amount of Lewis acid sites ^a (mmol/g-cat)			
		373 K	573 K	673 K	
8.0	439	0.411	0.061	0.042	
8.5	424	0.404	0.048	0.031	
9.0	437	0.423	0.035	0.022	
9.5	432	0.412	0.056	0.039	
10.0	425	0.415	0.045	0.029	
10.5	408	0.434	0.050	0.035	

^a The amount of Lewis acid sites was calculated by the method of Emeis [36] according to the IR absorption peak area of pyridine adsorbed on MoO₃/SiO₂ catalyst after desorption at different temperatures.



Fig. 1. FT-IR spectra of SiO₂ (a) (prepared by sol-gel method), MoO₃/SiO₂ prepared with ammonium hydroxide of (b) pH = 8.0, (c) pH = 9.0, (d) pH = 10.0, and (e) MoO₃ (calcined by ammonium heptamolybdate).

In the IR spectrum of pure bulk MoO₃, there are a band at 994 cm⁻¹ and two broad bands at 875 and 620 cm⁻¹ corresponding to the Mo=O group of MoO₃ phase, Mo–O–Mo asymmetric stretching vibration and Mo–O–Mo symmetric stretching vibration, respectively. These three IR absorption bands do not appear in the IR spectra of 10%MoO₃/SiO₂ catalysts, which indicates that bulk MoO₃ phase is not present in the prepared MoO₃/SiO₂ catalyst, which is consistent with the XRD results.

The bands at 915 and 960 cm⁻¹ in IR spectra of the MoO₃/SiO₂ samples are attributed to Mo–O–Si vibration and terminal Mo=O groups of surface molybdate phase [40]. The intensity of the band at 915 cm⁻¹ (Mo–O–Si) is clearly varied with the pH value of ammonium hydroxide, indicating that the interaction between Mo species and silica surface is affected by the pH value of synthesis solution in the sol–gel process. The IR absorption band at 915 cm⁻¹ on the surface of the catalyst (pH 9.0) has the highest intensity, that is, there is the strongest interaction between MoO₃ and SiO₂ on the catalyst (pH 9.0).

As shown in Fig. 2, the bands at 996, 821 and 667 cm^{-1} of crystalline MoO₃ are absent in the Raman spectra of MoO₃/SiO₂ catalysts, and the bands at ~873 and ~956 cm⁻¹ of surface polymolybdate species are observed remarkably. The broad band at 873 cm⁻¹ is assigned to the Mo–O–Mo stretching mode of polymerized three-dimensional surface molybdenum oxide species, such as Mo₈O₂₆^{4–} or Mo₇O₂₄^{6–} [29], and the band at 956 cm⁻¹ is attributed to the terminal Mo=O Raman stretching vibration of various octahedrally coordinated molybdenum oxide species (such as Mo₈O₂₆^{4–} or Mo₇O₂₄^{6–}) rather than isolated tetrahedral molybdenum species [41–43]. This indicates that only



Fig. 2. Raman spectra of MoO_3/SiO_2 catalysts prepared with ammonium hydroxide of (a) pH = 8.0, (b) pH = 8.5, (c) pH = 9.0, (d) pH = 9.5, and (e) pH = 10.0.

octahedrally coordinated molybdenum species exist on the surface of MoO₃/SiO₂ catalysts rather than tetrahedral coordinated molybdenum species.

4.3. FT-IR spectroscopy of adsorbed pyridine

To evaluate the type and strength of acid sites in MoO_3/SiO_2 catalysts, the FT-IR spectra of pyridine adsorbed on the catalysts were measured and the results are shown in Fig. 3. As it has been reported



Fig. 3. FT-IR spectra of pyridine adsorbed on MoO_3/SiO_2 catalysts after desorption at 373 K. L: Lewis acid sites; B: Brønsted acid sites.



Fig. 4. FT-IR spectra of pyridine adsorbed on MoO₃/SiO₂ catalysts prepared with ammonium hydroxide of (a) pH 8.0 and (b) pH 9.0 after desorption at 373–673 K. L: Lewis acid sites; B: Brønsted acid sites.

[44,45], the absorption bands at about 1451 and 1611 cm⁻¹ should be attributed to the absorption frequencies of pyridine interacting with the Lewis acid sites, and the bands at about 1540 and 1634 cm⁻¹ should be attributed to the absorption frequencies of pyridine coordinated in the Brønsted acid sites. The results in Fig. 3 show that only a band at 1451 cm⁻¹ appears on the MoO₃/SiO₂ catalysts after desorption at 373 K, suggesting that only Lewis acid sites exist on the MoO₃/SiO₂ catalysts and there are no Brønsted acid sites or its acid property is very weak.

After pyridine adsorbed on the catalyst (pH=8.0 and 9.0) was desorbed at 373 K, 573 K and 673 K, their FT-IR spectra are shown in Fig. 4, and the concentrations of Lewis acid sites on the all catalysts were calculated by the Emeis method based on the bands at 1451 cm^{-1} [36] and are listed in Table 2. With increasing desorption temperature, the amount of pyridine adsorbed on Lewis acid sites would decrease, because pyridine adsorbed on weaker Lewis acid sites would be desorbed at higher temperature; only pyridine adsorbed on relatively stronger Lewis acid sites can be kept. The results in Table 2 show that, pH of ammonium hydroxide has an influence on the strength distribution of the acid sites on the MoO₃/SiO₂ catalysts.

The results in Table 2 show that, with an increase in pH of ammonium hydroxide, the initial (or total) amount of Lewis acid sites on the MoO_3/SiO_2 catalyst is almost alike, but the acid amount has been varied after desorption at different temperatures, which shows that the precipitant pH value can affect the acid strength of surface acid sites of the MoO_3/SiO_2 catalyst. Among all catalysts, the catalyst (pH 9.0) possesses the lowest acid amount (0.022 mmol/gcat) after desorption at 673 K, that is, its Lewis acid strength is the weakest. The results in Table 1 show that the catalyst (pH 9.0) behaves the best performance, 91.5% PO selectivity and 79.1% PO yield. Relating the catalytic performance of the MoO_3/SiO_2 catalyst (Table 1) and its Lewis acid property (Table 2), it can be concluded that weaker Lewis acid sites on MoO_3/SiO_2 catalyst is in favor of the propylene epoxidation with CHP.

The data in Table 1 show also that, for the products (acetone and DMPC) resulted from the catalyzed decomposition of CHP, the concentrations over the catalyst (pH 9) are the lowest among all catalysts, which is agreement with the situation that the catalyst (pH 9) possesses the weakest Lewis acid sites (Table 2). It was reported that both Lewis acid strength and Lewis acid site density are important properties for the catalyst used in the CHP decomposition [46]. Because CHP is a Lewis base, the MoO₃/SiO₂ catalyst as a Lewis acid catalyze the CHP decomposition. Stronger acidity of the Lewis acid sites can accelerate CHP decomposition [47]. The PO selectivity can be improved when the stronger Lewis acidic sites are obviously reduced, such as the catalyst (pH 9). The increase in the concentration of strong Lewis acid sites promotes the catalyzed decomposition of CHP, which forms more acetone and DMPC byproducts, and also promotes the acid-catalyzed hydrolysis of PO to form the 1,2-propanediol.

The results above show that, the MoO₃/SiO₂ catalysts prepared with ammonium hydroxide of different pH values behave different concentration distribution and strength of their Lewis acid sites on the surface, resulting in different catalytic performances for the propylene epoxidation with CHP.

4.4. Effect of additive on the performance of MoO₃/SiO₂ catalyst

To modify the surface Lewis acidity to improve the catalytic performance of the MoO_3/SiO_2 catalyst, VIB elements (W, Cr) and rare earth elements (*e.g.*, La, Ce, Nd) were used as a promoter, and the catalytic properties of the modified catalysts are listed in Table 1S. The results show that the catalytic property of the MoO_3/SiO_2 catalyst (pH 9) can be improved after adding Nd. Using other elements as an additive to modify this catalyst, the selectivity to PO is reduced on the contrary. The effect of Nd loading on the catalytic performance of this catalyst was studied. It has been found that the optimal loading of Nd is ~0.5 wt%. Using 0.5 wt%Nd-MoO_3/SiO_2 (pH 9) catalyst, 91.4% CHP conversion and 91.1% PO selectivity can be obtained. When the Nd amount exceeds 1 wt% in this catalyst, its catalyst, its catalyst; property is severely deteriorate (Table 3).

The results in Table 3 show that, the moderate addition of Nd in MoO₃/SiO₂ catalyst affects hardly the PO selectivity, can increase the conversion of CHP and inhibit the PO hydrolysis, that is, 1,2-propanediol cannot be found in the products; and that acetone and DMPC from the CHP decomposition are almost unchanged. If the Nd amount in the catalyst is >0.7 wt%, the concentrations of acetone and DMPC in products are increased, which indicates that the surface Nd species may promote the CHP decomposition, resulting in no increase in PO selectivity. For acetophenone by-product, the addition of Nd has no obvious effect on its amount, because it results from thermal decomposition of CHP.

The Lewis acid concentrations of the Nd–MoO₃/SiO₂ catalysts were also measured by *in situ* FT-IR of adsorbed pyridine, and the results are shown in Table 3. As seen in Table 3, the presence of Nd in the MoO₃/SiO₂ catalyst does not vary the Lewis acid type on the surface of catalyst, but can affect the acid amount and acid strength of the catalyst. Comparing with unmodified MoO₃/SiO₂, the stronger Lewis acidic sites of Nd–MoO₃/SiO₂ is obviously reduced. When the Nd content is <0.7 wt%, the stronger Lewis acidic sites is gradually decreased with an increase in the Nd amount; when the Nd content

Nd (wt%)	X _{CHP} (%)	Selectivity (%)				Y _{PO} (%)	Amount o	fL-acid sites (mmol/g-cat) ^b	
		РО	1,2-Propanediol	Acetone	DMPC ^a	Acetophenone		373 K ^c	573 K	673 K
-	86.5	91.5	0.5	2.8	4.3	0.8	79.1	0.423	0.035	0.022
0.3	89.8	91.0	-	2.8	5.1	0.9	81.7	0.440	0.026	0.013
0.5	91.4	91.1	-	2.6	5.3	0.8	83.3	0.457	0.023	0.011
0.7	86.7	87.0	-	3.9	7.8	1.1	75.4	0.425	0.029	0.015
1.0	72.5	90.1	-	2.9	5.9	1.0	65.3	0.387	0.019	0.010
1.5	66.2	84.4	-	4.2	10.2	1.1	55.9	0.342	0.016	0.008

Amounts of Lewis acid sites and catalytic performances of Nd–MoO₃/SiO₂ catalysts for the propylene epoxidation.

Reaction conditions: 200 mg catalyst, 20 mL CHP, 40 mL tert-butanol, at 353 K for 4 h.

Table 3

^a The DMPC amount only results from thermal decomposition of CHP and excludes those formed in propylene epoxidation.

^b The amount of Lewis acid sites was calculated by the method of Emeis [36] according to the IR absorption peak area of pyridine adsorbed on Nd–MoO₃/SiO₂ catalyst after desorption at different temperatures.

is >0.7 wt%, total acid sites and the stronger Lewis acidic sites are all decreased with an increase of Nd amount.

Relating the catalytic performance and Lewis acidity of $Nd-MoO_3/SiO_2$ catalyst, we can see, the presence of Nd in the catalyst decreases the acid strength of the catalyst and increases amount of weak acid sites on the catalyst surface, inhibiting the PO hydrolysis thus largely eliminate 1,2-propanediol. When the Nd content exceeds 0.7 wt%, a decrease in total acid sites makes the CHP conversion notably fall, and a decrease in stronger Lewis acidic sites should improve the PO selectivity, but in fact the PO selectivity still decrease instead, which is possible that the presence of higher Nd loading promote CHP degradation to produce more acetone and DMPC.

4.5. Discussion of the active sites and effect of precipitant pH value

It has been proved that Mo-based catalysts possess Lewis acid sites in their highest oxidation state d^0 . These Lewis acid sites have a low redox potential and are labile to accept ligands. Olefin epoxidation by d^0 metal peroxo complexes is generally considered to proceed through an electrophilic attack of the oxygen on the electron-rich olefin.

In order to confirm that the Lewis acid sites serve as the active sites in the epoxidation of propylene, the catalytic activity of MoO_3/SiO_2 -Py pretreated with pyridine was studied. As it can be seen from Table 2S, after 2 mL pyridine was added in the reaction the conversion of CHP over MoO_3/SiO_2 is only decreased from 86% to 72%, but using MoO_3/SiO_2 -Py catalyst the conversion of CHP falls down to 4%, which is similar to the catalytic performance of SiO₂. This result indicates that the Lewis acid sites on the catalyst are the active sites to catalyze propylene epoxidation. The decrease in performance of MoO_3/SiO_2 -Py catalyst is due to pyridine on adsorbed on the catalyst blocking the Lewis acid active sites.

There may be three kinds of molybdate species in the MoO_3 -based catalyst, *i.e.*, tetrahedral species, tetragonal species, octahedral species and polymeric MoO_x species. The models of the possible surface molybdenum species can be demonstrated in Fig. 5. The models I and II represent the tetrahedral and tetragonal coordinated molybdenum species, respectively. The models III and IV represent the distorted octahedral configurations with pentacoordinated (MoO_5) species [48]. The Raman spectra reveal that only octahedral molybdenum species exist on the MoO_3/SiO_2 catalysts, which can be represented by model III and IV. Based on the structural models and Lewis acidity properties of the MoO_3/SiO_2 catalysts, we can conclude that the Lewis acid sites in the octahedral molybdenum species are the active catalytic sites.

In the octahedral molybdenum species in Fig. 5, the Mo (b) has stronger Lewis acidity than Mo (a) because of its lower electronic density. The hydrolysis and condensation of TEOS produce threedimensional structure network of SiO₄ at alkaline condition [49],



Fig. 5. Possible molecular structure of MoO_x cluster models: distorted tetrahedral coordination (I), distorted tetragonal pyramidal coordination (II) and distorted octahedral coordination (III and IV) [63].

and the pH value of the hydrolyzing environment (as precipitant) directly affects the silica structure. It is supposed that more highly cross-linked gels and short silica chain are obtained when ammonium hydroxide of pH 9.0 was used. Therefore, the MoO₃/SiO₂ catalyst prepared with ammonium hydroxide of pH 9.0 may contain more short chain molybdenum species (such as Mo (a) in model III) than other catalysts in the preparation of the MoO₃/SiO₂ catalyst. The FT-IR spectra (Fig. 2) show that there is the strongest interaction between MoO₃ and SiO₂ on the catalyst (pH 9.0), resulting in a formation of more short chain molybdenum species like Mo (a) after calcination. This is the reason that the 10wt%MoO₃/SiO₂ catalyst (pH 9.0) behaves the excellent catalytic performance for the epoxidation of propylene with CHP.

5. Conclusions

In summary, the high effective 10 wt% MoO_3/SiO_2 catalysts for the propylene epoxidation with CHP were successfully prepared by the sol-gel method using ammonium hydroxide as a precipitant. The results show that there are mainly Lewis acid sites on the surface of the MoO_3/SiO_2 catalyst, and these Lewis acid sites consisted of the octahedral molybdenum species are the active sites of propylene epoxidation. The concentration distribution and strength of Lewis acid sites are related to the catalyst performance of MoO_3/SiO_2 catalyst, and the total amount of Lewis acid on the catalyst surface is related with the CHP conversion and the weaker Lewis acid sites on MoO_3/SiO_2 catalyst is in favor of the propylene epoxidation with CHP. When the amount of Lewis acid sites on the catalyst surface is more and their acid strength is higher, the CHP degradation and PO acid-catalytic hydrolysis would be speeded up, resulting in a reduction of the selectivity to PO.

The concentration and strength of the Lewis acid sites on the MoO_3/SiO_2 catalyst are affected by pH of precipitant, and the catalyst prepared with precipitant of pH 9.0 possesses the most weakly Lewis acidic sites on the surface, resulting in the highest selectivity to PO (91.5%). The addition of Nd in the MoO_3/SiO_2 catalyst can

increase the weakly acidic sites to enhance CHP conversion and reduce strongly acidic sites to inhibit PO acid-catalytic hydrolysis. Using 0.5 wt% Nd-10 wt%MoO₃/SiO₂ catalyst, 91.4% CHP conversion and 91.1% PO selectivity can be obtained.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata. 2013.02.020.

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