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Selective propylene epoxidation in liquid phase using highly dispersed Nb catalysts incorporated in mesoporous silicates☆

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ABSTRACT

Selective propylene epoxidation to propylene oxide (PO) with hydrogen peroxide (H_2O_2) was carried out in a catalytic semi-batch reactor. High propylene epoxidation activity (44 h^{-1}) was observed over Nb based mesoporous silicate materials Nb-TUD-1 under mild operating conditions. The physical and chemical properties of the Nb based silicates characterized using BET, FTIR, TPD, TEM and UV-Vis revealed that the site isolation and surface acidity are crucial for PO production. Catalyst synthesis methods were investigated for their effects on PO productivity, PO selectivity and H_2O_2 utilization efficiency. It is found that Nb-TUD-1 material synthesized by the sol-gel method is more active and selective than impregnated materials for liquid phase propylene epoxidation. Surface characterization confirms that thus synthesized Nb-TUD-1 catalysts have more Lewis acidity and less Bronsted acidity compared to the catalysts by impregnation.

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1. Introduction

Propylene oxide (PO) is one of the most important industrial chemicals for the manufacture of a variety of commodity products including plastics, polymers, solvent and bio-active agents for fine chemical and pharmaceutical applications [1]. At present, industrial production of PO is mainly through the chlorohydrin process and peroxide promoted technologies. While the former is known for harsh reaction conditions, generation of significant toxic side-products and low production efficiency, the latter one has been extensively studied due to potentially high atomic efficiency and non-toxic by-product (H_2O) formation. Up to date, intensive research efforts are still focused on noble metal based catalysts (Au [2–20], Ag [21–26] and Pd [27,28]) for direct oxidation by H_2O_2 (or by H_2 – O_2 mixture [19,24]) in gaseous phase. The major issues, however, plaguing current metal-based catalytic processes include the use of expensive materials, poor catalyst durability and potential explosive risk induced by mixing of H_2 and O_2 . Some of recent work proved that direct oxidation of propylene to PO

is feasible in the presence of metal-based catalysts (e.g. Cu [1,29–38]). Although this provides an alternative process reducing the use of expensive and unrenewable H_2 , only limited progress has yet been achieved because of uncontrollable combustion, poor catalytic activity and selectivity when mixing propylene with O_2 under elevated reaction conditions.

Liquid phase epoxidation (LPE) of propylene to PO using H_2O_2 as oxidant under mild conditions ($<50^\circ\text{C}$) is an emerging technology exhibiting excellent atom efficiency and having productivity comparable with existing industrial processes. Busch and Subramaniam developed Re-based homogeneous catalysts and obtained $>99\%$ PO selectivity with zero CO_2 formation under 40°C and 3.5 MPa propylene pressure [39]. ENI, Evonik and DOW have developed H_2O_2 propylene oxidation (HPPO) technologies using TS-1 as catalyst with good selectivity towards PO [40]. Therefore, many research efforts have been put to enhance the performances of TS-1 catalysts by modifying their surface chemical properties [41–45], as well as understand the reaction mechanism on catalyst surface [15,29,46–49]. However, expensive cost for preparation of TS-1 catalysts restrained this technology from further development [47]. Economic and environmental analysis confirms that use of inexpensive catalytic materials with enhanced durability might debottleneck the further development of this technology. Therefore, rational design of cheaper catalysts is considered as a key factor that promotes practical application of the LPE process for PO manufacture.

Metal incorporated mesoporous materials have shown promising features in the area of heterogeneous catalysis of olefin epoxidation

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due to their remarkable catalytic properties and relatively cheaper precursors compared with those for TS-1 catalyst preparation [50–63]. For example, Ti modified MWW zeolite shows >99% selectivity to PO and 95% H_2O_2 efficiency during propylene epoxidation [40,64]. It is found that the formation of propylene glycol and block of pore channels might be the key factors in deactivating Ti-MWW catalysts. Ti modified HMS [50,65], SBA-15 [66] and MCM-41 [51] supports also show remarkable performances in propylene epoxidation (selectivity $S \sim 99\%$). Nb incorporated mesoporous materials have also exhibited promising performances in LPE for PO synthesis [67,68]. Held *et al.* [67] studied Nb doped SBA-3 mesoporous molecular sieves for selective oxidation of propylene in the presence of N_2O as an oxidant. The catalytic tests showed that propylene conversion and PO selectivity were affected both by the type and amount of transition metal ions introduced into the system. Experimental studies by Liu *et al.* [68] for Nb-HMS (Hexagonal Mesoporous Silica) using *n*-dodecylamine show that Nb-HMS material exhibited excellent catalytic activity and selectivity for PO with H_2O_2 as oxidant in MeOH medium. A propylene conversion of 41.3% and PO selectivity of 98.3% were obtained at 50 °C, and the efficiencies of the H_2O_2 utilization were higher than 98%. Under the same conditions, Nb-HMS showed higher activity and selectivity than Nb-MCM-41 (conversion $X = 33\%$, $S = 97\%$). But catalyst stability was not reported in their work.

Fundamental studies have shown that surface acidity/basicity is critical in tuning epoxidation activity and selectivity. It has been demonstrated that increasing total acidic sites will enhance overall catalytic epoxidation activity, while altering ratios of Bronsted and Lewis acidities will affect selectivity towards epoxides. We have recently shown that novel TUD-1 based mesoporous materials incorporated with highly dispersed Nb species for facile LPE of ethylene to ethylene oxide (EO). TUD-1 is an amorphous mesoporous silicate (named after Delft University of Technology) that has several advantages such as ease of preparation, wide pore size distribution, high thermal stability, and environmentally benign synthesis protocol [69]. The catalytic performances for metal incorporated TUD-1 show industrially comparable performances for EO synthesis even at 35 °C and 5.0 MPa ethylene pressure, because the surface acidity and basicity can be well manipulated by controllable doping of single sited metal species during catalyst synthesis [70,71]. To our best knowledge, there is no systematic study existing on TUD-1 supported Nb catalysts for LPE of propylene to PO under mild conditions. Therefore, in this work, we present detailed catalyst synthesis, characterization and activity test studies for facile PO synthesis in a batch reactor system. It is found that the surface and structural modification by Nb sites significantly enhances epoxidation performances of TUD-1 catalysts with excellent PO selectivity and H_2O_2 utilization efficiency.

2. Experimental

2.1. Chemical reagent

Methanol (MeOH) was used as received without further purification. High purify grade propylene was used as feedstock. H_2O_2 (30 wt % in H_2O), acetonitrile (AN, HPLC grade) niobium oxide (Nb_2O_5), niobium chloride (NbCl_5), niobium oxalate, triethanolamine (TEA), tetraethylammonium hydroxide (TEAOH, 35%), tetraethyl orthosilicate (TEOS), and anhydrous propylene glycol (PG) were purchased from Aladdin.

2.2. Synthesis of Nb-TUD-1

2.2.1. Sol-gel method

Nb-TUD-1 materials were synthesized following a procedure similar to that for siliceous TUD-1 [69]. In a typical synthesis, a mixture of TEA and deionized water was added to a solution of Nb precursor in ethanol under stirring. To this mixture, a predetermined amount of TEOS was

added and the stirring was continued for another 30 min. Finally, TEAOH was added dropwise, stirring the mixture vigorously for another 2 h. The resulting gel has the following molar composition ratio: 1 SiO_2 : (0.001–0.1) Nb: (0.35–0.5) TEAOH: 1 TEA: 11 H_2O . This gel was aged at room temperature for 24 h followed by drying at 100 °C for 24 h. The resulting solid was then transferred into a Teflon lined autoclave for hydrothermal treatment at 180 °C for 6 h. Finally, the template was removed by calcination in air at 600 °C for 10 h with a heating rate of 1 °C·min⁻¹. After the calcination, about 5 g of as prepared catalysts will be available after evaluation. The samples with various Si/Nb ratios are named as Nb-TUD-1(*x*), where *x* represents the Si/Nb atomic ratio.

2.2.2. Impregnation method

Impregnated Nb-TUD-1 was prepared by impregnating Si-TUD-1 with NbCl_5 . Si-TUD-1 was synthesized with following procedure. TEA, deionized water and ethanol were mixed under stirring. To this mixture, a predetermined amount of TEOS was added and the stirring was continued for another 30 min. Finally, TEAOH was added dropwise, stirring the mixture vigorously for another 2 h. The resulting gel has the following molar composition: 1 SiO_2 : (0.35–0.5) TEAOH: 1 TEA: 11 H_2O . This gel was aged at room temperature for 24 h followed by drying at 100 °C for 24 h. The resulting solid was then transferred into a Teflon lined autoclave for hydrothermal treatment at 180 °C for 6 h. Finally, the template was removed by calcination in air at 600 °C for 10 h with a heating rate of 1 °C·min⁻¹. For the impregnation method, two niobium precursors were studied. Si-TUD-1 was impregnated with desired amount of NbCl_5 or Nb oxalate (Nb mass percentage is about 1.6 wt% in the as prepared catalyst) in 20 g of ethanol for 5 h and air dry at room temperature. Each preparation provides 5 g of as prepared catalysts (particle size ~ 200 mesh). The samples synthesized with impregnation methods were named as Nb-TUD-1(*x*), with *x* representing the Si/Nb atomic ratio.

2.3. Catalyst characterization

Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2010 microscope. Brunauer–Emmet–Teller (BET) surface areas were measured using an ASAP 2020 instrument with nitrogen as the sorbate. FTIR spectroscopy was performed on a Nexus FTIR instrument to study the acidity of zeolite. Pretreatment of the sample was made in the cell at 300 °C under vacuum for 2 h. Then purified pyridine vapor was adsorbed onto the zeolite at room temperature. The excess of pyridine was removed under vacuum over two consecutive (1 h) periods of heating at 200 °C and 350 °C respectively, each of which followed by IR measurements. NH_3 -TPD was also employed as a measure of the acidity of catalysts on a CHEMBET-3000 TPR/TPD instrument. The sample (0.1 g) was loaded into a U-shaped microreactor and pretreated at 700 °C for 1 h in flowing He. After the pretreatment, the sample was cooled to 100 °C and saturated with NH_3 gas. Then the NH_3 -TPD was carried out under a constant flow of He (50 ml·min⁻¹) from 100 °C to 700 °C at a heating rate of 20 °C·min⁻¹. The desorbed ammonia was monitored continuously with a gas chromatograph equipped with a thermal conductivity detector. Nb content in different catalyst samples was determined by ICP (JY-2000, HORIBA), the method of which was previously reported [71,72].

2.4. Catalytic epoxidation

Propylene epoxidation reactions were conducted in a 50-mL reactor equipped with a magnetically driven stirrer, pressure transducer, and thermocouple. Briefly, a solution containing 30% $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ (13.5 g, 120 mmol), MeOH (20 g, 630 mmol) and internal standard acetonitrile (5 mmol) was charged into the reactor. Propylene was injected from the gas cylinder to pressurize the reactor up to 3.0 MPa. The inertness of AN was confirmed experimentally via blank runs. The reactor pressure was held constant by continuously replenishing the consumed propylene

from the external propylene reservoir. The reactor temperature was maintained at 40 °C. The impeller speed was kept at 1400 r·min⁻¹ to ensure the absence of mass transfer limitations. Isothermal, constant pressure semi-batch reactions last up to 5 h.

The following indexes are used in assessing the performance of the tested catalysts:

$$S_{PO} = \left(\frac{n_{PO}}{n_{PO} + n_{PG} + n_{MP}} \right) \times 100\%$$

$$U_{H_2O_2} = \frac{n_{PO} + n_{MP} + n_{PG}}{n_{H_2O_2}^0 - n_{H_2O_2}} \times 100\%$$

$$X_{H_2O_2} = \frac{n_{H_2O_2}^0 - n_{H_2O_2}}{n_{H_2O_2}^0} \times 100\%$$

where S_{PO} , $U_{H_2O_2}$, and $X_{H_2O_2}$ denote PO selectivity, H_2O_2 utilization towards products formation (also defined as the H_2O_2 utilization efficiency) and H_2O_2 conversion, respectively. n_{PO} , n_{MP} , n_{PG} denote the molar amounts of PO, methoxy propanol and propylene glycol formed, respectively. $n_{H_2O_2}^0$ and $n_{H_2O_2}$ are the initial and the final molar amounts of H_2O_2 , respectively. TOF is defined as moles of H_2O_2 converted per atom Nb per time [71,72].

3. Results and Discussion

3.1. Characterization of Nb catalysts

Fresh and used Nb-TUD-1 catalysts were characterized using BET, UV–Vis and NH_3 -TPD respectively. It is found in Table 1 that as Si/Nb ratio increases, surface areas of Nb-TUD-1 catalysts show significant enhancement. The pore volume of Nb catalysts also increases with Si/Nb ratios, suggesting lower Nb loading favors the formation of pores with larger diameter during catalyst synthesis. In addition, surface area, pore volume and pore diameter do not change significantly compared with fresh and used catalysts. Surface areas of Nb-TUD-1 catalysts prepared by impregnation method were also characterized and compared. It can be seen from Table 1 that Nb-TUD-1 (100) impregnated by chloride and oxalate precursors show smaller pore diameters compared with Nb-TUD-1 catalyst. Nb-TUD-1 (100) catalyst prepared by sol–gel method display good dispersion for Nb species as no detectable Nb nanoparticles are observed in TEM images (Fig. 1). The difference suggests that the sol–gel method favors Nb distribution within the network, thus larger pore size and volume can be formed (also confirmed in Fig. 2), while impregnation might block some mesoporous channels, thus both mean pore size and surface are lower.

Table 1
BET analysis of fresh and used Nb-TUD-1 catalysts

Si/Nb (molar ratio)		$S_{BET}/m^2 \cdot g^{-1}$	$V_p, BJH/ml \cdot g^{-1}$	$d_p, BJH/nm$
10	Fresh	358	0.67	7.5
	Used	357	0.65	7.3
20	Fresh	580	0.89	6.1
	Used	629	0.91	5.8
40	Fresh	505	0.99	6.8
	Used	514	0.89	6.2
100	Fresh	578	0.97	8.7
	Used	550	0.95	7.9
100 (NbCl ₅)	Fresh	478	0.91	6.1
	Used	550	0.91	5.9
100 (Nb oxalate)	Fresh	571	0.87	6.3
	Used	544	0.85	6.0

Diffuse reflectance UV–Vis spectra of Nb-TUD-1 samples show a significant absorption peak around 212–229 nm with a tail at 272 nm (Fig. 3). The absorption peak is attributed to well-defined NbO_4 tetrahedral

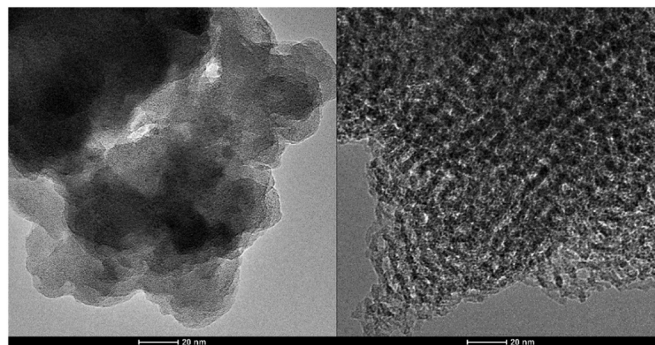


Fig. 1. TEM images of Nb-TUD-1 (100) catalysts.

units, whereas the tailing around 272 nm is due to oligomeric NbO_4 units. The absorption in the range of 272–325 nm may also be attributed to the possible exposure of catalyst sample to moisture, inducing the formation of penta- or hexa- coordinated Nb (V) species. Furthermore, the fraction of such species at 272 nm is relatively low compared to the tetrahedrally coordinated species. Since it is known that for commercial Nb_2O_5 powder, two absorption bands, one at 226 nm and a prominent one at 310 nm, are noticed [59,71,73], the lack of these footprint in Nb-TUD-1 samples suggests the absence of bulky Nb_2O_5 species in Nb-TUD-1 catalysts.

The influence of Nb loading on strength of acidic sites was also characterized using NH_3 -TPD technique. Particularly, the NH_3 desorption signals were collected at different temperatures and the results are shown in Figs. 3 and 4. We observed that TUD-1 without Nb loading shows negligible TCD signal. It is interesting to find that desorption peaks for Nb-TUD-1 (20) and (40) are both at 130–200 °C although peak shapes are slightly different. This result indicates that the effect of Nb loading on acidic strength is insignificant, suggesting Nb loading does not affect Nb-support interaction. However, this is not true for catalysts prepared by impregnation. We find from Fig. 5 that while Nb-TUD-1 (100) shows a wider desorption peak around 150–400 °C, Nb-TUD-1 (100) prepared using $NbCl_5$ for impregnation displays a higher NH_3 desorptive temperature with a small range from 210 to 280 °C. This unusual behavior is possibly induced by tunable Nb-support interaction within catalyst network. Although it is obvious that metal-support interaction is much stronger for Nb-TUD-1 (by the sol–gel method) samples. However, lower desorption peak for this sample implies that Nb presence in $-Si-O-Ni-O-Si-$ framework actually weakens the electron withdrawing capability in catalyst sample.

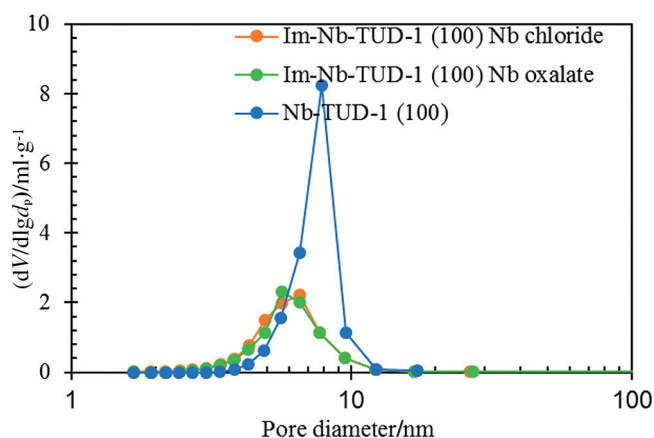


Fig. 2. Pore size distribution for Nb-TUD-1 catalysts prepared by sol–gel and impregnation methods.

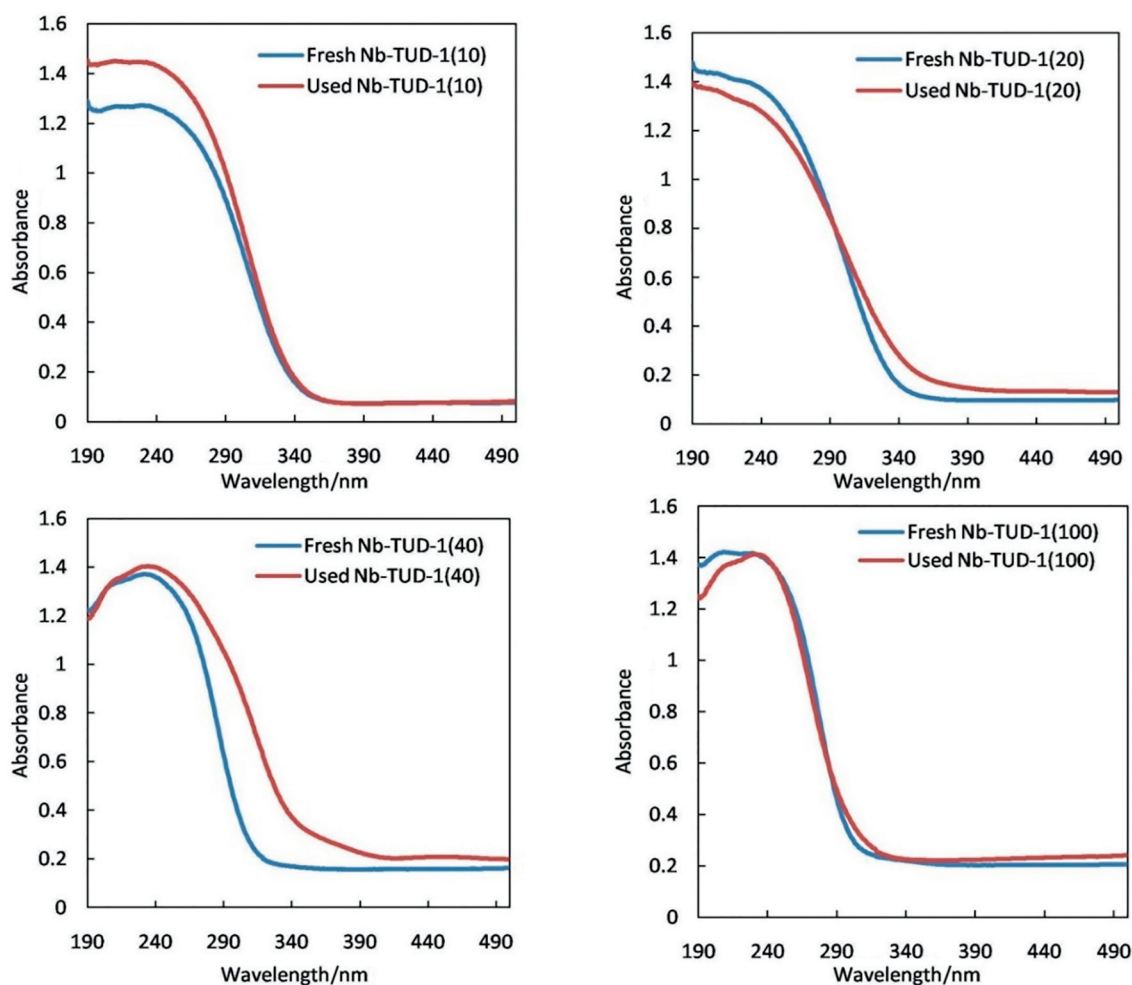


Fig. 3. UV-Vis of fresh and used Nb-TUD-1 catalysts.

On basis of surface area and acidic strength analysis, we further carried out FTIR to understand how the preparation method affects surface acidity (Fig. 6). Three bands are found in all investigated samples, exhibiting both Bronsted and Lewis acid sites. Nb-TUD-1 sample synthesized with the sol-gel method shows lower Bronsted acidity

compared with post synthesized Nb-TUD-1 samples by impregnation. The Bronsted acidity here is mainly assigned to Si—OH and Nb—OH groups. It might be due to less Nb species incorporation efficiency into the silica framework of post synthesis method.

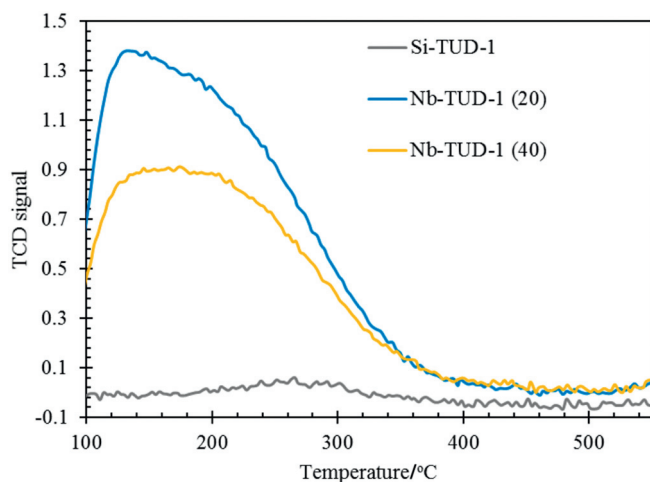


Fig. 4. NH_3 -TPD of Nb-TUD-1 (20) and (40) catalysts.

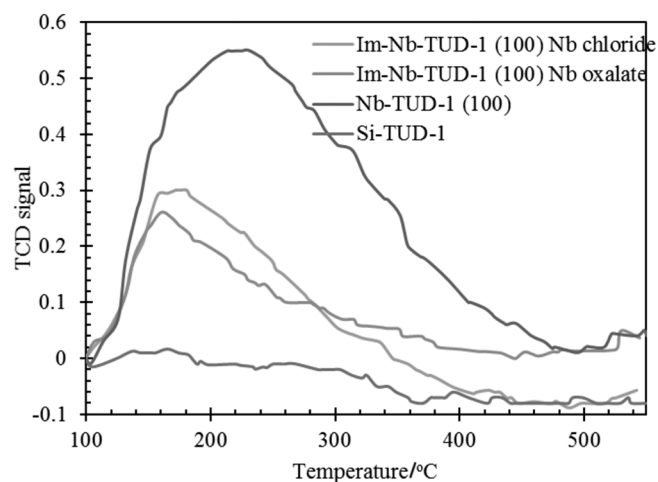


Fig. 5. NH_3 -TPD of Nb-TUD-1 catalysts prepared by sol-gel and impregnation methods.

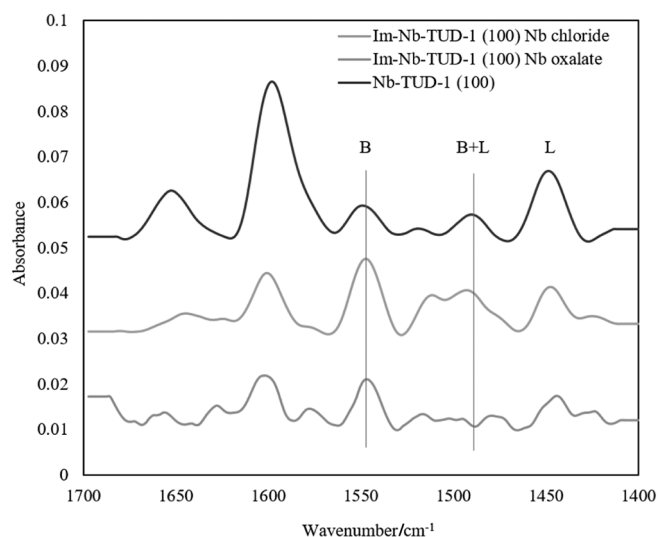


Fig. 6. Pyridine FTIR of Nb-TUD-1 catalysts.

3.2. Epoxidation of propylene over Nb-TUD-1 catalysts

3.2.1. Influence of Si/Nb molar ratio

The Nb-TUD-1 catalysts synthesized by different methods were tested and compared in the propylene epoxidation. Table 2 shows the effect of Si/Nb molar ratio on the catalytic performance of Nb-TUD-1 catalysts. Negligible PO formation and H_2O_2 decomposition were observed in a blank experiment with siliceous TUD-1 (Table 2, entry 1). Overall it is seen that framework incorporated Nb-TUD-1 catalysts (by sol-gel) displayed better performances for propylene epoxidation reactions compared with those prepared via impregnation (Table 2). This is because the sol-gel method generates better dispersed Nb catalysts, thus more active sites are available within the framework. In particular, Nb-TUD-1 (10), (20), (40) and (100) catalysts show 31.8%, 29.2%, 21.0% and 6.8% conversion for H_2O_2 at 40 °C and 3.0 MPa propylene pressure with catalytic activity being 19.4 h^{-1} , 30.1 h^{-1} , 44.1 h^{-1} and 32.4 h^{-1} . PO selectivity is found to be 54.1%, 57.4%, 72.1% and 77.4% respectively. The major by-products are propylene glycol (PG) and methoxy propanol (MP). In addition, Nb-TUD-1 (100) shows relatively better H_2O_2 utilization efficiency (53.9%) compared with Nb-TUD-1 (10), (20) and (40) catalysts. Although showing slightly lower catalytic activity (TOF: 18–20 h^{-1}), impregnated Nb-TUD-1 (100-NbCl₅) and (100-Nb oxalate) catalysts show higher H_2O_2 utilization efficiency compared with those obtained via sol-gel.

After a run of 5 h, catalysts were filtered, washed with methanol and dried at 100 °C. Propylene epoxidation experiments were carried out

with recycled catalysts under identical operating conditions as fresh catalysts. Further, the used catalysts were analyzed by the ICP-OES technique. Significant Nb leaching was observed for Nb-TUD-1. The used catalysts showed significant lower activity but relatively higher selectivity compared to the fresh catalysts due to the leaching of active Nb species to the solvent. This was confirmed by ICP-OES results. The Nb-TUD-1 (100) prepared by impregnation suffers more from metal leaching.

To further understand the influence of acidic sites on catalytic activity, the total acidity of Nb catalysts was compared with H_2O_2 conversion by carrying out control experiments without adding propylene. As shown in Table 3, increasing Nb loading from 1.6 wt% to 12.2 wt% leads to increases of total acidity from 0.2 to 0.4 $\text{mmol} \cdot \text{g}^{-1}$, which unfavorably cause more H_2O_2 decomposition. Particularly, no detectable H_2O_2 decomposition was observed over Si-TUD-1 in either the presence or the absence of propylene under similar operating conditions. However, even in the absence of propylene, approximately 18% H_2O_2 conversion was observed over Nb-TUD-1 (10) catalyst, implying that the acidity imparted by metal incorporation into the TUD-1 support is a causative factor for H_2O_2 decomposition. It is commonly known that homogeneous epoxidation catalysts that are exclusively Lewis acidic (MTO for example) utilize H_2O_2 effectively without decomposing it [39]. This may suggest that in the case of Nb-TUD-1 and other heterogeneous catalysts, the Brønsted acidity that increases with metal loading may play a role in decomposing H_2O_2 .

The effect of temperature on PO productivity was investigated with the Nb-TUD-1 (100) catalyst. As inferred from Table 4, whereas increasing the temperature from 40 to 60 °C has negligible effect on the PO

Table 3

Effect of acidity on H_2O_2 conversion on Nb-TUD-1 catalysts in absence of propylene

Nb-TUD-1	Nb loading/wt%	$\text{NH}_3/\text{mmol} \cdot \text{g}^{-1}$	$X_{\text{H}_2\text{O}_2}/\%$
Si-TUD-1	0	0.03	0
Nb-TUD-1 (100)	1.6	0.2	2.4
Nb-TUD-1 (40)	3.5	0.3	7.6
Nb-TUD-1 (20)	12.2	0.4	18.0

Reaction conditions: no propylene, other conditions similar to Table 2.

Table 4

Effect of temperature of propylene epoxidation over Nb-TUD-1 (100)

T/ °C	PO/mmol (± 3%)	$S_{\text{PO}}/\%$ (± 3%)	$X_{\text{H}_2\text{O}_2}/\%$ (± 3%)	$U_{\text{H}_2\text{O}_2}/\%$ (± 3%)
40	3.4	77.4	6.8	53.9
50	4.1	62.5	13.0	40.3
60	4.5	47.1	21.6	36.7

Reaction conditions: similar to Table 2.

Table 2

Epoxidation of propylene over Nb-TUD-1 catalysts

#	Si/Nb	Nb/wt%	PO/mmol	PG/mmol	MP/mmol	$\text{H}_2\text{O}_2/\text{mmol}$	$X_{\text{H}_2\text{O}_2}/\%$	S/%	U/%	TOF
1	Blank run	0	0	0	0	0	0	–	–	0
2	10	12.2	6.4	1.5	3.9	38.2	31.8	54.1	31.2	19.4
3	20	7.2	5.8	1.2	3.1	35.0	29.2	57.4	28.9	30.1
4	40	3.5	4.8	0.5	1.4	25.2	21.0	72.1	26.4	44.6
5	100	1.6	3.4	0.2	0.8	8.2	6.8	77.4	53.9	31.8
6	100-NbCl ₅	1.6	3.1	0.1	0.5	5.2	4.3	83.8	71.2	20.2
7	100-Nb oxalate	1.6	2.8	0.2	0.6	4.8	4.0	77.8	75.0	18.6
8	10 (used)	10.1	4.3	0.8	2.1	18.5	15.4	59.7	38.9	11.4
9	20 (used)	3.5	2.5	0.5	1	16.2	13.5	62.5	24.7	28.7
10	40 (used)	1.8	2.1	0.21	0.5	12.5	10.4	74.7	22.5	43.1
11	100 (used)	0.4	1.2	0.1	0.2	6.5	5.4	80.0	23.1	100.8
12	100-NbCl ₅ (used)	0.3	0.5	0.02	0.07	0.8	0.7	84.7	73.8	16.5
13	100-Nb oxalate (used)	0.2	0.3	0.02	0.06	0.5	0.3	78.9	76.0	15.5

[Reaction conditions: MeOH: 620 mmol, H_2O_2 : 120 mmol, AN: 5 mmol, catalysts: 300 mg, 40 °C, 3.0 MPa, 5 h, 1400 $\text{r} \cdot \text{min}^{-1}$].

productivity, and the PO selectivity decreased significantly from 77.4% to 47.1% as side reactions begin to dominate. In addition, enhanced H_2O_2 conversion ($X_{\text{H}_2\text{O}_2}$) but lower H_2O_2 utilization efficiency was achieved at the higher temperature.

Altering charging sequence of solvent, catalyst and oxidant can also affect H_2O_2 utilization efficiency (See Table 5). When adding catalysts in the mixture of MeOH and H_2O_2 , lots of bubbles generation was noticed. However, when adding H_2O_2 to the mixture of MeOH and Nb-TUD-1 catalyst, bubbles barely generated. The titration results showed that the H_2O_2 conversion decreased without loss of activity and the H_2O_2 utilization efficiency increased significantly.

Table 5

Effect of order of adding catalyst, solvent and oxidant

Operation mode	Nb/wt%	PO/mmol	$S_{\text{PO}}/\%$ ($\pm 3\%$)	$X_{\text{H}_2\text{O}_2}/\%$ ($\pm 3\%$)	$U_{\text{H}_2\text{O}_2}/\%$ ($\pm 3\%$)
MeOH + H_2O_2 + catalyst	3.5	4.8	72.1	21.0	26.4
MeOH + catalyst + H_2O_2	3.5	4.9	72.5	12.5	45.1
MeOH + H_2O_2 + catalyst	1.6	3.4	77.4	6.8	53.9
MeOH + catalyst + H_2O_2	1.6	3.4	76.9	4.3	85.0

Reaction conditions: similar to Table 2.

4. Conclusions

In this paper, selective epoxidation of propylene in liquid phase using Nb mesoporous catalysts were reported and studied within details. Nb-TUD-1 catalysts synthesized with both sol–gel and impregnation methods are active and have high selectivity towards PO. Impregnated Nb-TUD-1 catalysts showed slightly lower catalytic activity (TOF: 18–20 h^{-1}) but higher H_2O_2 utilization efficiency compared with those obtained via sol–gel. Furthermore, surface acidic strength strongly influences catalytic performances of Nb incorporated TUD-1 catalysts in terms of activity and H_2O_2 utilization. Experimental studies confirmed that Lewis acid sites are favorable for selective epoxidation of propylene while Brønsted acid sites promote H_2O_2 decomposition. Significant Nb leaching was observed for Nb-TUD-1 during a test of 5 h. The used catalysts showed significant lower activity but relatively higher selectivity compared to the fresh catalysts due to the leaching of active Nb species to the solvent. Future work of optimized design of Nb based catalysts will be focused on enhancing the stability of Nb species in the framework.

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