Catalysis Today 148 (2009) 6–11

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Synthesis and properties of a zeolite LEV analogue from the system—Na_2O–Al_2O_3–SiO_2–N,N-dimethylpiperidine chloride–H_2O

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ARTICLE INFO

Article history:
Available online 25 March 2009

Keywords:
Zeolite LEV analogue
N,N-dimethylpiperidine chloride
Synthesis
Hydration of propene

ABSTRACT

A new structure-directing agent (SDA) was firstly reported for the synthesis of a zeolite LEV analogue. N,N-dimethyl piperidine performed the SDA function, and induced the synthesis of products from a zeolite MOR with 12-ring channels to a zeolite LEV analogue with only 8-ring channels. The zeolite LEV analogue was synthesized from gels with initial compositions (5.0–6.0)Na_2O–Al_2O_3–(10–200)SiO_2–(4.0–8.0)N,N-dimethyl piperidine–400H_2O at 150 °C. The ^{29}Si NMR spectra showed that the relative intensities of the first line at −115 ppm for low Si/Al ratios were lower than that at high Si/Al ratios. Varying ion exchanges led to different acidities in the zeolite LEV analogue, with the acidity of H-LEV-HCl higher than that of H-LEV-$NH_3 \cdot H_2O$. Zeolite H-LEV in hydration of propene showed a higher selectivity of 1-propanol.

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1. Introduction

Zeolites possess special pore channels with dimensions comparable to those of reacting molecules and which are therefore effective for shape-selective reactions, in which the reaction pathway is strongly determined by the framework geometry and steric constraints. Toluene disproportionation, methanol ammoniation and cyclopentene hydration are good examples of shape-selective applications [1–3]. Zeolite LEV, whose pore dimensions are 3.6 × 4.8 Å, has good catalytic activity for small molecule conversion. H-Nu-3 (a zeolite LEV analogue) showed a high selectivity towards low olefins in the conversion of methanol to hydrocarbons [4].

Zeolite LEV was one of the first zeolitic structures discovered and synthesized using organic compounds [5]. Zeolite LEV can be prepared using a hydrothermal method by employing methylquinuclidine (1-methyl 1-azonia 4-azabicyclo[2,2,2] octane), or 2-hydroxyalkyltrialkylammonium chloride as the structure-directing agent (SDA) [6]. Zeolite LEV was also successfully synthesized in a solution containing fluoride with quinuclidine [7]. In Na_2O–B_2O_3–SiO_2–H_2O, the zeolite B-LEV may be synthesized using quinuclidine or 3-azabicyclo[3.2.2]nonane as the template [8]. Zeolite Al, B-LEV may be prepared in gel-Na_2O–methylquinuclidine–Al_2O_3–B_2O_3–SiO_2–H_2O [9].

Direct hydration of unsaturated bonds to form anti-Markovnikov products has attracted much attention. However, the catalytic hydration of olefins to primary alcohols remains a challenge. Our experiments showed the zeolite LEV analogue has good catalytic performance in the anti-Markovnikov reaction, i.e., enhancement in 1-propanol selectivity in propene hydration [10]. This paper reported the rather extensive work on the synthesis and characteristics of the zeolite LEV analogue in the Na_2O–Al_2O_3–SiO_2–N,N-dimethyl piperidine–H_2O system. Compared with these structure-directing agents for the synthesis of zeolite LEV analogues, N,N-dimethyl piperidine (denoted as DMP) is a more common, inexpensive industrial organic product, which has been used as the structure-directing agent in synthesis of zeolite NON [11]. The synthesized samples were characterized by X-ray diffraction, multinuclear NMR techniques, scanning electron microscopy, nitrogen adsorption, FT-IR, thermal analysis, NH_3-temperature programmed desorption, chemical analysis and catalytic tests of hydration of propene.

2. Experimental

2.1. Synthesis of the zeolites

The reagents used in the synthesis of zeolite LEV were N,N-dimethyl piperidine chloride (98 wt.%), and sodium hydroxide

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doi:10.1016/j.cattod.2009.02.017

(96 wt.%), both AR grade. Colloidal silica sol (6.05 mol SiO_2/L), $Al(OH)_3$ ($Al_2O_3 > 64.5$ wt.%) was the industrial product. These were purchased from commercial sources and used in all syntheses without further purification. Distilled water and the solution of sodium aluminate were made by our lab.

The gels were obtained by mixing the reagents in the following order: N,N-dimethyl piperidine chloride, distilled water, the solution of sodium hydroxide, the solution of sodium aluminate and colloidal silica sol. The resulting gels were stirred vigorously. The homogenized gels were loaded into 35 mL stainless steel autoclaves, and treated under static conditions at 100–220 °C for 5–12 days. The powder samples were recovered by filtration and washing with water.

Zeolite H-LEV was obtained by ion exchange from zeolite Na-LEV. The sample from gel Si/Al = 25.0 was chosen for conversion from Na-LEV to H-LEV. First, the zeolite Na-LEV was calcined in air at 550 °C for 5 h to remove the guest molecule, N,N-dimethyl piperidine chloride. Then the sample was exchanged with 1 mol/L hydrochloric acid (denoted as H-LEV(HCl)) or 1 mol/L ammonia (denoted as H-LEV($NH_3{\cdot}H_2O$)) six times. Zeolite H-LEV samples were obtained by calcination in air at 550 °C for 4 h. H-MFI(silica/alumina mole ratio of 25.0) was obtained from the Catalyst Plant of Nankai University, China. It was calcined in air at 550 °C for 3 h before use.

2.2. Characterization of the zeolites

X-ray powder diffraction (XRD) patterns were recorded with a Rigaku D/max 2500 diffractometer using Cu Kα1 radiation 40 mA, 100 kV. A scanning electron microscope (JEOL JSM-35C) was used for observing the morphology of typical samples coated with gold. The framework vibration of LEV analogue was recorded on a PerkinElmer 1730 FT-IR spectrometer using the KBr pellet method. Nitrogen adsorption was measured by at 77 K with a TriStar 3000 gas absorption analyzer. The samples were degassed at 200 °C and 6.7 Pa for 2 h prior to the measurement. The thermogravimetric analysis (TGA) was measured at a heating rate of 10 °C/min on a thermal analysis STA409C. The Si and Al contents were determined by gravimetric methods and volume methods, respectively.

Solid-state NMR experiments were carried out using a Varian Infinity-plus 400 spectrometer operating at a magnetic field strength of 9.4 T. Al chemical shifts were referenced to $Al(H_2O)_6^+$. Si chemical shifts were referenced to tetramethylsilane (TMS). C chemical shifts were referenced to HMB.

To determine the acidic properties of the zeolites, a NH_3-temperature programmed desorption (NH_3-TPD) was performed in a TP-5000 quartz microreactor (Tianjin-Xianquan, China) connected to a thermal conductivity detector (TCD) and a mass spectrometer (Omni Star 200). About 50 mg of sample was used in each measurement. The sample was first pretreated in situ in air at 500 °C for 1 h, followed by purging with nitrogen (50 mL/min) at the same temperature for 1 h and then cooling to 120 °C. Then it was saturated with dry ammonia through pulse injection. The sample was further flushed with nitrogen flowing at 120 °C for 30 min to remove any physically adsorbed ammonia. After that, the sample was heated to 550 °C at a ramp of 10 °C/min in the nitrogen flow. The exhaust gases were detected and monitored by TCD.

The hydration of propene was performed in a stainless steel tube reactor of 8.0 mm i.d. equipped with a backpressure regulator. Weight hourly space velocity (WHSV) (h^{-1}) = 0.84, H_2O/propene(mole) = 4.63, time on stream = 1 h, catalyst = 1 g, and temperature = 310 °C, reaction pressure = 7.0 MPa.

3. Results and discussion

3.1. Synthesis

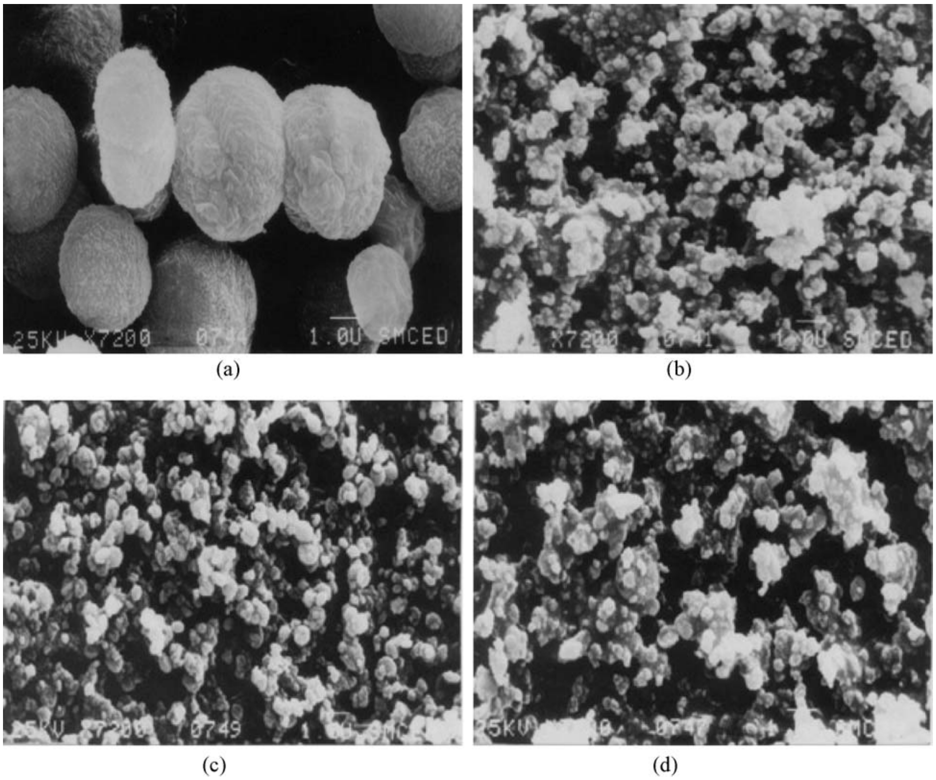
In experiments, the synthetic conditions of the zeolite LEV analogue were investigated by changing DMP/Si, Na/Si, Si/Al, the crystalline temperature and time (Table 1). Without DMP as the SDA, the synthesized products were only zeolite MOR. When DMP was added into the reactive gel, the synthesized products completely changed to the zeolite LEV analogue. Obviously, DMP had the function as SDA, which induced the synthesized products to convert from a large microporous zeolite with 12-ring channels (zeolite MOR) to a small microporous zeolite with only 8-ring channels (zeolite LEV analogue).

The effect of the Na/Si ratio was studied in the presence of DMP. The pure zeolite LEV analogue was obtained at Na/Si = 0.25–0.35. When the Na/Si ratio was equal to 0.40, ANA was obtained.

The influence of the gel Si/Al ratios on synthesis zeolite LEV analogue was investigated. Pure zeolite LEV analogue crystals were obtained at 150 °C for the reactive gel Si/Al ratios from 5.0 to 100.0. According to reference [6], the gel Si/Al ratio of the synthesised

Table 1
Typical synthesis conditions.

Reaction mixture composition (mole ratio)							
Na_2O	SiO_2	Al_2O_3	DMP	H_2O	Temperature (°C)	Time (days)	Phase
6.0	20.0	1.0	0.0	400	150	10	MOR
6.0	20.0	1.0	4.0	400	150	10	LEV
6.0	20.0	1.0	6.0	400	150	10	LEV
6.0	20.0	1.0	8.0	400	150	10	LEV
6.0	10.0	1.0	6.0	400	150	10	LEV
6.0	20.0	1.0	6.0	400	150	10	LEV
6.0	50.0	1.0	6.0	400	150	10	LEV
6.0	200.0	1.0	6.0	400	150	10	LEV
5.0	20.0	1.0	6.0	400	150	10	LEV
6.0	20.0	1.0	6.0	400	150	10	LEV
7.0	20.0	1.0	6.0	400	150	10	LEV
8.0	20.0	1.0	6.0	400	150	10	ANA
6.0	20.0	1.0	6.0	400	100	10	Amorphous
6.0	20.0	1.0	6.0	400	180	10	MOR
6.0	20.0	1.0	6.0	400	150	5	LEV + amorphous
6.0	20.0	1.0	6.0	400	150	7	LEV
6.0	20.0	1.0	6.0	400	150	12	LEV



(a) (b)

(c) (d)

Fig. 1. SEM images of typical samples from gel at different Si/Al mole ratios: (a) Si/Al = 5.0; (b) Si/Al = 10.0; (c) Si/Al = 25.0; (d) Si/Al = 100.0.

zeolite LEV was between 5 and 25 in the system $Na_2O–Al_2O_3–SiO_2$–methylquinuclidinium–H_2O. Also, the zeolite LEV analogue could be synthesized only with a narrow gel range of Si/Al ratio between 5 and 10 in fluoride media [12]. Certainly, the gels with Si/Al ratios range at the experiments are wider than reported data.

The gel Si/Al ratio of 5, 10, 25, and 100 resulted in actual Si/Al ratio of 3.4, 4.2, 7.4, and 10.6, respectively, in the as-synthesized zeolite LEV analogue. The data indicated increasing deviation of the actual values of Si/Al with the increase of that of gel composition.

Temperature effects were investigated in the synthesis system. Decreasing the temperature to 100 °C led to an amorphous solid, while increasing the temperature to 180 °C led to the zeolite MOR. The variation of structure type with increasing synthesis temperature correlates with an increasing framework density (FD) of the host structure. The zeolite LEV analogue (15.2 T/1000 $Å^3$) has eight-membered rings and a rather small channel (3.6×4.8 Å). The zeolite MOR (17.2 T/1000 $Å^3$) has 12-membered rings and middle-sized channel (6.5×7.0 Å) [13].

From the data of changing crystallization time, mixed phases of zeolite LEV analogue and amorphous solid were obtained after 5 days. As time went on, the phases became pure LEV analogue and the crystallization degree gradually increased until the highest relative crystallization was reached after 10 days. Further elongation of the crystallization time imposed no effect on the phase whereas the crystallization degree decreased slightly.

3.2. Morphology

The morphology of the zeolite LEV analogue with various Si/Al ratios was illustrated in Fig. 1. When the Si/Al ratio was equal to 5.0 in the gel, the shape of the crystals was the cobblestone form suggesting an agglomeration of smaller crystallites. The result is similar to reported data [6,9]. It can be seen that the crystals morphology was different with early data with Si/Al from 5.0 to 100.0 in the gel. Their morphology is irregular small particles. The reason may be that the content of the nucleation and the crystallization rates were decreasing with increasing Al concentration. Fewer nuclei were formed in the beginning of the reaction with high Al content, leading to the formation of larger crystals.

3.3. ^{27}Al and ^{29}Si NMR spectra

In Fig. 2, the ^{27}Al NMR spectrum of the as-synthesized samples clearly showed that only one NMR line at 55 ppm was detected, which is characteristic of tetrahedral coordination. The ^{29}Si NMR spectra are typical of the levyne structure (Fig. 3). The samples showed four NMR lines at −115, −108, −103 and −98 ppm. The first line at −115 ppm can be assigned to the Si (0Al) configurations of the T_2 sites [14]. Due to the influence of the framework of the aluminum atoms, the relative intensities of the first lines with low Si/Al ratios were lower than with high Si/Al ratios; the line widths with low Si/Al ratios were also greater.

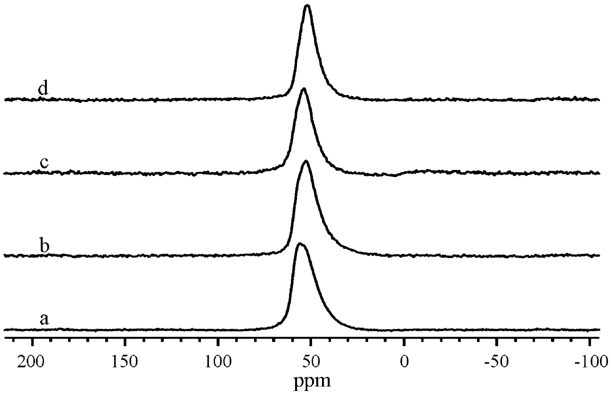


Fig. 2. ^{27}Al NMR spectrum of typical samples from gel at: (a) Si/Al = 5.0; (b) Si/Al = 10.0; (c) Si/Al = 25.0; (d) Si/Al = 100.0.

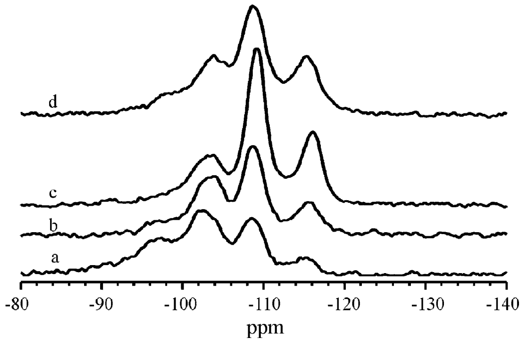


Fig. 3. ^{29}Si NMR spectrum of typical samples from gel at: (a) Si/Al = 5.0; (b) Si/Al = 10.0; (c) Si/Al = 25.0; (d) Si/Al = 100.0.

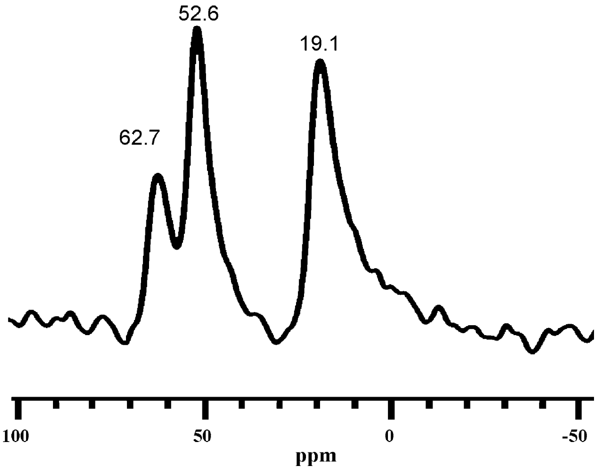


Fig. 4. ^{13}C NMR spectrum of the as-synthesized sample from gel at Si/Al = 25.0.

3.4. ^{13}C NMR and TG analysis

In the single pulse ^{13}C NMR spectrum (Fig. 4), three pronounced lines at 19.1, 52.6, and 62.7 were observed. The line at 62.7 ppm is assigned to the CH_2 group linked with N atom on piperidine ring. The line at 52.6 ppm is assigned to the methyl group linked with N atom. The line at 19.1 ppm is assigned to the CH_2 group at other positions of piperidine ring. So N,N-dimethylpiperidine should be a template included in zeolite LEV analogue framework.

Fig. 5 shows a TG curve of the typical sample obtained from the gel with Si/Al = 25.0. There were two major sections of weight loss observed on the TG curve. One was below 340 °C caused by dehydration, where the weight loss was 6.25%. Another was in the range 340–580 °C caused by combustion of DMP in the cage, for which the weight loss was 19.86%. According to weight loss of organic molecules and Al chemical analysis, N,N-dimethylpiperidine/Al is equal to 1.12. The calcination temperature was chosen to be 550 °C for the catalyst preparation.

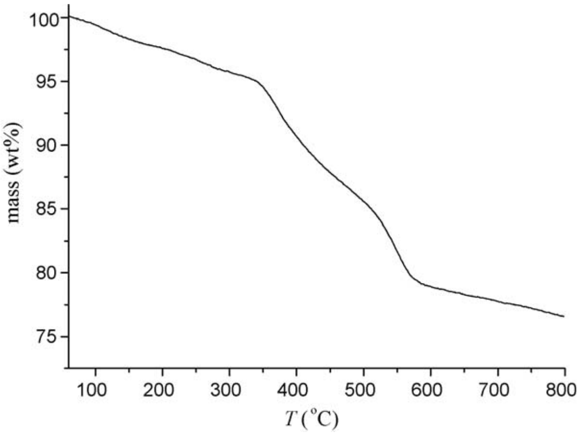


Fig. 5. TG curve of the as-synthesized sample from gel at Si/Al = 25.0.

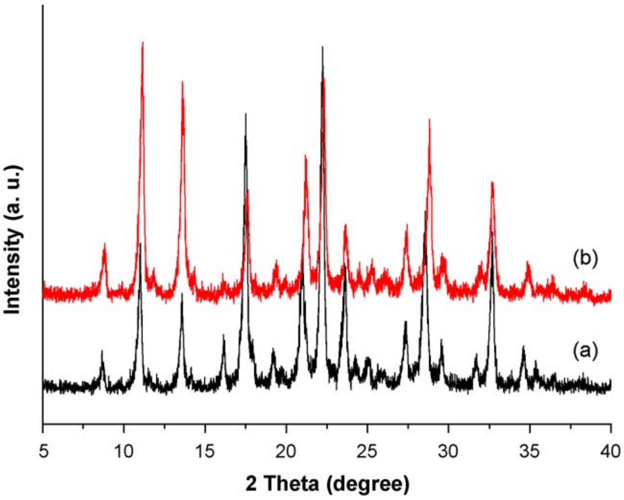


Fig. 6. XRD patterns of the as-synthesized sample from gel at Si/Al = 25.0 (a) as-synthesized; (b) calcined.

3.5. XRD analysis and nitrogen adsorption

Fig. 6 shows the XRD patterns of as-synthesized and calcined samples. From Fig. 6(a), the diffraction peak position and relative intensity are the same with reported data of zeolite LEV. So the synthesized sample is zeolite LEV analogue. Comparing Fig. 6(b) with Fig. 6(a), the relative diffraction intensity after calcination possess some change. After calcination, the diffraction intensity increases at 2θ = 8.6°, 11.0°, and 13.6°. And the diffraction intensity decreases at 2θ = 16.2°, 17.5°, 22.3°, and 23.6°.

The calcined zeolite LEV analogue was measured its nitrogen adsorption properties. Fig. 7 is its nitrogen adsorption/desorption curve. According to the data, its BET surface area is 480.0 m^2/g and its micropore volume is 0.192 cm^3/g.

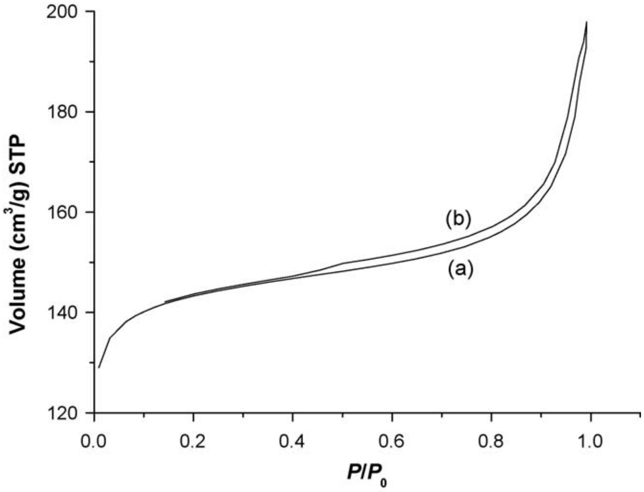


Fig. 7. Nitrogen adsorption (a)/desorption (b) curves of the as-synthesized sample from gel at Si/Al = 25.0.

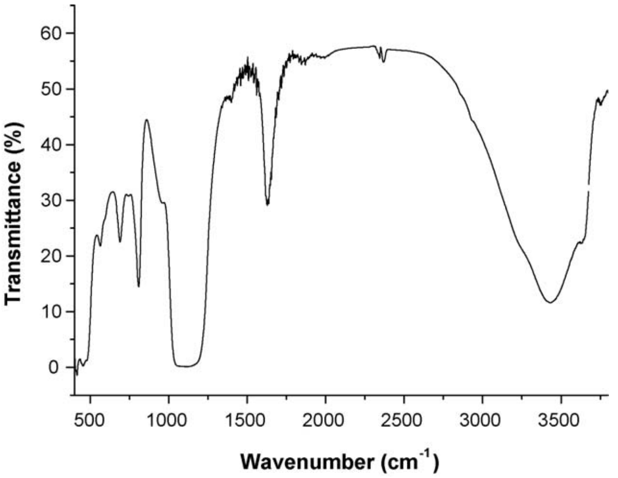


Fig. 8. FT-IR spectrum of the as-synthesized sample from gel at Si/Al = 25.0.

3.6. Framework vibration

The FT-IR spectrum of the as-synthesized zeolite LEV analogue in the framework region was shown in Fig. 8. According to Flanigen article's assigning method [15], there were the T–O band bending vibration, double ring stretching vibration, symmetric stretching and asymmetric stretching vibration of T–O–T in synthesized LEV. The vibrational data may be assigned as: T–O band bending vibration at 460, 421 cm^{-1}; double ring stretching vibration at 559 cm^{-1}; symmetric stretching vibration at 796, 685 cm^{-1}; asymmetric stretching vibration at 1088 cm^{-1}.

3.7. The acidic properties and catalytic properties

For the hydration of propene, the isomer 2-propanol predominates over 1-propanol in the products. To synthesize 1-propanol is a complex and indirect catalytic process [16,17]. The hydration of propene is generally believed to proceed via a mechanism of carbenium formation. 2-Propyl carbenium is much more stable than 1-propyl carbenium due to the large energy difference between them [18]. It is presumed that the yield of the anti-Markovnikov product 1-propanol in propene hydration may be enhanced by making use of the characteristics of zeolites with proper pore structure and acidity. The zeolite LEV analogue possesses small pores (3.6 × 4.8 Å) and proper acidity. Proper acidity of zeolites should be helpful to enhance the stability of the propyl carbenium and so change the distribution of the two propanol isomers. Different ion exchanges may lead to different acidity properties.

In experiments, the acidity was tested by integration of the NH_3-TPD profiles of different ion exchanged samples, as listed in Table 2. It can be seen that the peak temperature of the strong acid of H-LEV(HCl) was 459 °C and was 20 °C higher than that of H-LEV($NH_3{\cdot}H_2O$). The peak area of H-LEV(HCl) was 579 a.u. and was 230 a.u. larger than that of H-LEV($NH_3{\cdot}H_2O$). The data showed that the strong acidity of H-LEV(HCl) was greater than that of H-LEV($NH_3{\cdot}H_2O$). The sites of strong acidity may be responsible for the propene hydration. Strong acidity in zeolites is helpful to enhance the rate of propanol formation, which makes the distribution of propanol isomers closer to the equilibrium value. This may enhance the yield of 1-propanol. Therefore, H-LEV(HCl) was chosen for catalyst preparation in the early experiments [10].

Table 2
Integration of NH_3-TPD profiles of different ion exchanged samples.

Sample	Weak acid		Strong acid	
	Peak temp (°C)	Area (a.u.)	Peak temp (°C)	Area (a.u.)
H-LEV(HCl)	180	171	459	579
H-LEV($NH_3{\cdot}H_2O$)	190	301	439	349

Table 3
Conversion of propene and selectivities of propanol isomers and oligomers in propene hydration over H-LEV and H-MFI at 310 °C.

Catalyst	Propene conversion (%)	Selectivity (%)		
		2-Propanol	1-Propanol	Oligomer
H-LEV	4.9	90.2	6.1	3.7
H-MFI	52.8	10.6	0.4	89.0

Hydration of propene over H-MFI and H-LEV was carried out at 310 °C, 7.0 MPa, a propene WHSV of 0.84 h^{-1}, and Rw/p of 4.63, as shown in Table 3. Both propene conversion and oligomer selectivity for the hydration over H-LEV were much lower than those over H-MFI, while 1-propanol selectivity over H-LEV(6.1%) was higher than that over H-MFI(0.4%). This may be explained by the aperture difference between LEV(3.6 × 4.8 Å) and MFI(5.3 × 5.6 Å). And the propene conversion at 310 °C is lower than that at 280 °C [10]. The result matches with the thermodynamics calculation, which proves propene conversion will decrease with increasing reaction temperature.

4. Conclusion

Zeolite LEV analogue was successfully synthesized from gels containing N,N-dimethylpiperidine chloride as the SDA. The initial gel Si/Al ratios ranged from 10 to 100 for synthesis of the zeolite LEV analogue. The range is wider than that previously reported. The ^{29}Si NMR spectra showed that the relative intensities of the first line at −115 ppm of low Si/Al ratios were lower than those with high Si/Al ratios. It is experimentally proved that very strong acidity and great value of acid amount by H-LEV(HCl) exchange are realized compared to the case of employing H-LEV($NH_3{\cdot}H_2O$). Catalytic tests of zeolites H-MFI and H-LEV in hydration of propene indicate that the selectivity of 1-propanol is related to the pore structure and surface acidity of zeolites.

Acknowledgements

The authors are grateful to the National Natural Science Foundation of China (Grant no. 20373047) and the Science Foundation of Shanxi (20041024) for financial support.

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