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Two routes to 1,2-cyclohexanediol catalyzed by zeolites under solvent-free condition

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Abstract Two routes to 1,2-cyclohexanediol were studied. Specifically: (a) the hydrolysis of cyclohexene oxide and (b) the direct dihydroxylation of cyclohexene with aqueous hydrogen peroxide. Both reactions were carried out with zeolites as catalysts under solvent-free conditions, aiming to establish green routes for the synthesis of 1,2-cyclohexanediol. In the first route, H-Beta and H-ZSM-5 zeolites were used as catalysts, respectively. According to the results, H-ZSM-5 was a suitable catalyst for the hydrolysis of cyclohexene oxide. A 88.6 % yield of 1,2-cyclohexanediol could be obtained at a 96.2 % conversion of cyclohexene oxide under mild conditions, and the catalyst could be reused for three times. Compared with H-ZSM-5, H-Beta gave a much lower selectivity (63 %), although it was more active. In the second route, Ti-Beta zeolites with three different Ti loadings prepared via a simple two-step strategy were characterized and used. The results indicated that it was the framework Ti species which was responsible for the catalytic activity. The resultant Ti-Beta-3 % could give a 90.2 % cyclohexene conversion at a 66.2 % selectivity of 1,2-cyclohexanediol.

Keywords 1, 2-Cyclohexanediol · Hydrolysis · Dihydroxylation · Zeolites · Solvent-free

Introduction

1,2-cyclohexanediol is an important organic intermediate. It has two hydroxyl groups, which makes it widely used for the manufacture of polyester resins, a top grade diluter of epoxy resins, catechol and other products. Hydrolysis of

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cyclohexene oxide and dihydroxylation of cyclohexene are the two main routes to prepare 1,2-cyclohexanediol [1–4].

Cyclohexene oxide can be hydrolyzed to 1,2-cyclohexanediol using liquid acid or solid acid as catalysts. Liquid acid catalysts are not only corrosive to the equipment but also harmful to the environment [5, 6]. Recently, more attention has been paid to the solid acid catalysts recently which are environ-friendly and recyclable [7]. However, most of the solid acid catalysts exhibit low catalytic performance so that hydrolysis of cyclohexene oxide is generally carried out under rigorous conditions. A high mole ratio of reactants, a high temperature, and even the involvement of solvents are required to obtain high conversion as well as high selectivity. Especially, the use of much water or solvents will lead to a sharp increase of energy consumption for the separation of the products [8–10]. Recently, a solid acid catalyst, Sn-Beta zeolite, which was prepared via an improved two-step post-synthesis strategy was applied in the hydrolysis of epoxides for the first time and exhibited excellent catalytic performance [11]. However, the preparation of the Sn-Beta zeolite was rigorous and complicated, and the use of the expensive and toxic organometallic $(CH_3)_2SnCl_2$ was inevitable, which limited the large-scale preparation and applicability.

Herein, H-Beta and H-ZSM-5 zeolites will replace the Sn-Beta zeolite as catalysts for the hydrolysis of cyclohexene oxide due to their cheap and available sources. The reaction will be carried out without organic solvents. According to our knowledge, the hydrolysis of cyclohexene oxide to 1,2-cyclohexanediol catalyzed by H-Beta or H-ZSM-5 under solvent-free condition has never been reported in detail so far. According to the results, H-ZSM-5 was a suitable catalyst for the hydrolysis of cyclohexene oxide.

Another alternative pathway for the synthesis of 1,2-cyclohexanediol is the direct dihydroxylation of cyclohexene, which is abundant in sources and cheap in price. Traditionally, cyclohexene was directly oxidized to 1,2-cyclohexanediol using peracids [12]. However, peracids are not only expensive but also hard to handle. Current interest is on direct dihydroxylation to 1,2-cyclohexanediol from cyclohexene with H_2O_2 as a green oxidant due to the atom efficiency and the coproduction of water [13–15]. Generally, in the process, a two-step mechanism is considered which involves the epoxidation of cyclohexene with H_2O_2 over the catalyst and the rapid hydrolysis of cyclohexene oxide in the acid condition [16]. Recently, Antonetti et al. [17] reported the direct dihydroxylation of cyclohexene with H_2O_2 under a phase-transfer-agent and a tungstic acid/phosphoric acid catalytic system. However, the main drawback of this approach was the use of liquid acid, which was corrosive and could not be reused. Therefore, solid catalysts, which have bifunctional catalytic properties for the direct dihydroxylation of cyclohexene, are attractive to be explored. The oxidative property causes the epoxidation of cyclohexene and acidic sites leads to the hydrolysis of cyclohexene oxide.

The epoxidation of olefins with H_2O_2 over Ti-containing zeolites has been widely reported because of its significant importance in the oil and chemical industry [18–21]. Especially, Ti-Beta zeolites show active catalytic performance in the epoxidation of linear and cyclic olefins [22]. However, the preparation of Ti-Beta is always complicated and not environmentally friendly, which limits the large-scale
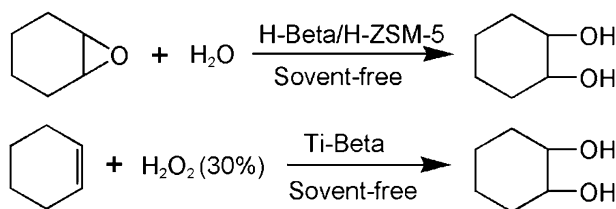
Fig. 1 The process of the preparation of 1, 2-cyclohexanediol

applicability [23–27]. Recently, Tang et al. [28] reported a novel and simple preparation of Ti-Beta zeolite by a two-step post-synthesis strategy, which consisted of the complete dealumination of the Beta zeolite and a tunable dry impregnation with Cp_2TiCl_2. The resultant Ti-Beta zeolite exhibited better catalytic performance in the epoxidation of olefins with H_2O_2 than other Ti-containing zeolites. However, most of the reports like this were confined to the epoxidation of olefins aiming at obtaining epoxides, in which the hydrolyzation to 1,2-diol should be inhibited. Moreover, organic solvents were required in the process, which would bring about environmental pollution [29]. In fact, except for oxidability, the resultant Ti-Beta zeolite also has acidity, which can lead to the further hydrolysis of cyclohexene oxide to 1,2-cyclohexanediol. Therefore, we aim to apply the similar catalytic materials for the direct dihydroxylation of cyclohexen to 1,2-cyclohexanediol. The results demonstrated that the Ti-Beta worked well in the one-step conversion of cyclohexene to 1,2-cyclohexanediol under solvent-free conditions (Fig. 1).

Experimental

Preparation of the catalysts

Commercial H-ZSM-5 zeolite ($SiO_2/Al_2O_3 = 25$) and tetraethylammonium BEA (TEABEA) ($SiO_2/Al_2O_3 = 25$) were both provided by Nankai University.

The catalysts for cyclohexene dihydroxylation were prepared as follows:

A H-ZSM-5 zeolite was used as received without further treatment.

A TEABEA zeolite was separated into two fractions. The first one was calcined in air at 823 K to remove the organic template, denoted as H-Beta. In order to investigate the effect of calcination temperature on the catalytic performance of H-Beta, the zeolites calcined at elevated temperatures (923 and 1023 K) were also prepared.

The second one was treated with HNO_3 solution at 353 K for 4 h to give the dealuminated organic-free Beta zeolite. The powder was then separated by centrifugation, washed thoroughly with distilled water until the filtrate became neutral, and dried at 353 K overnight under vacuum. In this paper, the zeolites

dealuminated with varying HNO_3 concentration (1.8–14.4 M) were prepared to investigate the influence of dealumination on the catalytic properties of H-Beta.

A Ti-Beta catalyst for direct dihydroxylation of cyclohexene was prepared by a simple two-step post-synthesis procedure. First, the H-Beta was dealuminated with HNO_3 solution at 373 K for 20 h to obtain Si-Beta. Then, the resultant Si-Beta was mixed with a certain amount of Cp_2TiCl_2 adequately. Finally, the mixture was calcined in air at 823 K for 6 h to derive Ti-Beta. In this study, Ti-Beta zeolites with three different Ti loadings of 1, 3, and 5 wt% were prepared, denoted as Ti-Beta-1 %, Ti-Beta-3 %, and Ti-Beta-5 %, respectively. For comparison, Ti-H-Beta-3 % was also prepared via a one-step procedure in which Ti is incorporated into H-Beta rather than Si-Beta in the same way.

Characterization of the prepared catalysts

Powder X-ray diffraction (XRD) patterns of the zeolites were collected on a Bruker D8 Advance X-ray diffractometer.

Diffuse reflectance ultraviolet–visible (UV–Vis) spectra were recorded in the region of 200–800 nm under air conditions and against $BaSO_4$ using a Shimadzu UV-3600 spectrophotometer.

X-ray fluorescence (XRF) chemical analysis was performed at room temperature on a S4 Pioneer spectrometer.

An infrared spectrum was recorded on a NEXUS 670 FT-IR spectrometer.

Catalytic experiment

All the reactions were carried out in a 25 mL three-necked flask with a cryogenic-liquid condenser under atmospheric pressure. After reaction, the catalyst was separated by centrifugation. The reaction products were analyzed by GC 6890 gas chromatography.
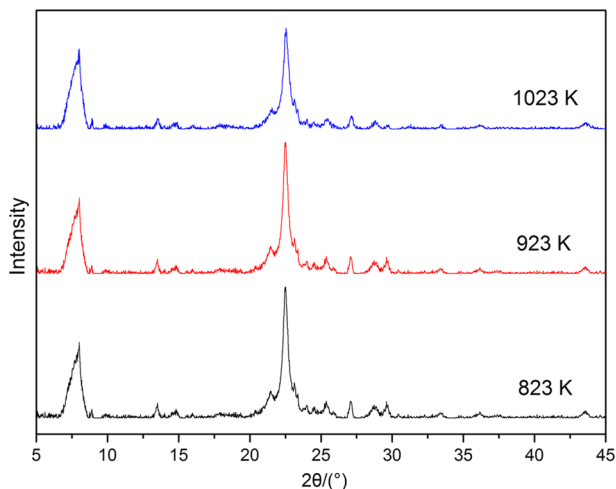
The procedure for the hydrolysis of cyclohexene oxide was as follows: The flask was charged with the mixture of cyclohexene oxide, water, and catalyst, and mixed vigorously by a magnetic stirrer at the desired reaction temperature.

In a typical dihydroxylation of cyclohexene to 1,2-cyclohexanediol, cyclohexene and catalyst were first mixed in the reaction flask. When the solution temperature was stable at the desired reaction temperature, H_2O_2 (30 wt%) was added into the flask under stirring.

Results and discussion

Structural properties of the catalysts for the hydrolysis of cyclohexene oxide

The XRD patterns of the zeolite samples are shown in Figs. 2 and 3. All the samples showed a typical BEA topology. Although calcination at high temperatures or acid treatment slightly decreased the diffraction intensities, the framework structure was definitely retained after the treatments.

Fig. 2 XRD patterns of calcined Beta zeolites at different temperatures
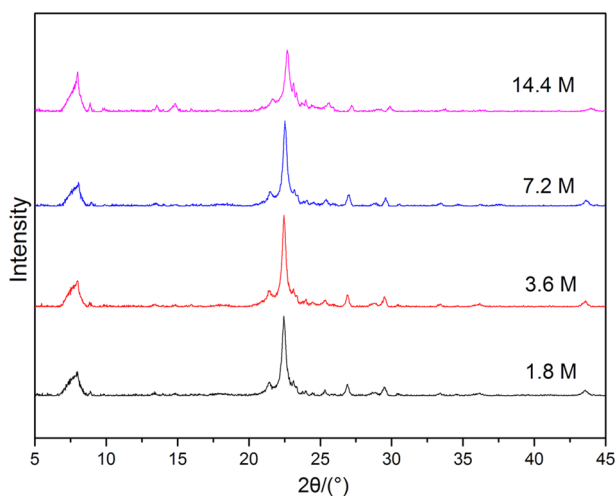
Fig. 3 XRD patterns of dealuminated Beta zeolite samples in varing HNO_3 concentration

The catalytic properties of the catalysts for the hydrolysis of cyclohexene oxide into 1,2-cyclohexanediol

H-Beta and H-ZSM-5 zeolites were used as catalysts in the hydrolysis of cyclohexene oxide to prepare 1,2-cyclohexanediol, respectively. The reaction produced polymer and ethers as by-products [10]. The catalytic properties of H-Beta and H-ZSM-5 were compared under identical reaction conditions, and the results are shown in Fig. 4. For both catalysts, the conversion of cyclohexene oxide always
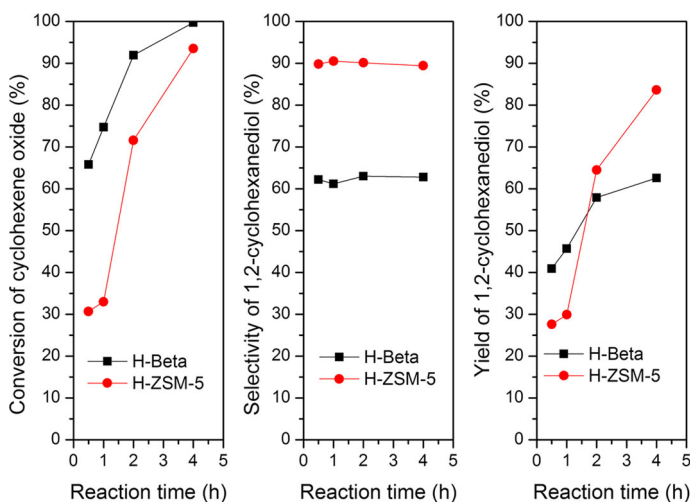
Fig. 4 Comparision of the catalytic properties of H-Beta and H-ZSM-5 under identical reaction conditions. Reaction conditions: 10 mmol cyclohexene oxide, 50 mmol H_2O, 0.05 g catalyst, temperature = 333 K

increased with time, while the selectivity of 1,2-cyclohexanediol remained basically unchanged. However, H-Beta exhibited higher cyclohexene oxide conversion but lower 1,2-cyclohexanediol selectivity. The 1,2-cyclohexanediol selectivity of the catalyst with H-Beta maintained only approximately 62 %, much lower than that with H-ZSM-5,(about 90 %). After reaction for 4 h, although a high conversion of 99.7 % could be obtained over H-Beta, the yield of 1,2-cyclohexanediol was only 62.6 %, much lower than that of H-ZSM-5 (83.6 %). Therefore, H-ZSM-5 was supposed to be more suitable for the hydrolysis of cyclohexene oxide.

The influence of the reaction conditions, such as catalyst dosage, reaction temperature, mole ratio of reactants, and reaction time on the catalytic properties of H-ZSM-5 zeolite were investigated. Controlling the variables method was adopted in which only one factor was changed at a time, so that the effect of that single factor could be determined. A typical reaction was carried out with H_2O (50 mmol), cyclohexene oxide (10 mmol) over catalyst (0.05 g) at 333 K for 1 h. The results are shown in Fig. 5. With the increase of catalyst dosage, mole ratio of reactants, reaction temperature or time, the conversion of cyclohexene oxide increased, while a high selectivity of about 90 % was preserved. So, a high conversion of cyclohexene oxide as well as a high selectivity of 1,2-cyclohexanediol could be obtained simultaneously under the proper conditions.

Then, H-ZSM-5 was used as catalyst for the hydrolysis of cyclohexene oxide under mild conditions, and the recycling ability of H-ZSM-5 was investigated. The reaction was carried out with 2:1 mol ratio of H_2O to cyclohexene oxide over 0.1 g H-ZSM-5 at 353 K for 2 h. After reaction, H-ZSM-5 was separated by centrifugation, washed with water, and dried at 353 K for the next run. As shown in Fig. 6,
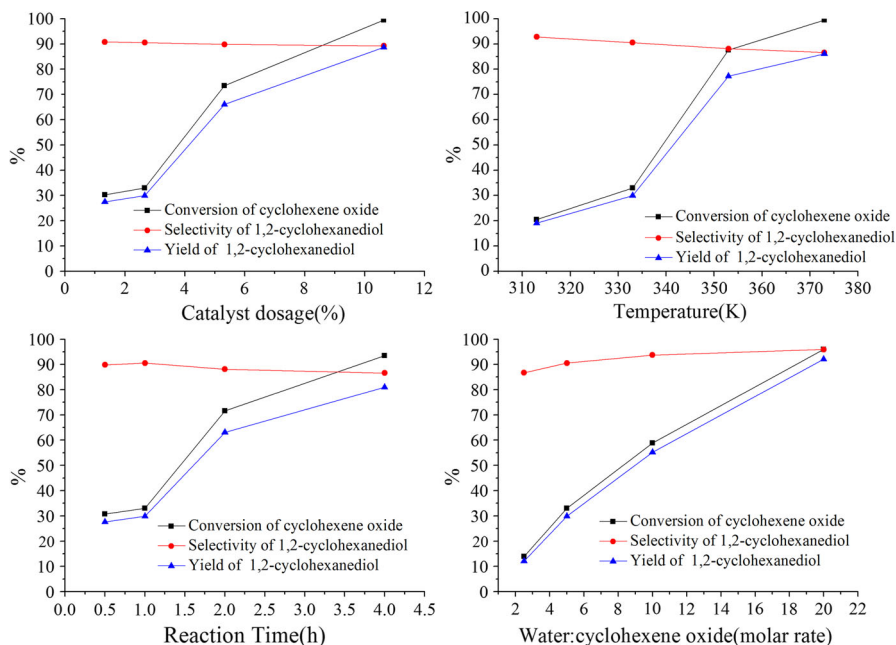
**Fig. 5** The influence of the reaction conditions catalyzed by H-ZSM-5
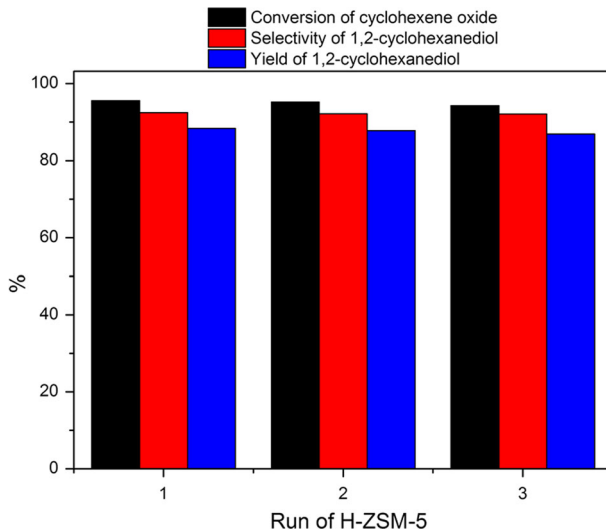
Fig. 6 Reaction conditions: 10 mmol cyclohexene oxide, 20 mmol H_2O, 0.1 g of catalyst, temperature = 353 K. reaction time = 2 h

after reaction, a 88.4 % yield of 1,2-cyclohexanediol could be obtained at a 96.2 % cyclohexene oxide conversion. H-ZSM-5 could be reused for three times; the yields did not reduce significantly.

In order to improve the 1,2-cyclohexanediol selectivity of H-Beta catalyst, the effect of calcination temperature on the catalytic performance of Beta zeolites was investigated. As shown in Fig. 7, the calcination temperature showed great impact on the catalytic performance of H-Beta in the hydrolysis of cyclohexene oxide. As the calcination temperature increased from 823 to 1023 K, the conversion of cyclohexene oxide decreased from 99.9 to 67.4 %, while 1,2-cyclohexanediol selectivity increased from 68.3 to 86.7 %. As reported, with increasing calcination temperature, Bronsted acid sites decreased but Lewis acid sites increased, and the total acid amount decreased [30, 31]. The decrease of activity might be owing to the decrease of the total acid amount, and the improved selectivity might be due to the decrease of Bronsted acid sites, which was responsible for the formation of byproducts.

In addition, another modification was also adopted, in which H-Beta zeolites were dealuminated in varying HNO_3 concentrations. By acid treatment, both the Bronsted acid sites and Lewis acid sites decreased, the acid concentration determined the final residual acid amount [32]. The results are shown in Fig. 8, the acid concentration showed an impact on the catalytic performance similar to calcination temperature. With the increase of HNO_3 concentration (from 1.8 M to 14.4 M), the conversion of cyclohexene oxide dramatically decreased from 96.6 to 23.4 %, while 1,2-cyclohexanediol selectivity was improved from 78.9 to 96.6 %. Accordingly, the decrease of conversion might be owing to the decrease of the total acid amount, and the improved selectivity might be due to the decrease of Bronsted acid sites. The formation of by-products was attributed to the strong Bronsted acid, which led to polymerization. Therefore, a better catalytic performance of H-Beta could be obtained by calcination at high temperature or dealumination with acid. H-Beta showed a talent for the hydrolysis of cyclohexene oxide.
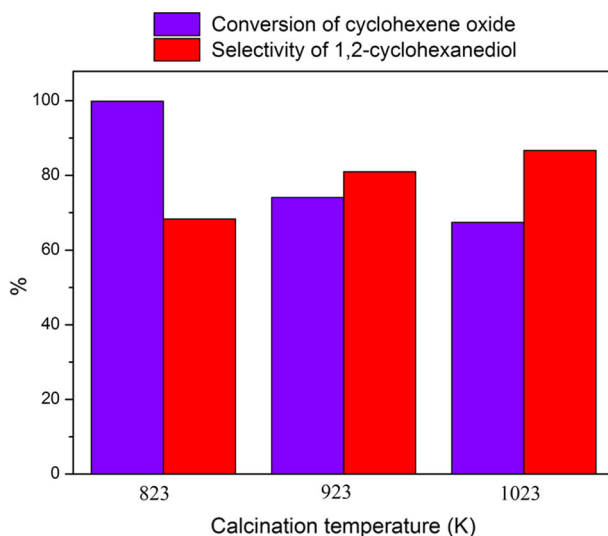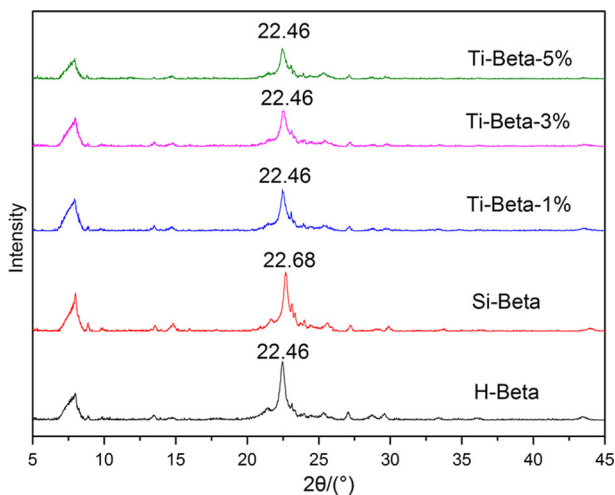

Fig. 7 Catalytic performance of H-Beta calcined at different temperatures
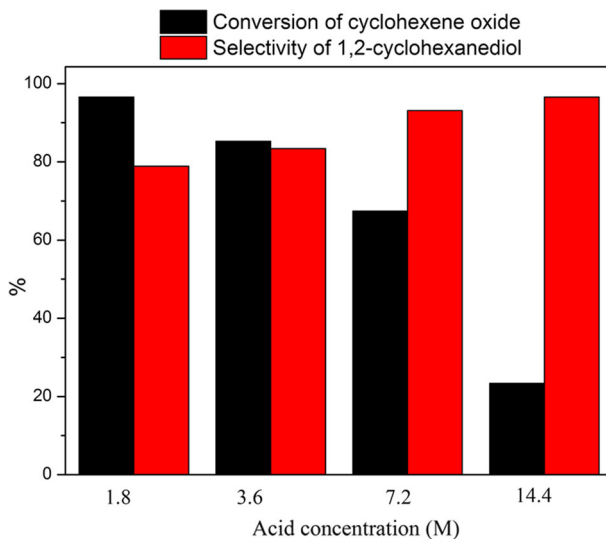
Fig. 8 Catalytic performance of H-Beta dealuminated in varying HNO_3 concentration

Fig. 9 XRD patterns of H-Beta, Si-Beta, Ti-Beta-1 %, Ti-Beta-3 %, and Ti-Beta-5 %

Structural properties of the catalysts for the direct dihydroxylation of cyclohexene

As shown in Fig. 9, XRD patterns of H-Beta, Si-Beta, Ti-Beta-1 %, Ti-Beta-3 %, and Ti-Beta-5 % typical of BEA zeolite were found to be similar, suggesting that the structure was not destroyed after dealumination or Ti incorporation.

The dealumination or Ti incorporation comes along with the framework of contraction/expansion and can be detected from the position of the diffraction peak at 22.46° [33, 34]. The diffraction peaks of H-Beta at $2\theta = 22.46°$ shifted to a higher 2θ value of about 22.68° after dealumination, suggesting a contraction upon dealumination. The incorporation of Ti into Si-Beta resulted in a shift from $2\theta = 22.68°$ to $2\theta = 22.46°$, revealing the expansion of the BEA structure. The results indicated that Ti had been successfully incorporated into the framework of Si-Beta.

To understand the existence state of Ti Species in Ti-Beta, the UV–Vis spectra of the synthesized Ti-Beta are presented in Fig. 10. All the samples showed a distinct absorption peak near 220 nm, which was attributed to the ligand-to-metal charge transfer from O^{2-} to Ti^{4+}, as reported earlier [27, 35]. This band corresponded to tetrahedral Ti(VI) in the framework. Moreover, the intensity of the band increased simultaneously with Ti content, directly indicating the successful incorporation of Ti into the zeolite frameworks. In addition, the absence of bands above 330 nm in the spectra indicated that the existence of bulky TiO_2 was not present.

The catalytic properties of the catalysts for the direct dihydroxylation of cyclohexene

The Ti content and the catalytic properties of the catalysts for the direct dihydroxylation of cyclohexene are shown in Table 1. Cyclohexene had no conversion when H-Beta or Si-Beta acted as catalyst, while 1,2-cyclohexanediol could be detected for all the Ti-containing Beta zeolites, but it is worth mentioning that no obvious cyclohexene oxide was detected during the whole process. The acidity of the Ti-Beta led to the rapid hydrolysis of cyclohexene oxide to
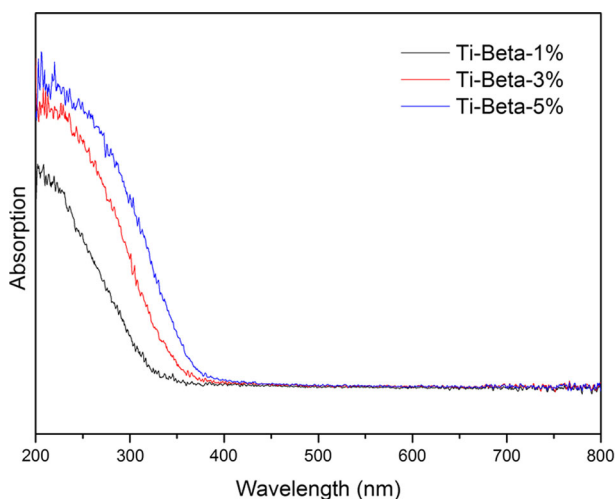
Fig. 10 UV-Vis spectra of Ti-Beta zeolites with varying Ti contents

Table 1 Catalytic properties of the Ti-Beta zeolites under study in the direct dihydroxylation of cyclohexene

Sample	Ti loading (wt%)[a]	Conversion (%)	Selectivity (%)
H-Beta	0	–	–
Si-Beta	0	–	–
Ti-Beta-1 %	1.1	18.7	69.7
Ti-Beta-3 %	3.0	29.7	70.1
Ti-Beta-5 %	4.8	30.5	70.7
Ti-H-Beta-3 %	3.1	19.2	18.3

Reaction conditions: 10 mmol cyclohexene, 15 mmol H_2O_2, 0.1 g catalyst, temperature = 333 K, reaction time = 2 h

[a] Determined by XRF

1,2-cyclohexanediol. The cyclohexene conversion increased from 18.7 to 29.7 % with increasing Ti content (1–3 wt%), indicating that it was the framework Ti species which was responsible for the catalytic activity. On the other hand, Ti-Beta-5 % gave a 30.5 % cyclohexene conversion similar to that of Ti-Beta-3 %, in spite of a higher Ti content. The results could be attributed to the limited amount of Ti incorporated in the zeolite frameworks. For all of the Ti-Beta zeolites, the selectivity to 1,2-cyclohexanediol appeared to be a constant (about 66 %) and had almost no change with the Ti content.

In addition, the catalytic performance of Ti-H-Beta-3 % prepared via one-step procedure was compared with that of Ti-Beta-3 %. The results showed that Ti-H-Beta-3 % was less active than Ti-Beta-3 % and cyclohexene conversion was only 19.2 % after 1 h. Moreover, the selectivity for 1, 2-cyclohexanediol was also only 18.3 %, much lower than that of Ti-Beta-3 % (70.1 %). So the two-step procedure was necessary for the preparation of Ti-containing Beta zeolites in order to obtain better catalytic performance.

Finally, Ti-Beta-3 % was used as catalyst for the direct dihydroxylation of cyclohexene. The reaction was carried out with cyclohexene (10 mmol), H_2O_2 (15 mmol) over Ti-Beta-3 % (0.1 g) at 333 K for different reaction times; the results are shown in Fig. 11. The conversion of cyclohexene oxide increased with time, but the selectivity of 1,2-cyclohexanediol was almost constant. After reaction for 10 h, a 90.2 % cyclohexene conversion could be obtained at a 66.2 % 1,2-cyclohexanediol selectivity.

The characterization of products

The product, 1,2-cyclohexanediol was characterized by melting point determination and infrared spectrometry (IR). It had a melting point of 102.9–103.0 °C, which was consistent with the literature values. The IR results are shown in Fig. 12, which is also the same as those reported in the literature [9].
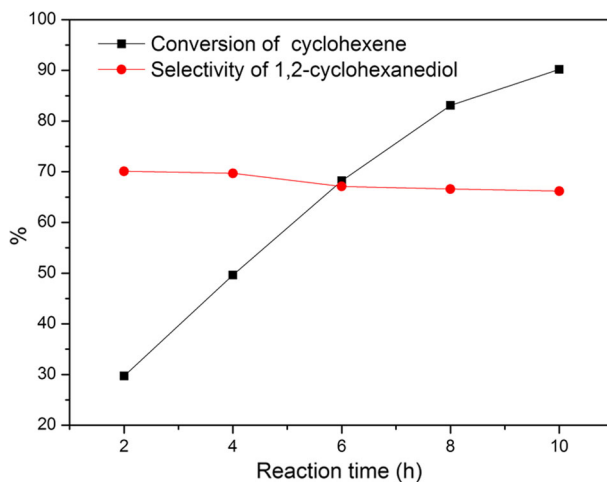
Fig. 11 Conversion of cyclohexene and selectivity of 1,2-cyclohexanediol in time with Ti-Beta-3 % as catalyst
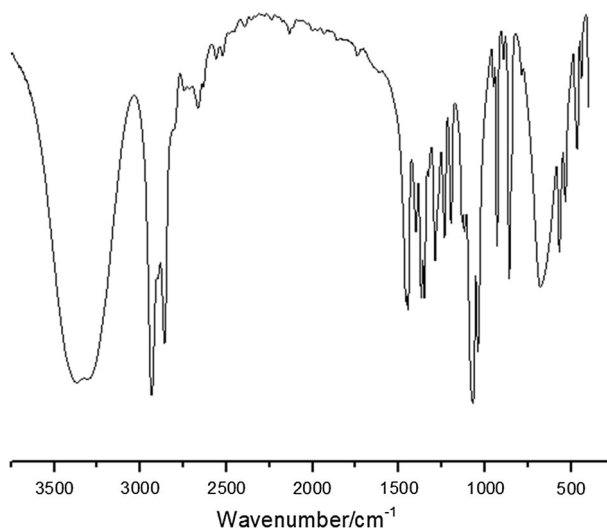
Fig. 12 IR of product

Conclusions

H-ZSM-5 was a suitable catalyst for the hydrolysis of cyclohexene oxide. A 88.6 % yield of 1,2-cyclohexanediol could be obtained at a 96.2 % conversion of cyclohexene oxide under mild conditions and H-ZSM-5 could be reused for three times. H-Beta showed a talent for the hydrolysis of cyclohexene oxide to 1,2-cyclohexanediol.

In the direct dihydroxylation of cyclohexene to 1,2-cyclohexanediol, a 90.2 % cyclohexene conversion could be obtained at a 66.2 % selectivity of 1,2-cyclohexanediol using Ti-Beta-3 % as catalyst.

References

1. A.V. Narsaiah, B.V.S. Reddy, K. Premalatha, S.S. Reddy, J.S. Yadav, Catal. Lett. **131**, 480 (2009)
2. J.M. Ready, E.N. Jacobsen, J. Am. Chem. Soc. **123**, 2687 (2001)
3. L. Emmanuel, T.M.A. Shaikh, A. Sudalai, Org. Lett. **7**, 5071 (2005)
4. K. Bergstad, S.Y. Jonsson, J.E. Backvall, J. Am. Chem. Soc. **121**, 10424 (1999)
5. H. Cavdar, N. Saracoglu, Tetrahedron **65**, 985 (2009)
6. P. Salehi, M.M. Khodaei, M.A. Zolfigol, A. Keyvan, Synth. Commun. **33**, 3041 (2003)
7. B. Tang, W.L. Dai, X.M. Sun, G.J. Wu, L.D. Li, N.J. Guan, M. Hunger, Chin. J. Catal. **36**, 801 (2015)
8. Z. Wang, Y.T. Cui, Z.B. Xu, J. Qu, J. Org. Chem. **73**, 2270 (2008)
9. H.Y. Tian, Y.D. Zhang, Z.X. Wang, Spec. Petrochem. **26**, 37 (2009)
10. Q.S. Yang, X. Yang, Y.J. Wang, H.O. Wang, Q.Y. Cheng, Res. Chem. Intermed. **38**, 2277 (2012)
11. B. Tang, W.L. Dai, G.J. Wu, N.J. Guan, L.D. Li, M. Hunger, ACS Catal. **4**, 2801 (2014)
12. R.H. Fan, X.L. Hou, Org. Biomol. Chem. **1**, 1565 (2014)
13. F. Cavani, J.H. Teles, ChemSusChem **2**, 508 (2009)
14. V. Nardello, J.-M. Aubry, D.E. De Vos, R. Neumann, W. Adam, R. Zhang, J.E. ten Elshof, P.T. Witte, P.L. Alsters, J. Mol. Catal. A **251**, 185 (2006)
15. I.W.C.E. Arends, R.A. Sheldon, Appl. Catal. A **212**, 175 (2001)
16. A.P. Zhang, S. Gao, Y. Lv, Z.W. Xi, Res. Chem. Int. **35**, 563 (2009)
17. C. Antonetti, A.M.R. Galletti, P. Accorinti, S. Alini, P. Babini, K. Raabova, E. Rozhko, A. Caldarelli, P. Righi, F. Cavani, P. Concepcion, Appl. Catal. A **466**, 21 (2013)
18. A. Corma, M.A. Camblor, P. Esteve, A. Martinez, J. Perez-Pariente, J. Catal. **145**, 151 (1994)
19. Q.H. Xia, X. Chen, T. Tatsumi, J. Mol. Catal. A **176**, 179 (2001)
20. A. Corma, M.T. Navarro, J. Perez-Pariente, J. Chem. Soc. Chem. Commun. **2**, 147 (1994)
21. T. Tatsumi, K.A. Noyano, N. Igarashi, J. Chem. Soc. Chem. Commun. **3**, 325 (1998)
22. T. De Baerdemaeker, B. Steenackers, D. De Vos, Chem. Commun. **49**, 7474 (2013)
23. M.A. Camblor, A. Corma, A. Martínez, J. Pérez-Pariente, J. Chem. Soc. Chem. Commun. **8**, 589 (1992)
24. N. Jappar, Q.H. Xia, T. Tatsumi, J. Catal. **180**, 132 (1998)
25. T. Blasco, M.A. Camblor, A. Corma, P. Esteve, A. Martínez, C. Prieto, S. Valencia, Chem. Commun. **20**, 2367 (1996)
26. J.P. Nogier, Y. Millot, P.P. Man, T. Shishido, M. Che, S. Dzwigaj, J. Phys. Chem. C **113**, 4885 (2009)
27. J.P. Nogier, Y. Millot, P.P. Man, C. Méthivier, M. Che, S. Dzwigaj, Catal. Lett. **130**, 588 (2009)
28. B. Tang, W.L. Dai, X.M. Sun, N.J. Guan, L. Li, M. Hunger, Green Chem. **16**, 2281 (2014)
29. K. Sarma, N. Borthakur, A. Goswami, Tetrahedron Lett. **48**, 6776 (2007)
30. R. Otomo, T. Yokoi, J.N. Kondo, T. Tatsumi, Appl. Catal. A **470**, 318 (2014)
31. R. Otomo, T. Tatsumi, T. Yokoi, Catal. Sci. Technol. **5**, 4001 (2015)
32. J. Dijkmans, M. Dusselier, D. Gabriëls, K. Houthoofd, P.C.M.M. Magusin, S. Huang, Y. Pontikes, M. Trekels, A. Vantomme, L. Giebeler, S. Oswald, B.F. Sels, ACS Catal. **5**, 928 (2015)
33. S. Dzwigaj, M.J. Peltre, P. Massiani, A. Davidson, M. Che, T. Sen, S. Sivasanker, J. Chem. Soc. Chem. Commun. **1**, 87 (1998)
34. S. Dzwigaj, M. Matsuoka, M. Anpo, M. Che, J. Phys. Chem. B **104**, 6012 (2000)
35. W.C.R.Z. Hua, T.G. Ge, X.X. Zhou, L.S. Chen, Y. Zhu, J.L. Shi, Chin. J. Catal. **36**, 906 (2015)