

Synthesis of HZSM-5 Catalyst by Template-Free Method for Hydration of Cyclohexene to Cyclohexanol

Runhu Zhang¹, Chao Hua^{2,*}, Fang Bai^{2,3}, Ping Lu² and Mencui Ning¹

¹Department of Chemical Engineering, Kunming Metallurgy College, Kunming 650033, China

²CAS Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

³School of Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100190, China

*Corresponding author e-mail: huachao@ipe.ac.cn

Abstract. In order to remain competitive, it is important to constantly optimize processes. The catalytic hydration of cyclohexene to cyclohexanol appears to be a promising alternative in the production of adipic acid. In this paper, the HZSM-5 was successfully synthesized without an organic template. Prepared H-ZSM5 catalysts were characterized using several techniques like X-ray diffraction (XRD), ammonia temperature-programmed desorption (NH₃-TPD) and Scanning electron microscopy (SEM). Prepared H-ZSM5 catalyst was found to offer the best performance regarding selectivity and activity. The conversion of cyclohexene reached to 12.38% and the selectivity of cyclohexanol was 99%.

1. Introduction

Cyclohexanol is an excellent organic intermediate used to produce adipic acid, caprolactam and other chemical products [1]. At present, there are three main methods of production of cyclohexanol: cyclohexane oxidation, phenol hydrogenation and cyclohexene hydration. In the process of cyclohexane oxidation, its safety is not high, the selectivity is poor, and energy consumption is relatively high [2, 3]. In the process of phenol hydrogenation, the production cost of cyclohexanol is relatively high, so the application is limited. In contrast, cyclohexene hydration is considered as the most promising pathway to produce cyclohexanol because it is a highly selective and low pressure reaction. Cyclohexene hydration to produce cyclohexanol is an acid catalyzed reaction, which requires a strong acid catalyst to provide enough protons for the proceeding of hydration reaction. It is well known that homogeneous acid catalysts such as sulfuric acid can provide high yield of cyclohexene hydration [4]. However, the catalyst cannot be industrialized because of the difficulty of product separation and corrosion of equipment. Various solid acids such as strongly acidic ion exchange resins and zeolites have been used for this reaction. Solid acid catalysts have many advantages such as high selectivity, small explosion hazards and convenient separation of the solid catalysts from the liquid mixture. The DuPont Co studied the use of perfluorinated sulfonic acid resins as catalysts for cyclohexene hydration [5]. The strong acid ion exchange resins were used for this reaction [6, 7]. However, ion exchange resins also could not be industrialized because of their low thermal stability. As one representative class of solid acid materials,



ZSM-5 is frequently employed for industrial processes in hydration reactions. ZSM-5 has a ten-membered ring channel structure (the pore diameter is 35 to 0.65 nm), which is equivalent to the molecular diameters of cyclohexene and cyclohexanol (58 nm and 0.60 nm, respectively), which have good selectivity, superior mechanical strength, and high thermal stability for the hydration of cyclohexene and have been studied in recent years [8-11]. Some organic templates as structural directing agents are often employed for the synthesis of ZSM-5 [12-14]. The use of organic templates can lead to difficult wastewater treatment, high energy consumption, and air pollution. Therefore, organic templates should be avoided in order to achieve more economical and environmentally friendly synthesis. Synthesis of HZSM-5 in the absence of organic template has been researched and developed. K.P. Dey et al. investigated synthesis of ZSM-5 zeolite through in-situ extraction of silica from rice husk ash in the absence of organic template by a simple hydrothermal condition at 150°C/72–96h [15]. Majid H. Nada and Sarah C. Larsen synthesized ZSM-5 successfully in high yield by using a seed-assisted method and without using the organic template [16]. A L. Figueiredo et al. obtained nanocrystalline ZSM-5 zeolites by a seed-assisted method from an organic-template-free system employing three different seeding strategies [17].

In this paper, we have developed a ZSM-5 catalyst for the hydration of cyclohexene to cyclohexanol, in which the catalyst has been prepared without employing organic templates. Our preparation method is easy to apply to ZSM-5 synthesis fields for industrial production. The catalysts exhibit higher activity and selectivity for cyclohexanol synthesis by cyclohexene hydration, which may be useful for commercial applications of the catalyst in the hydration of cyclohexene to cyclohexanol. The expected results provide some useful information to industrial researchers in studying hydration of cyclohexene to cyclohexanol.

2. Experimental

2.1. Catalyst preparation

ZSM-5 was synthesized from industrial aluminum sulfate, H₂SO₄ and water glass without any template. The synthesis procedure was reported in the previous reference [18]. A certain amount of water glass, aluminum sulfate, distilled water, crystal seeds (ZSM-5 zeolites), sulfuric acid were sequentially added to the reactor to form the gel mixture. Then the gel mixture was transferred into a Teflon-lined autoclave and hydrothermally treated at 160 ~ 180°C for 11~ 16h. H-ZSM-5 was obtained by ion exchange of ZSM-5 with an aqueous solution of HNO₃ three times, each at 80°C for 2 h, followed by calcination at 500°C in air for 6 h.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns of the HZSM-5 were collected by an X'pert Pro diffract meter (Panalytical, Almelo, Netherlands) using Cu K α radiation. The X-ray tube was operated at 40kV and 40mA and an angular range 2 θ from 5 to 60° was recorded. The surface morphology of the HZSM-5 was characterized by scanning electron microscopy (SEM). The SEM images were obtained using the Field Emission Scanning Electron Microscopy (JSM-6700F, JEOL, Tokyo, Japan). The acidity of the samples was measured by ammonia temperature-programmed desorption (NH₃-TPD) by a GC equipped with a TCD detector, in the range of 120–600 °C at a heating rate of 10 °C/min. The desorbed amount of NH₃ was continuously detected by TCD. Prior to the analysis, the samples were previously treated in argon at 500°C for 5 h. Elemental analysis of the HZSM-5 was conducted by ICP–AES apparatus (Spectro, Modular EOP) to identify the SiO₂/Al₂O₃ molar ratio.

2.3. Catalytic reaction

The activity of the HZSM-5 catalysts for cyclohexene hydration was performed in a 500 mL volume, high temperature, high pressure batch reactor (Parr 4575 series High Pressure/High Temperature reactor). In a typical experiment, 30g of catalyst, 5 mol of water and 0.64 mol cyclohexene were added to the reactor. The reactor was sealed and purged four times with nitrogen to evacuate the air. Then, the

initial pressure was controlled at 0.3 MPa with nitrogen and the temperature was raised to 125°C at which reactor pressure was 0.6 MPa. The rate of stirring was fixed at 600 r/min. After the reaction, the reactor was cooled to room temperature by circulating water and slowly depressurized to atmospheric pressure. The solid catalyst was separated by centrifugation, and the organic phase was analyzed using a gas chromatograph equipped with a flame ionization detector and a PEG20M packed capillary column (HP 6890, Agilent Technologies, and Santa Clara, CA, USA).

3. Results and Discussion

3.1. Characterization of the Catalyst

Figure 1 reports the XRD patterns for the HZSM-5 zeolites studied. The most important features of the diffractogram were observed at $2\theta = 7.9^\circ$, 8.8° , 23° , 23.9° , and 29.9° . It indicated that the catalyst had the characteristic peak of MFI-type zeolite and no amorphous material was present [19, 20]. These results show that the HZSM-5 has been prepared without using any organic templates.

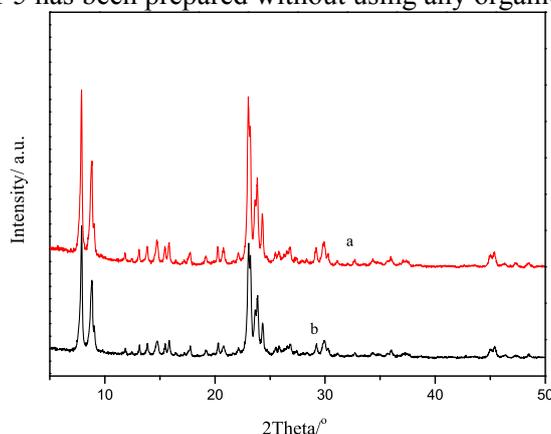


Figure 1. X-ray diffraction patterns of: (a) prepared HZSM-5 (b) commercial HZSM-5 catalysts.

Figure 2 shows the NH_3 -TPD profiles of the HZSM-5 zeolites. The similar curve is for the prepared HZSM-5 and commercial HZSM-5. The peak at the high temperature of about 420°C represents the strong Brønsted acid sites and the other at the low temperature of about 230 °C represents the interaction of Lewis acid sites with the NH_3 [21].

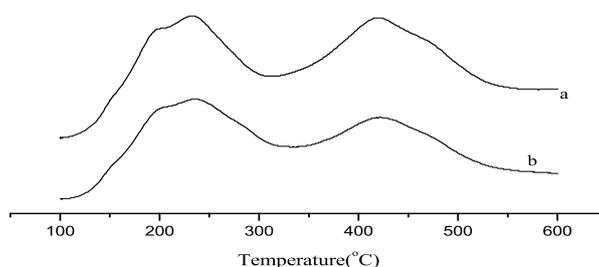


Figure 2. NH_3 -TPD profiles of (a) prepared HZSM-5 (b) commercial HZSM-5 catalysts.

Figure 3 presents SEM images of the prepared HZSM-5. The results indicate that The HZSM-5 particles possess rectangular morphologies, and these particles aggregate to form an olive-like shape.

These particles are intergrown with each other and are in the size range of 30–1000 nm. The micrographs also confirm the purity of the HZSM-5.

The chemical composition of the prepared HZSM-5 and commercial HZSM-5 zeolites, as measured by ICP–AES, is also reported in Table 1. As shown, the prepared HZSM-5 and commercial HZSM-5 zeolites have rather similar composition. The molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ is 28, and the ratio is also recommended for hydration of cyclohexene in the literature [9].

Table 1. $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of prepared HZSM-5 and commercial HZSM-5.

Catalyst	$\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio	Fe (%)	Na (%)
Prepared HZSM-5	28.0	0.02	0.10
Commercial HZSM-5	28.2	<0.01	0.14

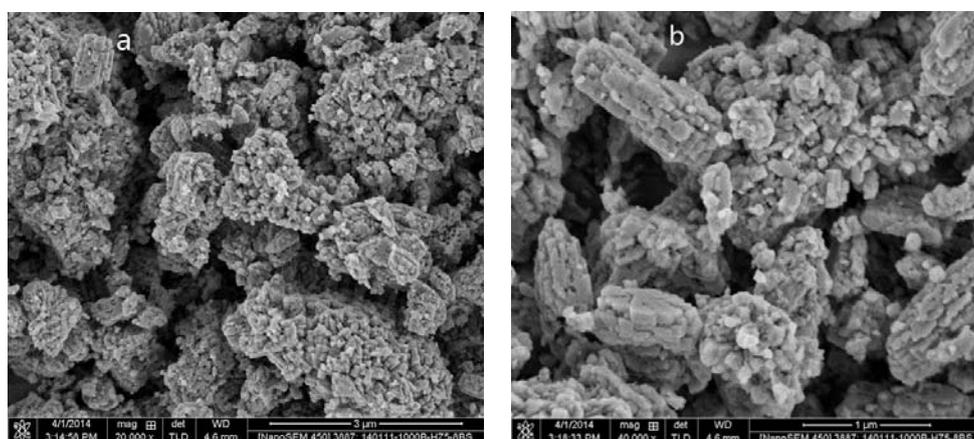


Figure 3. SEM images of the prepared HZSM-5: (a) magnify=20000 times (b) magnify=40000 times.

3.2. Catalytic Performance

The prepared HZSM-5 and commercial HZSM-5 catalysts were evaluated for their catalytic performance under the same reaction conditions. The reaction conditions are recommended in the reference. Figure 4 shows the conversion of cyclohexene over the prepared HZSM-5 and commercial HZSM-5 catalysts. For the prepared HZSM-5 catalysts, the conversion of cyclohexene varies from 6.7% to 12.38%. The conversion of cyclohexene over commercial the HZSM-5 catalysts is 6.6% to 12.15%. It is clear that the activity of the prepared catalyst is higher or equal to that of the commercial catalyst. Figure 5 displays the selectivity of cyclohexanol in the reaction. The selectivity of prepared HZSM-5 catalysts was obtained from 98% to 99%, which are also comparable to the commercial HZSM-5 catalysts.

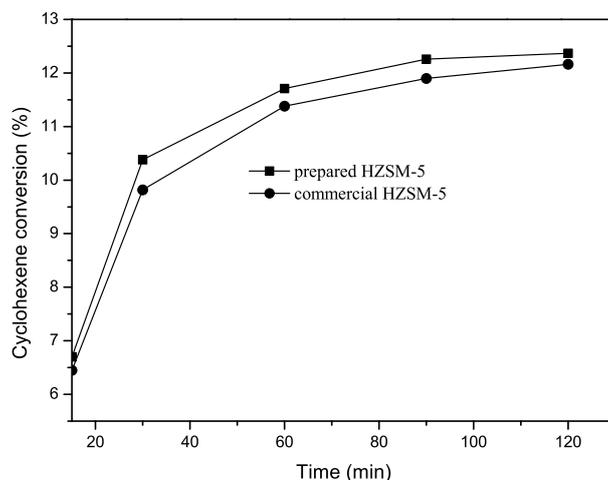


Figure 4. Conversion profiles of cyclohexene. Reaction conditions: Temperature: 125°C; Pressure: 0.6 MPa; stir speed: 600 r/min; cyclohexene: 64.6 ml, H₂O: 15 ml.

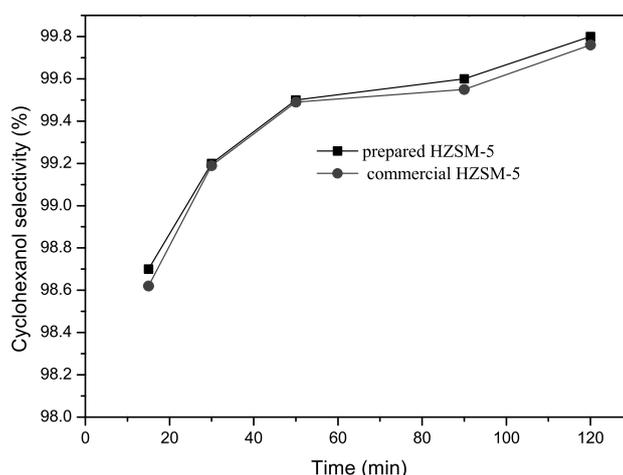


Figure 5. Selectivity profiles of cyclohexanol. Reaction conditions: Temperature: 125°C; Pressure: 0.6 MPa; stir speed: 600 r/min; cyclohexene: 64.6 ml, H₂O: 15 ml.

4. Conclusion

The HZSM-5 zeolite was successfully prepared by seed-induced synthesis from an organic-template free system. Prepared HZSM-5 catalysts were characterized by means of SEM, XRD and NH₃-TPD techniques. The prepared HZSM-5 and commercial HZSM-5 catalysts were tested for hydration of cyclohexene to cyclohexanol. The results illustrate that the prepared HZSM-5 catalysts are quite effective for the hydration of cyclohexene to cyclohexanol. The conversion of cyclohexene was up to 12.38% and the selectivity of cyclohexanol was 99% in 120 min, which would meet the demand of cyclohexene hydration catalyst in industrial applications.

Acknowledgments

The authors gratefully acknowledge the financial support of the Beijing Hua He Tuo Technology Co., Ltd. (20185301000029)

References

- [1] H. Ishida, Liquid-phase hydration process of cyclohexene with zeolites, *Catal. Surv. Jpn.* 1 (1997) 241-246.

- [2] Wen. Y, Potter.OE, Sridhar. T, Unanalyzed oxidation of cyclohexane in a continuous reactor, *Chem Eng Sci.* 52 (1997) 4593-4605.
- [3] H. Zhang, SM.Mahajani, MM. Sharma, T.Sridhar, Hydration of cyclohexene with solid acid catalysts. *Chem Eng Sci.* 57 (2002) 315-322.
- [4] H. Ishida, Y.Fukuoka, O.Mitsui, M. Kono, Liquid phase hydration of cyclohexene with highly siliceous zeolites, *Stud. Surf. Sci. Catal.* 83 (1994) 473-480.
- [5] F. H. Waller, U.S. Patent 4, 595, 786. (1986).
- [6] F.Hiroshi, M. Fujinao and K. Masao, Japan Patent 02, 040, 334. (1990).
- [7] H.J. Panneman, AACM. Beenackers, Solvent effects on the hydration of cyclohexene catalyzed by a strong acid ion exchange resin. I. Solubility of cyclohexene in aqueous sulfolane mixtures, *Ind. Eng. Chem. Res.* 31 (1992) 1227-1231.
- [8] Y. Fukuoka and O. Mitsui, Japan Patent6, 010, 403. (1985).
- [9] M.Tojo and Y.Fukuoka, Japan Patent 61, 180, 735.(1986).
- [10] M. Kučera, M. Králik, M. Mařaš, P. Hudec, M. Hronec, Hydration of cyclohexene catalyzed by zeolites Collect, *Czech. Chem. Commun.* 60 (1995) 498-504.
- [11] T. Kaneshima and Y. Takamatsu, U.S. Patent 6552235B2. (2003).
- [12] S. Y. Sang, F. X. Chang, Z. M. Liu, C. Q. He, Y. L. He, L. Xu, Difference of ZSM-5 zeolites synthesized with various templates, *Catal. Today.* 729 (2004) 93-95.
- [13] J. Robert, A. George and R. Landolt U.S. Patent3, 702, 886. (1972).
- [14] Y. Gao, B.h. Zheng, G. Wu, F.w. Ma, C.t. Liu, Effect of the Si/Al ratio on the performance of hierarchical ZSM-5zeolites for methanol aromatization, *RSC Adv.* 6 (2016) 83581-83588.
- [15] K.P. Dey, S. Ghosh, M.K. Naskar,Organic template-free synthesis of ZSM-5zeolite particles using rice husk ash as silica source, *Ceram. Int.* 39 (2013) 2153–2157.
- [16] Majid H. Nada, Sarah C. Larsen, Insight into seed-assisted template free synthesis of ZSM-5 zeolites, *Microporous Mesoporous Mater.* 239 (2017) 444-452.
- [17] A L. Figueiredo, A S. Araujo, M. Linares, Á. Peralb, R A. Garcia, D P. Serranob, V J. Fernandes Jr, Catalytic cracking of LDPE over nanocrystalline HZSM-5 zeoliteprepared by seed-assisted synthesis from an organic-template-free system, *J. Anal. Appl. Pyrolysis.* 117 (2016) 132–140.
- [18] S.H. Sun, W. Ding, C.X. Li, li Wang, X.M. Pang, X.H. Gao, Synthesis of zeolites ZSM-5 by using water glass, *Petrochemical Technology & Application*25 (2007) 509-511.
- [19] Y. Jiao, C. Jiang, Z. Yang, J. Zhang, Controllable synthesis of ZSM-5 coatings on SiC foam support for MTP application, *Microporous Mesoporous Mater.* 162 (2012) 152-158.
- [20] A K. Aboul-Gheit, A E. Awadallah, S M. El-Kossy, ALH., Mahmoud, Effect of Pd or Ir on the catalytic performance of Mo/H-ZSM-5 during the non-oxidative conversion of natural gas to petrochemicals, *J. Nat. Gas Chem.* 17 (2018) 337-343.
- [21] W. L. Fanchiang, Y. C. Lin, Catalytic fast pyrolysis of furfural over HZSM-5 and Zn/HZSM-5 catalysts, *Appl Catal. A.* 419-420 (2012) 102-110.