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The Synthesis of 1,4-Diazabicyclo (2.2.2) Octane over a Pre-Treated Titanium Silicalite-1 Catalyst

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Abstract Potassium chloride salt pre-treated titanium silicalite-1 (TS-1) zeolite (K-TS-1) was prepared via an ion-exchange method. XRD, EDX and BET were used to identify the structure of the zeolite. The BET surface area and the adsorption/desorption cumulative pore volume of the K-TS-1 catalyst were about 297 m^2/g and 0.213 cm^3/g, respectively. The average pore diameter of the K-TS-1 catalyst was 29.49 Å. The catalytic activity of K-TS-1 catalyst was studied in the fixed-bed catalytic reactor. 1,4-Diazabicyclo (2.2.2) octane (DABCO) was prepared from ethylenediamine (EDA) over the K-TS-1 zeolite catalyst. The influences of various reaction parameters such as reaction temperature, space velocity and concentration of EDA were discussed. The conversion of EDA was more than 96% and the selectivity of DABCO and PIP were up to 64 and 30%, respectively, in the temperature of 340 °C and weight hourly space velocity of 1.5 h^{-1} in the presence of water.

Keywords 1,4-Diazabicyclo (2.2.2) octane · Potassium chloride · Titanium silicalite · Ethylenediamine

1 Introduction

1,4-Diazabicyclo (2.2.2) octane (DABCO, also was named: triethylenediamine, TEDA, CAS No.: 280-57-9) is a key intermediate and is used, among other materials, in the preparation of pharmaceuticals and plastics, in particular as a catalyst in the preparation of polyurethanes [1, 2]. DABCO exhibits certain unusual properties which are due to its bicyclic or 'cage' structure [3, 4]. The known processes for the preparation of DABCO essentially differ through the nature of the starting materials for example ethylenediamine (1,2-diaminoethane, EDA) or monoethanolamine (MEOA) in the presence of a zeolite catalyst which comprises one or more metals in oxidation state [5–11]. In particular, a zeolite of the MFI type is used, because of right pore diameters [2]. In a particular embodiment, the zeolites can be doped by applying transition metals of subgroups IA, IIA and IVB to VIII, preferably those of subgroups IA and IVB, particularly preferably K and Ti. Kim recently demonstrated that DABCO bonds, via hydrogen bonding, to surface Al-OH groups and discovered that there are two stages of DABCO adsorption by hydrogen bonding and these bonding modes are thought to involve the adsorption of either a single DABCO molecule of two DABCO molecules to a single Al–OH group [12–15]. The DABCO was hardly desorpted from the SiO_2/Al_2O_3 zeolite catalyst surface due to the hydrogen bonds of Al–OH···(DABCO) and Al–OH···$(DABCO)_2$, which resulted in the low activity of the SiO_2/Al_2O_3 zeolite catalyst.

Titanium silicalite-1, a Ti-containing zeolite which have an MFI structure, shows a remarkable high efficiency and molecular selectivity in oxidation reactions under mild conditions such as the conversions of ammonia to hydroxylamine, of secondary alcohols to ketones and of secondary

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amines to dialkylhydroxylamines or reactions such as the phenol hydroxylation, the olefin epoxidation, the ketone ammoximation and also sulfide and disulfide oxidation [16–19]. The titanium isomorphously replaces silicon in a tetrahedral site of the MFI silicate lattice. TS-1 combines the advantages of having the high coordination ability of Ti^{4+} ions with the hydrophobicty of the silicate framework, while retaining the spatial selectivity and specific local geometry of the active sites of the molecular sieve structure. In the presence of TS-1, the DABCO was prepared by the reaction of EDA and piperazine (PIP) [20]. For these reasons, potassium chloride salt pre-treated titanium silicalite-1 (TS-1) zeolite (K-TS-1) was prepared.

The aim of our work was to prepare potassium chloride salt pre-treated titanium silicalite-1 (TS-1) zeolite (K-TS-1) via an ion-exchange method. The samples were characterized using XRD, EDX and BET. To test the activity of the catalyst, the K-TS-1 zeolite was used to conversion of DABCO in the presence of EDA in a fixed-bed reactor. The influences of various reaction parameters such as reaction temperature, space velocity and concentration of EDA were discussed.

2 Experimental

2.1 Catalyst Preparation

The TS-1 catalyst, obtained from SINOPEC Changling Company, China, had a titanium and silica molar content of 0.88. The TS-1 catalyst was water-treated and calcined at 550 °C before potassium chloride treatment. The K-TS-1 catalyst was prepared via an ion-exchange method, and was treated under reflux condition in potassium chloride aqueous solution, and then separated by decantation and filtration, rinsed under water reflux three times, dried at 110 °C for 5 h and then calcined. The calcined catalyst was pressed at 20 MPa to form pellets and the pellets were crushed to form small-sized particles with particles size ranging from 0.5 to 0.7 mm for characterization and identification by X-ray powder diffraction (XRD) (Fig. 1), energy dispersive analysis of X-ray (EDX) (Fig. 2) and Brunauer–Emmett–Teller (BET).

2.2 Characterization

The physicochemical and catalytic behavior of zeolites could be modified by changing their framework composition [21]. The advent of crystalline titanium silicates with zeolite properties had enlarged the domain of zeolite catalysis in hydroxylation, ammoximation and oxidation reactions [22–

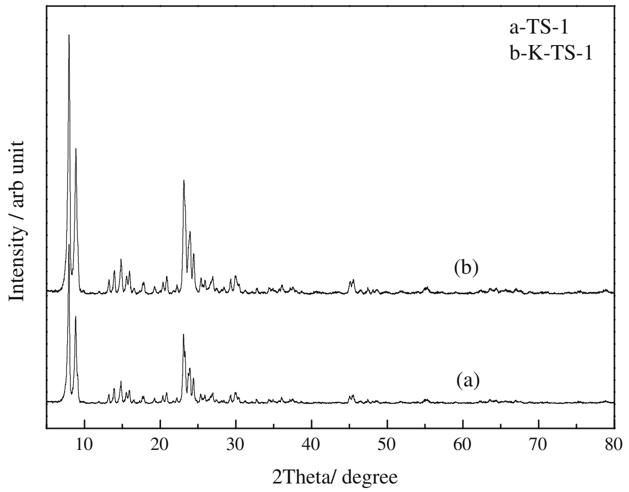
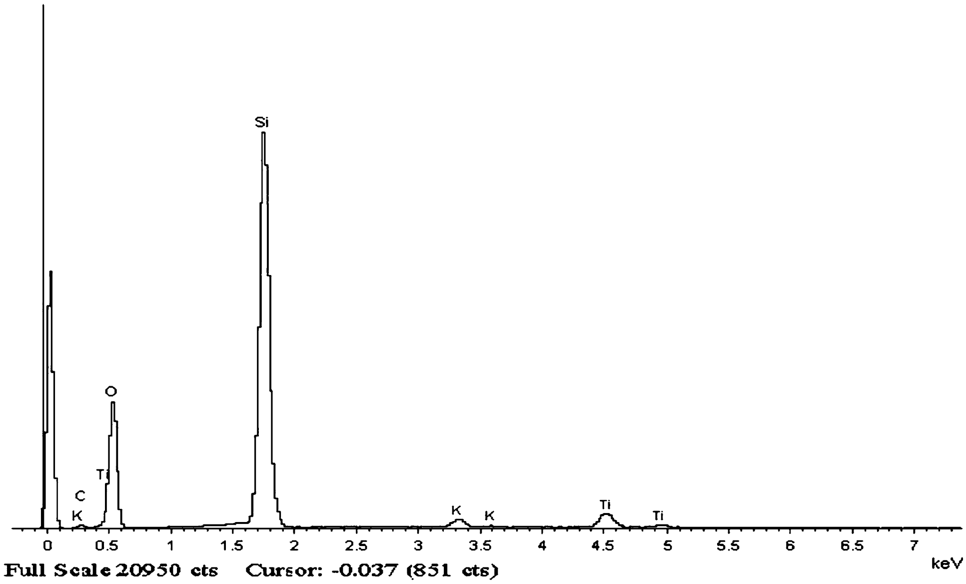


Fig. 1 X-ray diffraction patterns of TS-1 and K-TS-1

Fig. 2 EDX spectroscopy of K-TS-1



24]. XRD was used for structural identification and phase purity of the zeolite samples. X-ray diffraction was carried out on a Rigaku, D-Max/III-VC model using the Cu–Ka radiation (1.5418 Å) with Ni filter, scanning from 5° to 80° (2θ). EDX and BET surface area (Quanta chrome autosorb instrument) were also used to characterize the zeolite.

2.3 Catalytic Test

The reactions were carried out in a down-flow, fixed-bed silica reactor at atmospheric pressure and 300–400 °C. Prior to each run of the reactor, the catalyst (3 g, 0.3–0.7 mm) was calcined for 3 h in a flow of dry air and then cooled to the reaction temperature in a flow of N_2. Aqueous EDA solution (EDA/H_2O molar ratio) was introduced into the reactor via an ISCO pump (Model 500D, USA) with a flow rate of 3 mL/h. The temperature was measured by a thermocouple which was located in the catalyst bed. The products were cooled by an ice-cooled water bath and collected in the receiver, and were analyzed on SP 6890 gas chromatograph (SP 6890 with a FID detector, 30 m, CP-Sil-5 Chrompack column, id: 0.25 mm, coating 0.25 lm, column temperature 150 °C, injector temperature 200 °C and FID temperature 250 °C) [25]. The products were identified by GC–MS (Varianinc GC/MS 2100).

3 Results and Discussion

3.1 Characterization of K-TS-1 Catalysts

3.1.1 XRD Analysis

The X-ray powder diffraction pattern of the calcined TS-1 zeolites was produced in Fig. 1. It was similar to that of standard HZSM-5 zeolites confirming orthorhombic symmetry and location of Ti in zeolite framework. The XRD patterns of the zeolite sample TS-1 was all highly crystalline and matched with the reported literature [26]. In comparison with TS-1 and potassium chloride modified TS-1, it is clear from B = L ratio that the number of Lewis acid sites (LAS) are high in K-modified catalysts; however, the number of Brönsted acid sites (BAS) are low on K-TS-1 catalyst indicates that all the exchangeable sites are occupied with K. K-impregnation also leads to K-exchange to a good extent was evident from the decrease in BAS. Introduction of metal cations in the TS-1 produced changes in the number of BAS, the intensity of BAS clearly decreased when potassium cations were added [27, 28]. The presence of K^+, even in very small amounts, severely retards the catalytic oxidation activity [28].

3.1.2 EDX Analysis

The study was performed with a view to examine the behavior and performance of TS-1 by doping it with K. EDX spectrum of potassium chloride modified TS-1 is shown in Fig. 2. The chemical analysis by EDX measurement taken as an average of five different sites over an area of 15 μm × 15 μm shows C = 24.43%, O = 55.91%, Si = 18.54%, Ti = 0.77%, K = 0.34% giving Si/Ti atomic ratio to be 24.08.

3.1.3 BET and Average Pore Size Analysis

The adsorption–desorption isotherms and pore size distributions of the samples are displayed in Fig. 3. BET specific surface area, obtained by N_2 adsorption at the liquid nitrogen temperature, was 297 m^2/g, revealing that the K-TS-1 catalyst could provide high surface areas. The total

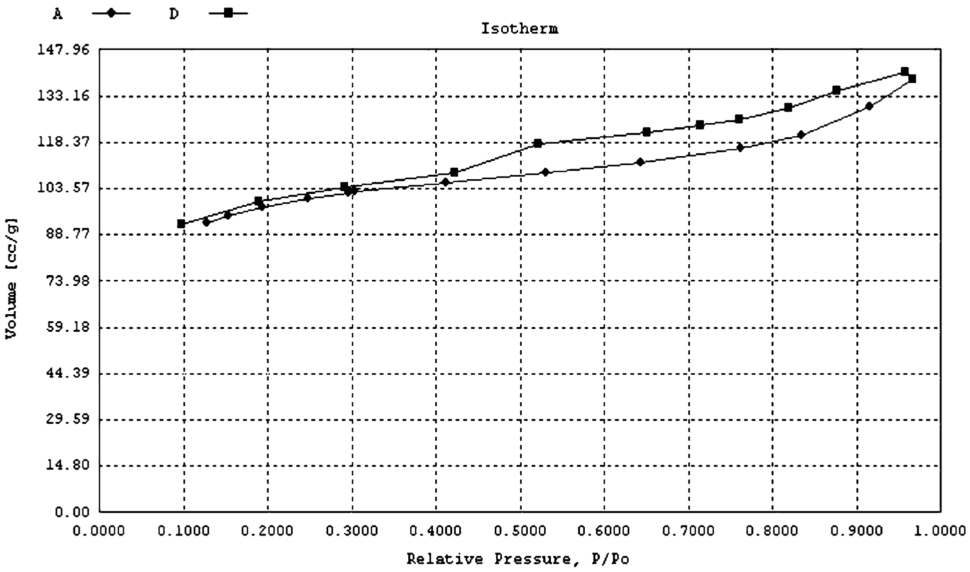


Fig. 3 N_2 adsorption/desorption isotherms of K-TS-1; *A*, ●: adsorption; *D*, ■: desorption

pore volume was 0.213 cm^3/g, revealing that the K-TS-1 catalyst had a high absorption/desorption capacity. The average pore diameter was 29.49 Å. The pore sizes were appropriate for the catalytic characteristics of DABCO.

3.2 Catalysis Results

3.2.1 Influence of Temperature

The catalytic activities for the EDA conversion and product selectivity of DABCO over K-TS-1 and TS-1 zeolites in the temperature range of 300–400 °C were exhibited in Table 1. With the increase of the temperature, the conversion of EDA increased on both of the zeolite catalysts. The TS-1 showed higher conversions of EDA (above 96%) than that of K-TS-1 at the same temperature. The selectivity of DABCO was higher on TS-1 than that of K-TS-1, but the selectivity of PIP was lower on TS-1 than that of K-TS-1. PIP synthesized by EDA can be reused to prepare DABCO in the presence of the catalysts. The total yield of DABCO was higher catalyzed by K-TS-1 than that of TS-1. To get the max economic benefits, K-TS-1 would be a better catalyst.

In the case of K-TS-1, the conversion of EDA increases from 90.93% at 300 °C to 99.43% at 400 °C with an increase in temperature, correspondingly the selectivity of DABCO increases from 61.37% at 300 °C to 65.26% at 400 °C. The selectivity of PIP increases from 25.04% at 300 °C to 30.80% at 340 °C and decreases to 26.00 at 400 °C. These are formed by the decomposition and transformation of DABCO. The low boiling by-products include methyl amine, ethylene diamine, ethylene imine, ammonia and ethylene as identified by GC-MS. These compounds are formed by the decomposition of PIP or DABCO over the acid sites of the zeolites. In order to obtain the most benefit, the optimum temperature was 340 °C for the high selectivity of DABCO (64.06%) and PIP (30.82%).

Table 1 Effects of reaction temperature on EDA conversion and products selectivity over TS-1 and K-TS-1

Catalyst	*T* (°C)	Conv. EDA	Selectivity (%)	
			PIP	DABCO
TS-1	300	94.50	8.45	56.58
	320	96.52	9.67	60.52
	340	97.94	11.82	63.31
	360	98.21	9.90	67.89
	400	99.47	9.79	70.56
K-TS-1	300	90.93	25.04	61.37
	320	94.22	28.70	61.74
	340	96.11	30.82	64.06
	360	98.95	26.85	64.54
	400	99.43	26.00	65.26

Reaction conditions: the molar ratio of EDA/H_2O = 1; WSHV = 1.5 h^{-1}

3.2.2 Influence of WHSV

The changes in EDA conversion and products selectivity over K-TS-1 at WHSV (h^{-1}) ranging from 0.5 to 2.5 were shown in Fig. 4. There were no external mass transfer limitations as evident by the linear increase in EDA conversion with contact time. However, the selectivity to DABCO and the sum of the selectivity of DABCO and PIP increased with increase in contact time, reaching 64.09 and 94.86% respectively, at a conversion of 96.06% EDA for WHSV = 1.5 h^{-1}. Thus keeping in view of DABCO selectivity and the sum of the selectivity of DABCO and PIP, it could be concluded that optimum WHSV was found to be 1.5 h^{-1}.

3.2.3 Influence of the Molar Ratio of EDA/H_2O

The influence of EDA/H_2O molar ratio in the feed was investigated over K-TS-1 at 340 °C. As it was shown in Table 2, a decrease in the molar ratio of EDA/H_2O in the aqueous solution of the feed improves the selectivity of DABCO and PIP. At a high concentration of EDA (EDA/H_2O molar ratio = 3), the conversion as well as the yield of DABCO was poor and the formation of by-products was high. At a low concentration of EDA (EDA/H_2O molar ratio = 0.5), the conversion of EDA and the selectivity of

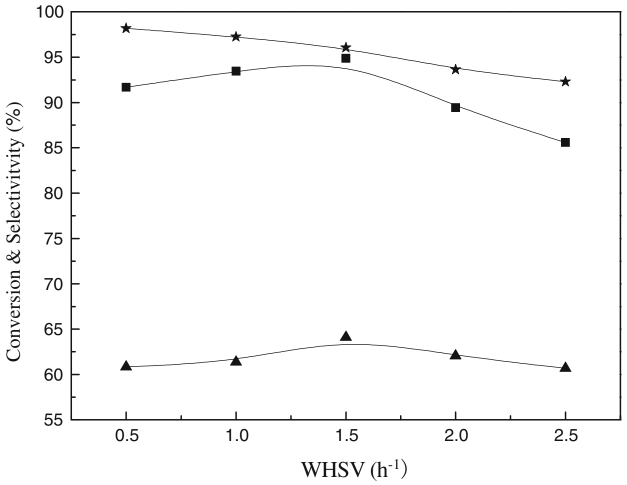


Fig. 4 Influence of space velocity on EDA conversion and products selectivity over K-TS-1. ▲, the selectivity of DABCO; ■, the sum selectivity of DABCO and Piperazine (PIP); ★, the conversion of EDA. Reaction conditions: the molar ratio of EDA/H_2O = 1; Temperature = 340 °C

Table 2 Influence of EDA/H_2O molar ratios on the conversion of EDA and the selectivity of PIP and DABCO using K-TS-1 as a catalyst

EDA/H_2O molar ratio	Conv. EDA	Selectivity (%)	
		PIP	DABCO
0.5	96.97	31.32	65.34
1.0	96.09	30.82	64.06
1.5	95.08	27.62	62.17
2.0	89.55	26.42	58.48
3.0	85.01	25.52	55.86

Reaction conditions: Temperature = 340 °C; WSHV = 1.5 h^{-1}

DABCO and PIP were good. But there will be more energy and time consuming during the next distillation step to remove the water which was introduced into the process in the catalysis synthesis step. So the optimum molar ratio of EDA/H_2O was 1.

4 Conclusions

Potassium chloride salts pre-treated titanium silicalite-1 zeolite catalyst was prepared via an ion-exchange way. The catalyst was characterized by XRD, EDX and BET. The BET surface area and the adsorption/desorption cumulative pore volume of the K-TS-1 catalyst were about 297 m^2/g and 0.213 cm^3/g, respectively. The average pore diameter of K-TS-1 catalyst was 29.49 Å. The catalytic activities for the EDA conversion and product selectivity over K-TS-1 were studied. The K-TS-1 zeolite catalyst was selective for the formation of DABCO. The catalyst showed high conversions of EDA (above 96%) and high selectivity of DABCO (64.06%) and PIP (30.82%) as the major products at the optimum reaction parameters (Temperature = 340 °C; WSHV = 1.5 h^{-1}; the molar ratio of EDA/H_2O = 1).

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References

1. Matthias F, Bernd B (2006) US Patent 7,115,742 B2
2. Anand R, Rao BS (2002) Catal Commun 3:479–486
3. Reichle WT (1993) J Catal 144:556–568
4. Farkas A, Mills GA, Erner WE, Maerker JB (1959) Ind Eng Chem 51:1299–1300
5. Matthias F, Bernd B (2003) US Patent 6,562,971 B2
6. Buysch HJ, Botta A, Puppe L (1991) DE 3,934,459
7. Li HX, Santiesteban JG, Armor JN (1998) US Patent 5,731,449
8. Santiesteban JG, Li HX, Armor JN (1998) US Patent 5,741,906
9. Armor JN, Santiesteban JG, Li HX (1998) US Patent 5,756,741
10. Li HX, Santiesteban JG, Emig LA, Armor JN (1999) EP 952,152
11. Li HX, Santiesteban JG, Emig LA, Armor JN (2000) US Patent 6,084,096
12. Kim S, Byl O, Yates JT Jr (2005) J Phys Chem B 109:3499–3506
13. Kim S, Byl O, Yates JT Jr (2005) J Phys Chem B 109:3507–3511
14. Kim S, Byl O, Yates JT Jr (2005) J Phys Chem B 109:6331–6333
15. Maspero F, Romano U (1994) J Catal 146:476–484
16. Hulea V, Moreau P, Di Rienzo F (1996) J Mol Catal A 111: 325–332
17. Adam W, Corma A, Reddy TI, Renz M (1997) J Org Chem 62:3631–3637
18. Clerici MG, Ingallina P (1998) Catal Today 41:351–364
19. Thangaraj A, Kumar R, Mirajkar SP, Ratnasamy P (1991) J Catal 130:1–8
20. Matthias F, Bernd S (2002) DE 10,061,863 A1
21. Taramasso M, Perego G, Notary B (1983) US Patent 4,410,501
22. Reddy JS, Kumar R, Ratnasamy P (1990) Appl Catal 58:L1–L4
23. Boccuti MR, Rao KM, Zecchina A, Leofanti G, Petrini G (1989) Stud Surf Sci Catal 48:133–144
24. Reddy JS, Kumar R (1991) J Catal 130:440–446
25. Zhao D, Duan E, Zhang X, Zhang J, Wang J (2007) J Chem Eng Data 52:1483–1485
26. Saxena S, Basak J, Hardia N, Dixit R, Bhadauria S, Dwivedi R, Prasad R, Soni A, Okram GS, Gupta A (2007) Chem Eng J 132:61–66
27. Capel-Sanchez MC, Campos-Martin JM, Fierro JLG (2003) Appl Catal A: Gen 246:69–77
28. Tatsumi T, Koyano KA, Shimizu Y (2000) Appl Catal A: Gen 200:125–134