ELSEVIER

Catalysis Today 51 (1999) 103–111

CATALYSIS TODAY

Attempts to create new shape-selective solid strong base catalysts

Jianhua Zhu*, Yuan Chun, Ying Wang, Qinhua Xu

Department of Chemistry, Nanjing University, Nanjing 210093, China

Abstract

Loading of KF on zeolite NaY leads to a similar basicity to that of KOH/NaY, but no strongly basic sites formed on the composite due to the negative effect of SiO_4 tetrahedra in NaY which form species with low base strength. Using $AlPO_4$-5 or NaY coated with Al_2O_3 to support KF could avoid the effect of SiO_4 tetrahedra and increased the base strength of the sample. KNO_3 loaded on NaY created basic sites after decomposition at 673 K with a redox method, and KNO_3/KL was found to have superbasicity. For preparation of strongly basic zeolites, microwave irradiation was employed to disperse MgO on zeolites, and the resulting materials showed high activities in the decomposition of isopropanol or the isomerization of *cis*-but-2-ene at 273 K.

Keywords: Strongly basic zeolite; KF modification; Loading of KNO_3; Dispersion of MgO; Microwave irradiation

1. Introduction

Owing to their ability of catalyzing a lot of reactions in mild conditions, strong solid bases, especially strongly basic zeolites, are desired for developing environmentally benign catalytic processes to minimize pollutants. A successful application of basic zeolite for the direct production of a pharmaceutical, 4-methylthiazole, has recently been reported [1]. Unfortunately, the number of shape-selective base catalysts in industry is very limited, due to the difficulty in obtaining strongly basic zeolites in a straightforward way. Regarding base catalysis by zeolites, it is generally known that the average oxygen charge or basicity increases with increasing aluminum content of the zeolite and with increasing ionic radius of the alkali cation [2]. However, the lack of strongly basic sites on the zeolite X, even exchanged with Cs cation [3], implies the necessity of introducing a basic guest into a zeolite host to form strongly basic catalysts. On the other hand, many methods, which can be used on oxides such as alumina to create strongly basic sites [4,5], do not work on zeolites, and the reason has not been well understood so far. Although many novel zeolites containing nanophase cesium oxide [6] or metallic sodium clusters [7] had been prepared in the laboratory and exhibited strong basicities, the high cost and/or oxygen sensitivity limited their application on an industrial scale. It is clear that the preparation of strongly basic zeolites becomes the key step for developing shape-selective base catalysis. In the work described here, we attempt to disperse neutral potassium salts such as KF or KNO_3 along with MgO on various zeolites, in order to develop novel ways for preparing new shape-selective solid strong base catalysts.

---

*Corresponding author.

0920-5861/99/$ – see front matter
PII: S0920-5861(99)00012-7

2. Experimental

2.1. Samples and agents

Various types of zeolites (NaY (Si/Al=2.86), NaX (Si/Al=1.40), KL (Si/Al=2.90), NaZSM-5 (Si/Al=24.3), Naβ (Si/Al=15.2) and NaM (Si/Al=5.2)) were used as starting materials. KX, KY and Kβ were obtained from the parent zeolite by an ion exchange method described previously [8]. $AlPO_4$-5 and $AlPO_4$-11 were synthesized according to patented methods [9]. The SiO_2, obtained by hydration and calcination of $Si(OEt)_4$, and γ-Al_2O_3 (Merck) were also used to support KF or KOH. Commercial MgO, purchased from Dunhuang Factory (China), was dried at 373 K prior to use. An impregnation method [10], using an aqueous solution of KF, KOH, KNO_3 or Na_2CO_3 followed by drying at 353 K, was employed to prepare the supported catalysts. In the process of dispersing Al_2O_3 or MgO by use of microwave irradiation, powder of Al_2O_3 or MgO was ground in mortar with zeolite at a given weight ratio, then irradiated in a microwave oven (2450 MHz) for 20 min.

Gases used here were nitrogen (99.99 wt%) and helium (99.999 wt%), both purified by passing over 5A zeolite. Isopropanol and the other agents were of AR grade, and their purities were higher than 99.5 wt%. *cis*-But-2-ene was purified by repeated freeze-thaw cycles.

2.2. Analytical methods

X-ray diffraction patterns were obtained with a Rigaku D/max-rA diffractometer employing Cu K_α radiation. XRD peak of MgO(2 0 0) was compared with zeolite KL(1 0 0) or NaY(1 1 1), and the intensity ratio was denoted as factor R to characterize the dispersion of MgO on zeolite.

IR spectra were recorded on a Nicolet FT-IR 510P spectrometer at 4 cm^{-1} resolution; Room-temperature spectra were obtained with a high-vacuum cell which allowed pressed sample wafers of 6 mg cm^{-2} to be pretreated in a heated region and then moved magnetically into the IR beam.

To measure the basicity of solid bases, samples of 0.05 g were shaken for 5 min in 0.02 M aqueous HCl (5 ml), and the remaining acid was then titrated with standard base (0.02 M aqueous NaOH). Base strength of the samples (H_-) was determined by using Hammett indicator [11]. In the experiment characterizing the water stability of solid base, the sample was washed by distilled water and filtered until the solution did not show basicity in titration; then the residual basicity of sample was titrated by use of a standard HCl solution.

2.3. Catalytic reactions

Decomposition of isopropanol was carried out in a conventional flow reactor with a WHSV of 3.30 h^{-1} [8]. A 50 mg portion of the catalyst, in 20–40 meshes, was activated at a given temperature for 2 h in a flow of N_2 prior to reaction. Nitrogen was used as carrier gas, and the total pressure was 0.1 MPa while the partial pressure of isopropanol was 9.1 kPa. The products were analyzed with an on-line gas chromatograph (GC) equipped with a Porapak T column ($\Phi 3 \times 4000$ mm) and a TCD, and the analysis data were normalized by using a HP3390A integrator.

A glass closed recirculation reactor, connected to a conventional vacuum line and to a GC, was employed for the isomerization of butene at 273 K [10]. Prior to reaction, the catalyst was evacuated under ca. 10^{-3} Pa at an elevated temperature for 2 h. Reaction products were analyzed by GC with a VZ-7 column ($\Phi 3 \times 2000$ mm) and a TCD, and the initial ratio of *trans*-but-2-ene to but-1-ene (*t*-B/1-B) in the products was obtained by extrapolation to zero conversion.

3. Results and discussion

3.1. Dispersion of potassium compounds or magnesia on zeolite

KF could be highly dispersed on zeolite NaY, NaX and $AlPO_4$-5. 16%KF/NaY, 17%KF/NaX and 5%KF/$AlPO_4$-5 had the same XRD pattern as that of parent zeolite, and no obvious distortion was found in their frameworks even when they were calcined at 773 K. However, the interaction between KF and the AlO_4 and SiO_4 tetrahedra of zeolite was accelerated at high temperature, therefore the characteristic XRD peaks of NaY disappeared after the 16%KF/NaY sample was evacuated at 923 K (Fig. 1), indicating the collapsing of framework. Evacuation at high temperature also

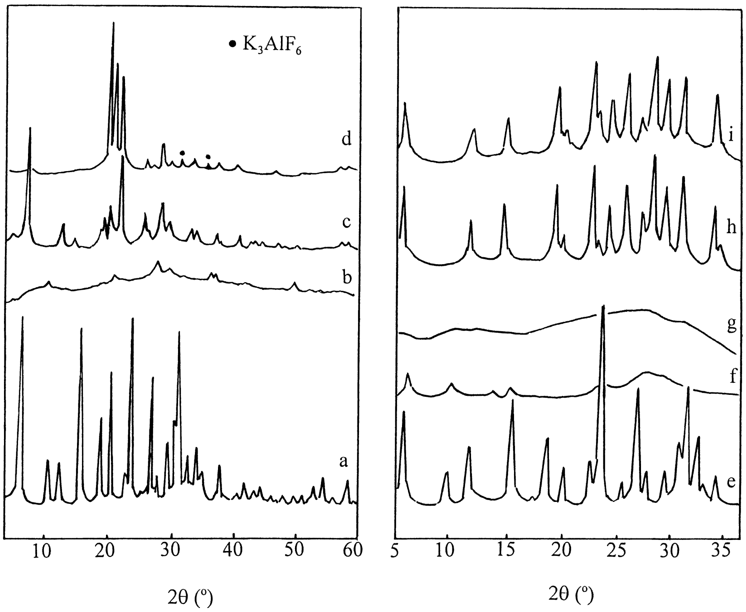

Fig. 1. XRD patterns of (a) NaY, (b) 16%KF/NaY evacuated at 923 K, (c) $AlPO_4$-5, (d) 5%KF/$AlPO_4$-5 evacuated at 873 K; 11%KOH/KY (e) before and (f) after calcination at 873 K, (g) 13%KOH/NaY calcined at 873 K, and 11%KOH/KL (h) before and (i) after calcination at 873 K.

damaged the framework of 5%KF/$AlPO_4$-5. Although the structure of KF/$AlPO_4$-5 persisted in the evacuation at 873 K, remarkable distortion emerged in the XRD pattern shown in Fig. 1, accompanied by the peaks of K_3AlF_6 resulting from the reaction between KF and the surface of support. Besides, the surface K/P atomic ratio of 5%KF/$AlPO_4$-5 was increased from 0.17 to 0.30 by the evacuation at 923 K, while the F/P ratio decreased from 0.50 to 0.37 [12]. It is very likely that KF has an intensive interaction with $AlPO_4$-5 at high temperature, forming K_3AlF_6 and resulting in surface enrichment of potassium species.

Neither KNO_3 nor new phase such as $K_2[Al(NO_3)_5]$ was observed in the XRD pattern of 21%KNO_3/NaY [13], indicating the well dispersion of KNO_3 on zeolite. Moreover, no considerable distortion was found in the structure of KNO_3/KL [14] and KNO_3/NaY, even when the sample was heated at 873 K. For a comparison, KOH was supported on zeolite NaY, KY and KL, and the composites were calcined at 873 K. As shown in Fig. 1, only KOH/KL sample kept the original XRD pattern after calcination, while KOH/NaY and KOH/KY became amorphous. It is clear that using KNO_3 as a modifier can avoid intensive interaction with the surface of host, keeping the pore structure and the shape-selectivity of zeolites that are necessary for catalysis.

Alumina was coated on zeolite NaY through hydrolysis of aluminum isopropoxide [15], in order to cover the surface of zeolite and prepare a novel porous support, denoted as Al_2O_3–NaY, for loading of KF or KNO_3. Microwave irradiation was proven to be an efficient method for the preparation of Al_2O_3–NaY porous materials. For example, 24 h were requited to disperse the Al_2O_3 of 20 wt% on zeolite NaY by use of isopropoxide hydrolysis, whereas only about 1 h was needed using microwave irradiation to obtain a NaY sample with the Al_2O_3 of 29 wt% being highly dispersed [16].

MgO could be dispersed on zeolite by the use of microwave irradiation, but it was more difficult than to disperse Al_2O_3. For instance, Al_2O_3 of 29 wt% could be well dispersed on NaY, whereas a considerable peak of MgO(2 0 0) remained on the XRD pattern of 22%MgO/NaY sample, with a R-value of 0.56 under the same condition. However, no new phase such as $MgAl_2O_4$ was detected on MgO/NaY, and the host kept its original framework structure. Loading MgO of 20 wt% on zeolite NaY decreased its surface area from 766 to 560 $m^2\ g^{-1}$. In a contrast, loading of Na_2CO_3

with the same amount by impregnation method made the surface area of NaY decreased to 408 $m^2 g^{-1}$.

The dispersion of MgO on zeolite depends strongly on the structure of support. No characteristic peak of MgO was observed on the XRD pattern of MgO/KL until the loading amount exceeded 5 wt% (3.2 $Mg^{2+} nm^{-2}$); Therefore the spontaneous dispersion threshold of MgO on zeolite KL was tentatively estimated to be 5 wt%. If the threshold value was given in units of $\mu mol\ m^{-2}$ for comparison, it was about 5.3 $\mu mol\ m^{-2}$ on KL zeolite, smaller than that on NaZSM-5 (8.1 $\mu mol\ m^{-2}$) [17]. A complex situation was found on MgO/NaY samples where a trace amount of bulk MgO remained even the loading amount of MgO was 5 wt% (1.0 $Mg^{2+} nm^{-2}$). In the case of a loading amount below 20 wt% that equals to 8.2 $\mu mol\ m^{-2}$, the *R*-value remained below 0.1 as revealed in Table 1. However, when the amount of MgO exceeded 20 wt%, a very strong XRD peak of MgO(2 0 0) appeared on the XRD pattern, and the *R*-value dramatically increased from 0.08 (20%MgO/NaY) to 0.56 (22%MgO/NaY) as shown in Table 1. Different *R*-values were observed on the MgO/NaY and MgO/KL sample with similar surface density of MgO, e.g. zero on 2%MgO/KL and 0.06 on 5%MgO/NaY, or 0.13 on 10%MgO/KL and 0.80 on 25%MgO/NaY. Same phenomenon was also found on these samples before microwave irradiation: for instance the *R*-value of 0.19 was observed on the precursor of 7%MgO/KL, while the 0.42 value was found on that of 20%MgO/NaY. The reason for the different dispersion of MgO on zeolite KL and NaY is not clear yet, however, and a further investigation is required.

Table 1
Dispersion of MgO on zeolite KL and NaY

Zeolite	Amount of loaded MgO		*R* value
	(wt%)	($\mu mol\ m^{-2}$)	
KL[a]	0	0	0
	2	2.1	0
	5	5.3	0
	7	7.7	0.07
	7[b]	7.7	0.19
	10	11.3	0.13
	10[b]	11.3	0.22
	20	25.4	0.20
	20[b]	25.4	0.29
NaY[c]	0	0	0
	3[b]	1.0	0.10
	5	1.7	0.06
	10	3.6	0.07
	20	8.2	0.08
	20[b]	8.2	0.42
	22	9.2	0.56
	25	10.9	0.80
	30	14.0	0.94
	40	21.8	1.22

[a] The surface area of zeolite KL is 246 $m^2 g^{-1}$.
[b] This sample was ground but not irradiated by microwave.
[c] The surface area of zeolite NaY is 766 $m^2 g^{-1}$.

3.2. *Basicity of the modified zeolites*

KF modification remarkably enhanced the basicity of zeolite. For instance NaY zeolite has a weak basicity (0.14 $mmol\ g^{-1}$), but 16%KF/NaY has an increased basicity (1.10 $mmol\ g^{-1}$) similar to that of 16%KOH/NaY (1.0 $mmol\ g^{-1}$) [18]. The KNO_3 dispersed on NaY zeolite was difficult to be thermally decomposed even during the evacuation at 873 K [13], hence only a weak basicity of 0.16 $mmol\ g^{-1}$ was produced (Table 2). However, if the KNO_3/NaY sample was contacted with a reducing agent such as isopropanol at 673 K, the characteristic IR bands of nitrate at 1761 and 1390 cm^{-1} disappeared, while strong bands of acetate emerged at 1581 and

Table 2
Titrimetric analysis on the basicity of modified zeolites

Sample	Basicity ($mmol\ g^{-1}$)
NaY	0.14
16%KF/NaY	1.10
21%KNO_3/NaY	0.16
	0.95[a]
20%MgO/NaY	6.81
20%Na_2CO_3/NaY	3.92
11%KOH/KL	1.73
	1.76[b]
13%KOH/NaY	1.84.
	0.45[b]
11%KOH/KY	1.62
	0.88[b]
11%KOH/Kβ	1.47
	1.15[b]
13%KOH/SiO_2	1.98
	0.72[b]

[a] This sample was pretreated with isopropanol at 673 K for 10 min.
[b] This sample was calcined in air at 873 K for 2 h.

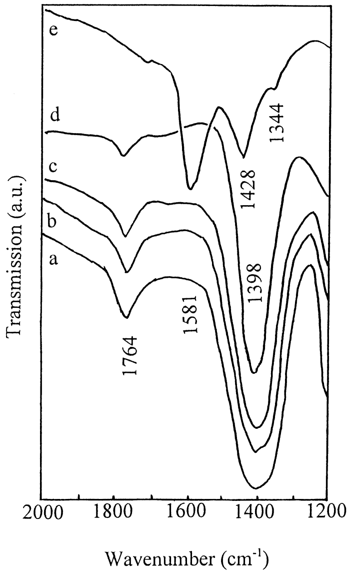

Fig. 2. FTIR spectra of 21%KNO_3/NaY evacuated at (a) 673 K and (b) 873 K, 21%KNO_3/KL evacuated at (c) 673 K, (d) 773 K, and (e) 21%KNO_3/NaY contacted with isopropanol at 673 K.

Table 3
Basic strength of zeolite and relative porous materials modified by potassium compounds

Sample	T_p[a] (K)	Basic strength (H_-)
NaY, NaX, Naβ	873	<7.2
16%KF/Al_2O_3	673	22.5
13%KOH/Al_2O_3[b]	–	18.4
16%KF/SiO_2	673	9.3
13%KOH/SiO_2[b]	–	9.3
16%KF/Al_2O_3+16%KF/SiO_2[b,c]	673	9.3
16%KF/NaY	673	9.3
17%KF/NaX	673	15.0
16%KF/Al_2O_3–NaY	673	17.2
16%KF/Naβ	673	9.3
21%KNO_3/NaY	873	15.0
21%KNO_3/Al_2O_3–NaY	873	18.4
21%KNO_3/KX	873	18.4
29%KNO_3/NaZSM-5	873	15.0
5%KNO_3/KL	873	27.0
10%KNO_3/KL	873	27.0
21%KNO_3/KL	673	17.2
	773	27.0
	873	27.0
	973	27.0
(Activated in O_2)	873	27.0
(Activated in H_2)	873	27.0
30%KNO_3/KL	873	27.0
21%KNO_3/Kβ	873	15.0

[a] T_p is the temperature of activation.
[b] Base strength of soluble basic species obtained from the filtrate of the sample.
[c] This sample is the mixture of KF/Al_2O_3 and KF/SiO_2.

1428 cm^{-1} as shown in Fig. 2. Besides, NO and NO_2 were detected in gas phase. The formation of acetate indicates the combination of acetic acid (one of the oxidized products of isopropanol) and K_2O (one of the products of decomposition of KNO_3), and suggests the cleavage of α-carbon atom in isopropanol molecule during the oxidation process [19]. The loaded KNO_3 was decomposed on NaY zeolite in this redox process, producing a larger amount of base (0.95 mmol g^{-1}) than that of the sample evacuated at 873 K (0.16 mmol g^{-1}). In contrast to what observed on untreated KNO_3/NaY, however, the IR band of nitrate on 21%KNO_3/KL sample declined after treating at 773K (Fig. 2), indicating the decomposition of KNO_3 and formation of K_2O [14].

Loading MgO of 20 wt% on zeolite NaY increased the basicity from 0.14 to 6.81 mmol g^{-1}. By comparison, the basicity of 20%Na_2CO_3/NaY was 3.92 mmol g^{-1}, smaller than the counterpart. Besides, high water-stability is the specific feather found on all of the catalysts derived from supported MgO. For example, 5%MgO/KL sample had a larger basicity (2.13 mmol g^{-1}) than 13%KOH/KL (1.17 mmol g^{-1}). However, 1826 ml g^{-1} water was needed to remove 10% of the basicity from the former when they were washed, but only 10 ml g^{-1} water removed about 20% of that from the latter [20].

Table 3 shows the base strength of various zeolites and relative porous materials modified by potassium compounds. KF or KNO_3 modification generated a higher base strength on Al_2O_3 than that on SiO_2. Moreover, if KF/Al_2O_3 was mixed with KF/SiO_2, the resulting material only had the low base strength (H_-=9.3) same as to KF/SiO_2. KF/NaY zeolite, with both AlO_4 and SiO_4 tetrahedra in the framework of NaY, possessed a weak base strength similar to the KF/SiO_2. Since the higher aluminum content of zeolite was beneficial for generating strong base [2], KF or KNO_3 loaded on zeolite NaX could produce a higher base strength than that on NaY. Besides, coating of Al_2O_3 on the surface of zeolite NaY could enhance the base strength (H_-) from 9.3 to 17.2.

KNO_3 loaded on zeolite NaY, Kβ, NaZSM-5, KY and KX induced base strength (H_-) in the range 15.0–18.4; however, superbasic sites with the strength of $H_-=27.0$ were found on KNO_3/KL upon activation at 773 K [14]. According to Tanabe's [21] definition, they can be assigned to superbasic sites, and this is the first observed evidence of the superbasic property of zeolite modified by KNO_3. In order to clarify if the superbasicity of KNO_3/KL resulted from some unusual oxides of potassium such as K_nO ($n>2$) or K_2O_m ($m>1$) other than K_2O, some 21%KNO_3/KL samples were activated in H_2 or O_2 prior to the measurement of base strength. It was interesting to find that all of the KNO_3/KL samples had superbasicity as shown in Table 3, which excluded the possible role of unusual oxides such as K_nO ($n>2$) or K_2O_m ($m>1$) for the superbasicity. Otherwise, the base strength of the sample should be changed because the K_nO ($n>2$) or K_2O_m ($m>1$) would be destroyed in the special atmosphere used in activation [13]. Therefore, the K_2O species derived from KNO_3 supported were suggested as the main basic species on the KNO_3/KL.

3.3. *Catalytic properties of the modified zeolite*

Table 4 summarizes the catalytic properties of various samples in the decomposition of isopropanol at 673 K. Dehydration of isopropanol is known to occur on the acidic sites of solid catalysts to form water and propene, while the dehydrogenation takes place on basic sites to produce acetone and H_2 [6]. No acetone was detected in the products on zeolite NaY, whereas the acetone yield of 23.6 mol% was observed on 16%KF/NaY at 673 K, closely matching the value on 16%KOH/NaY (27.1 mol%). The similar acetone yield on the KF/NaY and KOH/NaY in the range 623–773 K meant that KF loaded on zeolite NaY could generate a comparable basicity to that of KOH/NaY [18].

As shown in Table 4, the yield of acetone on KNO_3/NaY sample was slightly higher than that on KOH/NaY in the decomposition of isopropanol at 673 K under the same reaction conditions. The temperature of activation had no remarkable effect on the acetone yield of KNO_3/NaY, since it was not necessary to decompose the loaded KNO_3 on NaY zeolite in the activation. When the KNO_3 contacted with isopropanol in the reaction, it could completely decompose through redox process within few minutes, with no influence on the "induction period" and product distribution [19]. Loading of MgO on zeolite NaY suppressed the dehydration of isopropanol, therefore acetone became the dominant product though its yield was low. On the samples of MgO/KL, the yield of acetone increased with increasing amount of MgO especially in the range 473–620 K, higher than that on MgO and zeolite KL as demonstrated in Fig. 3.

Table 4
Results of catalytic decomposition of isopropanol reaction conditions (0.1 MPa, WHSV=3.3 h^{-1})

Sample	$T_{activation}$ (K)	$T_{reaction}$ (K)	Yield of acetone (mol%)	Yield of water (mol%)
16%KF/NaY	773	623	8.1	3.4
		673	23.8	13.6
		773	53.5	32.4
16%KOH/NaY	773	623	8.7	2.1
		673	27.1	26.1
		773	52.6	21.5
21%KNO_3/NaY	673	673	41.4	36.1
	723	673	35.1	33.0
	773	673	32.8	25.2
	823	673	40.1	20.6
20%MgO/NaY	873	673	6.4	0

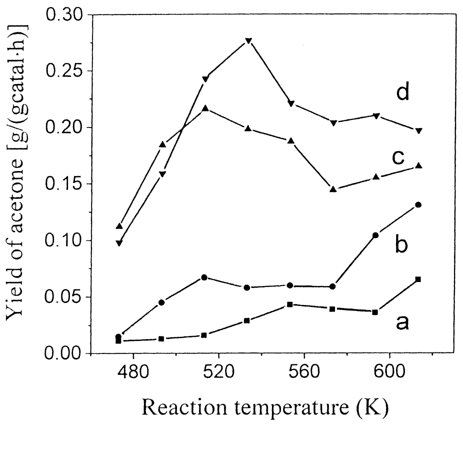

Fig. 3. Yield of acetone in the decomposition of isopropanol on (a) KL, (b) MgO, (c) 2%MgO/KL and (d) 5%MgO/KL vs. reaction temperature.

The isomerization of *cis*-but-2-ene at 273 K is a model reaction for probing strong basicity or acidity of solid samples [13]. For solid base, the value of initial *t*-B/1-B ratio of products reflects the base strength: The value of *t*-B/1-B below 1.0 is the characteristic of common base [22], while the ratio higher than 1.0 indicates the existence of superbasic sites on the sample [23]. KF/Al_2O_3 exhibited a high activity in this reaction [10], but KF/NaY and KF/NaX as well as KF/SiO_2 showed practically no activity.

With no silicon in its framework, 5%KF/$AlPO_4$-5 showed a weak activity upon evacuation at 873 K [10], accompanied with an initial *t*-B/1-B ratio of zero. When the sample 5%KF/$AlPO_4$-5 was evacuated at 923 K, the initial rate increased from 0.002 to 0.03 mmol (g min)$^{-1}$, which results probably from the surface enrichment of potassium species on the sample, because these species were believed to be the active sites for base-assisted reactions [24]. In addition, the initial *t*-B/1-B ratio was increased to about 5, close to that observed on the superbase CaO [23]. However, further increase in the evacuation temperature decreased the activity of the sample (Table 5). Based on the different catalytic behavior of KF/NaY and KF/$AlPO_4$-5, it is clear that KF dispersed on $AlPO_4$-5 can create stronger basic sites than on the analogous zeolite.

Among the catalysts supported KNO_3, KNO_3/NaY and KNO_3/Al_2O_3–NaY were inactive while KNO_3/Al_2O_3 showed a high activity in the isomerization of *cis*-but-2-ene at 273 K [14]. As expected, 21%KNO_3/KL exhibited a high initial rate (0.05 mmol (g min)$^{-1}$) in this isomerization, accompanied with the initial *t*-B/1-B ratio of 3.0 which results from the existence of superbasic sites with the base strength of H_{-}=27.0. Unlike KNO_3/KL sample, MgO/NaY showed a higher initial rate but a lower initial *t*-B/1-B ratio (Table 5). The initial ratio of *t*-B/1-B on MgO/NaY sample increased from 0.26 to 0.55 as the amount of MgO increased from 10 to 20 wt%, close to that on bulk MgO (0.60). Same tendency was observed on MgO/KL samples: their initial reaction rates increased as the loading amount of MgO rose, but the initial *t*-B/1-B ratio was kept below 1.0 (Table 5). These facts meant that no superbasic sites formed on the basic zeolite derived from MgO supported, and further confirmation came from the measurement of base strength, in which no superbasic sites with H_{-}=27.0 was found on the MgO/KL samples [20].

Table 5
Isomerization of *cis*-but-2-ene on basic zeolites at 273 K

Sample	T_p[a] (K)	Initial rate (mmol g^{-1} min^{-1})	Initial ratio of *t*-B/1-B
NaY	873	0	–
NaX	873	0	–
KL	773	0	–
5%KF/$AlPO_4$-5	873	0.002	0
	923	0.032	4.9
	1073	0.003	3.0
16%KF/NaY	873	0	–
16%KF/NaX	873	0	–
16%KF/Al_2O_3–NaY[b]	773	0	–
	873	0	–
KF, KNO_3	773–923	0	–
MgO	773	3.0	0.3
9%KNO_3/$AlPO_4$-5	773–923	0	–
21%KNO_3/NaY	873	0	–
21%KNO_3/Al_2O_3–NaY[b]	873	0	–
21%KNO_3/KL	773	0.05	2.6
10%MgO/NaY	773	0.29	0.3
20%MgO/NaY	773	0.65	0.6
2%MgO/KL	773	0.10	0.1
5%MgO/KL	773	0.26	0.2
10%MgO/KL	773	0.31	0.2
5%MgO/$AlPO_4$-11	773	0.02	0

[a] Temperature of evacuation prior to reaction.

[b] The amount of Al_2O_3 coated on the NaY zeolite was 18 wt%.

It should be pointed out that dispersion of MgO made $AlPO_4$-11 to be active in the isomerization of *cis*-but-2-ene upon evacuation at 773 K, whereas KF/$AlPO_4$-5 needed to be activated at 923 K to exhibit a similar activity while KNO_3/$AlPO_4$-5 was inactive under the same condition [10,13]. The decrease in the activation temperature of basic zeolite is beneficial not only for saving energy, but also for precluding degradation of zeolite structure that usually occurs at high temperature. Although the activity of sample 5%MgO/$AlPO_4$-11 is quite low, it is nonzero and reveals the possibility of creating strongly basic site on aluminophosphate in a simple and clean way, which will be discussed elsewhere in detail [25].

3.4. *Influence of zeolite structure on the formation of strongly basic sites*

Two specific features of zeolite structure cause more difficulties for the generation of strongly basic sites on zeolite than on common oxide supports: the first one is the existence of SiO_4 tetrahedra, and the second is the high crystallinity of zeolite. Neither KF nor KNO_3 modification can create strong basicity on SiO_2 till now [26], because silica reacts with the guest to form the species with a low base strength [18]. A similar process may occur on KF supported zeolite where both AlO_4 and SiO_4 tetrahedra exist. During the KF modification on zeolite, KOH is liberated through the guest–host interaction, but the SiO_4 tetrahedra in the zeolite competitively react with the KOH and preferentially form the species with low base strength [18]. This is the main reason why no strongly basic sites formed on the KF modified X and Y zeolites, and it is thus expected that using a host without silicon such as $AlPO_4$-5, or covering the surface of zeolite by a layer of Al_2O_3 can increase the base strength of resulting material.

Different catalytic behavior of KNO_3/Al_2O_3, KNO_3/NaY and KNO_3/Al_2O_3–NaY in the isomerization of *cis*-but-2-ene at 273 K should be attributed to their different intrinsic property of structure. There are octahedral vacant sites on γ-type alumina, and K^+ cation of KNO_3 can insert these sites and disperse dissociately to form strongly basic sites [13,26]. However, zeolites are "framework" aluminosilicates, which are based on an infinitely extending three-dimensional network of AlO_4 and SiO_4 tetrahedra linked to each other by sharing all of the oxygens [27]. No octahedral vacant site exists in the framework of NaY zeolite owing to the high crystallinity, therefore the KNO_3 cannot form strongly basic sites even though it has been well dispersed. For the Al_2O_3–NaY, it is not sure if there is any octahedral vacant site existing, because the Al_2O_3 has been highly dispersed and the structure should be different [13]. Consequently, KNO_3 loaded on Al_2O_3–NaY cannot be decomposed as that on the bulk Al_2O_3, producing a weaker basicity than that of KNO_3/Al_2O_3. The reason why KNO_3/KL exhibits superbasicity is still not yet clearly understood. There was no direct experimental evidence on the existence of octahedral vacant sites in the framework of zeolite KL. Recently, the SiO_4 tetrahedra in zeolite KL has been found to be more stable than those in the other zeolites, because they do not have an intensive interaction with KOH even at 873 K, and the sample KOH/KL kept the original XRD pattern as shown in Fig. 1. Moreover, only KOH/KL sample kept the original basicity after calcination at 873 K, whereas the other samples lost their basicities, similar to KOH/SiO_2 as shown in Table 2. These features of sample KOH/KL should be attributed to the unusual microenvironments around these SiO_4 tetrahedra providing by the KL zeolite, but their influences on the formation of superbasicity need to be explored in future.

Compared with the impregnation of KF or KNO_3, dispersion of MgO by microwave irradiation is a better way for preparing strongly basic zeolite. Unlike KF modification, MgO does not intensively react with the AlO_4 and SiO_4 tetrahedra of zeolite under the irradiation condition, and causes no damage on the framework of zeolite. Different from supporting of KNO_3, MgO itself can be strong basic sites which does not need either the decomposition procedure or the special structure of support. Moreover, this method costs less time, energy and money [20], and avoids the formation of pollutants such as NO_x or F^- species in the modification process.

4. Conclusions

1. SiO_4 tetrahedra of zeolite hinder the formation of strongly basic sites in KF modification, which can be overcomed by using $AlPO_4$-5 support or covering the surface of zeolite with a layer of Al_2O_3.
2. KNO_3 loaded on zeolite NaY can be decomposed at 673 K by contacting with a reducer such as isopropanol, and form a larger amount of basicity than thermal decomposition at 873 K.
3. The KNO_3 dispersed on zeolite KL can form superbasic sites with $H_-=27.0$.
4. MgO can be dispersed on zeolite by microwave irradiation to form strong base being active in *cis*-but-2-ene isomerization at 273 K.

Acknowledgements

The National Advanced Materials Committee of China and National Natural Science Foundation of China under Grant 29773020 supported this work. We are also grateful to Research Institute of Petroleum Processing-SINOPEC-Beijing for the financial support and to Prof. T. Yamaguchi in Ehime University for his help.

References

[1] M.E. Davis, Acc. Chem. Res. 26 (1993) 111.
[2] D. Barthomeuf, Stud. Surf. Sci. Catal. 65 (1991) 157.
[3] H. Tsuji, F. Yagi, H. Hattori, Chem. Lett. (1991) 1881.
[4] T. Ando, S.J. Brown, J.H. Clark, D.G. Cork, T. Hanafusa, J. Ichihara, J.M. Miller, M.S. Robertson, J. Chem. Soc., Perkin Trans. II (1986) 1133.
[5] T. Baba, H. Handa, Y. Ono, J. Chem. Soc., Faraday Trans. 90 (1994) 187.
[6] P.E. Hathaway, M.E. Davis, J. Catal. 117 (1988) 497.
[7] L.R. Martens, P.J. Grobet, W.J. Vermeriren, P.A. Jacobs, Stud. Surf. Sci. Catal. 28 (1986) 935.
[8] J.L. Dong, J.H. Zhu, Q.H. Xu, Appl. Catal. 112 (1994) 105.
[9] S.T. Wilson, B.M. Lok, C.A. Messina, T.R. Cannan, E.M. Flanigen, J. Am. Chem. Soc. 104 (1982) 1146.
[10] J.H. Zhu, Y. Wang, Q.H. Xu, H. Hattori, J. Chem. Soc., Chem. Commun. (1996) 1889.
[11] N. Kikuchi, Y. Yoneda, J. Catal. 21 (1971) 164.
[12] J.H. Zhu, Q.H. Xu, Acta Chim. Sinica 55 (1997) 474.
[13] J.H. Zhu, Y. Wang, Y. Chun, X.S. Wang, J. Chem. Soc., Faraday Trans. 94 (1998) 1163.
[14] J.H. Zhu, Y. Chun, Y. Wang, Q.H. Xu, Mater. Lett. 33 (1997) 207.
[15] J.H. Zhu, Y. Chun, Q.H. Xu, Y. Qin, Mater. Lett. 33 (1998) 331.
[16] J.H. Zhu, D.K. Sun, J. Shi, Y. Chun, Q.H. Xu, Chin. Sci. Bull. 43 (1998) 703.
[17] X.Y. Long, B.Y. Zhao, Y.C. Xie, Acta Phys. Chim. Sinica 13 (1997) 301.
[18] J.H. Zhu, Y. Chun, Y. Qin, Q.H. Xu, Microporous Mesoporous Mater. 24 (1998) 19.
[19] Y. Chun, J.H. Zhu, Q.H. Xu, Kexue Tongbao 41 (1996) 1858.
[20] J.H. Zhu, Y. Wang, Y. Chun, Z. Xing, Q.H. Xu, Mater. Lett. 35 (1998) 177.
[21] K. Tanabe, in: B. Imelik, C. Nacceche, G. Condurier, Y. Ben Taarti, J.C. Vedrine (Eds.), Catalysis by Acids and Bases, Elesvier, Amsterdam, 1985, p. 1.
[22] N.F. Foster, R.J. Cvetanovic, J. Am. Chem. Soc. 82 (1960) 4274.
[23] T. Iizuka, Y. Endo, H. Hattori, K. Tanabe, Chem. Lett. (1976) 803.
[24] C.V.A. Duke, J.M. Miller, J.H. Clark, A.P. Kybett, J. Mol. Catal. 62 (1990) 233.
[25] Y. Wang, J.H. Zhu, J.M. Cao, Y. Chun, Q.H. Xu, Microporous Mesoporous Mater. 26 (1998) 175.
[26] T. Yamaguchi, J.H. Zhu, Y. Wang, M. Komatsu, M. Ookawa, Chem. Lett. (1997) 989.
[27] D.W. Breck, Zeolite molecular sieves, John & Sons Inc., 1974, p. 514.