Basic properties of a KF modified $AlPO_4$-5 molecular sieve

Jian Hua Zhu,*[a] Ying Wang,[b] Qin Hua Xu[a] and Hideshi Hattori[c]

[a] *Chemistry Department, Nanjing University, Nanjing 210093, China*
[b] *Department of Applied Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790, Japan*
[c] *Centre for Advanced Research of Energy Technology, Hokkaido University, Sapporo 060, Japan*

Dispersion of KF on $AlPO_4$-5 molecular sieve creates strong basic sites and basic catalytic activity for the isomerization of butenes at 273 K.

Owing to the difficulty in obtaining zeolites possessing strong basic sites, basic catalysis utilizing zeolites is a developing area. A zeolite-like material with a positive framework was recently shown not to exist[1] while dispersion of metallic sodium particles in zeolites is difficult and the resulting materials oxygen sensitive.[2] Although zeolites can host basic guest materials, *e.g.* nanophase caesium oxide,[3] to form basic catalysts, the dispersion of neutral alkali-metal salts such as KF in molecular sieves to create strong basic sites has not received much attention. Despite the fact that KF supported zeolites have been used for *o*-methylation of phenol,[4] their basic properties have not yet been clearly understood.

KF has been supported on Al_2O_3,[5–7] ZrO_2,[8] CaF_2[9] and montmorillonite clay.[10] However, in the isomerization of but-1-ene at 273 K which was utilized as a probe reaction to evaluate the presence of solid strong basic sites,[11] only KF/Al_2O_3 and KF/ZrO_2 were found to be active.[8] To extend KF modification with molecular sieves and to create new solid strong bases with large surface areas, we attempted to disperse KF on NaX, NaY and $AlPO_4$-5 (abbreviated as APO-5), and found that only in KF/APO-5 were active sites present for butene isomerization at 273 K.

APO-5 was synthesized according to ref. 12 while the Si/Al ratio of NaX and NaY was 1.24 and 1.67, respectively. An impregnation method using an aqueous solution of KF followed by drying at 373 K was used to prepare 5%KF/APO-5 and the other KF supported catalysts. But-1-ene and *cis*-but-2-ene were purified by repeated freeze–thaw cycles and a closed recirculation reactor was employed to perform isomerization of butenes at 273 K.[11] In TPDE (temperature programmed decomposition experiments),[13] samples were evacuated at room temp. for 1 h, then TPDE was performed up to 1173 K at a heating rate of 10 K min^{-1}.

Identical XRD patterns of APO-5 and 5%KF/APO-5 indicate that loading of KF up to 5 mass% does not cause considerable distortion in the bulk structure of APO-5. After 5%KF/APO-5 was evacuated at 923 K, the IR band of KPF_5 (726 cm^{-1}) and the XRD pattern of K_3AlF_6 were observed which revealed an obvious interaction between KF and APO-5.

The results of but-1-ene isomerization at 273 K are listed in Table 1. Due to lack of strong acidic or basic sites APO-5 showed practically no activity, while 5%KF/APO-5 exhibited a weak activity which increased with the temperature of pretreatment (T_p). *cis*-But-2-ene was the only product formed on the 5%KF/APO-5 pretreated at 823 or 873 K suggesting that basic sites on these samples were active for but-1-ene isomerization at 273 K.[11] The activity of 5%KF/APO-5 was obviously enhanced by pretreatment at 923 K (Fig. 1) with *trans*-but-2-ene as a byproduct. Under the same reaction conditions, KF/Al_2O_3 was very active although its activity decreased with increasing T_p. On the other hand, KF/NaY and KF/NaX pretreated at 773–923 K were inactive. The presence of silicon in zeolites seems to hinder the formation of strong basic sites upon KF modification.

In *cis*-but-2-ene isomerization at 273 K, 5%KF/APO-5 showed a weak activity with an initial rate of 0.0017 mmol $(g\ min)^{-1}$ after evacuation at 873 K, and the initial *trans*/1 ratio of products was zero confirming the basic characteristic of the catalyst.[14] For the sample pretreated at 923 K, the initial rate was enhanced to 0.0324 mmol $(g\ min)^{-1}$. Since *cis*-but-2-ene isomerization at 273 K over solid bases has been established to occur on strong basic sites[15] and 5%KF/APO-5 shows basic catalytic behaviour in this isomerization, it is clear that KF dispersed on APO-5 can create some strong basic sites. By comparison, the activity of 9%KNO_3/APO-5 with the same K^+ density as that of 5%KF/APO-5 was not appreciable for isomerization at 273 K, upon pretreatment at 773–923 K.

APO-5 does not chemisorb CO_2 while CO_2 adsorbed on 5%KF/APO-5 led to an IR band due to bidentate carbonate at 1654 cm^{-1}.[16] The intensity of this band increased with T_p from 773 to 873 K mirroring the activity in but-1-ene isomerization. As expected no CO_2 was chemisorbed on 9%KNO_3/APO-5 pretreated at 873 K. Clearly the anion of the potassium salt plays

Table 1 Isomerization of but-1-ene at 273 K over KF supported catalysts

Catalyst	T_p/K	Initial rate/ mmol $(g\ min)^{-1}$	Initial *cis*/*trans*
5%KF/APO-5	823	0.0026	—
	873	0.0054	—
	923	0.0511	1.1
5%KF/Al_2O_3	723	53.1	4.3
	873	0	—
KF	773	0	—
5%KF/NaX	773	0	—
17%KF/NaX	873	0	—
	923	0	—
16%KF/NaY	873	0	—
	923	0	—
APO-5	773	0	—

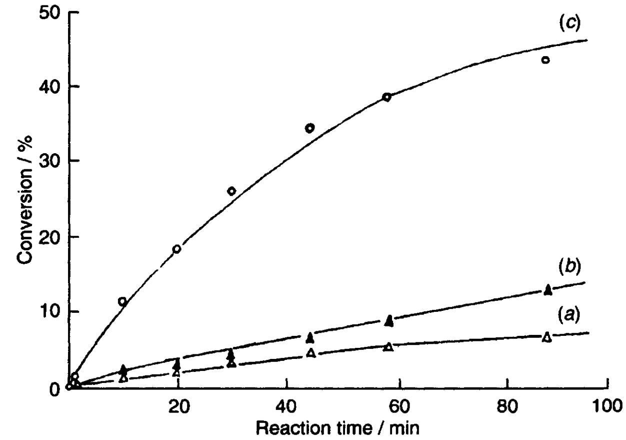

Fig. 1 Isomerization of but-1-ene at 273 K on 5%KF/APO-5 pretreated at (*a*) 823, (*b*) 873 and (*c*) 923 K

an important role in the creation of strong basic sites on molecular sieves.

During TPDE no CO_2 was desorbed from APO-5, but on 5%KF/APO-5 (Fig. 2), CO_2 adsorbed from the atmosphere during preparation, was desorbed in three stages at 383, 733 and 838 K.

The catalytically active basic sites of KF/APO-5 are assumed to be different from those of KF/Al_2O_3 on the basis of two facts. First KF/APO-5 shows much weaker activity than KF/Al_2O_3 in but-1-ene isomerization at 273 K, and the dependence of the initial rate for KF/APO-5 and KF/Al_2O_3 on T_p, as shown in Table 1, is the opposite. Secondly, the [Al–OH···F⁻] structure has been proposed[6] and recognized recently to be the main active site on KF/Al_2O_3 in but-1-ene isomerization.[7] In the TPDE process of KF/Al_2O_3,[7] a slight increase of mass due to H_2O appeared when CO_2 was desorbed at *ca.* 840 K indicating the destruction of the [Al–OH···F⁻] structure *via* dehydroxylation. No such phenomenon was observed on 5%KF/APO-5 which precludes the existence of [Al–OH···F⁻]. However, further investigation is required to identify the active basic centres on KF/APO-5.

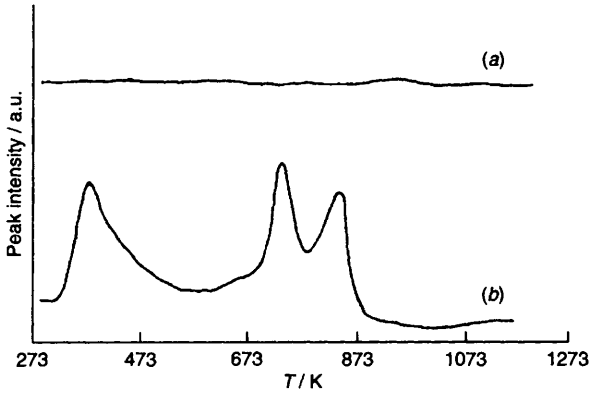

Fig. 2 Mass signal characteristic of CO_2 during the TPDE process of (*a*) APO-5 and (*b*) 5%KF/APO-5

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