Catalysis Letters Vol. 86, Nos. 1–3, March 2003 (© 2003)

Alkylation of benzene with long-chain olefins catalyzed by fluorinated β zeolite

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Received 20 February 2002; accepted 19 November 2002

The effects of fluorination on Hβ zeolite and alkylation of benzene with long-chain olefins catalyzed by fluorinated β zeolite are investigated. The lifetime of the catalysts depends on the surface area and pore volume rather than acidity. When the fluorine content is 0.5%, the lifetime improves by 30%, when the catalyst has maximum specific surface area and pore volume.

KEY WORDS: β zeolite; fluorination; alkylation; linear alkylbenzenes.

1. Introduction

Linear alkylbenzenes (LAB) are valuable industrial chemicals used in the manufacture of detergents. These are usually mixtures of C_9–C_{14} alkyl benzenes synthesized by alkylation of benzene with mixed linear olefins using anhydrous HF as catalyst [1]. Due to the hazardous nature of anhydrous HF, efforts have been made to find environmentally safer catalysts like solid acid catalysts [2–8]. In addition, during the alkylation of benzene with long chain olefins (C_9–C_{14}), a mixture of alkylbenzenes with the phenyl group attached to different carbon atoms is obtained. Of the different isomers, the most preferred component in detergent manufacture is the 2-phenyl isomer because such compounds when sulfonated have long "tails" which provide enhanced solubility and detergent properties. When alkylating benzene with long-chain olefins over zeolites, there is a possibility of producing more of the less bulky 2-phenyl isomer than the others, due to the narrow pore dimensions.

The disadvantage of the solid catalyst is that it is easily deactivated because the by-products are gum-polymers that tend to accumulate in the channels of the catalyst and block reactive sites [9]. It can be readily appreciated that such catalyst-deactivating agents or "poisons" are an unavoidable adjunct of aromatic alkylation, and hence catalyst deactivation is also unavoidable. Therefore, the industrial usability of solid catalysts depends on their regenerability.

High-silica zeolites are known to be important potential catalysts on account of their higher thermal, hydrothermal and acid stabilities, and good resistance to aging. β Zeolite is one of a few high-silica zeolites to have a fully three-dimensional 12-ring pore system [10], its structural nature determines that the deactivating materials deposited in the channels can readily be desorbed by washing the catalyst with the aromatic reactant, and the activity can be completely restored under a suitable regeneration condition [9]. In addition, for the alkylation of benzene with long-chain olefins, the 2-phenyl isomers amount to about 50% when catalyzed by Hβ zeolite, but less than 20% by anhydrous HF [9]. So Hβ zeolite is a very promising catalyst for the synthesis of LAB in industry. If the lifetime of Hβ zeolite catalyst for one reaction cycle is more than 24 h, two fixed-bed reactors can be employed for the operation of reaction and regeneration alternately, using a 24 h switch cycle. However, the actual lifetime of Hβ zeolite catalyst is less than 24 h, so it is inconvenient for this process to be used industrially.

Fluorine is often used as a component or modifier of catalysts [11]. Aneke *et al.* [12,13] studied a catalyst consisting of H-Y zeolite, β-AlF_3 and Cu, and found that the presence of fluorine resulted in an increase in the selectivity for toluene disproportionation. Lok and Izod [14] modified zeolites using F_2 gas, Araya and Dyer [15] described the treatment of zeolites with molten fluorides and Sariev and co-workers [16–18] reported the modification of zeolite catalysts with diluted hydrofluoric acid, which usually increased the catalytic activity. Information concerning zeolite catalysts modified with fluorine can also be found in the patent literature [19]. However, all of the above reports are little concerned about the relationship between fluorination and catalyst lifetime.

In this paper, Hβ zeolite is modified by different aqueous solutions of HF to prolong the lifetime, and is used for the alkylation of benzene with linear long-chain olefins. The effects of hydrofluoric acid treatment

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1011-372X/03/0300-0081/0

on the structure and acidity are investigated, and the relationship between HF modification and the lifetime of Hβ zeolite catalyst is reported.

2. Experimental

2.1. Catalyst preparation

A commercial catalyst, a mixture of 85% Hβ zeolite and 15% binder, was used as the starting material. In order to get several fluorine loadings, aqueous HF (table 1) was used at different concentrations for the fluorination, which took place at room temperature in Teflon beakers. After impregnation, the catalyst was left for 3 h, washed with plenty of water until the pH of the solution was 7, then dried at 423 K for 6 h and activated at 773 K for 4 h. The compositions of the fluorinated catalysts are given in table 1.

2.2. Zeolite characterization

X-ray powder diffraction patterns of the samples were recorded using a Norelco-Philips diffractometer over a range of 5–60 degrees at a scan rate of 2 degrees/min, using FeKα radiation. The elemental compositions of the samples were measured using an XRF-1700 X-ray fluorescence spectrometer. Surface areas and pore volumes were measured with N_2 as adsorbate using an ASAP2010. The values of surface areas and pore volumes of the micropores were calculated using the methods of Horvath–Kawazoe and Dubinin–Astakhov respectively, and of larger pores by BJH desorption.

In situ diffuse reflection infrared spectra of the zeolite were obtained at 2 cm^{-1} resolution using a Nicolet Nexus 670 spectrometer (smart collector, environmental chamber, MCT detector). The sample was loaded into an *in situ* cell, heated to 773 K for 4 h for activation, then cooled to 423 K, where its spectrum for use as a background was collected.

The total acid amount was measured by NH_3-TPD under the conditions of a 423 K adsorption temperature, temperature ramp of 30 °C/min using He as a carrier gas with a velocity of 40 m/min. For weak acid sites the desorption temperature was less than 723 K; for strong acid sites the desorption temperature was more than 723 K. The ratio of Brønsted acid to Lewis acid sites was measured by *in situ* diffuse reflection infrared spectroscopy after adsorption of pyridine to saturation.

2.3. Catalyst testing

A C_{10}–C_{14} olefin/paraffin mixture was provided by Fushun Petrochemical Corp., with 9.6% olefin content, and benzene was provided by Beijing Yanshan Petrochemical Ltd, of 99.0% purity.

The alkylation reaction was carried out in a stainless steel fixed-bed reactor (SS316, inside diameter 12 mm), down-flow type. The catalysts were always dried at 773 K for 4 h in dry air, then cooled to the reaction temperature in a flow of dry N_2. Benzene was injected prior to the feeding of actual alkylation mixture (olefins + benzene). The exact reaction parameters used in different experiments are presented along with the data in later sections.

The analysis of the reactants and products was carried out using a quartz capillary column (SE30, 50 m) in a gas chromatograph or GC–MS (Agilent 6890-5973N).

3. Results and discussion

3.1. Composition and structure

Elemental analysis shows that after impregnation by HF solution the fluorine content increases while the aluminum content decreases (table 1), which illustrates that some aluminum is removed from the catalysts. In addition, with the increase of fluorine concentration in the HF solution, the weight losses of the catalysts increase. Because the weight losses for all the modified catalysts vary from 11.5 to 56.3%, both aluminum and silica are removed from the catalysts. Therefore, Hβ zeolite is partly dissolved by HF solution.

The diffractograms of different catalyst samples analyzed by XRD are shown in figure 1. From the patterns obtained we observe that all of the samples give rise to the typical diffraction peaks of β zeolite

Table 1
Composition of the fluorinated catalysts

Sample	HF solution used to treat catalysts (wt%)	Composition (wt%)			SiO_2/Al_2O_3	Weight loss (%)
		F	SiO_2	Al_2O_3		
S-0	0	0	81.0	18.1	4.48	–
S-1	1	0.3	82.6	15.2	5.43	11.5
S-2	2	0.5	85.2	13.7	6.22	16.5
S-4	4	0.65	89.0	9.9	8.99	32.0
S-6	6	0.89	93.4	5.5	17.0	48.5
S-8	8	0.95	93.8	5.0	18.8	56.3

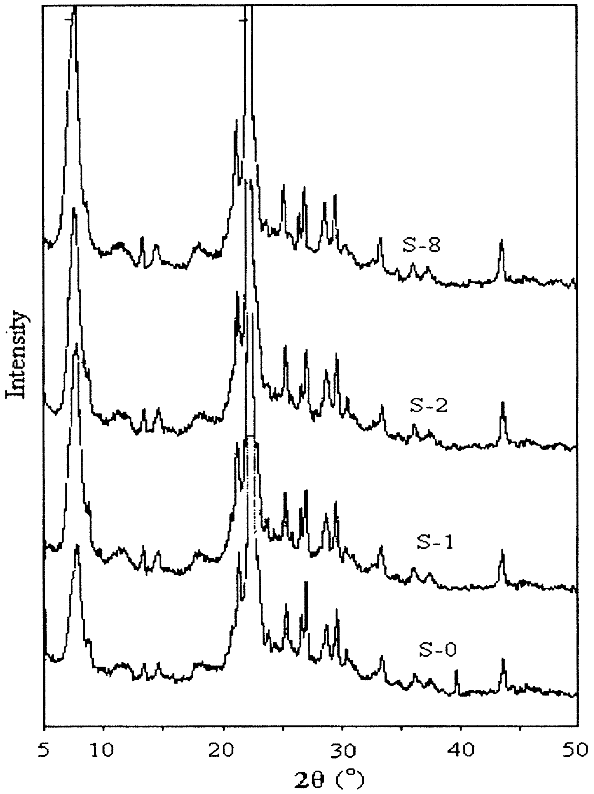

Figure 1. XRD patterns of different catalysts.

($2\theta = 7.62°$ and 22.50°). The patterns obtained for fluorinated catalysts have no peak at 39.58° but sample S-0 has. The peak at 39.58° may be attributed to the presence of $3Al_2O_3{\cdot}2SiO_2$ [20,21], which is formed in the preparation of the catalysts. Since no change of the crystallinity of β zeolite is noticeable, $3Al_2O_3{\cdot}2SiO_2$ must be an extra-lattice species. When impregnated by HF solution, the $3Al_2O_3{\cdot}2SiO_2$ in the catalysts is dissolved first, then the Hβ zeolite.

The evolution of the surface area and pore volume of fluorinated catalysts modified by HF solution is given in table 2. It can be seen that after impregnation by HF solution the surface area and pore volume of the catalysts have changed. They increase at first and then decrease with the extent of modification. Figure 2 indicates that the micropore volume of Hβ zeolite is the largest, and that it decreases after preparation. When impregnated by low-concentration HF solution, the extra-lattice species formed in the preparation of the catalysts are dissolved, so the specific area and pore volume increase. However, with the increase of HF concentration, not only the extra-lattice species are dissolved, but also Hβ zeolite reacts with HF and forms AlF_3 or other fluorinated compounds which deposit in the catalyst, so the specific area and pore volume decrease.

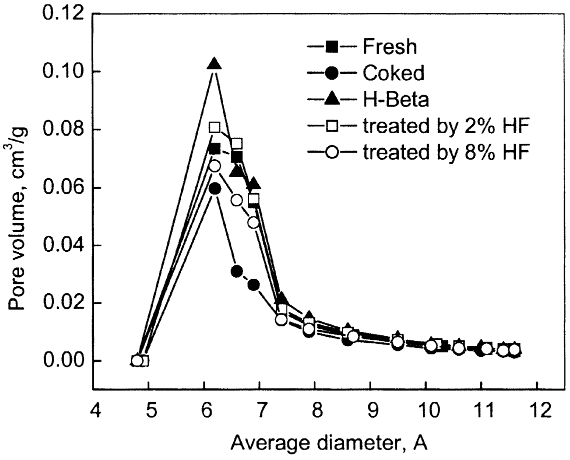

Figure 2. Variation of micropore volume with average pore diameter for the different catalysts.

3.2. *Effect of HF treatment on the hydroxyl groups of β zeolite*

The hydroxyl groups were characterized by IR spectroscopy. The spectra are shown in figure 3 as difference spectra, sample with adsorbed pyridine minus sample without adsorbed pyridine, of the samples at 423 K. Five types of hydroxyl groups are seen, which are strongly acidic bridging hydroxyl groups ($3605\,cm^{-1}$), OH groups bonded to extra-lattice aluminum (3660–$3680\,cm^{-1}$), internal SiOH groups at framework defects ($3730\,cm^{-1}$), terminal SiOH groups ($3745\,cm^{-1}$) and a "very high frequency" (VHF) absorption ($3782\,cm^{-1}$) [22].

Table 2
Variation of surface area and volume on the HF-treated catalysts

Catalyst	Specific surface area (m^2/g)			Volume (ml/g)		
	Micropore	Larger pore	Total	Micropore	Larger pore	Total
S-0	444	78	522	0.185	0.326	0.511
S-1	449	80	529	0.188	0.355	0.543
S-2	475	87	562	0.197	0.380	0.577
S-2 (deactivated)	279	79	358	0.132	0.374	0.506
S-4	419	61	480	0.173	0.339	0.512
S-6	407	60	467	0.170	0.337	0.507
S-8	397	58	455	0.166	0.334	0.500

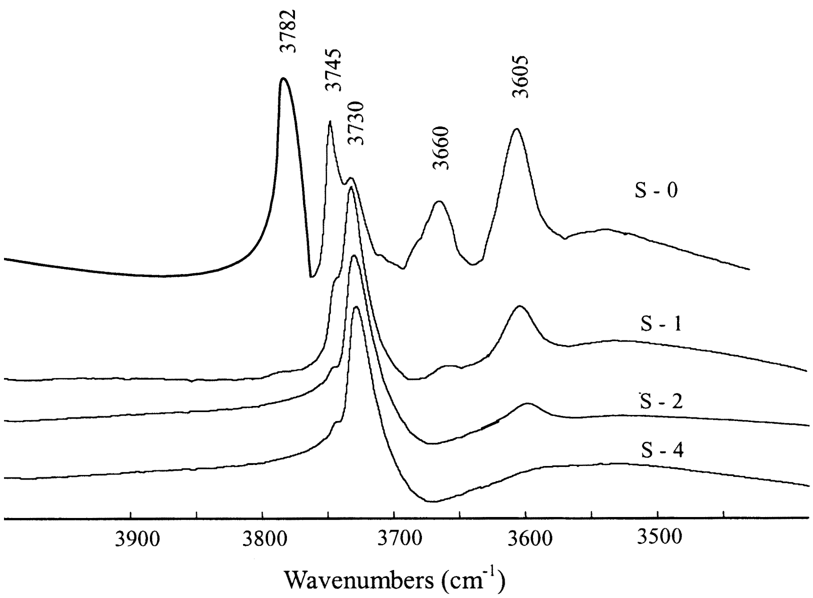

Figure 3. Differential IR spectra of catalysts in hydroxyl region after pyridine adsorption.

When the catalyst is treated by dilute HF solution, the OH groups bonded to extra-lattice aluminum at $3660\,\mathrm{cm}^{-1}$ and unstable lattice aluminum at $3782\,\mathrm{cm}^{-1}$ disappear first, then bridging hydroxyl groups at $3605\,\mathrm{cm}^{-1}$. Obviously, extra-lattice and unstable lattice species can readily react with HF, and the OH groups bonded to these species disappear quickly. When the extra-lattice aluminum and unstable lattice aluminum are removed, specific surface areas and pore volumes increase.

The bridging hydroxyl groups decrease gradually with the extent of modification, because they are substituted by fluorine atoms. This result is the same as that of previous studies [23–25] of the fluorination of the zeolite.

Figure 4 shows the IR spectra of the lattice structure region at $950–1000\,\mathrm{cm}^{-1}$, the bands of which are due to asymmetric stretching of bonds to the tetrahedron and which increase with the increase of Si/Al ratio [22,26]. It is seen that the band at about $950\,\mathrm{cm}^{-1}$ increases with the extent of modification, so we can conclude that some lattice aluminum is removed. Similarly, the elemental analysis in table 1 shows that the Si/Al ratio increases with the increase of the fluorine content, which also indicates that some lattice aluminum is removed.

3.3. Acidity

The variation of acidity with the fluorine content is shown in table 3 and figure 5. It is seen that the total number of acid, Lewis acid and Brønsted acid sites gradually decreases and finally becomes constant, the ratio of strong acid to weak acid sites increases, and the ratio of Brønsted acid to Lewis acid sites decreases.

The initial remarkable decrease of Brønsted acid sites is due to the substitution of bridging hydroxyl groups ($3605\,\mathrm{cm}^{-1}$) by fluorine atoms and the removal of unstable lattice aluminum from the lattice due to fluorination. Furthermore, it can be seen from figure 3 that the OH groups of the $3730\,\mathrm{cm}^{-1}$ band can adsorb pyridine, so it possess acidity. This result is similar to that of Kiricsi *et al.* [22]. Figure 3 shows that the hydroxyl groups bonded to Si ($3730\,\mathrm{cm}^{-1}$) are more stable than bridging hydroxyl groups and VHF hydroxyl groups, so strong Brønsted acid sites decrease less than weak Brønsted acid sites.

The weak Lewis acid sites gradually decrease, but the strong Lewis acid sites increase when the modification

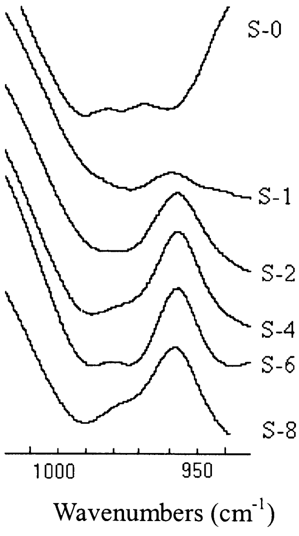

Figure 4. Differential IR spectra of catalysts in structural region after pyridine adsorption.

Table 3
Variation of acid sites with F content on the HF-treated catalysts

Catalyst	F content (wt%)	Brønsted acid ($\times 10^{20}$ sites/g cat)			Lewis acid ($\times 10^{20}$ sites/g cat)			Total acid ($\times 10^{20}$ sites/g cat)
		Strong	Weak	Total	Strong	Weak	Total	
S-0	0	0.55	0.78	1.33	0.67	1.93	2.60	3.93
S-1	0.3	0.50	0.52	1.02	0.51	1.40	1.91	2.93
S-2	0.5	0.48	0.20	0.68	0.53	1.48	2.01	2.69
S-4	0.65	0.35	0.16	0.51	0.70	1.18	1.88	2.39
S-6	0.89	0.31	0.12	0.43	0.86	1.08	1.93	2.36
S-8	0.95	0.38	0.11	0.49	0.84	1.08	1.92	2.41

increases, which may be due to the formation of AlF_3 or other fluorinated compounds. Thus, the increase of the strong Lewis acid sites causes the decrease of the ratio of Brønsted acid to Lewis acid sites. At the same time, the ratio of strong acid to weak acid sites increases.

3.4. Relationship between characterizations and catalyst lifetime

To evaluate the lifetimes of different fluorinated catalysts used for the alkylation of benzene with long-chain olefins, we define that the catalysts have deactivated when the conversion of dodecene is less than 95%. Figure 6 shows the variation of lifetime of the catalysts with different fluorine contents. It can be seen that suitable modification lengthens the lifetime, while excess modification shortens the lifetime, and the most suitable fluorine content is about 0.5% which improves the lifetime by 30%.

Comparing the lifetime (figure 6) with pore structure (table 2) and acidity (table 3) of the catalysts with different fluorine contents, we can see that it depends on pore volume and specific surface area, but the acidity has less effect on the lifetime. With the increase of pore volume and specific surface area, especially for micropores, the lifetime increases. So it is necessary for extending the lifetime of the catalysts to improve internal diffusion.

With the increase of fluorine content up to 0.5%, the acid sites decrease and the lifetime increases; when the fluorine content is larger than 0.5%, however, most acid sites are almost constant and strong Lewis acid sites even increase, but the lifetime decreases. This indicates that acidity, especially strong Lewis acidity, does not benefit the lifetime of the catalyst in this work.

Table 2 and figure 2 also give the specific surface area and volume of deactivated catalysts where the conversion of olefins is less than 60%. It can be seen that the surface areas and volumes of micropores decrease, while those of the larger pores almost do not change. So we can conclude that the main reason for the deactivation of the catalysts is micropore blocking.

Figure 7 shows that, with the increase of fluorine content, the yield of the 2-phenyl isomer and to a lesser extent of the 3-phenyl isomer decreases, while the yields of the others increase. This means that the HF modification weakens the selectivity of the catalysts. Because the distribution of the isomers depends on the shape selectivity that relates to the ratio of micropore volume to total volume, the yield of the 2-phenyl isomer decreases with the decrease of the ratio of micropore volume to total volume, which is shown in figure 7.

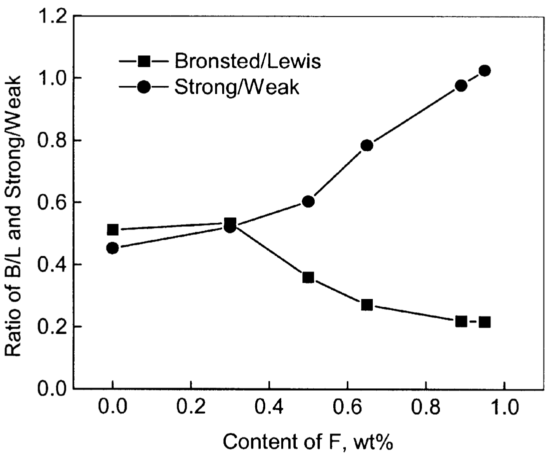

Figure 5. Variation of ratio between Brønsted and Lewis acid sites and between strong and weak acid sites with F content.

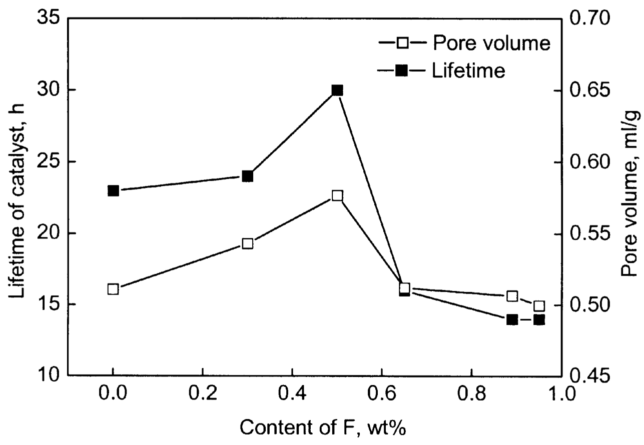

Figure 6. Effects of F content and pore volume on the lifetime the catalysts (150 °C, 2 MPa, WHSV = 2.5 h^{-1}, mole ratio of benzene to olefins = 15 : 1).

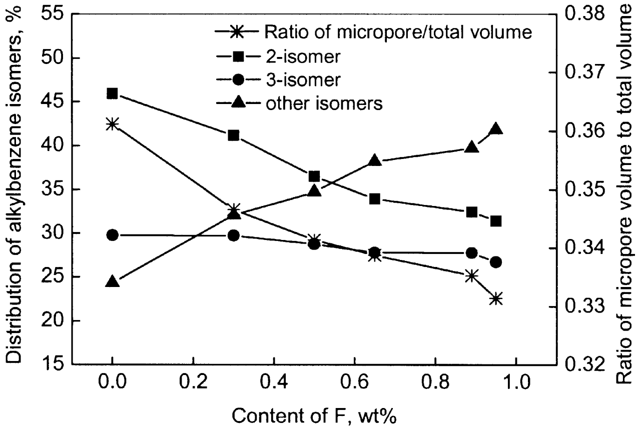

Figure 7. Effects of F content o the distribution of products (150 °C, 2 MPa, WHSV = 2.5 h^{-1}, mole ratio of benzene to olefins = 15 : 1).

To get more 2-phenyl isomer, the fluorine content should not be too high.

4. Conclusion

The effects of hydrofluoric acid treatment on the structure and acidity of β zeolite was investigated by XRD, BET measurements, FTIR, TPD, elemental analysis and catalyst testing. When impregnated by low-concentration HF solution, the extra-lattice species, such as $3Al_2O_3{\cdot}2SiO_2$, are dissolved by HF solution, so the specific area and pore volume increase. However, with the increase of HF concentration, both β zeolite and the extra-lattice species are dissolved and form AlF_3 or other fluorinated compounds which deposit in the catalyst, so the specific area and pore volume decrease.

With the extent of modification, the total acid amount gradually decreases and then becomes constant. The initial remarkable decrease of Brønsted acid sites is due to the substitution of bridging hydroxyl groups (3605 cm^{-1}) by fluorine atoms, and the removal of unstable lattice aluminum from the lattice due to interaction with fluorine atoms, which also causes the disappearance of the VHF hydroxyl groups (3782 cm^{-1}). Because the hydroxyl groups bonded to Si (3730 cm^{-1}) are more stable than bridging hydroxyl groups and VHF hydroxyl groups, strong Brønsted acid sites decrease less than weak Brønsted acid sites. The weak Lewis acid sites gradually decrease, but the strong Lewis acid sites increase when the modification increases, which may be due to the formation of AlF_3 or other fluorinated compounds.

The lifetime of the catalysts used for the alkylation of benzene with long-chain olefins is mainly dependent on the surface area and volume rather than acidity. When the fluorine content is 0.5%, the lifetime can improve by 30% when the catalyst has maximum specific surface area and pore volume.

References

[1] P.R. Pujado, in: *Handbook of Petroleum Refining Process*, ed. R.A. Meyers (McGraw-Hill, 1986).
[2] S. Sivasanker, A. Thangaraj, R.A. Abdulla *et al.*, J. Catal. 138 (1992) 386.
[3] J.L. Goncalves de Almeida, M. Dufaux, Y.B. Taarit, and C. Naccache, Appl. Catal. A: General 114 (1994) 141.
[4] Z. Cui, M. Han, W. Chen and Y. Jin, Petrochemical Technol. 28 (1999) 657.
[5] M. Han, Z. Cui, W. Chen and Y. Jin, Petrochemical Technol. 28 (1999) 734.
[6] L. Jose and B. Tejero, US Patent 5,146,026, 1992.
[7] A. Uppal, US Patent 5,365,009, 1994.
[8] B.V. Vora, P.R. Pujado and T. Imai, Chem. Ind. 19 (1990) 187.
[9] M. Han, Z. Cui, C. Xu, W. Chen and Y. Jin, Appl. Catal. (submitted).
[10] M.M.J.Treacy and J.M.Newsam, Nature (London) 332 (1988) 249.
[11] V.R. Choudhary, In. Eng. Chem. Prod. Res. Dev. 16 (1977) 12.
[12] L.E. Aneke, L.A. Gerritsen and P.J. Van der Berg, J. Catal. 59 (1979) 26.
[13] L.E. Aneke, L.A. Gerritsen and J. Eilers, J. Catal. 59 (1979) 376.
[14] B.M. Lok and T.P.J. Izod, Zeolites 2 (1982) 66.
[15] A. Araya and A. Dyer, Zeolites 1 (1981) 35.
[16] I.T. Sariev and V. Penchev, in: *Proc. 4th Int. Conf. on Heterogeneous Catalysis* (Bulgarian Academy of Science, Sofia, 1979) p. 391.
[17] V. Penchev, I.T. Sariev and M. Zhelazkova, Kinet Katal. 22 (1981) 732.
[18] M. Zhelazkova, I.T. Sariev and S.A. Koralska, in: *Proc. 5th Int. Conf. on Heterogeneous Catalysis* (Bulgarian Academy of Science, Sofia, 1983) p. 467.
[19] J.A. Kocal, US Patent 5,196,574, 1993.
[20] X. Liu, Hydrocarbon process publishing house, Beijing, 1990 (in Chinese).
[21] Powder Diffraction File, Joint Committee on Powder Diffraction Standards. American Society for Testing and Materials, International Center for Diffraction Data, 1988.
[22] I. Kiricsi, C. Flego, G. Pazzuconi *et al.*, J. Phys. Chem. 98 (1994) 4627.
[23] R.B. Borade and A. Clearfield, J. Chem. Soc. Faraday Trans. 91 (1995) 539.
[24] S. Kowalak, J. Chem. Soc. Faraday Trans. 84 (1988) 2035.
[25] A.K. Ghosh and A.K. Ronald, Zeolites 10 (1990) 766.
[26] J.P. Shen, Y. Li, and T. Sun, Chem. J. Chinese Universities 6 (1995) 943 (in Chinese).