Bull. Chem. Soc. Jpn., 69, 1429—1435 (1996)

Characteristics of Alkali-Exchanged Y Zeolites, Montmorillonite, and Al-Pillared Montmorillonite, Studied by Physical and Chemical Methods

István Hannus,* István Pálinkó,† Gyula Tasi, Attila Béres, and Imre Kiricsi

Applied Chemistry Department, József Attila University, Rerrich B. tér 1, Szeged, H-6720, Hungary

†Department of Organic Chemistry, József Attila University, Dóm tér 8, Szeged, H-6720, Hungary

(Received October 12, 1995)

Microporous catalytic materials with various surface acidities have been prepared and characterized with instrumental methods as well as chemical reactions. The catalysts were LiY, NaY, KY, CsY, RbY, Na-montmorillonite (Na-mor), and Al-pillared montmorillonite (Al-PILC). Structural characterization involved atomic absorption and X-ray fluorescence spectroscopies, X-ray diffractometry, infrared spectroscopy in the region of framework vibrations, and thermogravimetric and BET measurements. Infrared spectroscopy of adsorbed pyridine and the acid-catalyzed isomerization of cyclopropane was used for testing surface acidity. The instrumental methods suggested a decreasing acidity order with increasing cationic radii, while the chemical reaction showed that the acidity decreased in the Al-PILC>LiY>NaY>CsY>KY≈RbY sequence. On the first two catalysts oligomerization followed isomerization, and the activity of isomerization decreased in the above order.

In the last decades zeolites and related porous materials gained tremendous importance both in various fields of chemical industry as well as in fundamental and development-oriented academic research. Investigations are mainly focused on the syntheses of new substances with various pore size distributions, the modification of existing structures, and their catalytic use. Zeolites and related materials like, e.g., layered clays have relatively well-defined intersecting channel networks, giving rise to shape selectivity in molecular sieving as well as in catalysis. These materials are mostly considered to be acidic, therefore they mainly catalyze reactions proceeding through carbenium ions.

However, the acidity of, e.g., zeolites can be fine tuned and eventually it can be changed to be of basic character through ion-exchanging appropriate alkali cations. A substantial amount of work was devoted to the synthesis, characterization, and catalytic application of alkali-exchanged X-type,[1—10] Y-type,[1,2,6—10] ZSM-5,[4,11,12] and other (beta, EMT)[9] zeolites. The importance of acid–base properties in catalytic applications of appropriately modified zeolites was also pointed out in two recent reviews.[13,14]

The main objective of this work was to compose a group of catalysts with a wide range of acid–base properties with the aim of using them in the synthesis of fine chemicals in reactions requiring acidic and/or basic sites of various strength. To achieve this goal, we used Na-montmorillonite and NaY as starting materials. Going to the acidic end was attempted by the preparation of Al-pillared montmorillonite, while exchanging the sodium ions in NaY to the other alkali ions extended the range towards the basic end. Further use of these materials are only possible after appropriate characterization by physical as well as chemical methods. A substantial number of spectroscopic methods supplemented with thermogravimetric and BET measurements were used on one hand, while on the other, the isomerization of cyclopropane[15—18] and occasional oligomerization of the isomerization[19] product propylene were used as catalytic test reactions. Using these reactions we attempted to establish the role of Lewis acid sites beside that of the Brønsted sites. In this paper the results of this complex approach are detailed.

Experimental

Materials. The zeolites were prepared by conventional ion exchange of Na^+ ions in NaY (Union Carbide) for Li^+, K^+, Cs^+, or Rb^+ in 0.2 $mol\,dm^{-3}$ solution of the appropriate metal chloride for the first three cations and 0.1 $mol\,dm^{-3}$ of RbCl for the last. Ion-exchange was repeated twice. Unit cell composition (Table 1) showed that sodium ions in site I (situated in the double six rings) were never exchanged because that site is the most difficult to reach (and consequently ions there are firmly held), especially when the wet ion-exchange method is used, i.e., hydrated ions approach the various exchange sites.

Na-montmorillonite (Na-mor) was prepared from bentonite originated from Kuzmice (Czechoslovakia) by fractionation of a Na_2CO_3 (2.5%) treated suspension followed by dialysation (pH = 7.6).

Al-PILC was made following the method of Lahav et al.[20] $AlCl_3 \cdot 6H_2O$ (Reanal) was dissolved in double-distilled water (0.25 $mol\,dm^{-3}$) and 1 $mol\,dm^{-3}$ of NaOH solution was added to it until $OH/Al = 2$. One hundred cm^3 of this solution was aged for 24 h. These solutions were added to a well-stirred suspension of Na-mor and stirring was prolonged for an additional hour. Then the suspension was filtered and washed with double-distilled water until it became free of chloride. The resulting solid substance was dried at room temperature and calcined at 573 K for one hour.

All the catalysts were stored over saturated solution of NH_4Cl.

Methods of Characterization. Residual alkaline metal ion

Table 1. Characteristic Data on Alkali-Exchanged Zeolites, Na-mor and Al-PILC

Catalyst	Unit cell composition	Adsorbed N_2	Water content	Positions of the structure sensitive				
		STP $cm^3\ g^{-1}$	%	IR bands/cm^{-1}				
NaY	$Na_{58}Al_{58}Si_{134}O_{384}$	230	28.8	1019	792	580	507	
LiY	$Li_{38}Na_{20}Al_{58}Si_{134}O_{384}$	238	31.4	1022	792	580	509	
KY	$K_{54}Na_{4}Al_{58}Si_{134}O_{384}$	180	23.6	1016	787	576	503	
RbY	$Rb_{42}Na_{16}Al_{58}Si_{134}O_{384}$	174	23.6	1013	787	575	502	
CsY	$Cs_{50}Na_{8}Al_{58}Si_{134}O_{384}$	144	17.6	1008	785	574	501	
				Characteristic bands/cm^{-1}				
Na-mor	a)	21.9	25.2	1617	1435	906	$776^{d\ b)}$	706
Al-PILC	a)	193.2	25.4	1612	—	906	$776^{d\ b)}$	694

a) not available. b) d: doublet.

concentrations were measured by atomic absorption spectroscopy (AAS 3, Carl Zeiss Jena). The extent of ion exchange (Table 1) was calculated from these data.

The composition of the zeolite samples was analyzed by X-ray fluorescence (XRF) spectroscopy as well, using analytical standards. The results coincided with those calculated on the basis of AAS measurements. Only qualitative analysis could be done for Na-mor and Al-PILC. The spectra were taken in the 1-8 keV range.

X-Ray diffractiograms (XRD) were measured on a DRON 3 diffractometer using Cu $K\alpha$ radiation.

Thermal behavior of the substances was investigated by thermogravimetry (TG) with a Derivatograph-Q instrument. The powdered samples were placed on a platinum sample holder and studied under the following conditions: mass of sample 100 mg, heating rate 10 degree min^{-1}, temperature range 300 to 1270 K. Before measurements samples were kept above saturated NH_4Cl solution.

The KBr pellet technique was used for monitoring the framework vibrations of the substances. Infrared (IR) spectra were obtained in the range of 400—1200 cm^{-1} on FTS-65A/896 Bio-Rad FT-IR spectrometer with a liquid nitrogen cooled MCT detector.

Surface acidity was tested by pyridine adsorption. Self-supported wafers of 10 mg cm^{-2} thickness were used for measurements. They were treated in a vacuum system attached to an IR cell. 1.33 kPa of pyridine was adsorbed at 473 K for 1 h, then the IR spectra of the samples were run after the following treatments: (i) 1-h evacuation at 473 K, (ii) 1-h evacuation at 523 K, (iii) 1-h evacuation at 573 K. Bands around 1450 and 1540 cm^{-1} were monitored with a Specord 75 spectrometer.

BET measurements were done in a conventional volumetric adsorption apparatus at the temperature of liquid N_2. Before measurements, the clay and zeolite samples were treated in vacuum at 573 or 673 K, respectively. Results are summarized in Table 1.

Kinetic Measurements and Analytical Technique. Kinetic measurements were done in a conventional closed recirculation reactor. Usually 100 mg of catalyst was placed in the reactor and was pretreated for 4 h under vacuum at 573 K for the clays and 673 K for the zeolites.

Reactions were run at the temperature of this treatment for the clays and at 623 K for the zeolites. The reactant was 13.3 kPa of cyclopropane, which was purified by several freeze-thaw-pump cycles before each run. At certain times samples were withdrawn and analyzed by gas chromatography (Hewlett Packard 5710A GC and Hewlett Packard 3380S integrator). For a straightforward comparison the same temperature should have been used, however, the clays were extremely active at 623 K, while the zeolites were not active at all at 573 K.

For analysis, a 3.6 m long all-glass column was used, packed with 20% bis(2-methoxyethyl) adipate on Chromosorb PAW 80/100 mesh. Temperature of analysis was either 298 or 323 K. Product identification and calibration was made by pure reference samples.

Results

XRD Measurements. XRD measurements of the various samples showed excellent crystallinity. All the reflections described in the literature for NaY were found.[21] The other ion-exchanged samples did not show new reflections, i.e., the basic structure was not altered, however, the intensities were sensitive to the cation. Table 2 shows examples of highly as well as moderately sensitive reflections. It is clear that cations with increasing radii shadowed certain reflections dramatically, while others just to a smaller extent. As far as Al-PILC is concerned, XRD measurements showed that pillaring was successful: basal spacing, calculated from the (001) reflection, increased from 1.10 nm of Na-mor to 1.55 nm of Al-PILC.

TG Measurements. TG curves for the zeolite samples are displayed in Fig. 1. As it was expected dehydration occurred upon the elevation of the temperature. This process was continuously taking place with the increase of tempera-

Table 2. Typical X-Ray Reflections of Alkali-Exchanged Zeolites (intensities in arbitrary unit)

	XRD reflections														
	111	220	311	331	333	440	620	533	642	733	822	751	840	664	931
LiY	300	70	58	136	62	92	26	128	100	38	59	114	40	40	17
NaY	260	62	54	113	54	77	21	110	76	35	50	103	36	31	18
KY	220	55	34	78	51	34	26	116	71	22	39	64	45	25	16
RbY	120	40	38	42	70	14	18	75	70	49	30	42	48	36	7
CsY	35	13	13	9	57	—	—	38	40	39	8	14	15	25	—

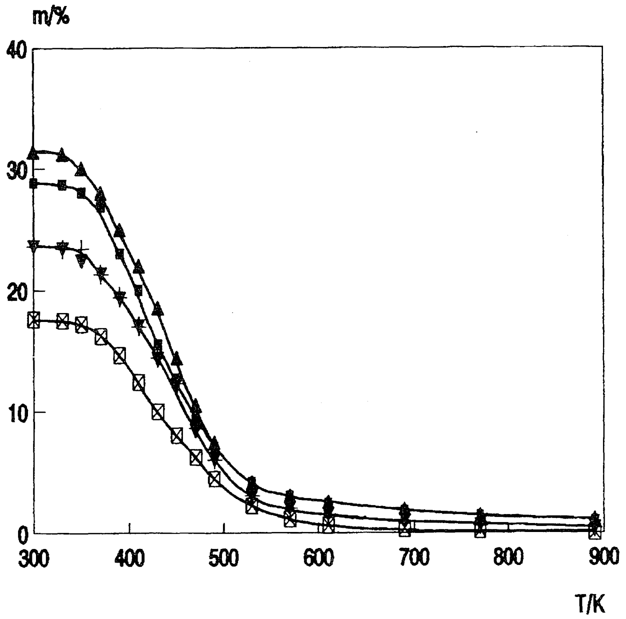


Fig. 1. Thermogravimetric curves for LiY (▲), NaY (■), KY (▼), RbY (+), CsY (□).

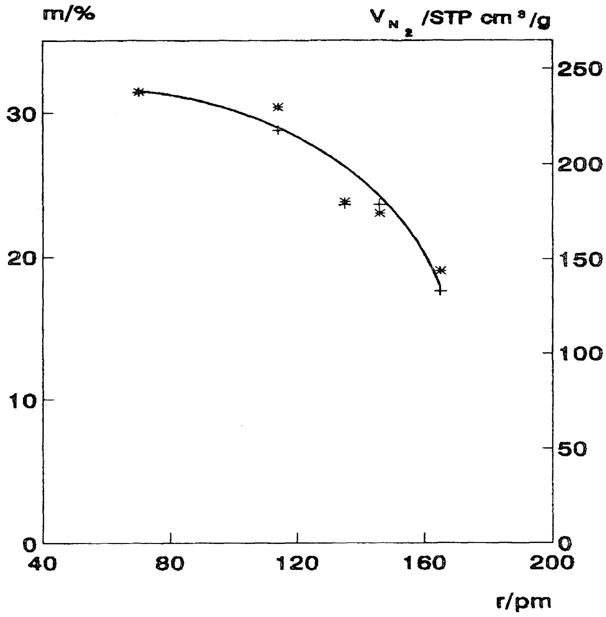


Fig. 2. Water content (+) or volume of adsorbed N_2 (∗) vs. cationic radii for the alkali-exchanged zeolites.

ture. The mechanism of dehydration and its dependence on exchange cations is discussed elsewhere.[22)]

Figure 1 clearly shows that the cations strongly influenced the water content of the zeolites. It increased with the decrease of the ionic radii, reflecting the extent of hydration. After complete dehydration the zeolitic structure remained intact up to about 1100 K. The exact temperature of structural collapse slightly depended on the cation.

TG measurements showed two characteristic weight-loss steps for both the starting montmorillonite and the Al-PILC: Na-mor (383 K, 963 K), Al-PILC (378 K, 853 K). The first step is due to dehydration while the second means the collapse of the sheet-silicate structure. A flat plateau could be observed between 500 and 800 K for Al-PILC indicating a slow but continuous process, probably due to the gradual dehydroxylation of the pillaring polyhydroxy cations.

BET Measurements. The results of BET measurements are in the third column of Table 1. As far as the zeolites are concerned, the highest value was obtained for LiY and the volume of adsorbed N_2 decreased with increasing ionic radii just like the water content of the air-dried materials (Fig. 2).

The BET results for the clays also verified that pillaring was successful, since the specific surface area was significantly higher for Al-PILC than for Na-mor.

Framework IR. Framework IR measurements also showed excellent crystallinity. In the analysis of the absorption bands in the region of framework vibrations (400—1200 cm^{-1}), the position of the bands in NaY was taken as the base of comparison. The SiO_2/Al_2O_3 ratio of our sample was 4.6, and IR absorptions (or shoulders) were found at 1147, 1019, 792, 734, 712, 580, 507, 459 cm^{-1}. These positions were very close to a NaY sample of $SiO_2/Al_2O_3 = 4.87$ described by Flanigen et al.[23)] Obviously, exchanging sodium ions for other alkali ions must influence the vibrations of zeolitic structural units to some extent. Accordingly, data in Table 1 (columns 5,6,7, and 8) showed systematic changes upon ion exchange, i.e., their position decreased in frequency with the increasing size, i.e., with decreasing polarizing power, of the cation. The position of the other bands did not change upon ion exchange.

IR Spectroscopy of Adsorbed Pyridine. For the zeolites studied, ion exchange should influence surface acidity. This should have been reflected in the IR spectra of pyridine adsorbed on these materials. However, neither the combination band of Lewis and Brønsted acid sites bonded pyridine nor adsorbed pyridine on Lewis acid sites were detected on any of our zeolite samples.

There was no band indicating Brønsted acidity either, on any of the catalyst (including Na-mor and Al-PILC), except LiY (Fig. 3). Here, a shoulder appeared at 1540 cm^{-1} on a band centered at 1590 cm^{-1} after 1-h evacuation at 473 K and became more pronounced after an additional hour of evacuation at 523 K. Nevertheless, a further 1-h evacuation at 573 K removed each form of adsorbed pyridine except a band at 1440 cm^{-1} which was thought to be pyridine attached to Li^+. A similar band (between 1430 and 1440 cm^{-1}) could be observed for each catalyst but it survived evacuation at 573 K only for LiY. From CsY, for instance, it could be removed by a 1-h evacuation at 523 K. The observed band was solely due to the interaction of pyridine with the exchanged cations.[24)]

On Na-mor neither Brønsted nor Lewis acidity could be detected by pyridine adsorption, while a band appeared at 1430 cm^{-1} on Al-PILC, indicating Lewis acidity. This band survived a 1-h evacuation at 573 K.

Catalytic Reaction. The cyclopropane molecule was used for probing catalyst acidity via chemical transformations. The catalysts could be divided into two groups. Only isomerization of cyclopropane to propylene took place on

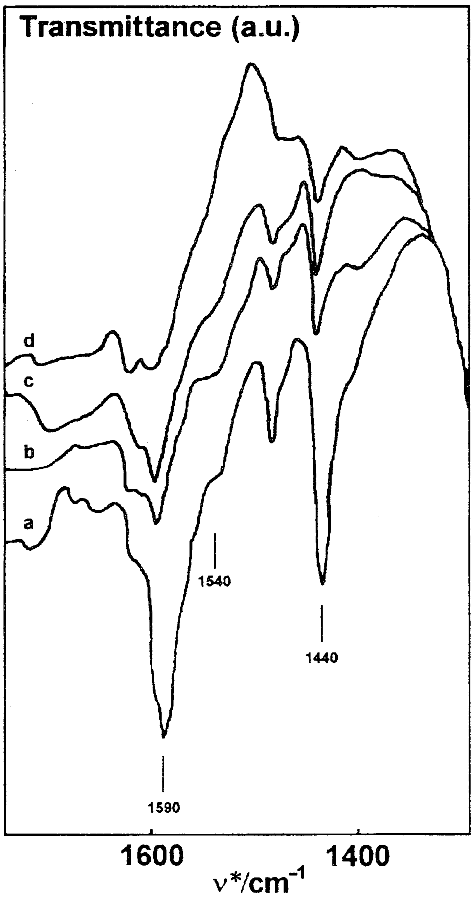


Fig. 3. IR spectra of adsorbed pyridine on LiY after the following treatments: (a) 1-h evacuation at 473 K, (b) 1-h evacuation at 523 K, (c) an additional hour at 523 K, (d) 1-h evacuation at 573 K.

NaY, KY, CsY, RbY, and Na-mor (Fig. 4), while oligomerization of propylene followed isomerization on LiY (Fig. 5) and Al-PILC (Fig. 6).

Figure 4 displays propene yield vs. time curves for the first group, where propene yield was normalized to 1 g of pretreated catalyst. It is to be seen that NaY was the most active catalyst. At the low-activity end, the behavior of KY and RbY was identical. Intuitively, CsY was expected to be the most basic, nevertheless, it displayed higher activity in this acid-catalyzed reaction than KY, RbY or Na-mor.

The two members of the second group showed in part similar and in part different behavior. They are similar in that propylene originated from cyclopropane isomerization underwent oligomerization and subsequent cracking resulting in the same products: propene (main product), 2-methylbutane, 2-methylpropene, and 2-methylpentane (minor products). However, they did differ in the quantity of the minor products: while 2-methylpentane was the most abundant minor product on Al-PILC, it was 2-methylbutane on LiY. It is noteworthy, that 2-methylpentane appeared first (among the minor products) on Al-PILC and the last on LiY. It is also remarkable that 2-methylpropene and 2-methylbutane started to form at the same time on Al-PILC, while each product appeared at different stages of the run on LiY.

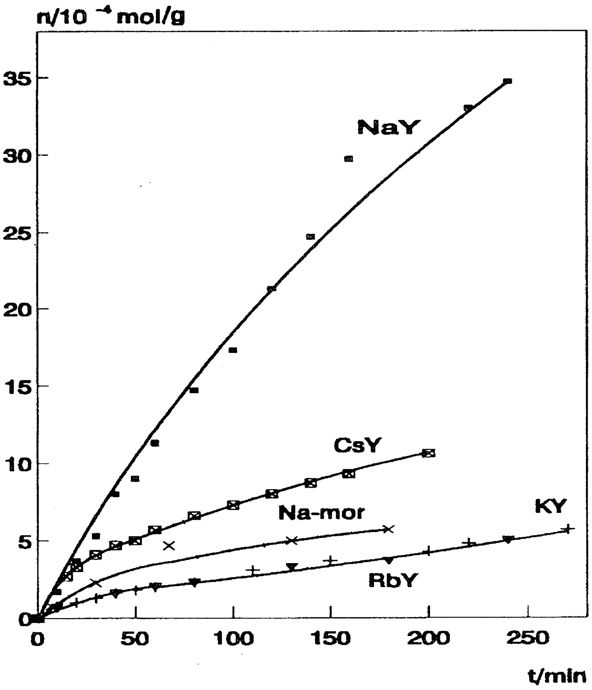


Fig. 4. Accumulation of propylene in cyclopropane isomerization at 573 K on Na-mor and at 623 K on the alkali-exchanged zeolites.

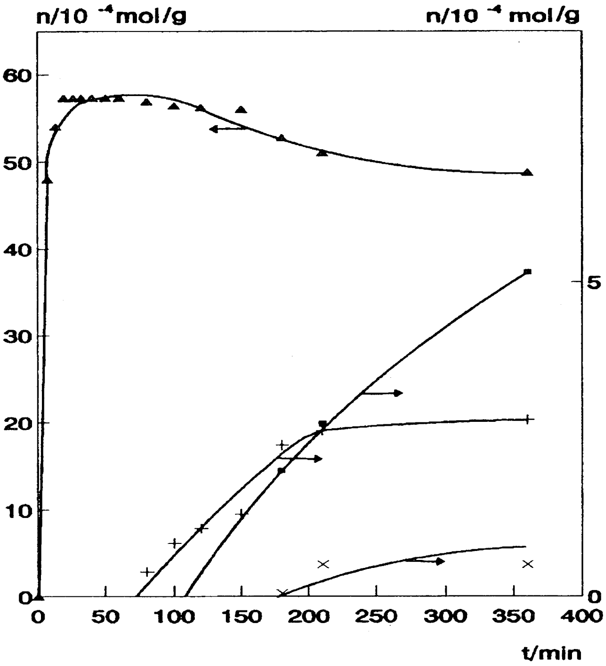


Fig. 5. Isomerization of cyclopropane followed by oligomerization and subsequent cracking of the propylene product on LiY at 623 K; propylene (▲), 2-methylbutane (■), 2-methylpropene (+), 2-methylpentane (×).

As far as oligomerization (and subsequent cracking) products are concerned, it is worth mentioning that *2-methylpropane was not detected* on any of the catalysts.

Visual inspection of the used catalyst revealed that coking was more severe on Al-PILC than on LiY.

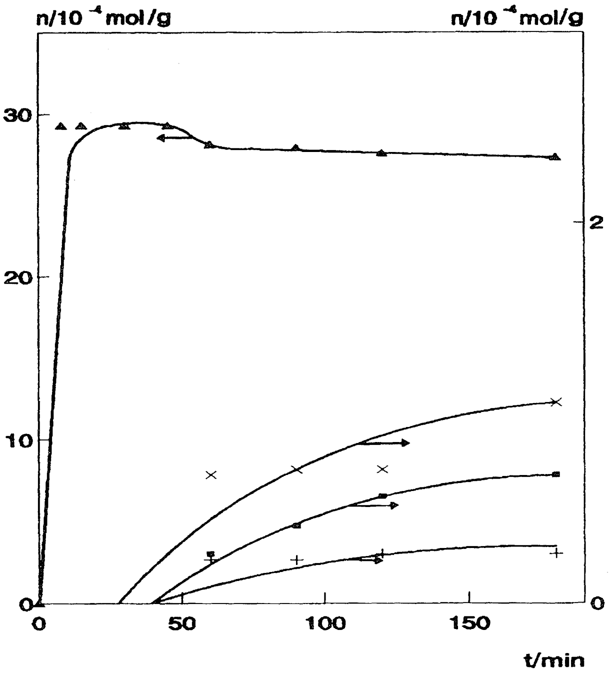


Fig. 6. Isomerization of cyclopropane followed by oligomerization and subsequent cracking of the propylene product on Al-PILC at 573 K; propylene (▲), 2-methylbutane (■), 2-methylpropene (+), 2-methylpentane (×).

Discussion

In this work two types of aluminosilicates were used in attempting to prepare a series of materials with a wide range of acidities. Acidity of NaY was varied by exchanging Na^+ with the other alkali ions. Na-montmorillonite was modified by exchanging sodium ions with Al-polyhydroxy cations to obtain Al-PILC, a known acidic substance.

Framework IR of the Y zeolites and the clays showed that the basic faujasite and sheet-silicate structures are just slightly modified by ion exchange.

As far as only the size of the exchanged cations are considered, one would suggest that acidity decreases in the following sequence: LiY>NaY>KY>RbY>CsY. Basically this was found by Barthomeuf[25] using pyridine and/or pyrrole as indicator reactants and by Ono[26] using dehydration of 2-propanol as a test reaction.

TG and BET measurements seem to agree well with this sequence. These measurements showed that cations with increasing size gradually became less hydrated (i.e., Lewis acidity due to the metal cations decreased with increasing cation size) and the volume of adsorbed N_2 was also decreasing with increasing ionic radii (Fig. 2).

IR study of pyridine adsorption did not seem to alter the suggested sequence, since an analysis of the spectra revealed that Brønsted acidic sites could only be found on LiY, and Lewis acidity on zeolites were only due to the cations. Thus, acidity detected this way reflected a sequence consistent with the ionic radii (i.e., pyridine remained bonded to Li^+ even at 573 K, while pyridine desorbed from CsY at 523 K).

Lewis acidity due to framework structure was only found on Al-PILC.

The intensities of selected XRD lines showed that an increase in cation size shadowed some reflections in the faujasite structure. The extent of shadowing may influence the acid–base properties of the faujasite skeleton since it is believed that the basic centers are the oxygen atoms of the framework. If extensive shadowing occurs, basicity may be decreased. Lewis acidity of the cations decrease by increasing size and so does the basicity of the framework, therefore this sequence may be altered somewhat.

The isomerization of cyclopropane to propylene and the oligomerization of this product are typical acid-catalyzed reactions: neither of them proceeds on the basic, sodium azide treated NaY zeolite.[17] It is also known that merely isomerization takes place on mildly acidic zeolites, while oligomerization of the isomerization product requires more acidic sites.[27] Thus, in view of the pyridine adsorption results it is not surprising that only isomerization takes place on every catalyst except LiY and Al-PILC. On these latter two oligomerization also proceeds, the cracking products of the adsorbed oligomer carbocations could be detected. As far as the mechanism of the transformations are concerned a simplified scheme (Scheme 1) may describe the most significant features. They are as follows:

(i) on LiY where Brønsted acidity was detected, ring opening takes place with the assistance of acidic OH groups with the formation of an isopropyl cation, which may lose a proton, and propene desorbs (route (a)),

(ii) ring opening also occurs on catalysts without Brønsted acid sites having only cations which can be considered as weak Lewis acid centers; the accurate mechanism of this transformation is not known, however, it cannot proceed with hydride ion abstraction (route (b)),[28]

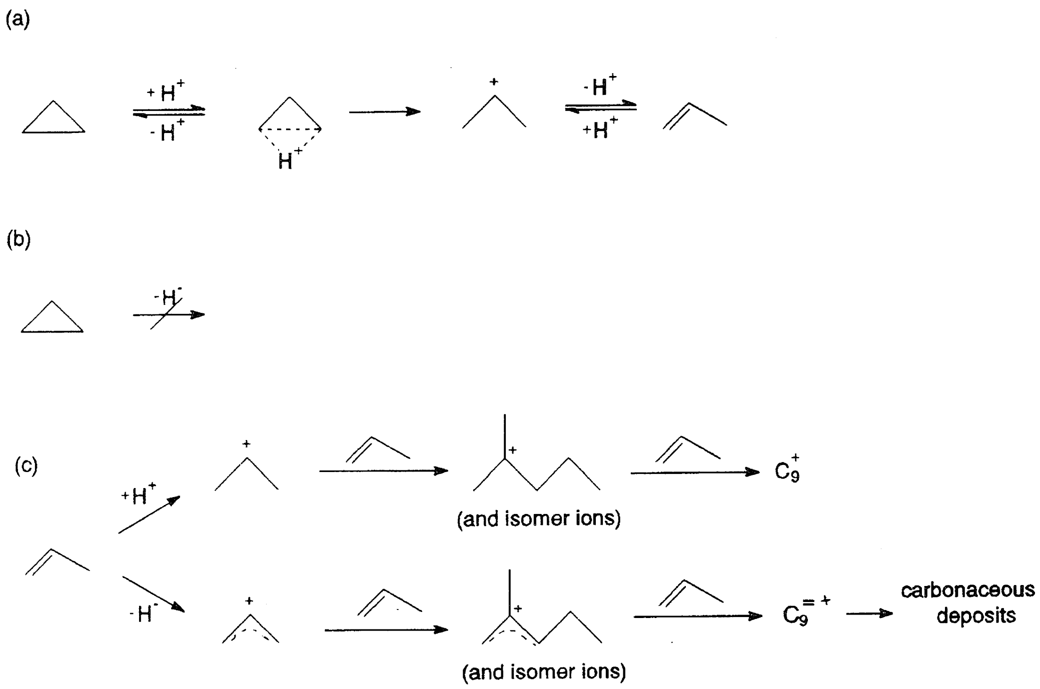
(iii) oligomerization may proceed with two mechanisms either with the assistance of Brønsted or Lewis sites on LiY and Al-PILC, respectively (of course the mixture of the two mechanisms may operate over LiY) (route (c)),

(iv) cracking of the surface bound carbocations probably occurs via β-scission and desorption either with the loss of proton or hydride ion acquisition from carbonaceous deposits of varying hydrogen content, and

(v) Lewis acid sites may not only be due to the framework structure and the cations but adsorbed carbenium ions may also serve as secondary Lewis acid centers.

Conclusions

During preparation and characterization of alkali-exchanged zeolites and Al-PILC a number of observations have been made. First, these modified microporous materials do provide a group of catalysts with changing acid–base properties. Second, it has been found that although instrumental methods give important information to an appropriate description of the fundamental attributes of these materials, catalytic test reactions are essential for learning about their actual performance. It is found that for the zeolites, the expected decreasing acidity sequence (LiY>NaY>KY>RbY>CsY) based



Scheme 1. The mechanism of the ring-opening reaction of cyclopropane on surfaces with Brønsted (a) or Lewis acidic centers (b), and the most important oligomerization steps of the product propylene on these surfaces (c).

on increasing ionic radii is altered in the test reactions (LiY>NaY>CsY>KY≈RbY). This experimental observation is attributed to the shadowing of basic sites (framework oxide ions) by the large cations, which in turn provide more accessible cationic Lewis centers. Third, these sites are not strong enough to facilitate oligomerization of the isomerization product. Either framework Lewis acid centers (Al-PILC) or Brønsted acid sites (LiY) are needed. The mechanisms of ring opening oligomerization and subsequent cracking are different on these sites. A possible route for the Lewis acid site catalyzed transformations, rarely considered explicitly before, is also suggested. Finally, in spite of the considerably lower reaction temperature (573 K), Al-PILC proved to be a very effective acidic catalysts with an activity comparable to that of LiY at 623 K.

Financial support provided for this work by the National Science Foundation of Hungary through grant OTKA T014275/1994 is gratefully acknowledged.

References

1) P. E. Hathaway and M. E. Davis, *J. Catal.*, **116**, 263 (1989).

2) M. Huang, A. Adnot, and S. Kaliaguine, *J. Catal.*, **137**, 322 (1992).

3) A. N. Vasiliev and A. A. Galinsky, *React. Kinet. Catal. Lett.*, **51**, 253 (1993).

4) M. Huang and S. Kaliaguine, *Catal. Lett.*, **18**, 373 (1993).

5) H. Tsuji, F. Yagi, H. Hattori, and H. Kita, *J. Catal.*, **148**, 759 (1994).

6) Zi-Hua Fu and Y. Ono, *J. Catal.*, **145**, 166 (1994).

7) Bao Lian Su and D. Barthomeuf, *Appl. Catal. A: General*, **124**, 73 (1995).

8) A. Corma, F. Llopis, J. B. Monton, and S. Weller, *J. Catal.*, **142**, 97 (1993).

9) P. R. Hari Prasad Rao, P. Massiani, and D. Barthomeuf, *Catal. Lett.*, **31**, 115 (1995).

10) C. J. Blower and T. D. Smith, *J. Chem. Soc., Faraday Trans.*, **90**, 931 (1994).

11) M. Otremba and W. Zajdel, *React. Kinet. Catal. Lett.*, **51**, 481 (1993).

12) R. B. Borade, M. Huang, A. Adnot, A. Sayari, and S. Kaliaguine, "Proc. 10th Int. Congr. Catal.," "New Frontiers in Catalysis," ed by L. Guczi, F. Solymosi, and P. Tétényi, p. 1625 (1992).

13) W. F. Hölderich, "Proc. 10th Int. Congr. Catal.," "New Frontiers in Catalysis," ed by L. Guczi, F. Solymosi, and P. Tétényi, p. 127 (1992).

14) H. Hattori, *Stud. Surf. Sci. Catal.*, **78**, 35 (1993).

15) B. H. Bartley, H. W. Habgood, and Z. M. George, *J. Phys. Chem.*, **72**, 1689 (1968); Z. M. George and H. W. Habgood, "Proc. Soc. Chem. Ind. Conf. Mol. Sieves," London (1968), p. 130; Z. M. George and H. W. Habgood, *J. Phys. Chem.*, **74**, 1502 (1970).

16) S. L. Suib and Z. Zhang, *ACS Symp. Ser.*, **368**, 569 (1980); M. W. Simon, A. M. Efstathiou, C. O. Bennett, and S. L. Suib, *J. Catal.*, **138**, 1 (1992).

17) P. Fejes, I. Hannus, I. Kiricsi, and K. Varga, *Acta Phys. Chem.*, **24**, 119 (1978).

18) H. Förster, S. Franke, and S. Seebode, *J. Chem. Soc., Faraday Trans. 1*, **79**, 373 (1983); P. Fejes, I. Kiricsi, Gy. Tasi, and K. Varga, *Acta Phys. Chem.*, **31**, 405 (1985).

19) I. Kiricsi, I. Hannus, K. Varga, and P. Fejes, *J. Catal.*, **63**, 501 (1980); H. Förster and J. Seebode, *Acta Phys. Chem.*, **31**, 413 (1985); I. Kiricsi and H. Förster, *J. Chem. Soc., Faraday Trans. 1*, **84**, 491 (1988).

20) N. Lahav, U. Shani, and J. Shabtai, *Clays Clay Minerals*, **26**, 107 (1978).

21) "Collection of Simulated XRD Powder Patterns for

Zeolites," ed by R. von Ballmoos and J. B. Higgins, Butterworth-Heinemann, London (1990), p. 392S.

22) G. Tasi, I. Kiricsi, F. Evanics, E. Nagy, and P. Fejes, *Acta Chim. Hung.*, **128**, 119 (1991).

23) E. M. Flanigen, H. Khatami, and H. A. Szymannski, *ACS Symp. Ser.*, **1971**, 201.

24) J. W. Ward, in "Zeolite Chemistry and Catalysis, ACS Monograph 171," Washington (1976), p. 185.

25) D. Barthomeuf, *J. Phys. Chem.*, **88**, 42 (1984).

26) Y. Ono, in "Catalysis by Zeolites," ed by B. Imeliket al., p. 19, 1980.

27) I. Kiricsi, I. Hannus, K. Varga, and P. Fejes, *J. Catal.*, **63**, 501 (1980), and references therein.

28) P. Fejes, H. Förster, I. Kiricsi, and J. Seebode, *Zeolites*, **4**, 259 (1984); P. Fejes, I. Kiricsi, K. Varga, H. Förster, and J. Seebode, *Zeolites*, **5**, 365 (1985).