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Alkane cracking reactions in zeolites with coadsorbed metal halides

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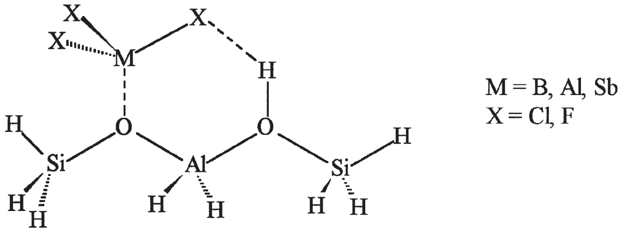
HY which is loaded with SbF_5, BCl_3, or BF_3 at low coverages, one metal halide molecule per Brønsted acid site, is shown to be active in the isomerization and cracking of n-hexane and n-butane at room temperature. In contrast, NaY with the same metal halide loading shows greatly reduced activity under identical reaction conditions. The cracking reaction was repeated with DY in place of HY, demonstrating deuterium incorporation into the hexane isomer and light alkane products through interaction with the Brønsted site. Flow reactor studies demonstrate that the conversion is not constant as a function of time on stream, going through an induction period, reaching a maximum, at around 400 s, and then decaying to ∼1% after 1 h.

Keywords: Lewis acid, Brønsted acid, metal halide, zeolite, HY, boron trichloride, boron trifluoride, antimony pentafluoride, alkane, cracking

1. Introduction

Alkane cracking and isomerization reactions at low temperatures require highly active catalysts. For example, metal-promoted sulfated zirconia has been shown to isomerize pentane and butane even below room temperature [1]. Another interesting and potentially very useful family of materials are prepared by incorporating metal halides into mixed oxides [2,3]. As an example, HY which has been doped with aluminum trichloride is significantly more active in the carbonylation of benzene with CO than the pure, undoped zeolite [4]. Interestingly, preliminary spectroscopic data suggests that some metal halide-doped zeolites are similar to “magic acid” in terms of the ability to protonate coadsorbed molecules [5].

In our previous study of the zeolite/metal halide composite material, we used gravimetric techniques to demonstrate that metal halides form stable 1 : 1 complexes at the zeolite Brønsted acid sites [5]. It is likely that the 1 : 1 complex is the active site in the carbonylation [4] and ethene polymerization reactions [5]. The proposed structure of the 1 : 1 complex **1** was determined from electronic calculations[1] [4], and provides some insight into the nature of the enhanced reactivity. This complex is similar to that presented by Makarova et al. [6] and also to that proposed by Adeeva et al. to describe the active site in sulfated zirconia [7]. One interesting result which follows from the calculations is that the partial charge on the Brønsted hydrogen atom is increased to 0.535 in the BCl_3 complex compared to 0.520 in the isolated site, due to the strong electron-withdrawing effects of the metal halide. The increase in the partial positive charge of the Brønsted hydrogen atom suggests an increase in the ability of the site to donate a proton to a co-adsorbed base molecule.



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Our results demonstrate synergy between the zeolite and the metal halide that apparently enhances the zeolite Brønsted site [8]. First, we establish the reactivity of the 1 : 1 zeolite/metal halide composite material in n-hexane and n-butane isomerization and cracking reactions at room temperature and at 273 K. The reactions were studied with both batch and differential plug-flow reactor methods, using gas chromatography and mass spectroscopy to analyze the reaction products. Second, we found that if the sodium form of the zeolite is used in the preparation of the composite material instead of the hydrogen form, the resulting material shows significantly reduced reactivity in the alkane cracking and isomerization reactions. Third, use of deuterated zeolite results in deuterium exchange into the alkane molecules at room temperature. These results, when taken collectively, are consistent with the Brønsted description of the active site in the composite material. Finally, we discuss the enhancement in the chemical reactivity in terms of acetone NMR chemical shifts, as a probe of the relative strength of the acid sites in both metal halide-doped and undoped zeolite.

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[1] Preliminary electronic calculations were performed on the cluster MX_3–$H_3SiOAlH_2OHSiH_3$ using *Gaussian 94*, version E, at the Hartree–Fock level with MP2 electron correlation energies. The calculated decrease in energy on formation of the complex from isolated molecules is 26 kcal/mol for BCl_3, and is highly dependent on the choice of metal and halide atoms.

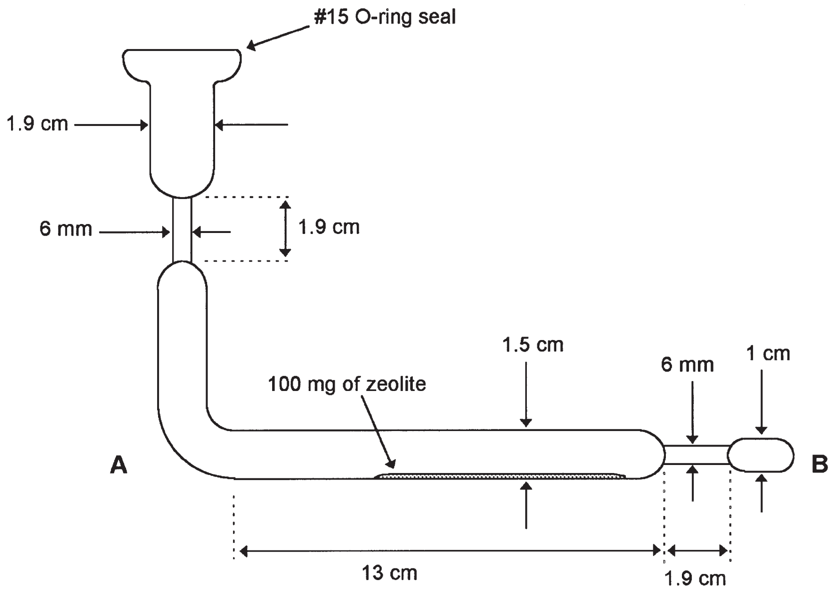

Figure 1. Glass tube used in the preparation of the samples for the alkane cracking reactions and acetone NMR measurements.

2. Experimental

Two different zeolite samples obtained from the PQ Corporation were used in this study. The HY sample has a bulk Si/Al_2 ratio of 5.3 and was steamed until the lattice parameter was 24.52 Å, corresponding to $\sim$30 Al atoms per unit cell [9]. The porosity of this sample was 0.321 cm^3/g as measured with O_2 uptake at $P/P_0 = 0.4$ and 77 K. The Brønsted site concentration of this material, determined using TGA of isopropylamine [10], was 850 μmol/g. The porosities of the 1 : 1 composite materials prepared from SbF_5, BCl_3, and BF_3 were 0.177, 0.173, and 0.232 cm^3/g, respectively [5]. The NaY sample was also obtained from PQ and also had a bulk Si/Al_2 ratio of 5.3. This sample was unsteamed and does not contain Brønsted sites as measured with the isopropylamine TGA technique [11].

The batch alkane cracking reactions were conducted over zeolite samples that were sealed in small glass ampoules. The zeolite was first weighed under vacuum at 750 K, and then carefully placed into L-shaped glass sample tubes [12], shown schematically in figure 1. The sample was spread in a thin layer along the horizontal portion of the tube, labeled as A in figure 1. The tubes containing the zeolite were then evacuated for $\sim$12 h at 750 K until the vacuum manifold reached its background pressure of 1.0×10^{-5} Torr. The samples were cooled to liquid nitrogen temperature and exposed to calibrated volumes of metal halide vapor so that the metal halide coverage on the sample was 1.0 molecule per Brønsted site. The samples were warmed to room temperature, exposed to 70 Torr of n-hexane or n-butane vapor, and sealed with a gas torch. The samples were then tapped into the small ampoule, section B in figure 1, and sealed a second time. Care was taken to keep the ampoules cold during the sealing process.

The ampoules were transferred under an inert atmosphere into a sealed glass tube equipped with a rubber septum, shown schematically in figure 2. After various lengths of time, the ampoules were cracked with the steel rod and the desorbing gases were analyzed using gas chromatography. The gas chromatograph was a Hewlett Packard model 5890 equipped with an AT alumina column, a flame ionization detector, and a mass spectrometer. The column was held at 60 °C for 1 min, ramped to 160 °C at 50 °C/min, and held at 160 °C for 2.5 min. For the flow re-

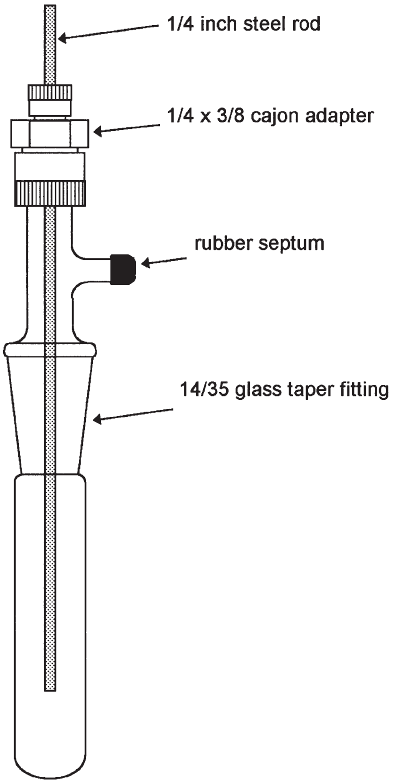

Figure 2. Apparatus used to crush the ampoules containing the zeolite/hexane mixture without exposure to significant amounts of room air.

actor experiments described below, the gas chromatograph was run isothermally at 160 °C in order to decrease the waiting time between runs.

In order to study the role of the zeolite Brønsted acid site in the cracking reactions in the modified zeolites, the cracking reactions were repeated using deuterated zeolite. The HY sample was first outgassed as described above, cooled to room temperature, and then exposed to 15 Torr of D_2O vapor for 30 min. The sample was evacuated and then exposed to D_2O a second time. Deuterium exchange into the zeolite Brønsted site using this technique has been previously verified with infrared spectroscopy [13]. The deuterated sample was then outgassed at 750 K, treated with metal halide vapor and n-hexane, and then sealed as described earlier.

In attempt to more carefully quantify the kinetics of the alkane cracking reaction, we examined the conversion of n-hexane in a differential plug-flow reactor. The reactor consisted of a 12 inch length of 3/8 inch diameter steel tubing with thermocouples attached to the external surface at various positions along the length of the tube. The reactor was filled approximately halfway with finely ground quartz chips, a small piece of pyrex wool, 100–120 mg of catalyst sample, and another piece of glass wool. The balance of the reactor volume was filled with additional quartz chips. The quartz chips served to preheat the reactant gases and to reduce the residence time of the reactor. Reactant gases were introduced by bubbling nitrogen carrier gas through a gas-tight bottle of n-hexane maintained at 0 °C in an ice bath. The nitrogen pressure was regulated at 10 psig, which was sufficient to maintain a flow rate of 10 cm^3/min through the reactor. Reactant and product gases were analyzed online using the chromatography techniques described earlier. For the low temperature 0 °C reactions, the entire reactor was immersed in an ice bath and equilibrated under flowing N_2 for 1 h prior to the introduction of n-hexane.

3. Results

3.1. Batch n-hexane and n-butane cracking and isomerization reactions

The results of the batch n-hexane cracking and isomerization reactions are reported in table 1 for HY and NaY treated with 1 molecule per Brønsted site of SbF_5, BCl_3, and BF_3. The conversion over 1 : 1 HY/SbF_5 after 1 h at room temperature is 71.7% and increases to 91.0% if the sample is warmed to 373 K. The conversion over HY treated with BCl_3 or BF_3 is somewhat lower, 31.0 and 15.7%, respectively. Under identical conditions but in the absence of metal halide, the HY starting material shows a conversion of only 0.6%, and this is probably due to a small amount of thermal cracking which probably occurred on flame sealing the glass ampoules. The untreated HY shows significant conversion only at elevated temperatures for prolonged periods. We observe 9.3% conversion when the sample is heated to 373 K for 15 h.

Table 1
Results of the batch n-hexane cracking experiments.

Sample	Reaction conditions	Conversion[a] (%)
HY/SbF_5	295 K, 1 h	71.7
HY/SbF_5	373 K, 4 h	91.0
HY/BCl_3	295 K, 1 h	31.0
HY/BF_3	295 K, 1 h	15.7
HY	295 K, 1 h	0.6
HY	373 K, 15 h	9.3
NaY/SbF_5	295 K, 1 h	10.2
NaY/BCl_3	295 K, 1 h	0.5
NaY/BF_3	295 K, 1 h	0.3
NaY	295 K, 4 h	0.2

[a] The GC analysis was conducted on the vapor phase. The standard deviation in the measurement was less than 0.9% in all cases.

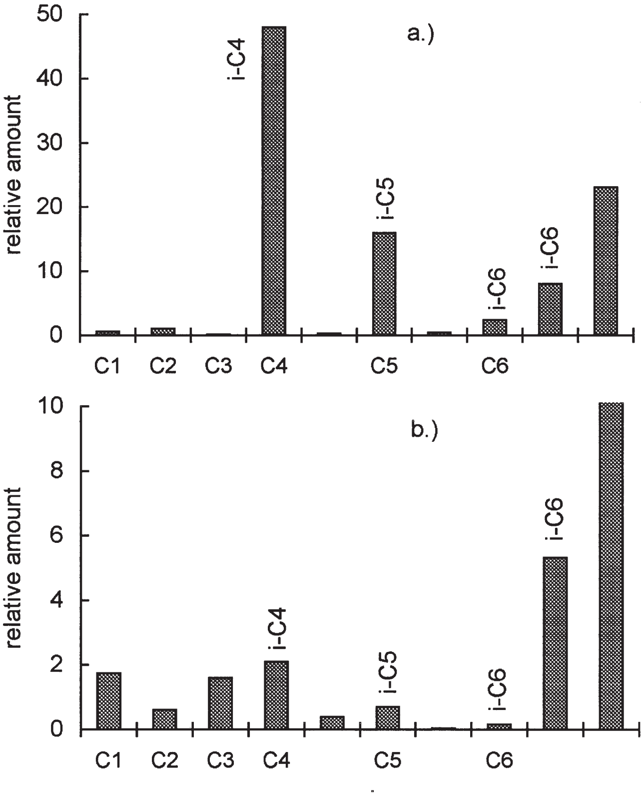

Figure 3. Product distributions in the alkane cracking reaction, measured over (a) 1 : 1 HY/SbF_5 and (b) HY.

A representative product distribution for the n-hexane cracking reaction is shown in figure 3(a). The products of the n-hexane cracking reaction on the various metal halide-treated zeolites were primarily 2-methylpropane and 2-methylbutane. We also observed smaller amounts of methane, ethane, propane, n-butane, and n-pentane. Significant quantities of 2-methylpentane and 2,2-dimethylbutane also form during the reaction. The relatively large amount of 2-methylpropane and 2-methylbutane without corresponding amounts of ethane or methane suggests that these products are not derived from the direct cracking of n-hexane, but rather from a higher molecular weight alkylated intermediate. The product distribution obtained from the undoped zeolite is shown in figure 3(b) for comparison. The main difference here is the appearance of a significantly greater amount of methane, ethane, and propane as primary cracking products.

Previous thermogravimetric studies suggest that the metal halide molecules are coordinating with the zeolite Brønsted sites on adsorption from the gas phase [5]. An important question is whether this complex is responsible for the observed catalytic activity of the composite material in the cracking reaction. We examined the role of the zeolite Brønsted acid site by substituting NaY for HY, and the results are shown in table 1 for comparison with the results obtained with HY. Of the samples examined, only SbF_5/NaY shows appreciable reactivity, with a conversion of 10.2%, most likely due to a Lewis acid alkane cracking pathway. The BCl_3- and BF_3-treated NaY samples are inactive and are indistinguishable from the pure NaY used in our study. As another reference state, one could compare the activity of the metal halide in the absence of zeolite. Olah and co-workers [14–16][2] have shown that SbF_5 yields a total conversion to products in isobutane cracking of 3.6% after 280 h at room temperature. SbF_5 was the most active of the metal halides used in this study.

To further explore the nature of the acid site, we compared the HY and deuterated HY zeolite, both treated with 1 : 1 SbF_5, in the n-hexane isomerization and cracking reactions. Deuterium exchange into hydrocarbons from deuterated HY has been reported previously, although at higher temperatures [17]. While deuteration of alkanes does not directly prove that the Brønsted site is actually involved in the cracking reaction, proton transfer to the alkane is widely regarded as a first step in the cracking process. Our results demonstrate that the zeolite/metal halide complex is capable of transferring a proton to the adsorbed alkane molecule, even at room temperature, and even though alkanes have a relatively low proton affinity [8]. The reaction products were analyzed with the mass spectrometer, and representative mass spectra for the 2-methylpentane isomer product are shown in figure 4. Figure 4(a) shows the results obtained for the undeuterated HY. The position and relative intensity of each of the primary mass spectral features are in excellent agreement with the published mass spectrum for 2-methylpentane [18]. Figure 4(b) shows the results obtained from the deuterated HY sample. Each of the primary mass spectral features appears to have increased by one mass unit, consistent with deuterium incorporation into the alkane molecule. For example, we see significant signal in the parent peak region, at $m/z = 85$, 86, and 87 in the undeuterated sample. The same m/z region has features at 85, 86, 87, 88, and 89 when DY is substituted for HY. As another example, we observe large features at $m/z = 70$, 71, 72, 73, and 74 for the deuterated zeolite, while the undeuterated sample shows features at $m/z = 70$, 71, and 72.

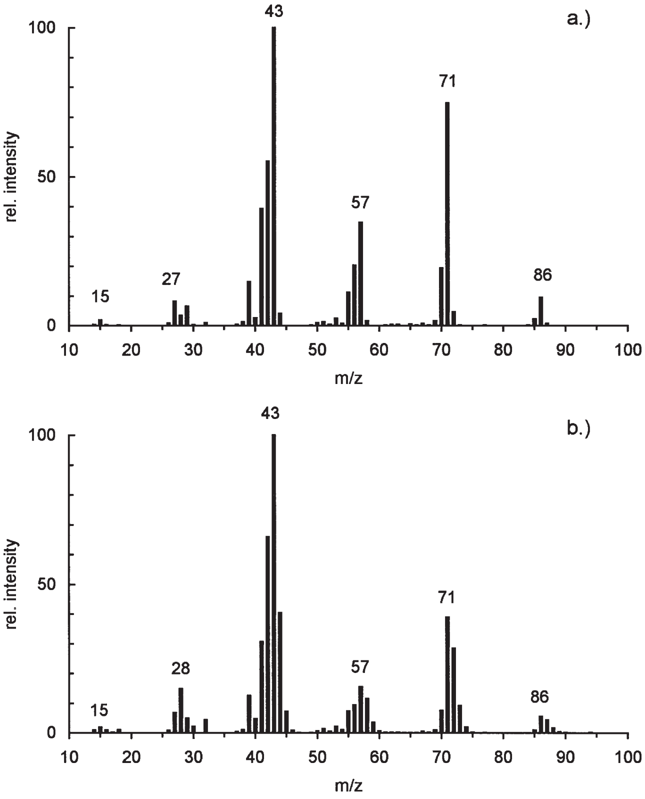

Figure 4. Mass spectral data for 2-methylpentane product peak in the (a) undeuterated and (b) deuterated HY samples.

Table 2
Results of the batch n-butane cracking experiments.

Sample	Reaction conditions	Conversion[a] (%)
HY/SbF_5	295 K, 1 h	15.9
HY	295 K, 1 h	0.6
NaY/SbF_5	295 K, 1 h	0.2

[a] The GC analysis was conducted on the vapor phase. The standard deviation in the measurement was less than 0.9% in all cases.

The cracking experiments were repeated using n-butane in place of the n-hexane for the SbF_5-treated materials, and the results are shown in table 2. As in the case of n-hexane, we see that the HY/SbF_5 sample is significantly more active in the cracking reaction than either the pure HY or the NaY/SbF_5 samples. Once again, the absence of significant quantities of reaction products in NaY/SbF_5 compared to HY/SbF_5 suggests that the zeolite Brønsted acid site is playing an important role in the reaction.

3.2. Plug-flow reactor

In order to examine the stability of the catalyst as well as turnover in the alkane cracking reaction, we examined the reaction using a differential plug-flow reactor. In these experiments, we measured the total conversion of n-hexane as a function of time on stream. Representative data are shown in figure 5. The conversion of n-hexane increased toward a maximum at 400 s. This is most likely an induction period similar to that reported for metal-promoted

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[2] An extensive review of reactions of alkanes on Lewis acids can be found in [16].

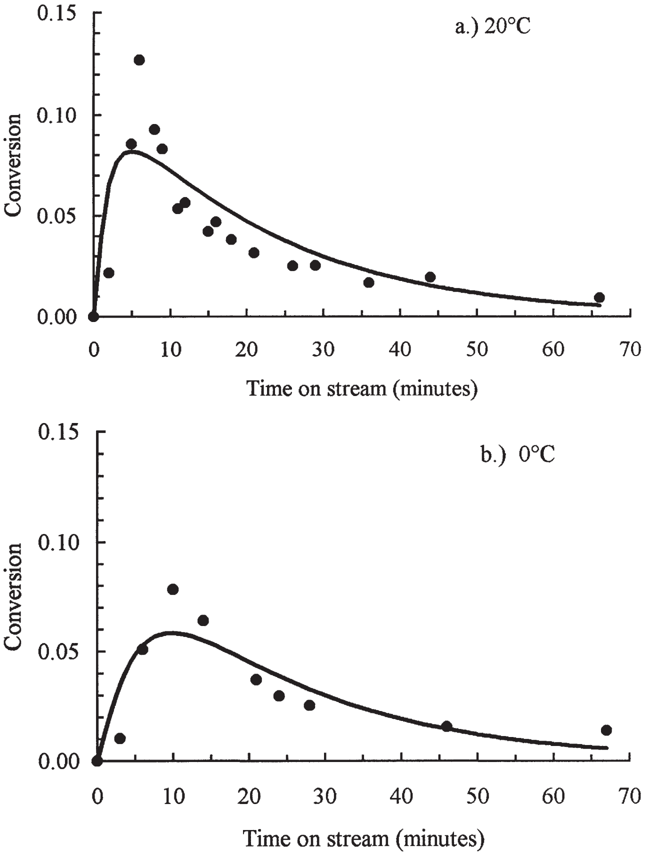

Figure 5. Conversion versus time on stream for the n-hexane cracking reaction in a differential plug-flow reactor measured at (a) room temperature and (b) 0 °C.

sulfated zirconia catalysts [1]. Other possibilities include deactivation due to coking or loss of HF or HCl from the catalyst. However, we note here that neither HF nor HCl was observed in the mass spectra of the desorbing species. After the induction period, the conversion decreases as a function of time on stream, from a maximum of 12.7% to a value of ~1% which persists for up to three hours, the longest time used in our study.

We have modeled the reactor response using an open system, transient mass balance assuming first-order decomposition of n-hexane. The results are shown as the smooth curves in figure 5. We also assumed that the catalyst is deactivated by a coking-type mechanism, perhaps by formation of a polymeric film on the catalyst surface which then blocks active sites. In this case the activity of the catalyst is given by $a = 1/(1 + k_\mathrm{d}t^2)$, with the rate of decomposition of n-hexane then given as $r' = ra$ [19]. We also tried using a non-zero activity at infinite times, obtained as a non-zero steady-state activity [20], but this did not significantly improve the fit at short times. Under these conditions, the fitted values for the first-order rate constant are 2.4 and 0.59 min^{-1} at 20 and 0 °C, respectively, giving an activation energy of 11.2 kcal/mol. The deactivation rate constant k_d was 0.40 min^{-1} at 20 °C and 0.031 min^{-1} at 0 °C, giving and activation energy of 20.3 kcal/mol. Finally, we note that the concave-up nature of the conversion data at very short times can be modeled with series kinetics, which provides time for the buildup of reactive intermediates. This will necessarily involve many more parameters in the curve fit, that is, adsorption and desorption rates for each species would have to be accounted for. This would obviously provide a much more accurate curve fit, but is beyond the scope of this initial study.

4. Discussion

The incorporation of metal halides into solid oxide supports is a very attractive idea [2–6,21–26]. The handling of materials such as BF_3 or SbF_5 is greatly simplified if they can be bound to solid supports. It may also be possible to replace HF in chemical processes with H-zeolite or other Brønsted acid solids, to prepare solid acids analogous to HF/BF_3 or HF/SbF_5. The use of zeolites in particular has other distinct advantages because of the large variety of highly uniform pore structures that are available. Earlier work with zeolites has shown that the acidity of the Brønsted site, as measured with CO adsorption, can be enhanced by coadsorption of metal halides [6]. However, application of a zeolite-based catalyst in chemical reactions has been somewhat limited [2,3].

In a recent study, Getty and Drago [3] examined $AlCl_2$-functionalized oxides, including silicalite and Y-zeolite, with both batch and flow reactor studies of small alkanes, and observed significant isomerization and cracking reactions as low as 100 °C. In one series of flow reactor experiments in [3], HCl was used in the feed and produced conversions as high as 75% at 175 °C. The strong Lewis acid sites in the materials probably interact with HCl to produce tetrahedral Brønsted sites of the type depicted in structure **1**. Our earlier study [5] provided experimental evidence for the formation of this complex on initial adsorption of the metal halide. The present paper establishes that this complex provides significantly more acidic sites, capable of protonating and cracking alkanes at room temperature and below. While the composite materials in our study do not appear to be as stable as those formed on removal of a molecule of hydrogen halide from the complex, much higher activity is apparently achieved. Given the wide diversity of metal halides and zeolites available for the formation of the complex, it should be possible to produce a stable co-acid system by this route.

In another important study which was very similar to this one, Tanab et al. [2] observed that “only non-ion-exchanged molecular sieves 13X became a superacid, while other zeolites, such as ion-exchanged Y- and A-type zeolites, did not exhibit superacidity on SbF_5 treatment”. In [2], superacidity was examined using Hammett bases and probe reactions of alkanes. We note that those results are significantly different from what is reported in the present study. We propose that pore blockage may be significant at the higher metal halide loading used by Tanabe. In our previous study, we noted that zeolites will adsorb metal halides

Table 3
Comparison of n-hexane cracking conversions and acetone NMR shifts.

Sample[a]	Partial charge on Brønsted hydrogen[b]	Acetone C2 ^{13}C chemical shift[c]	Conversion (%) on HY/MX$_n$
HZSM5/SbF$_5$	–	249.3	71.7
HZSM5/BCl$_3$	0.535	236.5	31.0
HZSM5/BF$_3$	0.552	230.0	15.7
HZSM5	0.520	223.6	–
HY[d]	0.520	233, 223	0.6

[a] The HZSM5 sample is fully described in [5].
[b] Determined using methods outlined in footnote 1.
[c] Measured in ppm from TMS, as in [5].
[d] See [27]. Unsteamed HY shows a chemical shift of 219 ppm.

at room temperature until the zeolite pores are essentially filled [5]. It is our opinion that only at very low concentrations, near or below one molecule per acid site, is sufficient porosity available to accommodate adsorbate molecules for use as probes of acidity. Even at moderately low coverages it is possible for local concentrations to be high enough to significantly restrict mass transport within the pores.

In our previous work, the acidic properties of the metal halide-treated zeolites were investigated using ^{13}C NMR of adsorbed acetone [5]. The chemical shift of the carbonyl carbon of acetone dissolved in acidic solvents is known to be influenced by the nature of the solvent. In weak solvents, changes in the chemical shift are due to an increase in the deshielding of the carbonyl carbon as the strength of the hydrogen bonds between acetone and the solvent molecules is increased. In very strong acids, where the fraction of protonated acetone molecules is significant, the chemical shift is dominated by the protonated acetone molecule. In pure untreated zeolites, one observes that the acetone carbonyl shift is consistent with the hydrogen-bonding model. In zeolite which has been doped with SbF$_5$, the chemical shift of the carbonyl carbon in acetone corresponds very closely to that observed in superacids.

The carbonyl chemical shifts of acetone adsorbed in metal halide/zeolite composites are listed in table 3, along with a comparison with the conversions in the batch alkane cracking reactions from table 1. H-ZSM-5 was chosen as a co-acid for this comparison since the smaller pore size suppresses bimolecular side reactions and the absence of non-framework Al simplifies interpretation of the NMR data. The extent of conversion in the closed, batch system is used as a measure of catalyst activity [3]. The chemical shift, which corresponds with the deshielding of the carbonyl carbon, seems to be closely correlated with the conversion. Even though in some cases the chemical shift of adsorbed acetone is not as high as that observed in AlCl$_2$-functionalized silica [26], significant alkane cracking is observed. These data suggest that the activity of the metal halide/zeolite composite can be altered by the choice of metal halide, providing the potential of the development of a stable solid superacid, and for significant control over catalyst activity.

5. Conclusions

In this work, we have demonstrated that zeolites that are doped with small amounts of metal halides are active in the cracking and isomerization of n-hexane and n-butane at room temperature. Sodium-exchanged zeolites which are doped with metal halides at comparable coverages are relatively inactive in the reaction, demonstrating that the materials are Brønsted acids. This conclusion was further verified with deuterium exchange into the catalyst.

Acknowledgement

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References

[1] S. Rezgui and B.C. Gates, Catal. Lett. 37 (1996) 5.
[2] K. Tanabe, H. Hattori and T. Yamaguchi, Crit. Rev. Surf. Chem. 90 (1990) 1.
[3] R.S. Drago and E.E. Getty, J. Am. Chem. Soc. 110 (1988) 3311; E.E. Getty and R.S. Drago, Inorg. Chem. 29 (1990) 1186.
[4] T.H. Clingenpeel and A.I. Biaglow, J. Am. Chem. Soc. 119 (1997) 5077.
[5] W.P. Fletcher, C.S. Gilbert and A.I. Biaglow, Catal. Lett. 47 (1997) 135.
[6] M.A. Makarova, S.P. Bates and J. Dwyer, J. Am. Chem. Soc. 117 (1995) 11309.
[7] V. Adeeva, J.W. de Haan, J. Janchen, G.D. Lei, V. Schunemann, L.J.M. van de Ven, W.M.H. Sachtler and R.A. van Santen, J. Catal. 151 (1995) 364.
[8] V.B. Kazansky, React. Kinet. Catal. Lett. 35 (1987) 237.
[9] J.R. Sohn, S.J. Decanio, J.H. Lunsford and D.J. O'Donnell, Zeolites 6 (1986) 225.
[10] W.E. Farneth and R.J. Gorte, Chem. Rev. 95 (1995) 615.
[11] A.I. Biaglow, D.J. Parrillo and R.J. Gorte, J. Catal. 144 (1994) 193.
[12] A.I. Biaglow, Ph.D. thesis, University of Pennsylvania (1993).
[13] W.E. Farneth, D.C. Roe, T.J. Gricus Kofke, C.J. Tabak and R.J. Gorte, Langmuir 4 (1998) 152.
[14] G.A. Olah, J. Kaspi and J. Bukala, J. Org. Chem. 42 (1977) 4187.
[15] G.A. Olah, US Patent 4,116,880 (1978).
[16] G.A. Olah, G.K. Surya Prakash and J. Sommer, *Superacids* (Wiley, New York, 1995) p. 261.
[17] C.J.A. Mota, L. Nogueira and W.B. Kover, J. Am. Chem. Soc. 114 (1992) 1121.
[18] S.R. Heller and G.W.A. Milne, *EPA/NIH Mass Spectral Data Base*, Vol. 1 (US Department of Commerce, 1978).
[19] H.S. Fogler, *Elements of Chemical Reaction Engineering* (Prentice-Hall, Englewood Cliffs, 1992) p. 289.
[20] G.A. Fuentes, Appl. Catal. 15 (1985) 33.
[21] R.M. Smith, US Patent 2,927,087 (1956).
[22] J.T. Kelly, W. Schoen and C.N. Sechrist, US Patent 3,248,343 (1966).
[23] J.W. Myers, US Patent 3,449,264 (1969).
[24] G.A. Olah and G. Messina, US Patent 3,993,587 (1976).
[25] S. Herbstman and A.N. Webb, US Patents 4,113,657 and 4,066,716 (1978).
[26] T. Xu, M. Kob, R.S. Drago, J.B. Nicholas and J.F. Haw, J. Am. Chem. Soc. 119 (1997) 12231.
[27] A.I. Biaglow, R.J. Gorte and D. White, J. Catal. 150 (1994) 221.