An evaluation of acid sites in fluorinated SmNaY zeolites

S. Kowalak, M. Łaniecki
A. Mickiewicz University, Faculty of Chemistry, Poznan, Poland

A.K. Khanmamedova and K.J. Balkus Jr.
University of Texas at Dallas, Department of Chemistry, Richardson, TX 75083-0688, USA

Received 14 July 1993; accepted 11 November 1993

A Sm(III) exchanged NaY zeolite prepared from aqueous $SmCl_3$ was modified with various amounts of fluorine using NH_4F. These fluorinated zeolites exhibit enhanced catalytic activity for the dealkylation of cumene. The evaluation of acid sites by infrared spectroscopy and pyridine adsorption was correlated with fluorine content.

Keywords: Zeolites NaY; fluorination; cumene cracking

1. Introduction

The gentle fluorination of oxide catalysts such as alumina, silica–alumina and zeolites has been shown to be an effective method for enhancing acid strength and catalytic activity [1]. Given the commercial importance of lanthanide exchanged zeolites we have initiated a study of RE-Y and X zeolites modified with fluorine. We have found the dehydration of methylbutyraldehyde catalyzed by SmNaY was improved upon fluorination [2]. We have also explored the effects of fluorine on other rare earth exchanged zeolite catalyzed dehydration processes [3] as well as model cracking reactions [4,5]. We were surprised to find the nature and behavior of Sm(III) exchanged NaY zeolites modified with fluorine were significantly different from other fluorinated zeolites [6]. In particular, SmNaY is stable during fluorination using a variety of fluorine sources. This is in sharp contrast to other polyvalent cation exchanged zeolites where substantial dealumination and loss of crystallinity occurs upon fluorination [7]. The stability of SmNaY appears to arise from the fact that the fluorine largely coordinates to the Sm(III) eventually generating intrazeolite SmF_3. We have found the nature of the exchanged Sm(III) affects the fluorination and reactivity of the zeolite. This can be further affected by the solution pH and counterion associated with samarium during exchange. In this paper we report the synthesis and characterization of fluorinated SmNaY where the zeolite was exchanged with $SmCl_3$. The zeolite acid sites were evaluated by pyridine adsorption and infrared analysis. The dealkylation of cumene was used as a model reaction to measure catalytic activity as a function of fluorine loading. Additionally, further evidence for the formation of SmF_3 is presented.

2. Experimental

The cation exchange of NaY (LZY-52, Si/Al = 2.7) using $SmCl_3$ was conducted as previously described [5]. NaY zeolite (112 g) was treated four times with 500 ml aliquots of a 0.07 M aqueous solution of $SmCl_3$ (Aldrich) at 65°C. The zeolite was stirred with each portion for 3 h. The initial pH was 2.5 which increased to 4 after the first exchange. The last exchange did not result in a solution pH change. The Sm(III) exchanged zeolite was suction filtered, washed with deionized water until the filtrate tested negative for chloride ion ($AgNO_3$) and then dried at 100°C overnight. This sample, SmNaY contains 11.07% Sm by weight.

The fluorination of SmNaY was conducted as previously described [5]. NH_4F was deposited in SmNaY using an incipient wetness technique. The impregnated samples were dried at 100°C for 15 h and then at 450°C overnight. The fluorine analyses for samples SmNaY-1, -2, -3, -4 and -5 are listed in table 1.

XRD powder patterns were obtained using a Scintag XDS 2000 diffractometer with CaF_2 as an internal standard. Infrared spectra were obtained from self supporting wafers (~ 3–4 mg/cm^2) using a Bruker IFS-133v and a Matson 2025 FT-IR spectrophotometer. The zeolite wafers were calcined at 450°C in a high temperature vacuum IR cell in a stream of helium for 3 h and then cooled under helium. After calcination pyridine (10 μl) was adsorbed at room temperature, purged with helium for 1 h at room temperature and then at 200°C for 2 h. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Catalytic cracking of cumene was evaluated using a pulsed microreactor interfaced to a Hewlett Packard model 5700A gas chromatograph equipped with an FID detector. The zeolite (10 mg) was loaded into the reactor and activated at

Table 1
Fluorine content of modified SmNaY zeolites

Sample	NH_4F/SmNaY (mg/g)	F (wt%)	F/Sm ratio
SmNaY-F-1	13.16	0.50	0.36
SmNaY-F-2	26.49	0.85	0.60
SmNaY-F-3	48.15	2.05	1.50
SmNaY-F-4	74.14	2.91	2.14
SmNaY-F-5	100.76	3.70	2.74

450°C for 30 min under a flow of nitrogen (30 ml min^{-1}). The reactor was cooled to 300°C then 1 μl of cumene was injected by syringe. Products were separated using a 1/8″ SS column, 1.5 m long, containing polyphenyl ether on chromsorb.

3. Results and discussion

The impregnation of NH_4F in SmNaY followed by calcination results in decomposition of the ammonium salt and the introduction of protons and fluorine to the zeolite lattice. Table 1 lists the amount of NH_4F used during impregnation and the resulting amount of fluorine in the zeolite after calcination. There is a near linear relationship between the amount of fluoride used and the level of fluorine incorporated. The molar ratio of fluorine to samarium approaches 3 : 1 at the highest loading. If the fluorine is coordinating to the samarium, then we anticipate the physical properties and reactivity might begin to deviate at this higher loading.

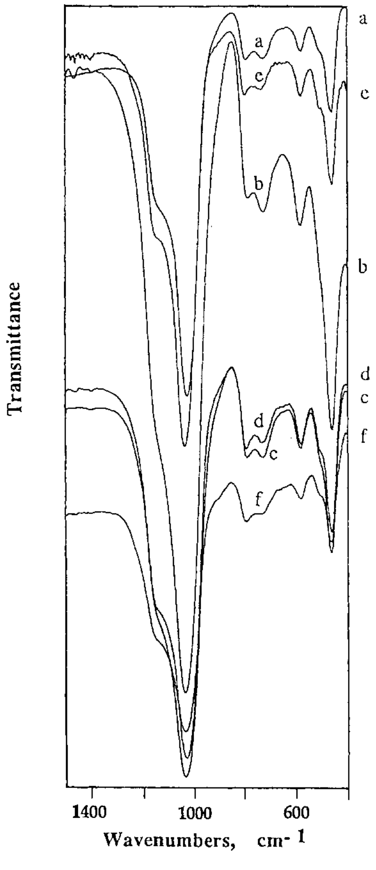

Fig. 1. FT-IR spectra of (a) SmNaY, (b) SmNaY-F-1, (c) SmNaY-F-2, (d) SmNaY-F-3, (e) SmNaY-F-4 and (f) SmNaY-F-5.

The fluorination of NaY zeolites exchanged with polyvalent cations has resulted in dealumination and partial decomposition of the framework [7]. Additionally, the deeper the fluorination level the worse the dealumination. This is presumably the result of fluorine coordination to aluminum and elimination of hydroxyl groups. In the case of Sm(III) exchanged NaY, both IR and XRD analyses indicate there are only minor effects on the lattice. The mid-FT-IR spectra shown in fig. 1 indicate there is an ~ 10 cm^{-1} shift to higher wavenumbers upon fluorination for all samples. However, the main asymmetric stretch (~ 1034 cm^{-1}) is invariant between samples regardless of fluorine loading. This is in sharp contrast to other polyvalent cation exchanged Y zeolites such as AlNaY where significant dealumination occurs even at low fluorination levels [1]. Therefore, it would appear the presence of Sm(III) serves to protect the lattice.

The XRD results indicate a slight decrease in the SmNaY crystallinity (~ 5% for samples 1–4 and ~ 20% for sample 5) upon fluorination. The lack of significant IR band shifts that would be associated with dealumination suggests the small decrease in pattern intensity reflects the formation of bulk SmF_3. Fig. 2 shows the XRD patterns for samples SmNaY-F-3 and SmNaY-F-5 which clearly indicate the presence of SmF_3.

In order to evaluate the fate of the generated protons and the effects of fluorine on these sites we have examined the FT-IR spectra of the Brønsted sites before and after pyridine adsorption. Fig. 3 shows the IR spectra of SmNaY and fluorinated samples in the region 3800–3450 cm^{-1}. The exchange of NaY with $SmCl_3$ results in

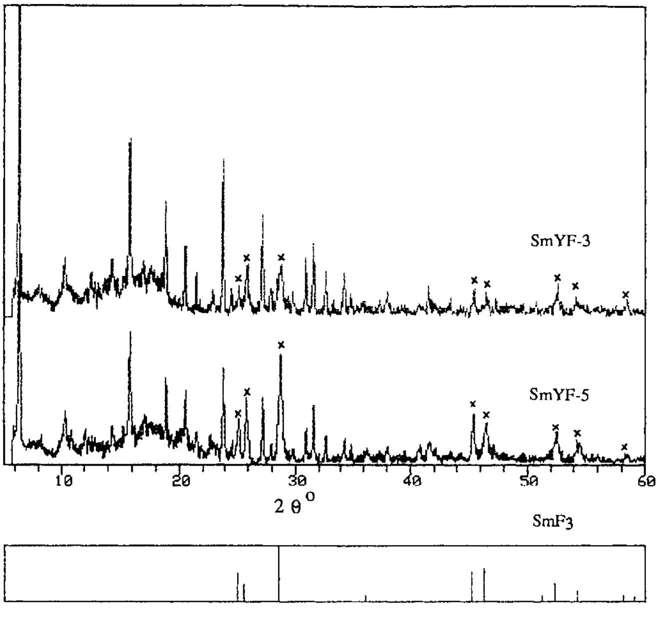

Fig. 2. XRD patterns for SmNaY-F-3 and SmNaY-F-5 where the reflections marked with an × correspond to SmF_3.

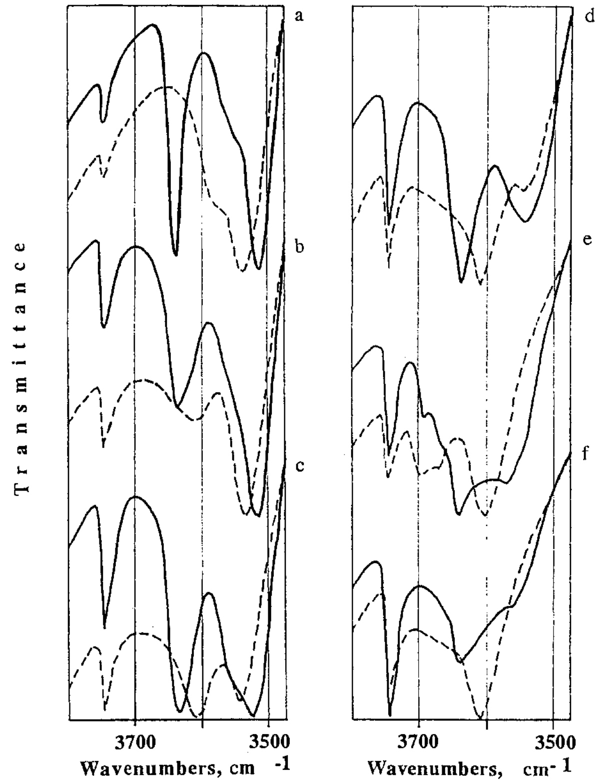

Fig. 3. FT-IR spectra of hydroxyl region before (——) and after (— — —) pyridine adsorption on (a) SmNaY, (b) SmNaY-F-1, (c) SmNaY-F-2, (d) SmNaY-F-3, (e) SmNaY-F-4 and (f) SmNaY-F-5.

formation of hydroxyls with IR bands at 3745, 3640, 3563(sh) and 3515 cm^{-1}. The assignment of these bands is generally well known [8–10]. The external silanols (3745 cm^{-1}) are unaffected by fluorination. The shoulder at 3563 cm^{-1} has not been assigned but does not seem to be influenced by fluorine modification. The supercage hydroxyls (3640 cm^{-1}) initially decrease in intensity upon fluorination but then increase with a maximum for sample SmNaY-F-4 as shown in fig. 4. The fluorine may react with these Brønsted sites but samarium competes for fluorine as evidenced by formation of SmF_3 noted above. Additionally, the added NH_4^+ ions create new hydroxyls. The 3515 cm^{-1} band is dramatically affected by fluorination and is virtually all but lost at high fluorine loadings. Two additional bands at 3690 and 3550 cm^{-1} grow in with increasing fluorine loading. The high frequency band is similar to adsorbed water but may also be supercage hydroxyls shifted by inductive effects. The fluorination of samarium may lead to more electron density in the oxide lattice which would result in stronger OH bonds. The 3550 cm^{-1} band may be D6R hydroxyls that shift to higher frequency with increasing fluorine content. The relative intensities of all the hydroxyl bands are summarized in table 2.

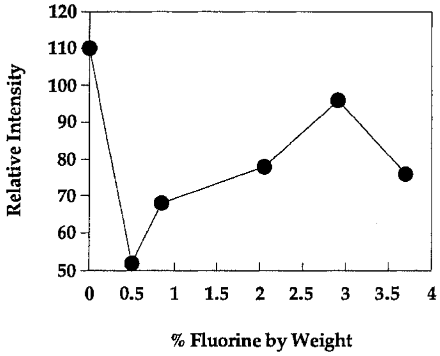

Fig. 4. Plot of peak intensity for the band at 3640 cm^{-1} versus zeolite fluorine content.

These results contrast samples prepared from samarium acetate where there was only a loss in supercage hydroxyls upon fluorination [5].

Fig. 3 also shows the IR spectra (broken lines) of SmNaY and fluorine modified samples after pyridine adsorption. For SmNaY (fig. 3a) the loss of the 3640 cm^{-1} band and a 20 cm^{-1} shift for the 3515 cm^{-1} band after pyridine treatment is a near textbook result. The shift in the 3515 cm^{-1} band has been attributed to an inductive effect from adsorbed pyridine [11]. Similar effects have been noted for adsorbed benzene [12]. The shoulder at 3563 cm^{-1} also shifts to 3573 cm^{-1}. For the fluorine modified samples the 3640 cm^{-1} band also disappears. The 3515 cm^{-1} shifts while the 3550 cm^{-1} band that appears with increasing fluorine content is lost upon pyridine adsorption (fig. 3 e and f). Additionally, a new band appears at 3600 cm^{-1} and increases in intensity with fluorine loading.

Pyridine adsorbs at both Brønsted and Lewis acid sites generating IR bands at 1542 and 1445 cm^{-1} respectively. The peak areas for these two bands listed in table 3 indicate an increase in the number of Brønsted sites but with a proportionately larger increase in the number of Lewis sites. Again these results are significantly different from samples prepared using samarium acetate where the Brønsted/Lewis acid ratio for the SmNaY sample was 4.9 and decreased even further with fluorine loading [5].

Table 2
Relative intensities of IR bands associated with hydroxyl groups

Sample	IR bands (cm^{-1})				
	3740	3690	3640	3550	3515
SmNaY	15	–	110	–	155
SmNaY-F-1	20	–	52	–	93
SmNaY-F-2	30	12	68	75	88
SmNaY-F-3	40	16	78	76	–
SmNaY-F-4	50	42	96	95	–
SmNaY-F-5	78	35	76	70	–

Table 3
Peak areas of IR bands associated with pyridine adsorption

Sample	$1524\,cm^{-1}$	$1445\,cm^{-1}$	B/L ratio
SmNaY	4.74651	0.07134	66.53
SmNaY-F-1	2.26862	0.15479	14.66
SmNaY-F-2	3.51086	0.17479	19.97
SmNaY-F-3	3.49211	0.28624	12.20
SmNaY-F-4	3.91092	0.47342	8.26
SmNaY-F-5	4.36631	0.63480	6.87

The dealkylation of cumene using a pulsed microreactor was employed as a model reaction to evaluate the acid sites. Fig. 5 shows a plot of cumene conversion after five pulses versus fluorine content. There is an initial decrease in activity followed by an increase with a maximum at sample SmNaY-F-3. This is similar to the plot of the number of supercage hydroxyls (fig. 4) and a faster flow rate actually results in a maximum in activity for SmNaY-F-4 but with a lower conversion. These results contrast the catalytic activity of fluorine modified SmNaY prepared from samarium acetate where there was no obvious enhancement in cumene conversion [5]. The pH of the exchange solutions were not adjusted and samarium acetate exchange occurred at pH ~ 7 while the $SmCl_3$ was at pH ~ 4. As the IR results indicate, there are more supercage hydroxyls formed in the modified SmNaY samples prepared from $SmCl_3$. This is not the result of ammonium ion introduced during fluorination as control experiments with ammonium carbonate do not lead to the observed activity enhancements [2].

4. Conclusions

The fluorine modification of samarium(III) exchanged NaY clearly affects the zeolite acid sites and catalytic activity. Although, they both depend on the nature of the exchanged metal ion. In this case the role of fluorine during catalysis appears

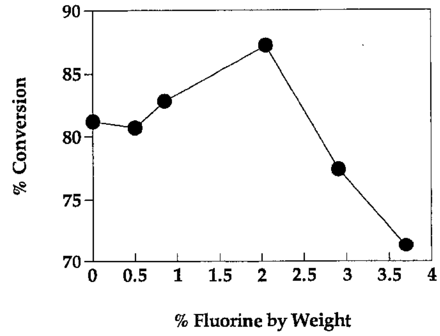

Fig. 5. Plot of cumene conversion versus zeolite fluorine content.

to extend beyond inductive effects. In order to rationalize the poor correlation between the number of supercage hydroxyls and catalytic activity a further understanding of the Sm and fluorine interactions is required. It is encouraging that a recent study of fluorinated USY catalysts suggests that strengthened Brønsted sites are not responsible for enhanced activity but rather some other as yet uncharacterized sites [13]. A unique aspect of our study is the presence of rare earth ions that appear to stabilize the lattice during fluorination. How these ions and resulting fluorides affect acid catalysis has become an interesting issue.

Acknowledgement

The financial support of the Polish Committee for Science Research (KBN) through grant No. 2-0765-91-01 is acknowledged (SK). Additionally, the support of the National Science Foundation (CHE-9157014) and the Robert A. Welch Foundation is greatly appreciated (KJB).

References

[1] S. Kowalak, Chemia Stosowana 34 (1990) 93.
[2] K.J. Balkus Jr., K. Nowinska and S. Kowalak, Catal. Lett. 9 (1991) 145.
[3] A.K. Khanmamdedova, K.J. Balkus Jr. and S. Kowalak, in preparation.
[4] K.J. Balkus Jr. and S. Kowalak, unpublished.
[5] S. Kowalak, M. Pawlowska and K.J. Balkus Jr., Collect. Czech. Chem. Commun. 57 (1992) 781.
[6] K.A. Becker and S. Kowalak, Stud. Surf. Sci. Catal. 52 (1989) 123.
[7] S. Kowalak, J. Chem. Soc. Faraday Trans. I 84 (1988) 2035.
[8] J.A. Rabo, C.A. Angell, P.H. Kasai and V. Schomaker, Discussions Faraday Soc. 41 (1960) 328.
[9] J.W. Ward, J. Phys. Chem. 72 (1968) 4211.
[10] J.W. Ward, J. Catal. 13 (1969) 321.
[11] P.E. Elberly Jr. and C.N. Kimberlin, Adv. Chem. Ser. 102 (1971) 374.
[12] P.A. Jacobs, J.A. Martens, J. Weitkamp and H.K. Beyer, Faraday Discussions Chem. Soc. 72 (1981) 351.
[13] S. Soled, G.B. McVicker, J.J. Ziemiak, G. DeMartin, L. Yacullo, K. Strohmaier and J. Miller, Petrol. Preprints 38 (1993) 546.