

## CATALYTIC PROPERTIES OF FLUORINE MODIFIED SmNa-Y ZEOLITES\*

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It is known that mild fluorination of zeolites, including those modified with polyvalent cations, increases their activity for acid catalyzed reactions. In this study we report the reactivity of fluorine modified Sm(III) exchanged zeolite NaY. Mild fluorination of SmNaY reduces the activity of strong protonic acid sites and increases the contribution of weak aprotic acid centres. Results for cumene cracking and toluene disproportionation as well as for 1-hexene isomerization are reported.

A substantial increase in acid strength has been found for mildly fluorinated alumina, silica-alumina and zeolites<sup>1-3</sup>. However, the crystallinity of sodium or hydrogen forms of low silicon zeolites (e.g. faujasites) is adversely affected by fluorination. It was found that the introduction of polyvalent cations (e.g. Al<sup>3+</sup>) into these zeolites before fluorine treatment prevents amorphization. The catalytic activity of fluorine modified Al-Y increases with fluorine content to a certain level, then further fluorination results in a decrease in activity. Catalytic reactivity as well as the nature of intrazeolite fluorine-containing species depends on the fluorination agent (e.g. gaseous CHF<sub>3</sub> or solution of NH<sub>4</sub>F) as well as on the type of zeolite and charge balancing cations.

The fluorinated species can play the role of an active site or interact with already existing centres (e.g. acidic OH groups). Rare earth-modified faujasite — type zeolites are widely employed as commercial catalysts. We are interested in effects of fluorination on the catalytic reactivity of these materials. Generally, Sm and Gd comprise a small percentage of REX and REY commercial catalysts. We have found that a mild fluorination of zeolite SmNa-Y (5% Sm) resulted in some activity rise for cumene cracking and toluene disproportionation<sup>5</sup>. The increase in activity, however, was not as dramatic as that for other fluorinated zeolites. In order to probe the

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influence of metal loading on the activity we have prepared zeolites with a higher Sm loading. The catalytic results for zeolite SmNa-Y (10.77% Sm) are presented in this study.

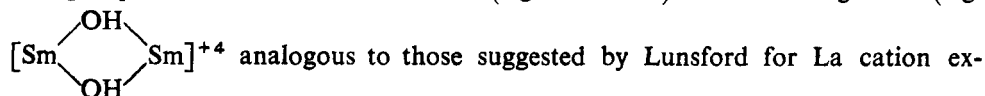
## EXPERIMENTAL

Zeolite Na-Y (LZY-52, Union Carbide) was treated three times with an aqueous solution of samarium acetate, then washed with deionized water and dried at 100°C. The resulting zeolite Sm-Y contained 10.77 wt. % Sm and 1.91% Na. The sample was treated with various amounts of NH<sub>4</sub>F using the incipient wetness technique. Sample Sm-Y-A-F-2 was calcined at 450°C for 16 h before fluorination in order to evaluate the effect of temperature treatment on stability. The fluoride treated samples were dried at 100°C and then calcined at 450°C in air for 16 h. Elemental analyses (Sm, Na, F) were performed by Galbraith Laboratories, Knoxville, TN.

Crystallinity of the modified samples was examined by XRD (TURM-62). Infrared spectra were recorded as KBr and polyethylene pellets on a Nicolet 5DX FT-IR and Bruker IFS-113v spectrophotometers. Spectra of OH groups (4 000–3 000 cm<sup>-1</sup>) were taken on Perkin Elmer 580 using self-supported wafers in a vacuum cell. Samples were evacuated at 450°C, 10<sup>-5</sup> torr, for six hours. Pyridine was absorbed at room temperature for an hour and then samples were evacuated at 150°C for two hours. The catalytic tests for cumene cracking, toluene disproportionation and 1-hexene isomerization have been carried out in a pulse microreactor attached to a gas chromatograph. The conditions are listed in Table I.

## RESULTS AND DISCUSSION

The SmNa-Y sample used in this study was calculated to have the following unit cell formula Sm<sub>12.5</sub>Na<sub>14.5</sub>(AlO<sub>2</sub>)<sub>52</sub>(SiO<sub>2</sub>)<sub>138</sub>. This formula does not include potential OH groups combined with Sm cations (e.g. SmOH<sup>2+</sup>) or cation oligomers (e.g.



change degree based on chemical composition was about 72%. Fluorine content in modified samples is listed in Table II.

TABLE I  
Reactor conditions

Reactant	Toluene	Cumene	1-Hexene
Catalyst, mg	10	10	10
He flowrate, ml/min	50	50	50
Activation temperature, °C	450	450	450
Reaction temperature, °C	450	350	150
Pulse, µl	0.5	1.0	1.0

XRD results indicate that the crystallinity of the fluorinated samples is preserved except for Sm-Y-F-6, where amorphization is evident. Contrary to earlier results on fluorinated zeolites, the XRD patterns of fluorine-rich samples indicate forming of a new crystalline phase. The new reflections are consistent with those for  $\text{SmF}_3$  (Fig. 1).

No significant influence of calcination before the fluorine treatment was observed. In the case of zeolites Al-Y calcination caused a reduction in crystallinity after fluorination<sup>4,6</sup> which was assumed to be the result of  $\text{Al}^{3+}$  cations migration and subsequent loss of the protective effect of these cations against fluorine. The only effect resulting from calcination is a slightly lower F content in sample Sm-Y-A-F-2 compared to Sm-Y-F-2.

TABLE II  
Fluorine content in zeolites SmNa-Y modified with  $\text{NH}_4\text{F}$

Sample	F, wt. %	mol F/mol Sm	mol F/unit cell
Sm-Y	—	—	—
Sm-Y-F-1	0.07	0.05	0.64
Sm-Y-A-F-2	0.41	0.30	0.75
Sm-Y-F-2	0.62	0.45	5.63
Sm-Y-F-3	0.93	0.68	8.50
Sm-Y-F-4	1.13	0.83	10.38
Sm-Y-F-5	2.34	1.72	21.50
Sm-Y-F-6	2.97	2.18	27.28

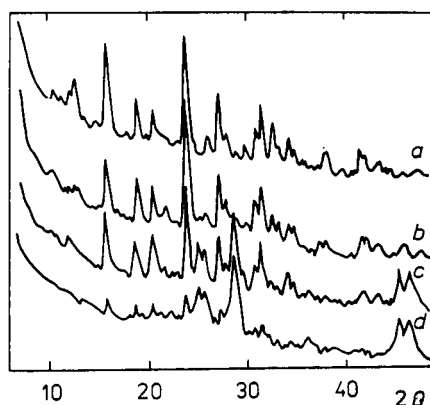


FIG. 1  
XRD patterns for selected samples: Sm-Y (a);  
Sm-Y-F-2 (b); Sm-Y-F-5 (c); Sm-Y-F-6 (d)

Similarly, in our recent study<sup>5</sup> on low samarium loaded zeolite Y we did not observe framework dealumination resulting from the fluorine treatment (except for sample Sm-Y-F-6). The mid-infrared spectra do not show any frequency shift of the stretching bands at ca 1 000 and 790  $\text{cm}^{-1}$  (Fig. 2). The IR spectra recorded in the range 500–100  $\text{cm}^{-1}$  do not indicate any changes resulting from fluorination (Fig. 3).

The IR spectra of OH groups (Fig. 4) show that fluorination drastically reduces the concentration of bridging OH groups. The band at 3 640  $\text{cm}^{-1}$  attributed to

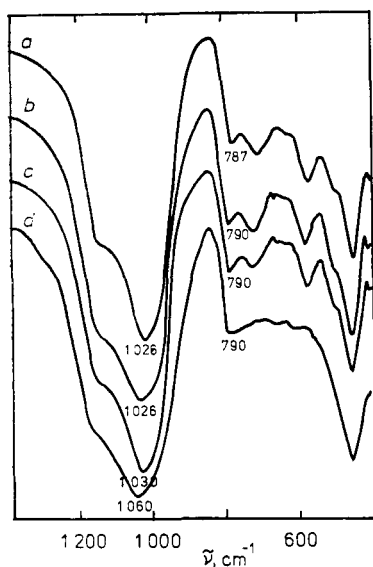


FIG. 2

IR spectra (KBr pellets) of the samples: Sm-Y (a); Sm-Y-F-X (b); Sm-Y-F-5 (c); Sm-Y-F-6 (d)

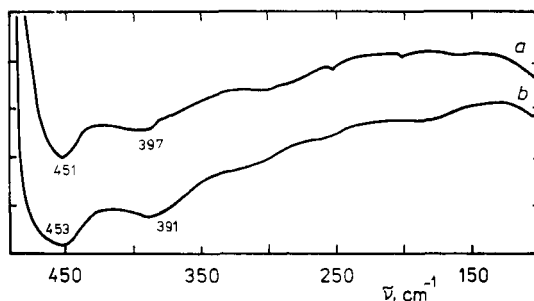


FIG. 3

IR spectra (polyethylene pellets) of samples Sm-Y (a) and Sm-Y-F-5 (b)

acidic OH groups in the supercage nearly disappears after introduction of 0.93% F. Further fluorination (e.g. sample Sm-Y-F-5) eliminates the band at  $3\,520\text{ cm}^{-1}$  associated with the least accessible hydroxyl groups. Only the silanol groups ( $3\,740\text{ cm}^{-1}$ ) remain after severe fluorine treatment.

The spectra of absorbed pyridine are consistent with the above spectral results and indicate a decreasing ratio of Brønsted/Lewis acid sites as a function of fluorine content (e.g. 4.9 for Sm-Y; 2.1 for Sm-Y-F-3; 1.3 for Sm-Y-F-5).

Catalytic cumene cracking and toluene disproportionation require strong protonic acid sites. Hexene isomerization can be catalyzed by weaker centres, including Lewis type. The activity of fluorinated samples did not vary as a function of pulse number for these reactions. However, the isomerization of hexene decreased with pulse number (Fig. 5).

Correlation between fluorine content and conversion of toluene and cumene differs substantially from those reported for other fluorinated zeolites. Generally, mild fluorination results in enhanced activity<sup>2</sup>. We have found that NaY zeolites containing lower loadings of samarium display enhanced catalytic properties.

The present results for toluene and cumene conversion (Fig. 6) show a decrease in activity after introduction of small amounts of fluorine (0.1%). Further fluorination brings about some increase in activity, but the maximum activity of fluorinated samples (2.34% F) is still lower than that of unmodified zeolite Sm-Y. Deeper fluorination results in reduction of activity which is coupled with a loss in zeolite crystallinity.

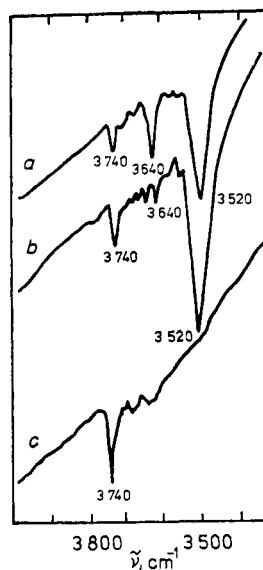


FIG. 4  
IR spectra of OH groups (self-supported wafers, vacuum cell) of the samples: Sm-Y (a); Sm-Y-F-3 (b); Sm-Y-F-5 (c)

Only the lowest loading (Sm-Y-F-1) shows an increase in activity for 1-hexene isomerization. Introduction of additional fluorine (up to 0.9% F) results in diminishing activity, and then conversion of hexene rises with fluorine content again. The other activity maximum is approached at 2.34% F. A similar correlation (two activity maxima) for alkene isomerization was reported<sup>4</sup> in case of fluorinated Al-Y, however, the initial activity was always higher than that of the unmodified Al-Y.

These results suggest that mild fluorination of Sm-Y eliminates the strong protonic acid sites, which is reflected in reduced activity for toluene and cumene reactions. This is consistent with the spectral data indicating elimination of acidic OH groups during fluorination. Spectra of adsorbed pyridine demonstrate the increasing contribution of the Lewis acid sites, which can be responsible for the activity rise in hexene isomerization. The nature of intrazeolite fluorinated species has not been resolved. However, a comparison with previous findings<sup>5,7</sup> clearly indicates there is a reactivity dependence on both samarium and fluorine loading.

In summary we have shown the catalytic behavior of fluorinated Sm-Y to be different from other reported fluorinated zeolites. Additionally, the rare earth modified zeolites appear to be stabilized during fluorination unlike  $H^+$ ,  $Na^+$  or other polyvalent cation forms of zeolite Y. Also, in contrast to other forms of zeolite Y there appears to be a competition between Sm(III) and hydroxyl groups

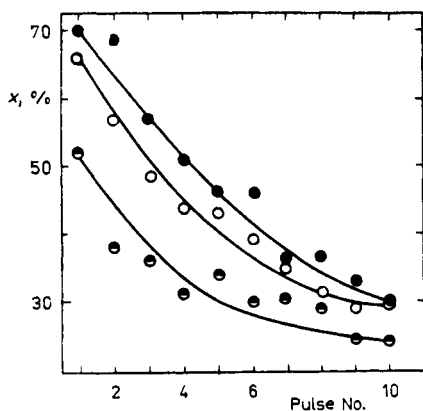


FIG. 5

Correlation between 1-hexene conversion and pulse number for the samples: Sm-Y (●); Sm-Y-F-3 (○); Sm-Y-F-5 (●)

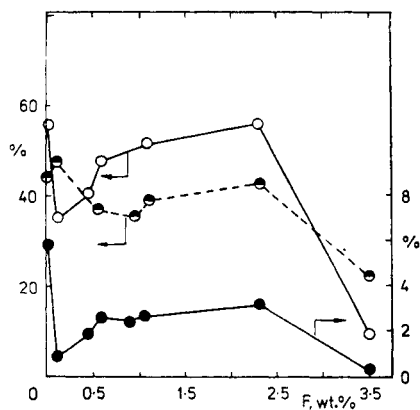


FIG. 6

Correlations between fluorine content and conversion for reactions of cumene cracking (○), toluene disproportionation (●) and 1-hexene isomerization (◐). These are mean conversion values estimated from the results of ten consecutive injections

for fluorine. Further metal loadings will be required in order to evaluate better the correlation between reactivity and  $\text{SmF}_3$  formation. Clearly the mild fluorination of high loading (10%) Sm-Y eliminates strong acidic OH groups, which is reflected in decrease in catalytic activity. Simultaneously, weak Lewis-type sites are created and they are responsible for increased activity in hexene isomerization.

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