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RESEARCH NOTE

Selective Removal of Surface Acidity in ZSM-5 Zeolite Using $(NH_4)_2SiF_6$ Treatment

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Ammonium hexafluorosilicate, $(NH_4)_2SiF_6$, has been found to be partially selective for removing surface acidity in zeolite ZSM-5. Under static digestion conditions using HZSM-5 extrudate, the zeolite was found to lose approximately 30% of its acid sites as determined by NH_3 desorption and hexane cracking results. However, tetrapropylammonium desorption and α-naphthyl red adsorption studies showed up to a 50% reduction in surface acid sites. This surface deactivation was conclusively demonstrated in propene oligomerization catalytic studies. Use of fluorosilicate-treated HZSM-5 in the surface acidity-sensitive reaction gave substantial viscosity index (VI) improvements in the C_{20}^{+} fraction due to more linear oligomerized products. It is believed that the static digestion procedure necessary to treat the HZSM-5 catalysts in this study allowed for increased reaction between the zeolite surface and the SiF_6^{2-} anion. If optimized, this method may be a useful technique to prepare catalysts for surface acidity-sensitive hydrocarbon conversion reactions. © 2000 Academic Press

Key Words: **hexafluorosilicate; ZSM-5; surface acidity; propene oligomerization.**

INTRODUCTION

For postsynthesis modification of zeolites, the metathesis reaction involving removal of Al^{3+} in T sites followed by Si^{4+} substitution using aqueous ammonium hexafluorosilicate, $(NH_4)_2SiF_6$, is well known. This method for modifying zeolites was first reported by Elliott (1) and the reaction chemistry later elucidated in detail by Skeels and Breck (2). The reverse reaction, i.e., the aluminum substitution into zeolites using fluoroaluminate complexes, was also reported at about the same time (3) and the entire system was found to exist as an equilibrium condition between Al and Si fluorides in solution (4). This use of aqueous metal fluorides has been shown to be a versatile method for insertion of Fe^{3+}, Ti^{4+} (5), Sn^{2+}, Cr^{3+} (6), Ga^{3+} (4, 7, 8), Be^{2+} (9), and B^{3+} (10) ions into the framework of zeolites such as ZSM-5 and Y. The only reported case where the use of aqueous metal fluorides for achieving isomorphous substitution into zeolite T-atom sites was unsuccessful involved the insertion of the substantially larger In^{3+} ion using aqueous InF_3 (11).

The determination of Al siting and distribution after dealumination reactions has been of interest since Al distribution in a zeolite could potentially impact its catalytic performance, depending upon the reaction in question. The early ways for determining surface acidity in zeolites included the controversial method of using dyes or indicators on surfaces (12–15) and catalytic techniques such as dehydration of 4-methyl-2-pentanol (16). Using fast atom bombardment mass spectrometry (FABMS), Dwyer *et al.* showed that the acid leaching of ZSM-5 zeolite left a surface enriched in Si while steaming and $SiCl_4$ treatment resulted in Al enrichment on the surface (17). It is well known that, under severe thermal and hydrothermal conditions, Al migration in zeolites is observed when defect sites allow such movement, resulting in a surface enriched with Al.

A highly sensitive method for determining the loss of surface acidity from pentasil zeolites is the catalytic shape-selective propene oligomerization reaction. In general, oligomerized products have reduced branching when the zeolite catalyst has reduced surface acidity due to minimization of surface side reactions such as isomerization. More linear products have been obtained in propene oligomerization by modifying the surface acidity of HZSM-5 zeolite with large molecules such as 4-methylquinoline and hexamethyldisilazine (18). Page *et al.* showed that linear hydrocarbons were obtained from propene by selective poisoning of HZSM-23 zeolite with 2,4,6-collidine (19, 20). Recently, Chen and Bridger (21, 22) reported that propene oligomerization over HZSM-5 gave a higher viscosity index (VI) C_{20}^{+} hydrocarbon product when the zeolitic surface was selectively poisoned with 2,6-di-*tert*-butylpyridine.

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The improved VI was attributed to the more linear product structure, which was confirmed by ^{13}C NMR analysis (22).

We report in this paper that, under the proper treatment conditions, the $(NH_4)_2SiF_6$ treatment of ZSM-5 gives a dealuminated zeolite enriched with Si relative to Al on the surface. As this reaction inserts Si^{4+} after dealumination, we believe this is a permanent modification to the surface of the zeolite catalyst. To confirm that ZSM-5 surface acidity has been reduced using the aqueous $(NH_4)_2SiF_6$ reaction, we have used two physical methods, tetrapropylammonium (TPA^+) ion exchange followed by TGA/TPD and α-naphthyl red adsorption measurement by UV/vis spectroscopy and the highly sensitive propene oligomerization reaction.

METHODS

The starting NH_4ZSM-5 catalyst ($SiO_2/Al_2O_3 = 70$) was a binder-free extrudate similar to that described earlier (22). To a zeolite/water slurry containing 14.0 g of binder-free NH_4ZSM-5 extrudate in 200 mL of deionized water was added 150 mL of 0.11 M aqueous $(NH_4)_2SiF_6$ solution. This reaction mixture was digested at 363 K for 17 h. The product was filtered, washed, and calcined at 811 K. XRD confirmed the product to be 100% crystalline based on comparing the average intensities for the five strongest peaks in the 23°–25° 2θ range (d spacing 4.0–3.5 Å) for the parent vs treated catalysts. The zeolite SiO_2/Al_2O_3 ratio was determined by elemental analysis and NH_4^+ TGA/TPD (23). As a further test of dealumination, the hexane cracking activity, or α-test (24), was determined for the parent and product catalysts.

To measure surface acidity by tetrapropylammonium desorption, the H^+ form of the zeolites was exchanged into the TPA^+ form by reacting 0.1 g of the zeolite with 20 mL of 1.0 M (TPA)Br overnight. The catalysts were washed copiously with water and dried at 393 K. TGA/TPD analyses were then obtained using the same method as that for NH_4^+ measurement above.

α-Naphthyl red [4-(phenylazo)-l-naphthylamine] was obtained from Aldrich with about 75% dye content and 25% inorganic salt content. The dye was extracted out in pure form with toluene and stripped of solvent. Standard solutions in toluene were then prepared and data taken on a HP-8450 UV/vis spectrophotometer. The λ_{max} of the dye dissolved in toluene is at 436 nm (22,940 cm^{-1}) with molar absorptivity $\epsilon = 8.35 \times 10^3$ liters mol^{-1} cm^{-1}. In a typical experiment, 0.0200 g of zeolite (ground to 100–200 mesh) in a test tube was covered with 5.00 ml of a 1.820×10^{-4} M standard solution of α-naphthyl red in toluene. The mixture was stirred for 30 s on a Fisher touch-mixer and then centrifuged. The solution was then pipetted out and its spectrum taken. Concentration calculations were performed in the spectrophotometer using a second-order calibration curve that compensates for deviations from Beer's Law at high sample concentrations. The amount of dye adsorbed was then calculated by the concentration drop against the original standard solution.

Catalytic testing was carried out in a standard fixed-bed microreactor. The catalyst (15.0 ml) was loaded into a 1.6-cm-i.d. stainless steel reactor and propene was reacted over the catalyst at ca. 500 K and 0.2–0.5 h^{-1} LHSV. Propene used was C. P. grade. Liquid products were analyzed by GC using a capillary column calibrated with hydrocarbon standards. The C_{20}^+ fraction was obtained by distillation under vacuum and kinematic viscosities measured at 313 and 373 K. The viscosity index (VI) is an empirical number derived from the viscosity measurements above which measures the variation in kinematic viscosity due to temperature changes. The VI values were determined as described in ASTM D2270. Two reference catalysts were used as base case comparisons in the catalytic testing. One was a commercial HZSM-5 extrudate containing 65 wt% HZSM-5 and 35 wt% alumina binder, similar to that used as the base catalyst in earlier propene oligomerization studies (22). The second comparison catalyst used was the HZSM-5 alumina extrudate from the above steamed with 100% steam at 755 K for 6 h.

RESULTS AND DISCUSSION

Table 1 shows the analytical data obtained for $(NH_4)_2SiF_6$-treated ZSM-5. The NH_4^+ exchange capacities given in Table 1 show a 30% drop in total acidity in the fluorosilicate-treated catalyst from the starting ZSM-5, with a corresponding 36% drop in the hexane cracking activity, α, from 200 to 128. To measure surface acidity quantitatively, two methods were used, tetrapropylammonium desorption and measurement of α-naphthyl red adsorption. TPA^+ cations have been found in our laboratory to exchange only on the surface of ZSM-5 because of its steric

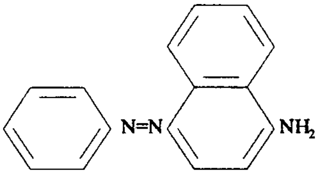
TABLE 1

Analytical Results for Parent and $(NH_4)_2SiF_6$-Treated ZSM-5

Method	Parent ZSM-5	$(NH_4)_2SiF_6$-treated ZSM-5
SiO_2/Al_2O_3 mole ratio by elem. analysis	70	106
Fluoride, wt% by elem. analysis	0.08	0.10
% Crystallinity by XRD	100	100
NH_4^+ exchange capacity (meq/g of zeolite)	0.44	0.31
α	200	128
TPA^+ exchange capacity (meq/g of zeolite)	0.040	0.020
α-Naphthyl red adsorbed (meq/g of zeolite)	0.017	0.0093

bulk (25). The TPA^+ exchange capacity was determined using TGA/TPD analysis using the assumption that 1 mol of TPA^+ would titrate as 1 mol of NH_3 desorbed after the thermally induced Hofmann elimination reaction of tetrapropylammonium to propene and ammonia. TPA^+ exchange data are also given in Table 1. The results of these experiments show a 50% decrease in the number of acid sites on the surface from the parent catalyst after fluorosilicate treatment. Since the overall acidity decrease was 30%, this indicates a partially selective surface acidity removal from HZSM-5 by aqueous fluorosilicate treatment.

Measurement of surface acidity by α-naphthyl red adsorption is similar in concept to TPA^+ desorption, i.e., use of a bulky probe molecule which cannot enter the ZSM-5 pores, except in the quantitative measurement procedure. The basic dye molecule ($pK_{ind} = 4.0$):



reacts with acid sites to form the conjugate acid on the surface of the zeolite. It is assumed that α-naphthyl red will react preferentially with the surface sites since the molecule has a bulky structure that prevents it from entering the pores of ZSM-5 (26). Measurement of the amount of dye adsorbed on the surface was made spectrophotometrically by following the change of absorbance in the visible range relative to a standard control solution. From the data in Table 1, it is shown that the amount of dye adsorbed on the zeolite has dropped by 45% in going from parent to fluorosilicate-treated ZSM-5. This 45% drop in surface acidity as measured by this technique agrees reasonably well with the TPA^+ exchange experiment and indicates selectivity in surface acidity removal using $(NH_4)_2SiF_6$ treatment when compared against the 30% change in overall acidity. Though the results for the two methods agree reasonably well for a determination of this nature, it is important to stress that the steric bulk of the two probe molecules used may give rise to problems in complete surface coverage. The concerns of using dye adsorption methods have been described previously (12, 15). Consequently, to demonstrate what we felt was permanent selective acidity removal from the surface, we decided to use a catalytic test that has been shown conclusively in the literature to be sensitive to zeolite surface acidity, namely, propene oligomerization.

In propene oligomerization, it is important to note that diffusion limitations can also play a role in determining product profiles. Thus, we were careful to use similar zeolites at similar crystal sizes to those described previously (22). Consequently, we expected the VI's of the C_{20}^+ products generated in these studies to be related to the linearity of the hydrocarbons obtained, which would in consequence be a function of the zeolite surface acidity. In addition, in our system we were able to run our catalytic tests using a conventional fixed-bed microreactor. The catalytic experiments reported by Chen and Bridger (22) were done in batch reactor mode due to the need to maintain a desired level of surface acidity poison, 2,6-di-*tert*-butylpyridine, in the system. As our fluorosilicate-treated ZSM-5 catalyst is *permanently* modified on the zeolite surface, the need for bulky poisons was obviated. However, the different reactor modes used preclude direct comparisons of our data vs the data of Chen and Bridger, as contact times for our system were significantly shorter.

TABLE 2

Propene Oligomerization Results for $(NH_4)_2SiF_6$-Treated, Unmodified, and Steamed ZSM-5 Catalysts

HZSM-5	$(NH_4)_2SiF_6$-treated			Unmodified		Steamed
Temperature, K		500		500		500
LHSV, h^{-1}	0.2	0.3	0.5	0.5	0.5	0.5
C_{20}^+ product, wt%	39	35	32	18	10	9
VI	83	86	93	73	70	43

The propene oligomerization data are given in Table 2. The VI's obtained from the fluorosilicate-treated HZSM-5 catalyst are consistently higher than those of the base case unmodified HZSM-5 at all space velocities, indicating a reduction in surface acidity. The steamed HZSM-5 catalyst gave an exceptionally low VI for the C_{20}^+ range product, indicating significant surface acidity and hence undesired side reactions that give branched products. Also observed was that increasing surface acidity for the parent and steamed catalysts relative to the fluorosilicate catalyst significantly reduced C_{20}^+ yield, likely again due to undesired surface reactions such as cracking. The increased surface acidity for steamed zeolites is consistent with the FABMS results reported by Dwyer *et al.* (17).

All tests, physical and catalytic, have shown that $(NH_4)_2SiF_6$ treatment is partially selective in removing Al from the surface of ZSM-5. The remaining issue then is, why is this method selective? This is unlikely due to any steric effects with the SiF_6^{2-} anion, as the species should be easily accommodated inside the ZSM-5 pore system. We postulate that this is due to the static treatment conditions we used on the ZSM-5 extrudate in our experiments. As ZSM-5 is more difficult to dealuminate/Si substitute with this treatment than other zeolites, e.g., Y, long digestion conditions were required for ZSM-5 to react with the $(NH_4)_2SiF_6$ reagent. However, stirring of the extrudates was avoided in the long digestion procedure due to concerns about maintaining catalyst integrity and shape with constant agitation. Consequently, it is possible that diffusion of the SiF_6^{2-} anion, while not prohibited, was not necessarily encouraged and a statistical majority of the zeolite Al/Si metathesis reactions occurred on or near the surface. This preparation has been reproduced several times at the scale reported in this paper; the surface selectivity effect of this digestion treatment on a larger scale is unknown at present.

Of interest is the potential process applicability of catalysts modified in this manner. As indicated earlier, this method is a permanent modification to the zeolite and thus removes the need for selective poisons in catalytic reactions requiring abatement of surface acidity. As such, reactors/processes used become simpler and catalyst productivity is considerably improved. If the experimental procedure is optimized, the $(NH_4)_2SiF_6$ treatment of ZSM-5 may prove to be a versatile method for preparing surface-deactivated catalysts.

CONCLUSIONS

Our studies suggest that $(NH_4)_2SiF_6$ treatment of zeolite ZSM-5 extrudates under static reaction conditions produces a resultant catalyst with reduced surface acidity. Measurements such as tetrapropylammonium desorption and α-naphthyl red dye adsorption show a 45–50% surface acid site removal as compared with a 30% overall acidity removal. This reduction in surface acidity clearly translates to catalytic performance, as $(NH_4)_2SiF_6$-treated ZSM-5 catalysts give substantially higher viscosity index C_{20}^{+} products in propene oligomerization. As this method is simple and provides a permanent catalyst modification, optimization of this preparative system may be a valuable synthetic pathway to surface-deactivated zeolites and catalysts.

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