rangement of the sultone $F_5S\overline{CHCF_2OS}O_2$, in a 25-mL Pyrex-glass round-bottomed flask, equipped with a stirring bar, was added the base $BF_3{\cdot}N(C_2H_5)_3$ (3.17 g, 18.8 mmol). The flask was attached to a vacuum-transfer line equipped with a 10-mL receiving flask that was cooled to −196 °C. The pressure in the system was lowered to 500 Torr, and the mixture was heated to 100 °C over a 25-min period. At ~85 °C a crystalline precipitate was observed in the homogeneous melt, which disappeared at ~90 °C, leaving an upper brown and a lower colorless liquid layer. Heating was continued at 100 °C (25 min). The product (4.45 g) was transferred under vacuum (30 min) to the 10-mL receiving flask cooled to −196 °C. The ^{19}F NMR and IR spectra showed that only the ketene was present; yield (based on the 14:86 mixture) 95%.

$F_5SC(SO_2F)=C=O$ in a Sealed Tube. The ketene (0.49 g, 1.96 mmol) was heated in an evacuated dry 50-mL Carius tube to 220 °C for 4 h. The liquid inside was slightly discolored, but 0.48 g of unchanged ketene was recovered.

$F_5SC(SO_2F)=C=O$ and 2-Propanol. To 118 mg of 2-propanol (1.94 mmol) in a 1-mL dry reaction vessel was added dropwise ketene **1** (497 mg, 1.92 mmol). Initially, the reaction was vigorous, but it subsided after addition of approximately half of the ketene. After addition was complete, the reaction vessel was kept at room temperature (0.5 h) and 568 mg of product was collected. The infrared and ^{19}F NMR spectra agreed with those found for ester **2**. Gas chromatography (Carbowax 20% on Chromosorb W, 110 °C) showed the product to be essentially pure (>95%).

$F_5SC(SO_2F)=C=O$ and 2,2,2-Trifluoroethanol. Into 0.50 g (2.0 mmol) of the ketene in a dry 30-mL Pyrex-glass reaction vessel, equipped with a Kontes Teflon valve, was condensed CF_3CH_2OH (0.24 g, 2.4 mmol) at −196 °C. The mixture was allowed to attain room temperature slowly and was heated to 83 °C for 1 h. The liquid product was transferred out and washed with water (2 × 0.5 mL); the lower layer was taken up with a pipet, transferred to a 5-mL flask, and dried (Na_2SO_4). The infrared spectrum of the product (0.59 g) was essentially identical with the published spectrum of $F_5SCH(SO_2F)C(O)OCH_2CF_3$.[2] The ^{19}F NMR spectrum revealed that the product was essentially trifluoroethyl ester with some $F_5SCH_2SO_2F$ as a minor impurity; yield 82% (NMR spectrum).

$F_5SC(SO_2F)=C=O$ and H_2O. Into a 100-mL reaction vessel, equipped with a Kontes Teflon valve and containing water (40.5 mg, 2.25 mmol), was condensed ketene **1** (485.3 mg, 1.94 mmol). The mixture was warmed to room temperature and remained there for 2 h. It was then cooled to −78 °C, and the infrared spectrum of the volatile material showed CO_2 to be present; 85.4 mg (1.94 mmol) of CO_2 with trace impurities was formed in 100% yield. The residue was transferred at elevated temperature and dried (Na_2SO_4). A total of 369.0 mg product was collected. A gas chromatogram (Carbowax, 20%, 6 ft, on Chromosorb W, 100 °C) showed only one product; its infrared and ^{19}F NMR spectra were identical with the published spectra of $F_5SCH_2SO_2F$;[2] yield 84.9%.

$F_5SC(SO_2F)=C=O$ and $(C_2H_5)_2NH$. The ketene (0.49 g, 1.96 mmol) was condensed into a 50-mL Pyrex-glass reaction vessel, equipped with a Kontes Teflon valve and containing 2 mL of dry CH_2Cl_2 at −196 °C. The vessel was warmed above the melting point of the solution, shaken, and cooled again to −196 °C, and diethylamine (0.142 g, 1.94 mmol) was added. Upon being warmed to the melting temperature, the solution was shaken, frozen (−196 °C), and allowed to slowly attain room temperature. During warming to room temperature, the solution turned brownish. At room temperature it was decanted, concentrated, and recrystallized from CH_2Cl_2, leaving 302 mg (0.93 mmol) of product $F_5SCH(SO_2F)C(O)N(CH_2CH_3)_2$: mp 108–110 °C; yield 47.7%.

^{19}F NMR spectrum ($CDCl_3$): multiplet, ϕ 72.2 ppm, area 4.8 (SF_5); multiplet, ϕ 62.3 ppm, area 1.0 (SO_2F).

^1H NMR spectrum: triplet, δ 1.19 ppm, $J_{H-H} = 7.1$ Hz, area 3.0 (CH_3); triplet δ 1.32, $J_{H-H} = 7.1$ Hz, area 3.0 (CH_3); multiplet, centered at 3.5 ppm, area 4.3 (CH_2); pentet, δ 6.00 ppm, $J_{H-F} = 4.0$ Hz, area 0.9 (CH).

Infrared spectrum: 2990 (w), 1661 (vs), 1460 (vw), 1432 (s), 1390 (w), 1363 (w), 1320 (w), 1278 (w), 1222 (m), 1212 (m), 1129 (w), 1096 (w), 1083 (vw), 953 (w), 899 (m), 860 (vs), 820 (m), 799 (m), 740 (w), 647 (w), 562 (m), 488 (w), 458 (w).

Mass spectrum (electron impact) (*m/e*, species, relative abundance): 323, M^+, 1.6; 308, $(M-CH_3)^+$, 12.1; 280, $C_6H_4F_6NO_3S_2^+$, 2.0; 231, $C_2F_5O_3S_2^+$, 4.6; 196, $M - SF_5^+$, 14.9; 176, $M - HF - SF_5^+$, 5.8; 127, $(SF_5, CFO_2S_2)^+$, 7.4; 125, $C_2H_2FO_3S^+$, 2.9; 112, $(CH_3CH_2)_2NCOC^+$, 2.9; 105, $C_2HO_3S^+$, 2.7; 100, $C_5H_{10}NO^+$, 5.8; 89, SF_3^+, 14.8; 73, C_2HOS^+, 2.0; 72, $NC_4H_{10}^+$, C_2OS^+, 42.4; 71, $NC_4H_9^+$, 3.4; 70, $NC_4H_8^+$, SF_2^+, 4.4; 67, FSO^+, 5.5; 58, $C_2H_4NO^+$, 100; 56, $NC_3H_6^+$, $C_2H_2NO^+$, 21.5; 54, C_2ON^+, 2.0.

Anal. Calcd for $C_6H_{11}F_6NO_2S_2$: C, 22.29; H, 3.43; F, 35.3; N, 4.33; S, 19.83. Found: C, 22.37; H, 3.54; F, 35.2; N, 4.26; S, 19.91.

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Contribution from the Research Department,
Paulsboro Research Laboratory, Mobil Research and
Development Corporation, Paulsboro, New Jersey 08066,
Research Department, Princeton Laboratory, Mobil Research
and Development Corporation, Princeton, New Jersey 08540,
and School of Chemical Sciences,
University of Illinois, Urbana, Illinois 61801

Stability of Synthetic Zeolite ZSM-5 to Dealumination with Chromium(III) Salt Solutions

W. E. Garwood,* P. Chu, N. Y. Chen, and J. C. Bailar, Jr.

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We have previously reported dealumination of dense zeolites such as erionite[1] and also the larger pore faujasites[2] by reaction of the zeolite with hot aqueous solutions of chromium(III) salts. The dealuminated dense zeolite residues are left with very little chromium, usually less than 1 wt %, while the dealuminated faujasite Y contains much more chromium, up to 7 wt %, with evidence that the chromium is "healing" to some extent the rupture in the silica alumina lattice created by hydrolysis and removal of the aluminum atoms.

We now find that the synthetic zeolite ZSM-5 undergoes less than 10% dealumination with $CrCl_3$ solutions under conditions giving greater than 40% dealumination of the dense zeolites and faujasite. In addition, the chromium content of the treated ZSM-5 is <0.1 wt %, demonstrating the intrinsic stability of this high silica zeolite in an acid environment.

Experimental Section

Hydrated chromium(III) chloride was obtained from Matheson Coleman and Bell.

Synthetic ZSM-5 was prepared by the method of Argauer and Landolt.[3] Analysis by weight: 97.0% SiO_2, 2.10% Al_2O_3, 2.7% Na; calculated SiO_2/Al_2O_3 molar ratio 77/1. In the first experiment 8.7 g of the powdered zeolite was added to 300 mL of refluxing (~101 °C) aqueous 2.0 N $CrCl_3$, pH 1.5, and the mixture was stirred for 2 h. The flask contents were then filtered through paper by suction, and the residue was treated twice more with 300 mL of $CrCl_3$ solution (total of 102 mL of solution/g of zeolite). In all cases, the filtrate remained clear. The final filter cake was water washed until chloride ion free and then dried overnight at 110 °C. Analysis by weight: 98.0% SiO_2, 1.98% Al_2O_3, <0.01% Na, 0.02% Cr; calculated SiO_2/Al_2O_3 ratio 84/1; alumina removal 8 wt %.

In a second experiment using more severe treatment conditions, 6.0 g of the zeolite was added to 600 mL of refluxing 4.0 N $CrCl_3$, pH 1.4, and the mixture was stirred for 48 h (100 mL of solution/g of zeolite). The flask contents were filtered as in the first experiment; the filter cake was water washed until chloride ion free and then dried overnight at 110 °C. Analysis by weight: 95.2% SiO_2, 2.00% Al_2O_3, <0.01% Na, 0.04% Cr; calculated SiO_2/Al_2O_3 ratio 8.1; alumina removal 5 wt %.

Discussion

In the earlier work dealuminating erionite with $CrCl_3$, it was found that treatment of the zeolite with HCl solutions of the same pH as the $CrCl_3$ solutions removed only about one-fourth as much alumina.[1] Further evidence was given of a complex of the chromium with the hydrolyzed alumina, accounting for its greater removal from the framework. Further, in the earlier work it was

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* To whom correspondence should be addressed at the Paulsboro Research Laboratory.

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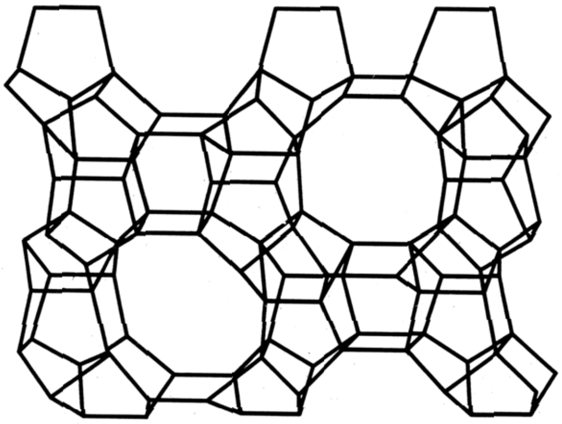

Figure 1. Line drawing of ZSM-5. Reprinted with permission from ref 4. Copyright 1978 Macmillan.

shown that alumina removal from both the dense zeolites[1] and faujasites[2] was 40% or more under reaction conditions with $CrCl_3$ less severe than those used above on ZSM-5.

In the two experiments reported here, as in the earlier work, the sodium to aluminum bond is first hydrolyzed and the Na^+ replaced by H+. The high stability of ZSM-5 to dealumination is related to its unusual structure and predominance of five-membered ring cages, shown in Figure 1,[4] where the apices represent aluminum and silicon atoms and the lines represent oxygen atoms. The small cages join together to create 10-membered rings and the pore structure shown in Figure 2, accounting for its unique shape-selective catalytic performance.[5]

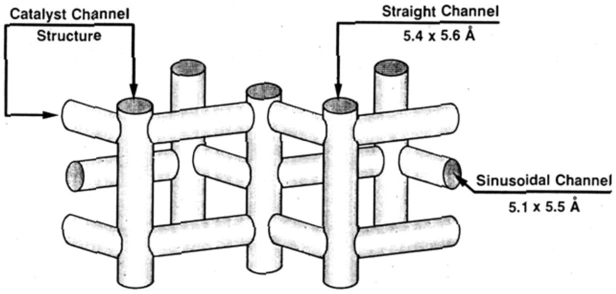

Figure 2. Pore structure of ZSM-5. Reprinted with permission from ref 4. Copyright 1978 Macmillan.

That high alumina content zeolites are more easily dealuminated than those containing less alumina is not limited to ZSM-5, whose pores restrict the entering of $Cr(H_2O)_6^{3+}$ ions. A large pore, high silica (SiO_2/Al_2O_3 ratio 88) zeolite, ZSM-12, first synthesized by Rosinski and Rubin[6] and described by LaPierre et al.[7] was also treated with $CrCl_3$ and also found to be resistant to dealumination. Alumina removal was 10% under the conditions giving 8% removal with the higher alumina content ZSM-5.

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