

for a more anionic NO ligand in $[\text{Co}(\text{NO})(\text{NH}_3)_5]\text{Cl}_2$, whereas these authors reported a value of 402.3 eV for a more cationic NO in $[\text{Co}(\text{NO})(\text{diars})_2](\text{ClO}_4)_2$ (diars = $\text{C}_6\text{H}_4\text{-}[\text{As}(\text{CH}_3)_2]_2$). It is difficult, however, to make a valid comparison between these absolute binding energies, particularly since Finn and Jolly did not report the value adopted for their carbon (pump oil) standard. The infrared bands in the 1800-cm^{-1} region are consistent with a minimum electron donation into the π^* orbital of the nitrosyl ligand. Therefore, on the basis of the infrared data and the photoelectron spectra of the cobalt ions, we believe that the nitrosyl ligands are effectively neutral in the cobalt complexes of the three zeolites.

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Registry No. Co^{2+} , 22541-53-3; CoNO^{2+} , 65036-07-9; $\text{Co}(\text{NO})_2^{2+}$, 65036-08-0; $[\text{Co}^{\text{III}}(\text{NH}_3)_6]^{3+}$, 14695-95-5.

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

Partial Dealumination and Healing of Faujasites by Chromium(III) Salt Solutions

W. E. GARWOOD, S. J. LUCKI, N. Y. CHEN, and J. C. BAILAR, JR.*

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When faujasite-type zeolites such as Y and X are partially dealuminated by refluxing in aqueous chromium chloride solutions, a portion of the chromium remains in the washed zeolite. Most of this chromium cannot be removed by ion exchange. If, instead of chromium chloride, EDTA is used as the complexing agent to remove aluminum from zeolite Y, a significant amount of silicon can subsequently be digested and removed with refluxing 1.0 N sodium chloride solution. In the case of chromium, the silicon is less readily removed, particularly after calcination at 540 °C. This is evidence that the chromium is "healing" the rupture in the lattice created by hydrolysis and removal of the aluminum atoms. Others (Maher et al., Peri, Gallezot et al.) have reported that some healing can occur simply by silicon atom migration following dealumination with EDTA. We propose the empirical formula $(\text{Na} + \frac{1}{3}\text{Cr})_x(\text{Al} + \text{Cr})_y\text{Si}_z\text{O}_w$, where the ratio $y:x$ is higher than in the starting faujasite, to describe these new materials (in dehydrated form) at up to about 40% aluminum removal. Different metal ions, such as silver and lanthanum, can be added to these materials by ion exchange.

Introduction

Dealumination of dense zeolites such as erionite with hot aqueous solutions of chromium(III) salts has been reported previously by us,¹ along with evidence for a complex between chromium and the removed aluminum. The dealuminated dense zeolite residues are left with very little chromium, usually much less than 1 wt %. We now find that the larger pore faujasites respond to treatment with chromium(III) salt solutions for aluminum removal, but the dealuminated faujasite contains much more chromium, up to 7 wt %, most of which is not removed by ion exchange. Further, we have evidence that the chromium is "healing" to some extent the rupture in the lattice created by hydrolysis and removal of the aluminum atoms. Ermolenko et al. have previously reported isomorphically substituted chromium in zeolites,² where a chromium compound is used in the crystallization of the zeolite.

* To whom correspondence should be addressed at the University of Illinois at Urbana.

Experimental Section

Procedure. As in the previous work on dense zeolites,¹ the powdered zeolites were added to chromium(III) salt solutions at either reflux or room temperature. At the end of the treatment period, the material was filtered through paper by suction and the filter cake was washed with water until the test for anion was negative. In all cases, the filtrate remained clear. The residue was dried overnight at 110 °C.

Materials. Hydrated chromium(III) chloride was obtained from Matheson Coleman and Bell. The synthetic sodium X faujasite was obtained from The Linde Co., and the sodium Y faujasite was synthesized by the procedure outlined in ref 3.

Results

Faujasite type zeolites have a large pore opening of 9 Å and a framework consisting of a tetrahedral arrangement of sodalite units linked by hexagonal faces with six bridge oxygen atoms.⁴ The apices of the sodalite cages are occupied by silicon and aluminum atoms, about five silicon to four aluminum atoms in faujasite X and five silicon to two aluminum atoms in faujasite Y. Siting of the aluminum ion in the lattice is

Table I. Dealumination of NaY, NaX, and Amorphous Silica-Alumina with Refluxing 1.0 N CrCl₃

	NaY	NaX	Amorphous silica-alumina
SiO ₂ :Al ₂ O ₃ ratio	5.1	2.5	15.3
mL of 1.0 N CrCl ₃ /g	15	15	15
Reflux time, h	2	2	6
Aluminum removed, wt %	32	46	48
Cr content of washed, dried residue, wt %	7.1	13.2	0.33

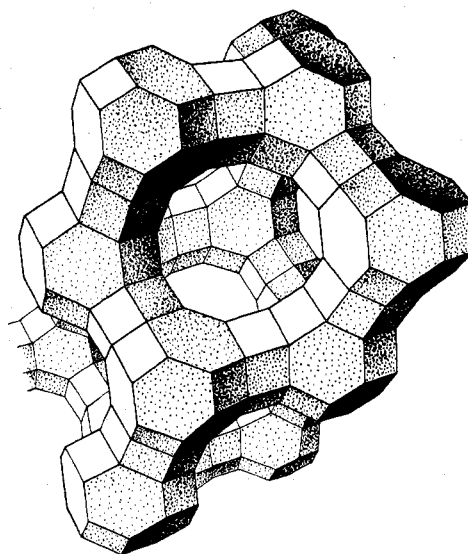
believed to be random but with four degrees of acid strength of the associated protons.⁵

Dealumination. Treatment of NaY and NaX with 15 mL of refluxing 1.0 N chromium chloride per gram of zeolite removes 32 and 46% of the aluminum, respectively, with 7 and 13 wt % chromium remaining in the washed residue (Table I). Amorphous silica-alumina dealuminates to the same extent but retains only 0.33 wt % chromium.

A study was made of the extraction of aluminum from NaY. Results at several temperatures, quantities of 1.0 N chromium(III) chloride solution, and times of heating are shown in Table II. Crystallinity is 75% of the original at 32% aluminum removal and decreases rapidly with further dealumination. Chromium retention is highest at 30–40% aluminum removal.

At room temperature, trivalent chromium cation exchanges with sodium ion available in the supercage sites. As shown by the data in Table III, about 67% of the sodium in the cationic sites has been replaced by Cr³⁺, and a good cation balance is observed. Little dealumination has taken place at this temperature. Under reflux conditions, however, framework aluminum is removed and more chromium is left in the washed, dried residue than can be accounted for as trivalent chromium cations. Assuming that Cr³⁺ cations occupy all the remaining cationic sites associated with framework aluminum, Na⁺ and Cr³⁺ would occupy 24 and 76% of the cationic sites, respectively, and an excess of about 2.9 wt % of chromium remains to be accounted for. If framework substitution of chromium for aluminum had taken place during the CrCl₃ treatment, then, in addition to 32% aluminum removal, about 9% of the framework positions previously occupied by aluminum will now be filled by chromium.

Not all the cationic chromium can be exchanged by silver ions. Treating the Cr(32% Al)Y sample twice with 1 N AgNO₃ solution at 82 °C for 2 h each replaces essentially all the sodium but only 62% of the total cationic sites. There remains 3.9 wt % of chromium in the sample. Balancing the remaining cationic sites with trivalent chromium ions leaves 2.1 wt % excess chromium which corresponds to about 8% of

**Figure 1.** Line drawing of faujasite structure.

the framework positions previously occupied by aluminum. Thus the calculated value of framework substitution is in close agreement with that estimated before the silver exchange.

The results of the silver exchange can also be interpreted to mean that only 62% of the aluminum is truly zeolitic framework aluminum and that the residual chromium has reacted with the nonframework aluminum to form a solid residue. This solid residue, which could have a stoichiometric composition of 1:1.4 Cr₂O₃:Al₂O₃, would amount to about 11 wt % of the sample. X-ray diffraction analysis of the sample before and after calcination does not indicate the presence of a nonzeolitic Cr_xAl_yO₂ phase or spinel formation.⁶ Since it is known that chromium-aluminum spinel contains chromium atoms and aluminum atoms in the same framework, we feel that it is quite possible for these two metals to replace each other in the zeolite framework. However, its positive identification with x-ray diffraction analysis has not been successful.

Most of the dealumination reaction is over in the first 30 min (Table IV). The sorption capacity for *n*-hexane and cyclohexane at that time is about half that of the original zeolite. After 24 h of reflux, *n*-hexane sorption is approaching the original, and cyclohexane sorption exceeds the original, evidence that further changes in the zeolite are occurring.

Desilication. The course of the dealumination reaction is pictured by Kerr⁷ as, first, H⁺ exchange, then acid hydrolysis of the Si–O–Al bonds, and finally removal of the hydrolyzed aluminum atoms (chelated with EDTA in his work) leaving the aluminum “ghost” site (Figure 1). We found, in the dense zeolite work,¹ that the dealuminated zeolite could then be

Table II. Treatment of NaY with Chromium Chloride Solution

CrCl ₃ soln (1.0 N), mL	None	600	600(x2)	750	1500	750	600	600(x2)
NaY, g		20	20	50	100	50	20	20
Temp		Ambient (~25 °C)		← Reflux (~101 °C) →				
Contact time, h		2	2(x2)	0.5	2	24	2	2(x2)
No. of treatments		1	2	1	1	1	1	2
Residue (washed, dried), g		19.2	18.3	43.4	95.6	42.4	15.0	11.1
Analysis of residue, wt %								
SiO ₂	63.6	66.9	67.4	71.4	71.6	74.0	81.5	96.8
Al ₂ O ₃	21.2	21.6	21.2	16.7	16.1	14.0	10.4	1.35
Cr		4.82	4.78	6.4	7.1	7.0	4.9	1.04
Na	8.55	3.14	2.34	1.4	1.7	1.4	0.95	0.02
Al removal, wt %		3	6	30	32	43	62	96
SiO ₂ :Al ₂ O ₃ ratio	5.1	5.3	5.4	7.3	7.6	9.0	13.3	122
Crystallinity, ^a %	100				75	63	25	<i>b</i>

^a Based on the comparison of the sum of the intensities of a series of diffraction lines with that of an arbitrary standard. ^b Mainly amorphous.

Table III. Effect of Temperature and AgNO₃ Exchange (2 h Contact)

	Ambi-ent (25 °C)	Reflux (101 °C)	After AgNO ₃ exchange
mL of 1.0 N CrCl ₃ /g of NaY	30	15	<i>b</i>
Al removal, wt %	3	32	32
SiO ₂ :Al ₂ O ₃ ratio	5.3	7.6	7.6
Equiv Na ⁺ :Al	0.33	0.24	0.005
Cr ³⁺ :Al	0.67	0.76	0.38
Ag ⁺ :Al			0.61
Excess Cr:Al ^a		0.09	0.08

^a 2/3 Cr³⁺:Cr₂O₃:Al₂O₃ (in NaY). ^b 25 mL of 1.0 N AgNO₃/g of zeolite at 82 °C, 2 h, two times.

Table IV. Effect of Time of Refluxing on Sorption Properties (15 mL of 1.0 N CrCl₃/g of NaY, Reflux)

	Time, h			
	0	0.5	2	24
Al removal, wt %	Nil	30	32	43
Cr, wt %		6.4	7.1	7.0
Equiv Na:Al	0.90	0.19	0.24	0.22
<i>n</i> -Hexane absorption, ^a wt %	17.5	9.3	11.0	13.7
Cyclohexane absorption, ^a wt %	15.4	8.9	14.1	17.8

^a Equilibrium at 20 mm, room temperature.

Table V. Stability of Silicon Digestion with 1.0 N NaCl (300 mL of 1.0 N NaCl/g of Dealuminated Y, 1 h Reflux, Three Times)

	Dealuminated with	
	CrCl ₃	EDTA
% Al removed	43	41
Subsequent treatment with 1.0 N NaCl, % Si removed	9	15

Table VI. Stabilization of Silicon by Calcination (540 °C for 16 h)(32% Dealuminated Y Treated with 1.0 N NaCl)

	Si re-moved, wt %	SiO ₂ :Al ₂ O ₃ ratio	Cr content, wt %
Dealuminated Y, as is ^a		7.6	7.1
Before calcination, NaCl treat ^b	8	6.9	5.7
After calcination, NaCl treat ^c	2	7.4	5.7

^a 150 mL of 1.0 N CrCl₃/g of NaY, 2 h reflux, washed, dried 110 °C. ^b 125 mL/g of dealuminated Y, 1 h reflux, three times.

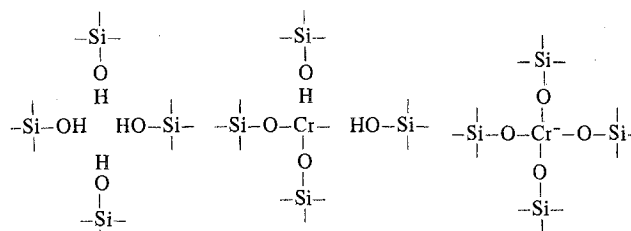
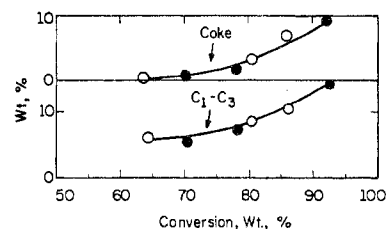
^c 300 mL/g of dealuminated Y, 1 h reflux, three times.

desilicated by reflux with a copious amount of 1.0 N NaCl solution. The dealuminated faujasites also desilicate (Table V), but to a lesser extent when chromium(III) chloride is used for dealumination than when EDTA is used. This is evidence that the silicon has been stabilized by reaction of one or more of the Si-OH groups with chromium. The silicon is stabilized further by calcination at 540 °C for 16 h (Table VI), evidence of further reaction between silicon and chromium.

Thus, the rupture in the lattice is "healed" to the extent that chromium reacts with the silicon to form Si-O-Cr bonds (Figure 2). This seems reasonable in view of a growing body of evidence⁸ that on heating EDTA-dealuminated faujasites, silicon migrates to form new Si-O-Si bonds, thereby healing the lattice vacancy. The atomic dimensions of chromium are such⁹ that it fits easily in the ghost site.

Proposed Empirical Formula. To account for the two environments of chromium we propose the empirical formula (Na + 1/3Cr)_x(Al + Cr)_xSi_yO_z where the ratio x:x is higher than in the starting faujasite, and aluminum removal is less than about 40%.

"ghost" site partially healed completely healed

**Figure 2.****Figure 3.** East Texas Light Gas Oil cracking: O, La-Cr dealuminated Y steamed 24 h at 650 °C; ●, rare earth Y steamed 24 h at 650 °C.

Catalysis. Gas Oil Cracking. A rare earth exchanged Y faujasite containing no chromium, and a 42% dealuminated Y containing 6.4% chromium and 4.6% lanthanum (by post exchange with LaCl₃) were used to crack 200–350 °C East Texas Light Gas Oil at 480 °C, atmospheric pressure, and several space velocities. Production of coke and C₁-C₃ gas over a 65–90% conversion range is plotted in Figure 3. Both are the same for either catalyst, even though the one contains 6.4% chromium. As little as 1.0 wt % chromium causes excessive formation of coke when it is on amorphous silica-alumina cracking catalysts.¹⁰ This is catalytic evidence that the chromium in these new materials is different from that previously observed.

Conclusion

The evidence presented here indicates that treating faujasite with chromium(III) chloride solution results in the replacement of sodium ion, the removal of part of the framework aluminum, and the replacement of a portion of aluminum(III) by chromium(III). This does not markedly alter the physical properties of the zeolite, and the replacement has not been demonstrated by x-ray analysis. However comparison of the catalytic behavior of the faujasite with amorphous aluminosilicates containing chromium(III) indicates that the chromium in faujasite structure is held in quite a different way.

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