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Aluminum Removal from Dense Zeolites by Aqueous Chromium(III) Salt Solutions

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The porosity of a number of dense zeolites which occur as natural ores, such as erionite and phillipsite, as well as some made synthetically, such as zeolite T, is increased by dealuminization with hot aqueous solutions of chromium(III) salts. Crystallinity is not lost at aluminum removals up to about 40%. Porosity is increased still further when aluminum removal is followed by desilication with a solution of NaCl or NH_4Cl. The removal of aluminum can be understood if it is assumed that the hydrated chromium(III) ion penetrates into the pores of the zeolite where it complexes with the hydrolyzed aluminum and solubilizes it. Evidence for the formation of a complex is furnished by experiments on the dissolution of aluminum hydroxide powder by refluxing aqueous solutions of chromium(III) chloride.

Introduction

The crystal lattices of zeolites are known to be attacked by mineral acids with the formation of amorphous material.[1,2] Kerr has developed a special technique for dealuminization, using ethylenediaminetetraacetic acid (EDTA).[3]

In this paper, we describe a technique in which dealuminization is effected by solutions of chromium(III) salts. This was followed in selected cases by silica removal. Throughout the entire process, crystallinity was retained to a high degree.

Experimental Section

Procedure. Powdered zeolites were added to boiling solutions of chromium(III) salts (in most cases, chloride). 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. Surface areas were measured by standard BET methods.

Materials. Hydrated chromium(III) chloride was obtained from Matheson Coleman and Bell. The green aqueous solutions turned blue-violet when they were allowed to stand or were heated, as was done before the addition of the zeolite. This change in color is due to an isomerization of the green salt (either $[Cr(H_2O)_5Cl]Cl_2{\cdot}H_2O$ or $[Cr(H_2O)_4Cl_2]Cl{\cdot}2H_2O$) to $[Cr(H_2O)_6]Cl_3$. The pH of a 1 N solution of the green salt was 1.9, while that of a corresponding solution of the violet-blue salt was 2.1.

The erionite came from Mt. Moses, Nev., and was shown by x-ray analysis to contain 20% clinoptilolite. Clinoptilolite, containing 20% phillipsite, was from the Mojave Desert. X-ray analyses showed that it also contained traces of silica and clay but no detectable phosphate.

Zeolite T was prepared by the procedure outlined in U.S. Patent 2950952 (Union Carbide). Its identity was shown by x-ray analysis.

The aluminum hydroxide powder was Baker's Analyzed Reagent grade.

Results

A. Erionite. 1. Removal of Aluminum by Chromium(III) Chloride. Aluminum removals between 8% and 64% were accomplished by contact of erionite with chromium(III) chloride solution (Table I). It is evident that removal of aluminum above 40% results in a considerable loss of crystallinity. It is also shown in Table I that clinoptilolite content is high in the dealuminized erionite, increasing from 20% in the original erionite to 30–40% after dealuminization.

2. Desilication Following Aluminum Removal. When the 38% dealuminized sample was refluxed with 1.0 N NaCl or 1.0 N NH_4Cl (150 ml of solution/g of zeolite), a portion of the silica in the structure was solubilized (Table II). The sorption capacity and the surface area increased in both steps.

3. Increase in Porosity. The nitrogen sorption isotherms (Figure 1) show the increase in porosity by successive removal of aluminum and silicon.

B. Clinoptilolite (Mixed with Phillipsite). The behavior of clinoptilolite (mixed with phillipsite) was similar to that of erionite (mixed with clinoptilolite) in that clinoptilolite content increased with dealuminization. Phillipsite was preferentially

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Table I. Treatment of Erionite with Chromium(III) Chloride

$CrCl_3$ soln (1.0 N), ml	None	120	600	1200(×2)	600(×3)	600(×3)	1200
Erionite, g		20	20	40	20	20	4
Reflux time, h		2	2	2(×2)	2(×3)	24(×3)	1
No. of treatments		1	1	2	3	3	1
Residue (washed, dried), g		16.9	15.0	27.6	13.5	12.7	3.2
Analysis, wt %							
SiO_2	66.8	73.4	75.1	80.6	82.2	86.6	80.5
Al_2O_3	15.4	15.5	13.8	11.6	10.6	7.1	12.0
Cr		0.21	0.16	0.17	0.30	0.42	0.35
Fe	1.95	2.30	2.12	2.0	1.56	2.05	1.98
K	3.7	3.93	3.4	2.1	1.82	7.25	1.8
Na	3.3	0.80	0.25	0.07	0.05	0.05	0.05
Ca	3.0	2.66	0.90	0.57			0.52
Mg	0.57	0.4	0.54	0.41		0.31	0.43
Al removal, %		8	20	38	44	64	35
$SiO_2:Al_2O_3$ ratio	7.3	8.0	8.3	11.8	13.2	23.9	11.4
n-Hexane absorption,[a] wt %	5.2	5.7	7.5	9.4	8.2	9.6	
Cyclohexane absorption,[a] wt %	1.7	2.2	2.7	3.7	5.8	7.4	
Crystallinity, x ray[b]							
% erionite	80	80	85	70	65	45	
% clinoptilolite	20	35	35	40	30	35	

[a] Equilibrium at 20 mm, room temperature. [b] Based on an arbitrary standard.

Table II. Some Properties of Treated Erionite

	Sorption, wt %			Surface area, m^2/g	Crystallinity, %
	H_2O	*n*-Hexane	Cyclohexane		
Erionite	13.3	5.2	1.7	286	80
Dealuminized	16.6	9.4	3.7	371	70
Then desilicated	17.9	10.7	6.8	408	85, 90[a]

[a] After ammonium exchange.

Table III. Sorption Capacity of Clinoptilolite

	Original	Dealuminized	Then desilicated
n-Hexane, wt %	0.9	3.2	4.5
Cyclohexane, wt %	0.8	4.0	5.6

attacked. After dealuminization and desilication, the clinoptilolite content was 95%.

The sorption capacities of the relevant materials are shown in Table III.

C. Zeolite T. A detailed study was made on the extraction of aluminum from synthetic zeolite T. The results are shown in Table IV. As in the case of erionite, subsequent desilication increased the sorption capacity.

Increase in time of reflux from 1 to 24 h and in normality of the extracting solution from 0.5 to 2.0 did not significantly increase the amount of aluminum removed, but increase in the total amount of chromic chloride did. The relationship is not linear.

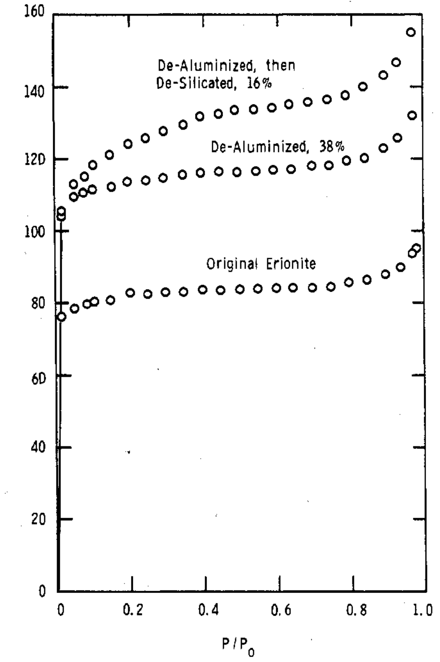


Figure 1. Nitrogen sorption isotherms.

D. Comparison of Ease of Aluminum Removal. The ease with which aluminum is removed from the dense zeolites is in the order synthetic T (easiest) > phillipsite > erionite >

Table IV. Treatment of Zeolite T with Chromium(III) Chloride

[$CrCl_3$ soln], N	None	1.0	1.0	1.0	1.0	1.0	1.0	0.5	2.0	2.0
Soln, ml		600	300	600	600	300	300	600	150	600
Zeolite T, g		40	20[a]	40	40	40	40	20	20	20
Reflux time, h		1	1	6	24	6	24	1	1	1
No. of treatments		1	1[b]	1	1	1	1	1	1	1
Residue (washed, dried), g		31.6	18.1	31.7	30.7	33.9	33.6	17.2	16.9	14.0
Analysis, wt %										
SiO_2	65.3	74.0	79.0	75.8	77.0	71.8	72.4	74.7	75.8	88.3
Al_2O_3	18.5	15.2	13.3	15.8	14.7	17.4	16.6	16.5	15.2	7.6
Cr		0.91	1.00	1.04	1.06	0.97	1.2	1.4	0.68	0.70
K	9.4	7.3	4.8	6.7	6.6	7.7	7.7	6.12	7.92	2.61
Na	2.3	0.24	0.04	0.23	0.20	0.37	0.32	0.18	0.35	0.02
Al removal, wt %		28	40[c]	27	32	15	19	22	28	70
$SiO_2:Al_2O_3$ ratio	6.0	8.3	10.1	8.2	8.9	7.0	7.4	7.7	8.4	15.4
n-Hexane absorption,[d] wt %	6.3	7.5	8.7	9.1	8.6	8.0	8.7	7.3	6.8	7.0
Cyclohexane absorption,[d] wt %	2.1	3.2	4.1	4.9	5.5	3.8	3.8	2.7	4.3	4.7
Crystallinity,[e] %	55	75	70	80	80	80	80	85	85	*f*

[a] 20 g zeolite from first treatment (preceding column). [b] Residue from first treatment. [c] Based on original amount of zeolite. [d] Equilibrium at 20 mm, room temperature. [e] Based on the same standard mentioned in Table I, footnote *b*. [f] Mainly amorphous.

Table V

	$CrCl_3$	$Cr(NO_3)_3$	$KCr(SO_4)_2$
pH of 1.0 N soln	2.1	2.3	2.7
Al removal, wt %	28	28	19

Table VI. Al Removal from Erionite

	$CrCl_3$			HCl
	A	B	C	D
Soln, ml/g of zeolite	6	30	30(×2)	150(×4)
No. of treatments	1	1	2	4
Total reflux time, h	2	2	2	20
% Al removed	8	20	38	2

Table VII. Al Removal from Zeolite T

	$CrCl_3$		HCl	
Soln, ml/g of zeolite	50	300	50	300
Reflux time, min	10	60	10	60
% Al removed	15	89	Nil	4

clinoptilolite. Clinoptilolite has five-membered rings,[4] which may explain its resistance to dealuminization by chromium(III) chloride.

Aluminum removal from amorphous silica–alumina, under the same conditions, was higher than for any of the dense zeolites.

E. Comparison of Chromium Salts. Chromium nitrate and potassium chromium sulfate remove aluminum in the same manner as chromium chloride (Table V).

The lower aluminum removal with solutions of higher pH $KCr(SO_4)_2$ indicates that a preferred procedure may be mild acid exchange of the zeolite to remove cations (K^+, Na^+, etc.) *first*, before contact with the aquochromium(III) ion. Kerr's theory states that hydrolysis can take place only after H^+ exchange,[3] and this is in agreement with the above results.

No aluminum was removed by treatment of natural erionite with a 0.7 N ammonium chromate solution.

F. Comparison of Aluminum Removal from Erionite and Zeolite T by Chromium(III) Chloride and Hydrochloric Acid. The results are shown in Tables VI and VII. In each case, the chromium(III) chloride solution was 1.0 N (pH 2.1) and the hydrochloric acid was 0.01 N (pH 1.9). In experiments A and D, the total chloride contents of the solutions were the same, and the pH values were approximately the same, but, in spite of the much longer contact time in D than in A, only one-fourth as much aluminum was removed.

Zeolite T also dealuminizes to a greater extent with the chromium(III) chloride solution than with hydrochloric acid (Table VII).

G. Comparison of Aluminum Removal with Chromium(III) Chloride and Ethylenediaminetetraacetic Acid (EDTA). Dealuminization of erionite with EDTA solution[3] and with $CrCl_3$ solution, to about the same level, gave materials of the same crystallinity and cyclohexane adsorption, but the product from the EDTA treatment gave a smaller *n*-hexane adsorption. Upon desilication with 1.0 N NaCl solution, however, the adsorption properties of the material from the EDTA treatment reverted to those of the original erionite (Table VIII). This shows that the EDTA anion, too big to enter the erionite pore, removed surface aluminum, leaving a silica "shell". Removal of this silica with sodium chloride uncovered the original erionite surface.

H. Composition of Extract. The extract solution, i.e., the filtrate from the reaction slurry, is clear blue-green and remains clear on standing for months. Two of these extract solutions were evaporated on a steam bath to thick viscous masses, which were dried overnight at 110 °C and analyzed. (See Table IX.)

Table VIII. Comparison of $CrCl_3$ and EDTA

	Dealuminization		
Treating agent	None	1.0 N $CrCl_3$	EDTA
% Al removed		38	44
Fe content, wt %	1.95	2.0	0.15
Cr content, wt %		0.17	
$SiO_2:Al_2O_3$ ratio	7.3	11.8	13.1
Adsorptions, wt %			
n-Hexane	5.2	9.4	6.7
Cyclohexane	1.7	3.7	3.6
Crystallinity, %	80	70	75
	Desilication		
Treating agent	None	1.0 N NaCl[a]	1.0 N NaCl[a]
% silica removed		16	22
$SiO_2:Al_2O_3$ ratio		9.9	9.8
Adsorptions, wt %			
n-Hexane	5.2	10.7	5.8
Cyclohexane	1.7	6.8	1.2
Crystallinity, %	80	85	90

[a] 300 ml of 1.0 N NaCl/g of zeolite, reflux for 1 h, three times.

Table IX. Composition of Extract

Al removed, wt %	28	32
Compn of dried extract, wt %		
Cr	50.3	56.1
Al_2O_3	8.9	11.6
SiO_2	1.94	2.32
Cr recovery,[a] wt %	83	90
Al recovery, wt %	89	97
Si:Al	0.2	0.2
Cr:Al(found)	5.6	5.2
Cr:Al(calcd)[b]	5.9	5.2

[a] If the chromium left in the zeolite is included, the recovery figures are 85% and 97%. [b] Based on Cr in the treating solution and loss of Al from the zeolite.

Table X. Dissolution of $Al(OH)_3$ by $CrCl_3$ Solution

Reflux time, h	$Al(OH)_3$ dissolved, wt %	pH of soln
0	0	1.33
1	7	1.70
24	37	2.09
72	59	2.30
96	65	2.32

The silica analysis shows that about one silicon atom is removed with every five aluminum atoms. The close agreement between the found and calculated Cr:Al ratios shows that the removed aluminum is all in the solution (but does not say what the complex is).

I. Solution of Aluminum Hydroxide in Chromium(III) Chloride Solution. Aluminum hydroxide powder (1 g) was added to a refluxing $CrCl_3$ solution (30 ml, 2 N), the pH of which was measured as the aluminum hydroxide slowly dissolved (Table X).

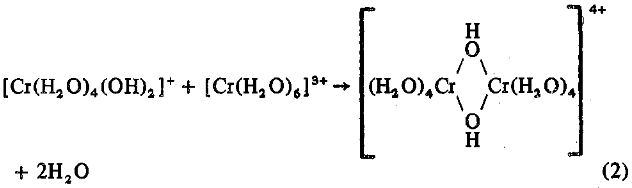
The experiment was repeated using 2 N sodium chloride in place of chromium(III) chloride. The solution was acidified to pH 2 with HCl. After 21 h, the pH rose to 2.68, and the solution was acidified to pH 2 again. After 20 h more of refluxing, the pH was 2.45, and the amount of the aluminum hydroxide dissolved was only 4 wt %. This shows that HCl was not used in significant quantities to destroy any free alkali in the original hydroxide.

If, instead of addition of aluminum hydroxide, sodium hydroxide is added to chromium(III) chloride solution, quite different results are obtained. The pH rises immediately and chromium(III) hydroxide precipitates. As the refluxing is continued over a period of some hours, the pH drops slowly, closely approaching the original value, and the precipitate goes back into solution. The resulting green solutions do not change in pH or color upon cooling and diluting. The color probably indicates that chloride is coordinated to the chromium.

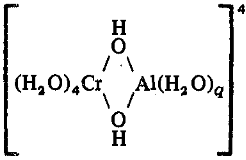
Discussion

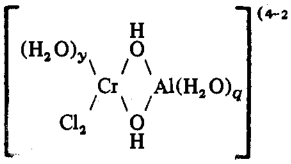
It is well known that polyvalent metal ions, in aqueous solution, are hydrated and that the coordinated water molecules readily lose hydrogen ions, which make the solution strongly acidic. Assuming that there are six water molecules in the complex, the reaction is written for chromium(III) as (1). The coordinated hydroxo group is a powerful complexing agent and may displace a water molecule from an adjacent complex ion. This process is known as olation[5] (eq 2). There may be one, two, or three "ol bridges" between the two metal ions. If the remaining coordinated water molecules lose hydrogen ions, further olation can take place, leading to the formation of large aggregates, even up to colloidal dimensions.

$$[Cr(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Cr(H_2O)_5OH]^{2+} + H_3O^+ \rightleftharpoons [Cr(H_2O)_4(OH)_2]^+ + H_3O^+ \rightleftharpoons \text{etc.} \quad (1)$$


(2)

The removal of aluminum from zeolites by chromium(III) chloride probably takes place through the formation of ol bridges in the pores of the zeolite. It is reasonable to picture the hydrated chromium(III) ion entering 5-Å pores (eight-membered rings) by temporary replacement of aquo groups. It is postulated that, once inside the pore, the aquochromium ion complexes with the hydrolyzed aluminum ions to form complexes of the type





which then diffuse out of the pore. Once outside the pore, olation with the excess chromium ions in the solution proceeds to the formation of particles containing five or six chromium ions for each aluminum ion. Aluminum removal must stop when all of the chromium is tied up in these large complexes or when the pH of the solution reaches a value which limits the number of hydroxo groups so much that olation no longer takes place.

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Registry No. Erionite, 12510-42-8; clinoptilolite, 12173-10-3; phillipsite, 12174-18-4; aluminum hydroxide, 21645-51-2; chromium(III) chloride, 10025-73-7; chromium nitrate, 13548-38-4; potassium chromium sulfate, 10141-00-1; hydrochloric acid, 7647-01-0; EDTA, 60-00-4; Al, 7429-90-5.

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Reactions of Molybdates with Polyphosphates. 1. Spectrophotometric and Electron Paramagnetic Resonance Studies of Molybdenum(V)–Pyrophosphate Complexation

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In the course of a general study of mediation of biologically important phosphorylation and hydrolysis reactions by polyvalent transition metal–oxo ions, we have investigated the formation of complexes between pyrophosphate and Mo species. Previously, complex formation had been established, but neither formulations of the complexes nor oxidation states of the Mo had been settled. Treatment of $Mo_2O_4^{2+}$ with aqueous solutions of polyphosphate ions gives rise to complexes exhibiting an absorption peak in the near-ultraviolet region of the spectrum which fades away rapidly in the presence of oxidants such as oxygen, perchlorate ion, and nitrate ion. In the case of pyrophosphate ion, and thus far only in that case, an EPR signal is observed exhibiting ^{31}P hyperfine splitting. Isotopically enriched ^{95}Mo samples exhibit six hyperfine lines each split into five superhyperfine lines by the interaction of an unpaired d electron with four equivalent phosphorus atoms. Bis(pyrophosphate) complexes of $Mo_2O_4^{2+}$ are formed at pH 4.5 and dissociate to an extent of only 5% to form $MoO_2(P_2O_7)_2H_n^{n-7}$. Values are $g = 1.952$, $a(Mo)/g\beta = 56$ G, and $a(P)/g\beta = 10$ G at pH 4.5 and room temperature. Frozen solutions of ^{95}Mo complexes gave EPR spectra characterized by small g anisotropy and large hyperfine anisotropy. No ^{31}P hyperfine lines are observed in frozen solutions. Solutions containing complexes of $Mo_2O_4^{2+}$ with triphosphate ion, ATP, and ADP give no EPR signals under comparable conditions.

Introduction

Molybdenum in oxidation states VI, V, and IV is a powerful catalyst for the reduction of oxy ions such as nitrates and perchlorates[1,2] and of nitrogen[3] and also for the enzymatic reduction of NO_3^- and N_2 and oxidation of xanthine, purines, SO_3^{2-}, and aldehydes.[4,5] It also catalyzes the hydrolysis of ATP[6]. The nature and reactivity of complexes of Mo(IV), -(V), and -(VI) with oxy ions is thus of fundamental significance. Recently oxidations of VO^{2+} have been coupled directly to polyphosphate hydrolyses.[7] These observations have prompted us to investigate interactions of another d^1 species, Mo(V), with polyphosphates. A primary objective is to produce labile P(V) by increasing the electron density on phosphorus(V) atoms.

This report describes a complex of Mo(V) with pyrophosphate which exhibits interaction of the d^1 electron with the ^{31}P nucleus. Although polyphosphates form complexes with most metal ions[8–10] and electroanalytical studies[11,12] reveal complex formation of molybdenum and pyrophosphate in aqueous solution, formulas and metal oxidation states in