ION-EXCHANGE OF MORDENITE-TYPE
ZEOLITE WITH Mg^{2+} AND La^{3+}

MASTER

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ABSTRACT

Special techniques were tried for ion-exchanging Mg^{2+} and La^{3+} into mordenite, which is an acid-stable zeolite of possible catalytic value to the coal industry. Electron microprobe analysis showed that ion-exchange occurred only along the main channels of the 100 μm long needles. Complete exchange was not achieved, and exchange was always higher at the ends of the needles. The highest content of Mg^{2+} is 3.7 atoms per unit cell (with 0.2Na and 1.0K residual), and the highest content of La^{3+} is 1.7 atoms per unit cell (with 1.7Na and 0.1K residual). Higher ion-exchange should be achievable for smaller crystals, such as are commonly made synthetically, but such crystals would be too small for routine X-ray structure analysis. Detailed structural data are given for an Mg^{2+} -exchanged crystal, but interpretation of the cation populations is equivocal.

Suggestions are made for further work using (a) X-ray powder techniques and (b) X-ray single-crystal techniques based on a rotating-anode X-ray generator.

SCOPE AND SUMMARY OF INVESTIGATION

The aim of the investigation is to determine whether mordenite-type zeolite can be prepared with La^{3+} and Mg^{2+} cations, and if so, to determine the crystal structures. Faujasite-type zeolites with these cations have proven to be important catalysts in the petroleum industry, and mordenite-type ones may prove useful in the acidic conditions expected in the coal industry.

Ion-exchange of significant amounts of Mg^{2+} and La^{3+} into mordenite has been achieved using special techniques, but complete exchange of the original cations was not achieved. Large, natural crystals were analyzed with an electron microprobe, and ion-exchange was found to occur only along the main channels. A crystal-structure determination of a partly-exchanged Na,Mg-mordenite was inconclusive.

It should be easier to obtain higher levels of ion-exchange for smaller synthetic crystals (e.g. 1-10 μm), but such crystals would be too small for routine single-crystal X-ray structural analysis. Further work could utilize (a) X-ray powder methods to follow the extent of ion-exchange (b) development of X-ray structure analysis of smaller crystals using a rotating-anode X-ray generator. For (a), it would be possible to use calculated X-ray powder patterns for assumed site occupancies, but some ambiguity would remain on the extent of ion exchange. For (b), it should prove possible to utilize crystals some 20-50 times smaller than the present ones, perhaps 50 x 10 x 10 μm . It would also be possible to set up diffusion models based on data for large crystals, and estimate the rate of ion exchange from small crystals. Termination of funding made it impossible to follow up these three possibilities under the present grant, but attempts will be made to raise the necessary funds.

EXPERIMENTS

All experiments were made on natural mordenite crystals from Challis Valley,

Idaho, because these are the only known crystals large enough for detailed crystal structure determination. The starting composition is $(\text{Na}_{3.9}\text{Mg}_{0.3}\text{K}_{0.4}\text{Ca}_{1.5})(\text{Al}_8\text{Si}_{40}\text{O}_{96}) \cdot x\text{H}_2\text{O}$.

No significant ion-exchange by Mg^{2+} and La^{3+} was achieved using aqueous salt solutions at 90°C . Special techniques were then developed for ion-exchange at higher temperatures.

Experiment #1

(1) Twenty crystals were placed in a watch glass with large excess of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and the watch glass placed inside a Petri dish. $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ melts at 89°C and loses water slowly at higher temperature.

(2) The crystals were heated to 200°C for 2 days, cooled to room temperature, and washed with deionized water to remove the Mg-salt which had dehydrated and solidified.

(3) A crystal was removed from each batch and analyzed with an ARL electron microprobe (solid-state detector).

(4) The procedure was repeated for additional periods of 4 days and 2 days.

(5) The data (Table 1) show that (a) ion-exchange proceeds from the end of the needles into the center, and (b) the maximum exchange results in ~ 3.2 Mg atoms per unit cell and ~ 0.5 residual Ca atoms which appear to be unexchangeable by this technique. The charge equivalent of the exchangeable cations (~ 7.4) is less than that of the framework (~ 8.2) suggesting the presence of undetected protons. We suggest that ions in the "side-pockets" are very difficult or impossible to replace by Mg.

Experiment #2

(1) Thirty crystals were placed in a pyrex tube which was filled with 2M MgCl_2 , and the tube was sealed with a gas-oxygen torch.

(2) The glass tube was placed in an oven at 180°C for 2 weeks after which

the capsule was opened and some crystals were analyzed (Table 2). (3) The tube was then resealed, and the procedure repeated for a further period of one month. Substantial but not complete exchange was obtained. (4) A similar procedure for 0.1M LaCl_2 for 2 weeks gave only slight exchange at the end of the crystals.

Experiment #3

This experiment was designed to attempt ion-exchange via a K-exchanged intermediary, which procedure has been found successful with several zeolites.

(1) Thirty crystals were placed in a test-tube filled with 1M KCl and heated for 3 days at 95°C.

(2) The crystals were washed and transferred to a watch glass. An excess of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added and the watch glass was placed inside a Petri dish and covered.

(3) The Petri dish was placed inside an oven hot enough (150° or 200°C) to melt the salt.

(4) After several days the sample was removed from the oven, the $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was washed away, and a crystal was analyzed (Table 3).

(5) Remaining crystals were heated to 300°C, and then treated again with molten salt.

(6) The procedure was then repeated twice with intermediate heating to 500°C.

Experiment #4

An attempt was made to prepare the fully ion-exchanged Mg^{2+} form by rapid heating of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ to 750°C hoping that the H_2O would be driven off and the MgCl_2 would melt (m.p. 708°C). Instead of melting, MgO was formed.

Experiment #5

Another experiment was designed to attempt ion-exchange via a K-exchanged intermediary.

(1) Thirty crystals were placed in a pyrex glass tube filled with 1M KCl, and heated for 3-days at 90°C.

(2) A microprobe analysis indicated that K had replaced Na, Mg and Ca.

(3) The crystals were washed and 0.5M MgCl_2 was added to the glass tube. The tube was sealed and placed in an oven at 180°C for 10 days.

(4) Results of the microprobe analysis are given in Table 4.

(5) A similar procedure was used in an attempt to prepare the La^{3+} form with the ion-exchange being carried out for 13 days. La^{3+} was detected only at the ends of the mordenite needles (Table 4).

Experiment #6

A final attempt was made to prepare a fully ion-exchanged Mg-mordenite using a Morey bomb in order to carry out the ion-exchanges at even higher temperatures.

(1) About 50 mordenite crystals were placed in two quartz tubes, one filled with 2M MgCl_2 and the other with 0.1M LaCl_3 . The quartz capsules were sealed with a gas oxygen torch, and placed in a Morey bomb along with some water and the bomb was sealed.

(2) The bomb was placed in a furnace for two days at 350°C.

(3) The bomb and the quartz capsules were cooled, opened and subjected to microprobe analyses. Results are given in Table 5.

(4) 50 crystals were placed in a quartz tube and filled with $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, sealed and placed in a Morey bomb and heated to 350°C for 6 days. The crystals decomposed.

(5) Number (4) was repeated for 1 day at 300°C and the crystals were analyzed (Table 5).

Crystal-structure analysis

Single-crystal X-ray data were obtained for a dehydrated Mg-bearing specimen from experiment #5, which had average composition $(\text{Na}_{2.9}\text{Mg}_{2.2}\text{K}_{0.3})(\text{Al}_{7.9}\text{Si}_{40.2}\text{O}_{96})$.

Although the refinement gave an excellent R-factor of 0.05, the interpretation of the electron density is inconclusive because of the similarity of the scattering factor of Na and Mg. Selected data are given in Table 6, and the remaining data are on file at Chicago.

PERSONNEL

The principal investigator has devoted about 5% of his time to supervising the project.

The main effort came from Joseph J. Pluth who devoted 40% of his time to the project, and from John L. Schlenker who spent 20% of his time on the project averaged over the nine-month term.

OTHER SUPPORT

Basic research facilities were provided by the Materials Research Laboratory, funded by the National Science Foundation.

Table 1. Electron microprobe analyses of products of expt. 1.

Sample	Position in crystal	T°C	Time	Na	Mg	K	Ca	Al	Si	O (assumed)	%	Total cation charge
untreated	uniform	-	-	3.9	0.3	0.4	1.5	8.3	39.8	96	86	7.9
first treatment	near end	200°C	2 days	-	1.9	-	1.32	8.1	40.3	96	81	6.4
second treatment	end	200°C	4 days	-	3.2	0.1	0.4	8.1	40.0	96	82	7.3
	1/4 along		extra	-	2.0	0.1	1.2	8.0	40.3	96	82	6.5
	center			-	0.2	-	2.2	8.1	40.5	96	82	4.8
third treatment	end	200°C	3 days	0.2	3.1	0.1	0.6	8.2	40.0	96	82	7.8
	1/4 along		extra	0.2	2.2	0.1	1.7	8.1	39.9	96	79	8.2
	center			0.2	3.1	0.1	0.7	8.4	39.7	96	81	7.9

Electron microprobe analysis. Solid-state detector. Reed-Ware program. 15kV. 0.07μA beam current. 50μm spot.

Table 2. Electron microprobe analyses of products of expt. 2.

Sample	Position in crystal	T°C	Time	Na	Mg/La	K	Ca	Al	Si	O (assumed) %	Total cation charge
untreated ^a	uniform			3.9	0.3	0.4	1.5	8.3	39.8	96 86	7.9
first treatment with MgCl ₂ ^b	end	180°C	2 weeks	0.2	2.9	0.1	0.9	8.9	39.4	96 83	7.9
	1/4 along			0.3	2.3	0.1	1.4	8.6	39.6	96 83	7.8
	center			0.0	1.3	0.0	2.5	8.7	39.6	96 84	7.6
second treatment ^b	end	180°C	1 month	-	2.7	-	0.8	8.3	40.0	96 84	7.0
	center			-	2.3	-	1.6	8.4	39.7	96 84	7.2
first treatment with LaCl ₃ ^b	end	180°C	2 weeks	0.7	0.4	0.1	1.8	8.5	40.3	96 82	5.6
	1/4 along			0.9	-	0.1	2.0	9.0	40.0	96 82	5.9
	center			1.2	-	0.3	1.9	8.4	40.4	96 83	5.3

Electron microprobe analyses. (a) Solid-state detector. Reed-Ware program. 15kV. 0.07μA. 50μm spot.

(b) Spectrometers. GLAB program.

Table 3. Electron microprobe analyses of products of expt. 3.

Sample	Position in crystal	T°C	Time	Na	Mg	K	Ca	Al	Si	O (assumed)	%	Total cation charge
untreated	uniform	-	-	3.9	0.3	0.4	1.5	8.3	39.8	96	86	7.9
first treatment (KCl)	uniform	95°C	3 days	-	0.1	7.7	0.4	8.3	39.6	96	88	8.6
second treatment	end	150°C	3 days	0.3	2.8	1.5	-	8.1	40.1	96	81	7.4
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	center			0.3	2.1	1.9	-	8.3	40.2	96	83	6.4
third treatment: heating to 300°C, then with molten salt.	end	200°C	2 days	0.4	2.7	1.5	-	8.2	39.9	96	84	7.3
				0.5	1.8	1.70	-	8.4	40.5	96	85	5.8
fourth treatment: heating to 500°C, then with molten salt.	end	200°C	3 days	0.2	3.7	1.0	-	8.1	39.7	96	89	8.6
	center			0.2	2.6	1.0	-	8.3	40.2	96	90	6.4
fifth treatment: heating to 500°C, then with molten salt.	end	200°C	3 days	0.1	3.0	1.0	-	8.2	40.0	96	86	7.1
	center			0.2	1.8	1.1	-	8.6	40.4	96	86	4.9

Electron microprobe analysis. Solid-state detector. Reed-Ware program. 15kV. 0.02 μ A beam current. 50 μ m spot.

Table 4. Electron microprobe analyses of expt. 5.

Sample	Position in crystal	T°C	Time	Na	Mg/La	K	Ca	Al	Si	O (assumed) %	Total cation charge
untreated ^a	uniform	-	-	3.9	0.3	0.4	1.5	8.3	39.8	96 86	7.9
first treatment ^a (1M KCl)	uniform	90°C	3 days	(little residual Na,Mg,Ca detected)							
second treatment ^a (2M MgCl ₂)	end	180°C	10 days	2.8	2.6	.2	-	7.9	40.1	96 85	8.2
	center			3.3	1.7	.2	-	8.0	40.3	96 84	6.9
first treatment ^b (1M KCl)	uniform	90°C	9 days	(little residual Na,Mg,Ca detected)							
second treatment ^b (0.1M LaCl ₃)	end	180°C	13 days	1.7	1.7	0.1	-	7.8	40.4	96 90	7.0
	center			2.8	-	.3	-	8.0	41.2	96 90	3.2

Electron microprobe analyses. (a) Solid-state detector. Reed Ware program 15kV 0.015μA 50μm spot
 (b) spectrometers. GLAB program 15kV 0.075μA 50μm spot.

Table 5. Electron microprobe analyses of products of expt. 6.

Sample	Position in crystal	T°C	Time	Na	Mg/La	K	Ca	Al	Si	O (assumed) %	Total cation charge	
untreated	uniform	-	-	3.9	0.3	0.4	1.5	8.3	39.8	96	86	7.9
treatment (2M MgCl ₂)	end	350°C	2 days	-	2.5	0.2	0.8	7.7	40.5	96	88	6.8
	center				1.9	0.1	1.5	7.6	40.6	96	86	6.8
treatment (.1M LaCl ₃)	uniform	350°C	2 days	-	-	-	1.7	8.1	41.1	96	88	3.4
treatment (Mg(NO ₃) ₂ ·6H ₂ O)	end	300°C	1 day	-	2.7	-	0.9	7.9	40.2	96	85	7.2
	center			-	0.9	-	2.1	8.0	40.5	96	86	6.0

Table 6. Positional and population parameters and selected interatomic distances and angles for a partially exchanged Mg mordenite. (Cell parameters Cmcn a 18.063(4), b 20.178(4), c 7.4755(14)).

	Type	Population	x/a	y/b	z/c
T(1)	(16h)	16	0.1966(1)	0.4267(1)	0.5423(2)
T(2)	(16h)	16	0.1969(1)	0.1906(1)	0.5450(2)
T(3)	(8g)	8	0.0853(1)	0.3827(1)	1/4
T(4)	(8g)	8	0.0848(1)	0.2244(1)	1/4
O(1)	(16h)	16	0.1234(2)	0.4141(2)	0.4282(5)
O(2)	(16h)	16	0.1245(2)	0.1945(2)	0.4262(4)
O(3)	(16h)	16	0.2609(3)	0.3769(2)	0.4877(5)
O(4)	(8g)	8	0.0899(3)	0.3034(3)	1/4
O(5)	(8g)	8	0.1718(3)	0.1947(3)	3/4
O(6)	(8g)	8	0.1753(3)	0.4187(3)	3/4
O(7)	(8e)	8	0.2259(3)	1/2	1/2
O(8)	(8d)	8	1/4	1/4	1/2
O(9)	(4c)	4	0	0.4095(5)	1/4
O(10)	(4c)	4	0	0.2005(4)	1/4
Mg(I)	(4b)	1.53(6)	0	1/2	0
Mg(II)	(4c)	0.28(5)	0	0.4438(4)	3/4
Mg(IV)	(4c)	0.39(5)	0	0.1897(3)	3/4
Mg(VI)	(8g)	0.54(6)	0.206(3)	0.044(2)	3/4

Interatomic Distances (Å) and Angles (°)

Framework

T(1)-O(1)	1.595(4)	O(1)-T(1)-O(3)	111.6(3)	T(2)-O(2)	1.582(3)	O(2)-T(2)-O(3)	110.8(2)
-O(3)	1.589(4)	-O(6)	107.6(3)	-O(3)	1.580(4)	-O(5)	107.6(2)
-O(6)	1.608(2)	-O(7)	108.4(2)	-O(5)	1.600(2)	-O(8)	110.3(2)
-O(7)	1.602(3)	O(3)-T(1)-O(6)	111.0(3)	-O(8)	1.572(2)	O(3)-T(2)-O(5)	109.2(3)
		-O(7)	107.0(3)			-O(8)	109.2(2)
		O(6)-T(1)-O(7)	111.3(2)			O(5)-T(2)-O(8)	109.8(2)
T(3)-O(1)	1.627(4)	O(1)-T(3)-O(1)	109.9(3)	2 T(4)-O(2)	1.617(4)	O(2)-T(4)-O(2)	109.1(3)
-O(4)	1.603(6) 2	O(4)	111.5(2)	O(4)	1.596(7) 2	O(4)	110.4(2)
-O(9)	1.632(4) 2	-O(9)	105.7(2)	O(10)	1.607(3) 2	O(10)	108.1(2)
		O(4)-T(3)-O(9)	112.4(4)			O(4)-T(4)-O(10)	110.8(4)

Cation

Mg(I)-O(9)	2.613(7)	Mg(IV)-O(5)	3.105(6)
-O(1)	2.874(5)	-O(2)	3.306(4)
Mg(II)-O(9)	2.96(8)	Mg(VI)-O(7)	2.41(3)
-O(6)	3.207(13)	-O(3)	2.46(3)
-O(1)	3.334(14)		