PROGRESS REPORT SUBMITTED TO UNITED STATES ENERGY
RESEARCH AND DEVELOPMENT ADMINISTRATION

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SCOPE 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. 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. Investigation is continuing of high-temperature exchange methods, and crystal structure determinations will be made of the most highly-exchanged crystals. Details of the experiments follow.

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 0.5M 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_3 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.

Crystal-structure analysis #1

Single-crystal data were obtained for a dehydrated specimen produced early in the investigation, which was found to have 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 scattering factor of Na and Mg. The data are on file at Chicago, and will be interpreted when further X-ray studies have been made.

ESTIMATE OF FUTURE WORK

Further attempts will be made to increase the degree of exchange by using longer times and higher temperatures. Crystal-structure analyses will be made of

the most Mg-rich specimens. The future of the work on La-exchange is quite speculative, but it is hoped that molten-salt exchange at $\sim 700^{\circ}\text{C}$ may be effective.

PERSONNEL

The principal investigator has devoted about 5% of his time to supervising the project, and will continue to do so for the balance of the project.

The main effort comes from Joseph J. Pluth who is devoting approximately 40% of his time to the project, and from John L. Schlenker who is spending about 20% 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. 0.07 μ A beam current. 50 μ m 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	-	0.80	8.3	40.0	96 84	7.0
	center			-	2.3	-	1.6	8.4	39.7	96 84	7.8
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			0.1	-	0.1	2.0	9.0	40.0	96 82	4.2
	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 $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	end	150°C	3 days	0.3	2.8	1.5	-	8.1	40.1	96	81	7.4
	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
	center			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. 0.07 μ A beam current. 50 μ m spot.