# REDUCTION OF INTERLAYER Ni²⁺ AND Cu²⁺ IN MONTMORILLONITE WITH HYDROGEN

All oxidation-reduction studies undertaken in various phyllosilicates other than vermiculite (Patel, 1978; Patel *et al.*, 1978) have been on the structural iron; no attempt has been made to study the reduction behavior of interlayer cations. The degree of reduction of transition metal-exchanged vermiculites increases with the decrease in the lattice charge. Thus, for structurally similar montmorillonites, reduction reactions may be carried out in the interlayer space. The present investigation is a kinetic study of the $H_2$ reduction of Ni²⁺ and Cu²⁺ exchanged in the interlayer space of montmorillonite between 190° and 250°C. These relatively small transition metal ions were chosen for study because they are (1) liable to migrate (Hofmann and Klemen, 1950; Calvet and Prost, 1971) into the octahedral layer and create a quasitrioctahedral environment around the octahedral cations, thereby giving added stability to the structure; and (2) easily reduced and form finely dispersed metal particles (Kermarec *et al.*, 1977).

This study also presents data on the structural rearrangement that can take place around vacant sites in the octahedral layer of montmorillonite as a result of the migration of interlayer cations following the thermal reduction treatment (Brindley and Brown, 1980).

## MATERIALS AND METHODS

The montmorillonite studied (Patel, 1975) is a Wyoming bentonite (No. 625, B.R.G.M., Orléans, France). The bentonite was washed free of quartz and other impurities and exchanged with Ni²⁺, Cu²⁺, or Ni²⁺ + Cu²⁺. The structural formula of the mineral before exchange was reported by Patel (1975) as:

$$(Si_{3.85}Fe^{3+}{}_{0.1}Al_{0.05})(Al_{1.79}Fe^{2+}{}_{0.05}Mg_{0.22})O_{10}(OH)_2Ca_{0.21} \cdot xH_2O$$
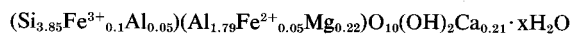
X-ray powder diffraction (XRD) and infrared (IR) analyses showed the presence of about 2% cristobalite impurity. The final suspension was lyophilized (Patel, 1981).

$H_2$ uptake was measured at various temperatures from the change of volume at fixed $H_2$ pressures (6.665 kPa). The pressure could be read with a precision of ±13.3 Pa and volume of ±0.1 cm³. Care was taken to prevent contamination of the solid surface by water and grease vapors during heating. Readings during the reduction process were preceded by filling the cold trap with liquid $N_2$ to condense the water molecules produced from the solid during reduction. In the absence of such a trap, $H_2$ uptake by the mineral proceeded in an irregular manner. All samples were pretreated at 250°C with a heating rate of 60°C/hr and for a duration of 20 hr under a vacuum of 0.133 Pa.

XRD analysis of various samples was carried out *in situ* wherein the treated samples were transferred to a Lindmann capillary tube and sealed under vacuum. A Guinier-Wolff camera with CuK$\alpha$ radiation was used.

## RESULTS AND DISCUSSION

Table 1 shows the interlayer cation composition (determined by atomic absorption spectrometry) of various exchanged montmorillonites. The last three columns of this table list the data in terms of number of metal atoms/g. Because the amount of $H_2$ taken up during reduction is of the order of $10^{-20}$ atoms/g, M²⁺ values have also been expressed in this manner.

The d(001) values obtained from XRD studies show that the interlayer distance decreases between 25° and 230°C to a constant value of 9.7 Å. Therefore, heating to at least 230°C is required for the complete elimination of interlayer water. Samples heated at 280°C under a vacuum of 0.133 Pa for 48 hr showed reversibility in swelling behavior as well as all characteristic XRD reflections. This reversibility was lost at higher temperatures.

The hydroxyl groups of dioctahedral montmorillonite are less strongly held than those of its trioctahedral counterpart, vermiculite. Thus, the dehydroxylation of montmorillonite should take place at a much lower temperature than the dehydroxylation of vermiculite, thereby limiting reduction kinetic studies in montmorillonite to below 250°C, compared to below 400°C for some vermiculites (Patel, 1978). Because reduction was carried out at or below the pretreatment temperature, interference in $H_2$ uptake by structural or interlayer was minimized. From the results of a blank experiment with Na-montmorillonite heated in helium, the above assumption was found to be valid. It was also presumed from this experiment that the amount of structural iron was too small to add significantly to the $H_2$ uptake of M²⁺ during reduction.

The time vs. nH (number of hydrogen atoms adsorbed) curves for all samples examined are similar; that for Ni²⁺-montmorillonite is presented in Figure 1. The linearity of $H_2$ adsorption vs. time was maintained fairly well up to the first two hours and to some extent up to the fifth hour. After 8 to 10 hr of reduction, the rate at which $H_2$ was adsorbed was very slow, leading towards a state of saturation. Because the curves for all samples were similar in shape, the same reaction mechanism is likely for all systems. The near absence of $H_2$ uptake after the tenth hour may be due to the inhibited diffusion of $H_2$ in the layered structure, probably due to the production of water molecules during the reaction. The following reaction mechanism is therefore likely (Mt = montmorillonite):

$$Mt-O-Ni(OH)^+ + H_2 \rightarrow Mt-O-\overset{H}{\underset{|}{N}}i-\overset{H}{\underset{|}{O}}-H \rightarrow Ni^0 + H_2O + Mt-OH,$$
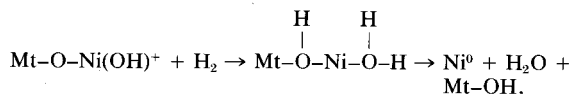
where O represents structural oxygen on the plane of silicate sheet. Although the amount of water produced by the reduction reaction was difficult to measure with precision, it increased with temperature or with an increase in the amount of M²⁺, supporting the above mechanism. In view of the similarity of the structures of montmorillonite and vermiculite, the reduction may have taken place through interlamellar diffusion of $H_2$ (Patel, 1978).

The energies of activation, calculated from the initial portions of the curves for the four systems are 17, 16, 16, and 18 kcal/mole for samples 1, 2, 3, and 4, respectively. From the values of nH₂ (15 hr) at various temperatures (190°–250°C) listed in Table 2, the $H_2$ uptake was proportional to the M²⁺ values, i.e.,

Sample 1 > Sample 3 > Sample 2 > Sample 4.

From the percentages of transition metal interlayer cations that were reduced after 15 hr (Table 3),

$$n_1/n_2 = 1.4 \text{ and } (nH_2)_1/(nH_2)_2 = 1.5,$$

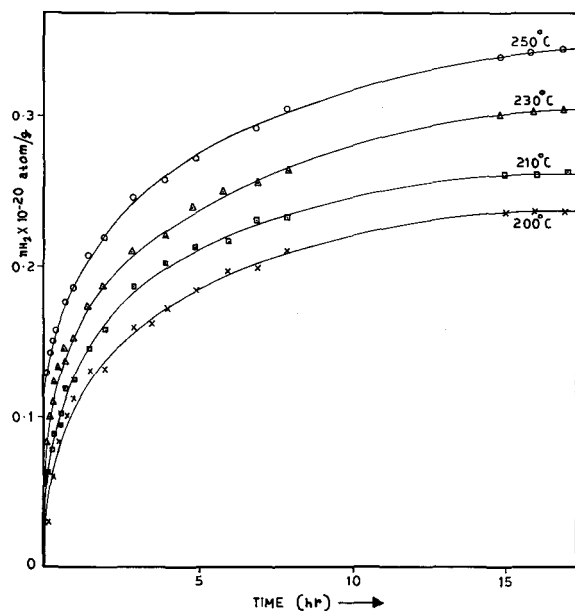Figure 1. H$_2$ uptake of Ni-montmorillonite (sample 1).

Table 2. H$_2$ uptake in various samples in 15 hr (atoms/g × 10$^{20}$).

| Tempera-ture (°C) | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Ni-vermi-culite |
|---|---|---|---|---|---|
| 250 | 0.337 | 0.276 | 0.280 | 0.266 | 0.452 |
| 240 | — | — | 0.262 | — | — |
| 230 | 0.288 | 0.242 | 0.240 | 0.232 | 0.250 |
| 210 | 0.258 | 0.206 | 0.203 | 0.192 | 0.236 |
| 200 | 0.226 | — | — | — | 0.215 |
| 190 | — | 0.172 | — | — | 0.188 |

Table 3. Percentage of interlayer cations reduced after 15 hr.

| Temperature (°C) | Sample 1 | Sample 2 | Sample 3 | Sample 4 |
|---|---|---|---|---|
| 250 | 13.69 | 15.55 | 12.74 | 11.74 |
| 230 | 11.70 | 13.63 | 10.95 | 10.24 |
| 210 | 10.48 | 11.60 | 9.24 | 8.50 |
| 200 | 9.18 | — | — | — |
| 190 | — | 9.71 | — | — |

Table 4. Values of proportionality constant (K) for various systems.

| Temperature (°C) | Sample 1 | Sample 2 | Sample 3 | Sample 4 |
|---|---|---|---|---|
| 250 | 0.1369 | 0.1555 | 0.1274 | 0.1170 |
| 240 | — | — | 0.1190 | — |
| 230 | 0.1170 | 0.136 | 0.109 | 0.102 |
| 210 | 0.105 | 0.116 | 0.092 | 0.085 |

where n is the number of interlayer reducible ions. In other words,

$$(nH_2)_{total} \propto (n) \text{ or } (nH_2)_{total}/(n) = K,$$

where K is a proportionality constant. K values (Table 4) increase with rise in reduction temperature in the following order:

Sample 2 > Sample 1 > Sample 3 > Sample 4.

For Ni-samples, the proportionality constant for Sample 2 is greater than for Sample 1, showing that the higher the n values, the lower is the degree of reduction. Although Samples 3 and 4 possess higher M$^{2+}$ values than Sample 2, they have smaller K values, possibly because Cu$^{2+}$ yields a less favorable reduction condition with H$_2$. It is less likely that Cu ions could have hindered the reduction of Ni$^{2+}$.

It is interesting to compare the H$_2$-uptake values of these montmorillonite samples with that of a trioctahedral vermiculite. The latter contains 3.98% Ni$^{2+}$ in the interlayer space, whereas the highest amount of Ni$^{2+}$ in the montmorillonite samples (Sample 1) is 2.4%. Therefore, the H$_2$-uptake value of Ni-vermiculite is expected to be greater than that for Ni-

Table 1. Analysis of interlayer cations (M$^{2+}$) in montmorillonites.

| Sample[1] | Cation (wt. %) | | | Metal atoms/g × 10$^{20}$ | |
|---|---|---|---|---|---|
| | Ni$^{2+}$ | Cu$^{2+}$ | Na$^+$ | Ni$^{2+}$ | Cu$^{2+}$ |
| 1 | 2.40 | 0 | 0.093 | 2.46 | 0 |
| 2 | 1.73 | 0 | 0.77 | 1.77 | 0 |
| 3 | 0.46 | 1.82 | 0.20 | 0.47 | 1.72 |
| 4 | 0 | 2.39 | 0.20 | 0 | 2.26 |

[1] Calcined at 1000°C.

montmorillonite. H$_2$-uptake values, presented in Table 2, show that this relationship does not hold, except at 250°C. The superiority in H$_2$-uptake value of montmorillonite over vermiculite in the reduction process at lower temperatures (≤230°C) indicates that although the Ni$^{2+}$ ions initially present in the interlayer space migrate partially to the vacant octahedral sites and to the pseudo-hexagonal cavities (Brindley, 1980) in montmorillonite, they remain equally accessible to the reduction process with hydrogen as in the trioctahedral vermiculite. Thus, it appears that the Ni$^{2+}$ ions that migrated into the vacant octahedral sites are unlikely to form similar bonds as in a normal trioctahedral mineral. At ≥250°C, the Ni-vermiculite is capable of adsorbing more H$_2$ than Ni-montmorillonite. The structural disorganization in montmorillonite, brought about at higher temperatures, apparently interferes in the H$_2$-reduction process of Ni$^{2+}$.

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