

*Short Communication*

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**DTA OF SOME REDUCEABLE METAL ION EXCHANGED  
MONTMORILLONITES**

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Stable montmorillonites with exchange of Cu, Ni, Ce, Ag, Pd and Pt are possible to be prepared. Ni<sup>2+</sup> only migrates into the octahedral space and thus stabilising the structure.

Pillard smectites have recently been of high catalytic interests [1-4] where the interlayer space becomes the core of catalytic activity because of exchanged surface active ions like Al<sup>3+</sup>. Another way of converting the mineral suitable for catalysts is by introducing transition metal ions such as Cu, Ni, Pt, Pd, etc., and then reduce them with H<sub>2</sub> to a finely divided state as in vermiculite and zeolite [5-8]. Thermal treatment of the minerals is to be done above the temperature of reduction in these samples.

The present note is intended to report montmorillonite mineral with some unusual metal ions such as Pt, Pd, Ce and Ag which were probably never prepared before. DTA of these samples as well as minerals exchanged with Cu and Ni are presented here. Cu and Ni-exchanged montmorillonite were studied before on their reduction kinetics with hydrogen [9]. The hydrogen-treated products have also been subjected to DTA. The results have thrown light on the migration phenomenon [10] in montmorillonite.

## Experimental

The exchange of the ions has been carried out through conversion of montmorillonite to protonic stage first in a resin column and then with respective salts of the metals. The exchanged mineral samples were repeatedly washed to eliminate the anions. The method of DTA measurement is described previously [11].

## Results and discussion

The montmorillonite used here is from bentonite of Wyoming, U.S.A. having the following structural formula:



The exchange mechanism of Cu and Ni and of Pt and Pd has been described previously [9, 11].

DTA curves of Cu and Ni prior to reduction and after reduction are shown in Fig. 1 while for Ag, Pd and Pt are shown in Fig. 2. The results before and after reduction in Ni-montmorillonite appears to be interesting. The last endothermic and exothermic peaks for the reduced sample are at temperatures much higher than in sample without subjected to reduction in hydrogen; 915 and 935° instead of 892 and 921°. The reduced sample was

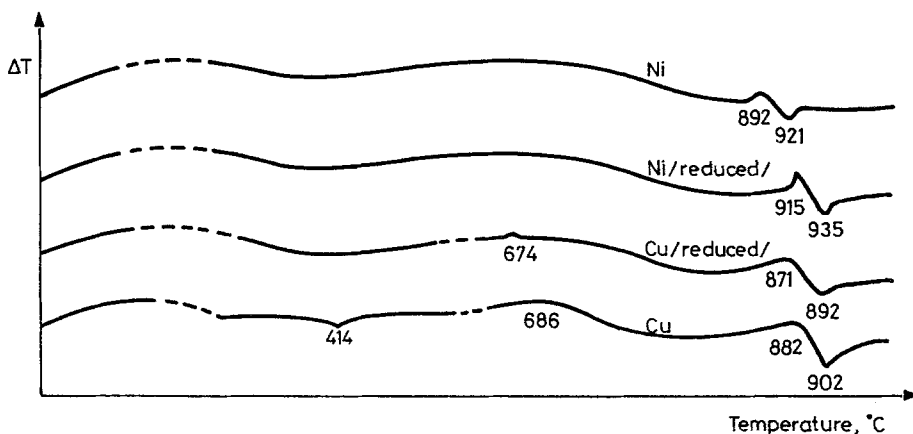


Fig. 1 DTA curves of Cu and Ni-exchanged montmorillonites

firstly evacuated at 250° and then reduced for 15 hours at the same temperature. At this temperature, the  $\text{Ni}^{2+}$  will migrate from its initial interlayer position to the vacant octahedral sheet and it is likely to form trioctahedral structure. This will result into a more stable structure than when in dioctahedral montmorillonite initially. The reduction process is likely to leave further  $\text{H}^+$  ions over the oxygen ions of the hexagonal cavities which may further stabilise the structure.

The ionic radius of  $\text{Ni}^{2+}$  is 0.68 Å which is 0.92 Å for  $\text{Cu}^{2+}$ . Ions of such higher ionic dimension may not migrate into the octahedral position as in case of Ni-montmorillonite. This may be the reason for the low temperature occurrence of these two peaks. It is surprising to note that after reduction the peak appears at lower temperature than in the initial sample without reduction. The reduction here takes place on metal ions present in the interlayer space; the  $\text{Cu}^{2+}$  is reduced to  $\text{Cu}^+$  (which has ionic radius of 0.96 Å) first and then to  $\text{Cu}^0$ . The metal state does not help in any way for stabilising the structure and therefore the temperatures for occurrences of these two peaks are at lower temperatures than in sample without reduction.

The other DTA curves shown in Fig. 2 are of sample without reduction.

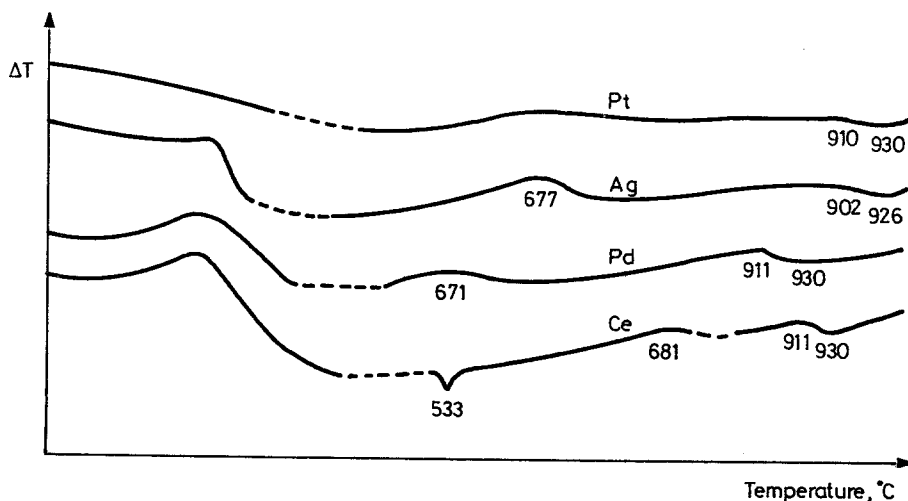


Fig. 2 DTA of Ag, Pd, Pt, CE-exchanged montmorillonites

These ions are also reducible but no kinetic measurements have been made on reduction of these samples. The ionic radius of  $\text{Ce}^{4+}$  is 1.01 Å and for  $\text{Ag}^+$ , it is 1.26 Å; for Pd and Pt also these dimensions are very high and they can not exhibit the migration phenomenon. However, the tempera-

tures for occurrences of the last two peaks are higher than in  $\text{Cu}^{2+}$ . These ions hold the interlayer space with strong co-ordinated water molecules apparently.

The initiation of dehydroxylation is marked at temperatures of 675-685° in different samples. In Ce-montmorillonite, one sharp small peak is observed at 533° which may be due to quartz impurity.

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