

THERMOGRAVIMETRIC INVESTIGATION Solid-state ion-exchange procedure of Cu^{2+} , Co^{2+} , Ni^{2+} and Fe^{2+} ions into montmorillonite

Á. Fudala, J. Halász and I. Kiricsi

Applied Chemistry Department, József Attila University, Rerrich B. tér 1, Szeged, Hungary

Abstract

Ion-exchange of transition metal ions into montmorillonite was investigated using two different ion-exchange procedures. Performing ion-exchange from aqueous solution of the respective metal ion leads to material possessing measurable Brønsted acidity, while the solid-state exchange materials show predominantly Lewis acidity.

Measurements by means of a derivatograph allowed us to construct a feasible reaction mechanism for solid-state ion exchange. Satisfactory correlation was found between the results calculated from the reaction steps assumed and the measurements by means of a derivatograph.

Keywords: ion-exchange procedure, montmorillonite, TG

Introduction

Thermal analysis is a widely used experimental method for studying various transformations taking place in the solid phase. Recently, a new ion-exchange method was developed and proposed to apply for catalyst preparation from zeolites [1].

The ion-exchange properties of clay minerals in the smectite family assure that they can be tailored towards various applications. Montmorillonites have ion-exchange capacity about 80 meq/100 g, however, very often, this value cannot be fully exploited. In these cases the use of the solid-state ion-exchange procedure is suggested [2].

Since the mechanism of this new ion-exchange procedure was studied exclusively for zeolites, we decided to widen this field and include the smectite family as well [3]. In order to get more insight into the nature of transformations actually occur upon heat treatment, investigation by means of a derivatograph was undertaken on metal salt-montmorillonite mixtures as well. Results of the investigation are presented in the followings.

Experimental

Sample preparation

Na-montmorillonite (Na-mont.), the parent montmorillonite sample was a product of LAPORT (Bentolit H). For conventional ion-exchange, 15 g of Na-

mont. was suspended in 2000 cm³ distilled water. After homogenization of the suspension by vigorous stirring, the solution of metal ions (Cu²⁺, Ni²⁺, Co²⁺, Fe²⁺ in 0.1 molar aqueous solution) was slowly added. After 24 h, stirring was stopped and the slurry was centrifuged. The solid material was washed free of chloride and dried in air.

For solid-state ion-exchange, 10 g of Na-mont. was mixed mechanically with 4% metal chloride salt. After having an intimate mixture, the preparation was heat treated at 773 K for 5 h. Then the sample was cooled to ambient temperature in an adhumator filled with saturated NH₄Cl solution.

Composition of the samples was determined by classical and instrumental analytical methods.

Characterization methods

For measuring the interlayer distances of the montmorillonites and their change upon various treatments, X-ray diffraction measurements were performed on a DRON 2 powder diffractometer.

Using the structure sensitive IR bands of montmorillonite, the crystallinity of the samples was also checked by IR spectroscopy. Spectra were taken on disc formed samples containing 0.5% montmorillonite in KBr matrix.

BET measurements were performed in an adsorption equipment allowing pretreatments in wide temperature range.

TG, DTG and DTA measurements were performed using a MOM Derivatograph-Q equipment operating in the 298–1273 K temperature range. Generally 100 mg of powdered sample was applied using ceramic sample holder. In some cases, measurements were performed under flowing nitrogen (flow rate: 20 cm³ N₂ min⁻¹).

Results and discussion

Characterization of the samples

The composition data showed, that metal chlorides reacted with the clay, since their metal content was 4%, exactly the value expected from the composition of the mixtures used for solid-state ion-exchange. For the conventionally ion-exchanged samples, the metal ion content was different.

IR spectra of the materials are to be seen in Fig. 1. They indicate no observable destruction of the layer structure after applying either ion-exchange method. This observation is in line with the results of X-ray diffraction.

In the range of OH vibrations (between 3400–3900 cm⁻¹) the spectrum of conventionally exchanged samples differs from those of solid-state exchanged materials. For the latter, no structured OH spectra were found. This can be explained by the lack of reaction between metal chloride and the clay, thus, OH groups are

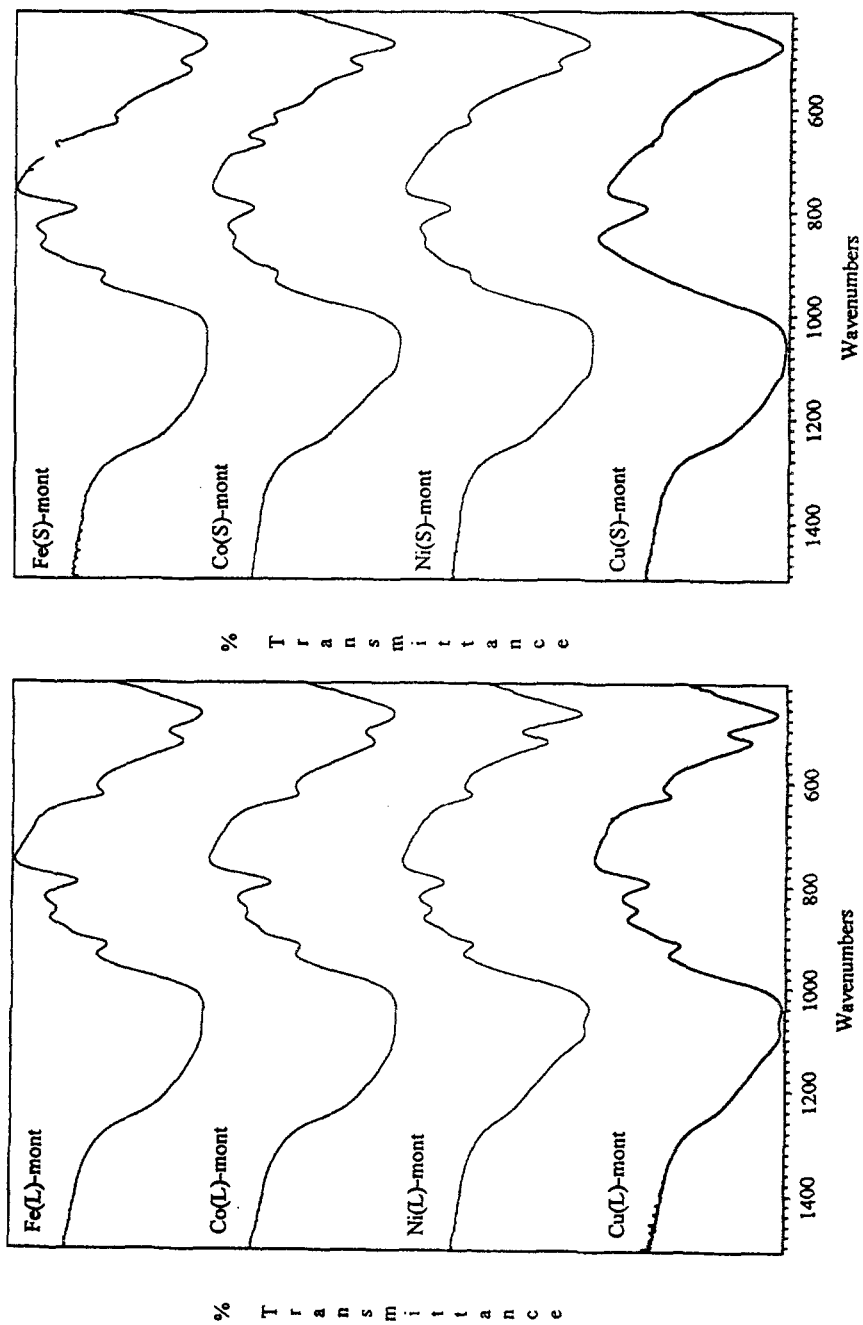


Fig. 1 IR spectra of conventionally (A) and solid-state (B) ion-exchanged materials

Table 1 Physical characteristics of the samples studied

Sample	Interlayer distances/nm		BET surface area /m ² g ⁻¹	
	Conventional	Solid-state	Conventional	Solid-state
Na-mont.	1.2628		116.6	
Fe-mont.	1.2663	1.2358	124.1	108.2
Co-mont.	1.4750	1.2278	150.1	108.4
Ni-mont.	1.4663	1.1999	134.8	90.0
Cu-mont.	1.2663	1.2628	133.4	97.8

not generated and consequently, HCl is not formed and, of course is not released.

The interlayer distances and the BET specific surface areas are summarized in Table 1. Comparison of these data show that BET values are somewhat smaller for materials ion-exchanged in the solid-state. This finding indicates the presence of some extra material in the interlayer space.

Thermogravimetric measurements

Conventionally exchanged materials

In Fig. 2 two weight loss steps are seen in TG curves of samples prepared by conventional ion-exchange. Temperatures indicated in the Figure reveal that the

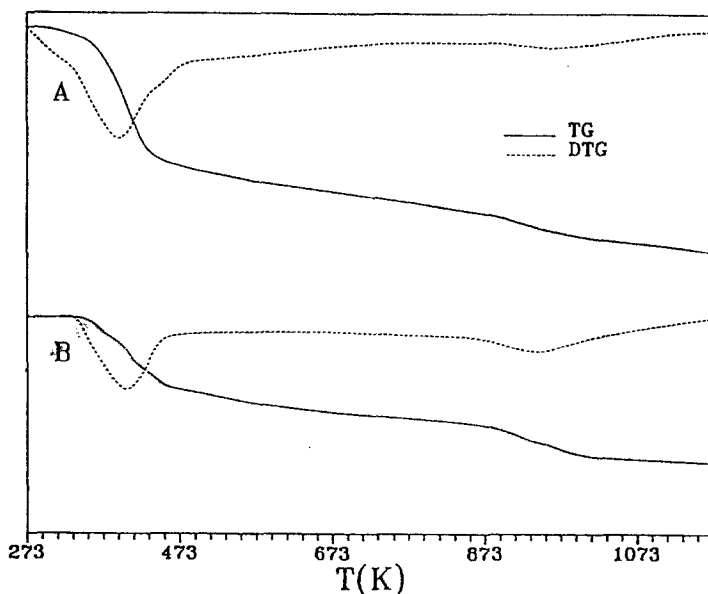


Fig. 2 Thermogravimetric profile of the conventionally exchanged Co-mont. (A) and Fe-mont. (B) sample

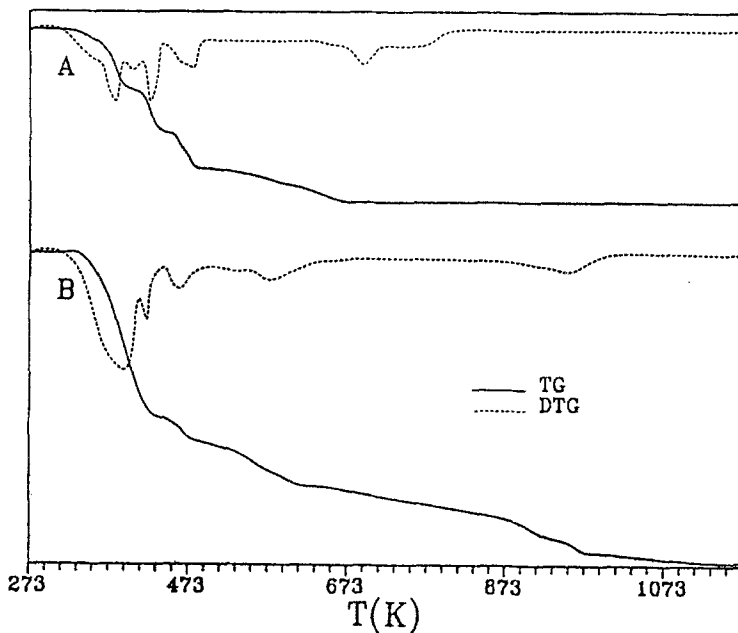


Fig. 3 Thermogravimetric curves of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (A) and the $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}/\text{Na-mont.}$ mixture (B)

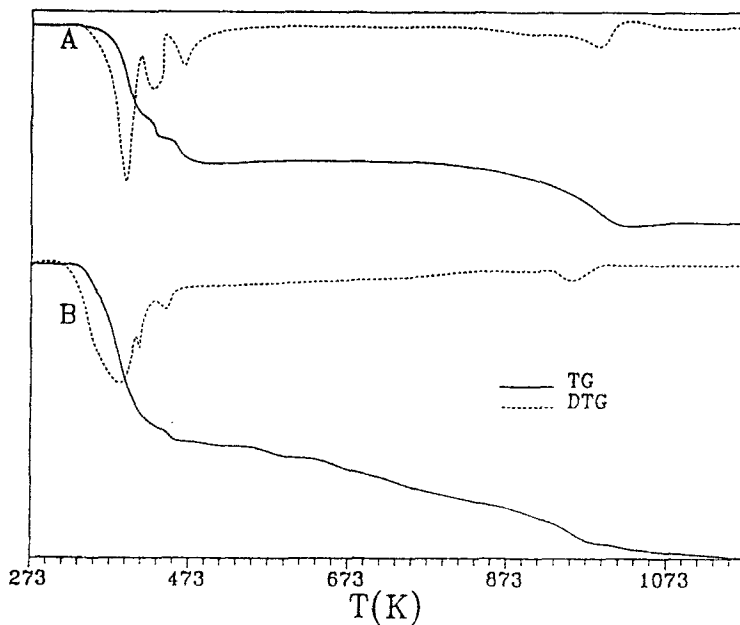


Fig. 4 Thermogravimetric curves of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (A) and the $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}/\text{Na-mont.}$ mixture (B)

first step is due to dehydration, since it occurs in a narrow temperature range, between 373–403 K. In this step the physisorbed, weakly bonded water is released.

The second step must be due to the dehydration of the samples. In this step water chemically bonded as OH groups leave the sample. The bond strength of these OH groups varies with the transition metal cations in-between the layers. This feature is reflected by the temperature variation of the temperature of the step from sample to sample. For these samples, Brønsted acidic OH groups were detected by IR spectroscopy.

Solid-state exchanged samples

It is known from the zeolite chemistry, that the solid-state ion-exchange method is advantageous in those cases where the simple ion-exchange procedure is ineffective. For clay minerals, however additional feature can be expected, namely the intercalation of the salt between the layers. As the extent of this process strongly depends on the time of homogenization of the salt-clay mixture, the anion of the salt and the baking temperature [4], the procedure should be optimized, otherwise amorphous product is obtained.

In the course of these measurements the thermal behaviour of metal chloride–Na-mont. systems was investigated. As was expected, weight variations observed were more complex in the low temperature range. However, contrary to the results obtained for the conventionally exchanged materials, the high temperature weight loss proceeded around 953 K for each sample. These materials possessed Lewis acid sites exclusively, detected by pyridine adsorption.

Table 2 Summary of the thermogravimetric measurements

Sample	Mass losses, <i>m</i> /%	
	Experimental	Theoretical
FeCl ₂ ·4H ₂ O/Na-mont.	20.0	23.7
CoCl ₂ ·6H ₂ O/Na-mont.	21.0	22.4
NiCl ₂ ·6H ₂ O/Na-mont.	22.6	24.2
CuCl ₂ ·2H ₂ O/Na-mont.	20.0	18.6

Analyzing weight losses taking place below 573 K, several elementary reaction steps should be taken into account. The following transformations are assumed to occur upon heating the metal chloride–Na-mont. mixtures: desorption of adsorbed water from the clay, release of the crystal water of metal chloride, formation and liberation of a small amount of HCl. Comparison of weight losses calculated on the basis of these reactions and those found experimentally shows fair agreement, as to be seen in Table 2.

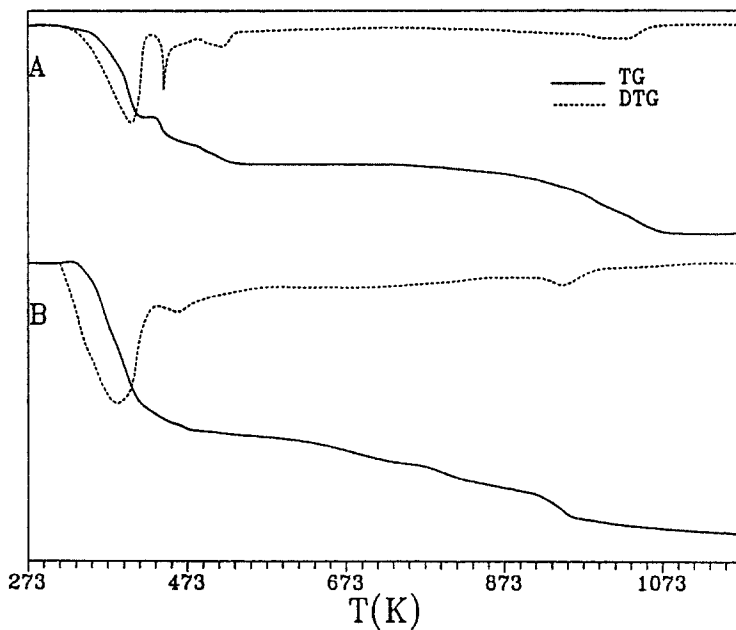


Fig. 5 Thermogravimetric curves of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (A) and the $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}/\text{Na-mont. mixture}$ (B)

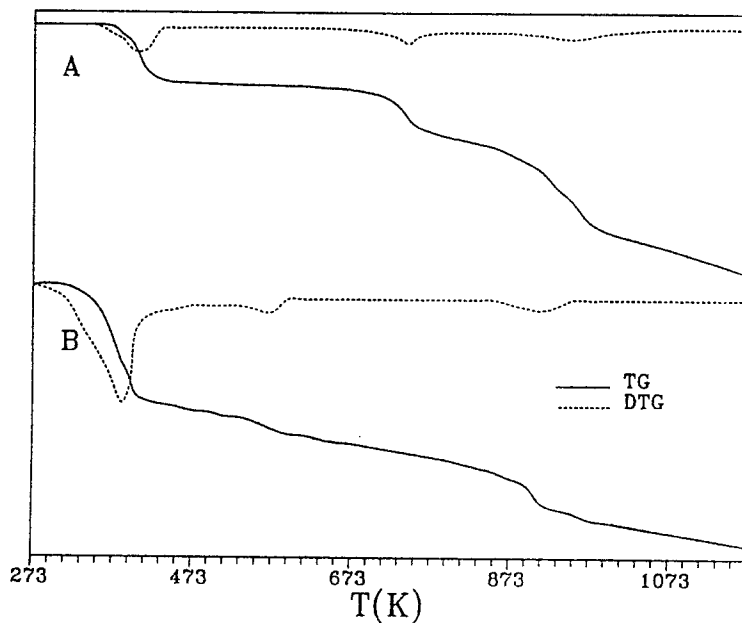
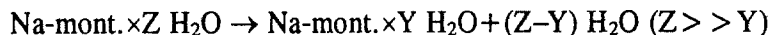


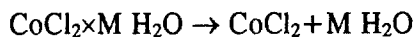
Fig. 6 Thermogravimetric curves of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (A) and the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}/\text{Na-mont. mixture}$ (B)

On the basis of this results the following elementary steps can be assumed to occur during the solid-state ion-exchange procedure.

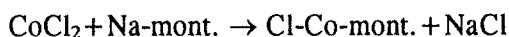
1. Partial dehydration of the clay:



2. Partial loss of crystal water of metal chloride



3. Reactions between the clay and metal chloride



Taking these reactions, the mechanism of solid-state ion-exchange becomes easy to interpret.

Investigations aimed to apply these materials as catalysts are in progress.

* * *

Financial support by the Hungarian Research Fund (OTKA T014275) is gratefully acknowledged. The skilful technical assistance of Kati Barna is highly appreciated.

References

- 1 H. G. Karge and H. K. Beyer, *Stud. Surf. Sci. Catal.*, 69 (1991) 43.
- 2 I. M. Natale and A. K. Helmy, *Clay and Clay Miner.*, 40 (1992) 206.
- 3 I. Pálincó, I. Kiricsi, Gy. Tasi and K. Varga, *J. Thermal Anal.*, 39 (1993) 197.
- 4 J. G. Thomson, N. Gabbitas and P. J. R. Uwins, *Clay and Clay Miner.*, 41 (1993) 73.