

# **THERMOGRAVIMETRIC CHARACTERIZATION OF SOLID-STATE ION-EXCHANGE PROCEDURE IN ZEOLITES**

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## **Abstract**

The solid-state ion-exchange procedures of zeolites with  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Co}^{2+}$  salts can be resulted in prosperous catalysts for NO decomposition. Reactions taking place in solid-state between four transition metal chlorides and H-ZS-5 zeolite were investigated by means of a derivatograph. The results showed that irreversible consumption of surface -OH groups occurred with simultaneous bonding of the transition metal in the zeolite channel structure.

**Keywords:** solid-state ion-exchange, TG and DTG measurements, zeolites, ZSM-5

## **Introduction**

Among other types of zeolites the metal ion-exchanged ZSM-5 zeolites were proved to be effective catalysts in NO decomposition [1, 2]. Beside the traditional procedures now the solid-state ion-exchange plays increasing role in the preparation of modified zeolites [3]. Several intensive investigations have been performed on their characteristics [4] and catalytic effects [5] but even the thermal behavior of these catalyst precursors has not been clarified yet.

The present study deals with the stoichiometry of the procedures taking place upon solid-state ion-exchange between metal chlorides and H-ZSM-5 zeolite.

## **Experimental**

Na-ZSM-5 zeolite was synthesized with a Si/Al ratio of 13.8. This parent material was transferred to  $\text{NH}_4^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Fe}^{3+}$  ionic forms by conventional ion-exchange procedure (these samples are denoted as Cu(L)ZSM-5, etc.). The  $\text{NH}_4$ -ZSM-5 sample was deammonized at 873 K. Solid-state ion-exchange was performed in the same way as suggested in [3]. In each case 5 m% of metal chloride salt was intimately mixed with an aliquot of H-ZSM-5 in an agate molten. This mechanical mixture was heat treated at 873 K for 8 h in air. The product was cooled to ambient temperature and washed chloride free, then

dried at 373 K (these samples are denoted as Cu(S)ZSM-5, etc.). Composition of samples was determined by classical methods and by X-ray fluorescence analysis.

Specific surface area of catalysts pretreated at 723 K in vacuum were determined on the basis of N<sub>2</sub> adsorption measurements at 77 K.

The thermal behavior of specimens was investigated using a Derivatograph-Q (MOM, Hungary) instrument in the 298–1270 K temperature range. Generally a plate series type sample holder made from Pt was applied. The measurements were run at 10 K min<sup>-1</sup> heating rate.

For characterization of the catalyst candidates by X-ray diffraction well-powdered samples were placed into the sample holder of a DRON 3 diffractometer and the X-ray patterns were registered in the 3° < 2θ < 45° range.

The KBr matrix technique of IR spectroscopy was utilized for characterization of materials in the framework vibration range (400–1600 cm<sup>-1</sup>). 100 mg of each sample made by solid-state ion-exchange was heated to 573, 673 and 773 K and held there in steam for 4 h. After this treatment their IR spectra were recorded.

## Results

### Sample characterization

Beside other physical characteristics, the composition and surface area of the samples prepared are to be seen in Table 1. The data show that the transition metal ion contents of (S)ZSM-5 and (L)ZSM-5 differ significantly, the (S)ZSM-5 samples containing much more transition metal ion than required for 100% ion-exchange. Apart from Cu(S)ZSM-5, therefore these samples are regarded as 'overexchanged' materials.

**Table 1** Sample characterization

Preparation method	Cu-ZSM5		Fe-ZSM5		Co-ZSM5		Ni-ZSM5	
	L	S	L	S	L	S	L	S
Metal ion content	0.55	0.32	0.017	4.69	0.72	4.71	0.72	5.06
Ion-exchange degree	73	46	0.82	152	22.2	145	22.5	154
BET area m <sup>2</sup> g <sup>-1</sup>	270	318	367	318	310	313	310	293
Crystallinity from X-ray	0.83		1.205		1.129		0.776	
Crystallinity from IR	0.754	0.794	0.785	0.757	0.802	0.770	0.775	0.769

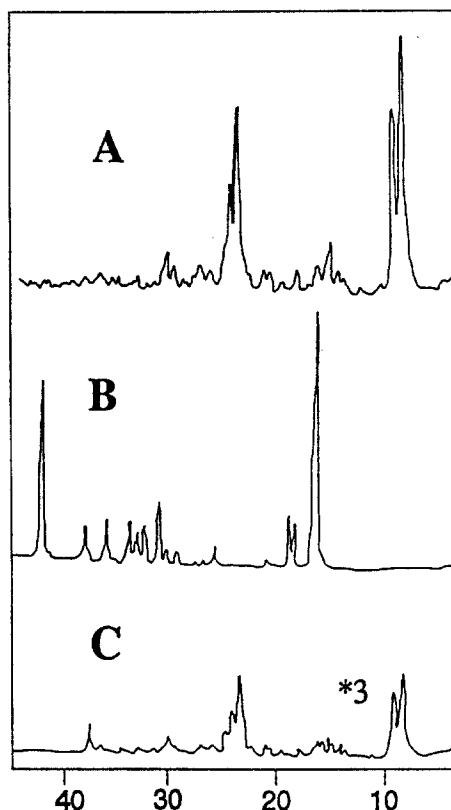


Fig. 1 X-ray diffractograms of H-ZSM-5 (A), NiCl<sub>2</sub>·6H<sub>2</sub>O (B) and Ni(S)ZSM-5 (C) samples

The BET measurements revealed that the solid-state exchanged samples possess very similar specific surface areas to those of the other samples. It follows that no destruction of the pore system occurred in consequence of the different ion-exchange methods.

Similar results were obtained from the X-ray diffraction studies. In Fig. 1, X-ray diffractograms registered before and after the NiCl<sub>2</sub> treatment are depicted. The diffractogram of H-ZSM-5 seems to be almost identical with that for Ni(S)ZSM-5. There is no common reflexion in the diffractograms NiCl<sub>2</sub>·6H<sub>2</sub>O and Ni(S)ZSM-5, proving the absence of crystalline NiCl<sub>2</sub> moieties in the channel system or intercrystalline phase. The same was observed for the other metal ions and this excludes the occurrence of partial crystal collapse due to the solid-state exchange.

Coudurier suggested to use the ratio of the IR bands at around 440–480 and 550–650 cm<sup>-1</sup> as a measure of crystallinity of zeolites [6]. For well-crystallized ZSM-5 type materials, this ratio should be around 0.72. As the data in Table 1 demonstrate, this is the case for our catalyst candidates.

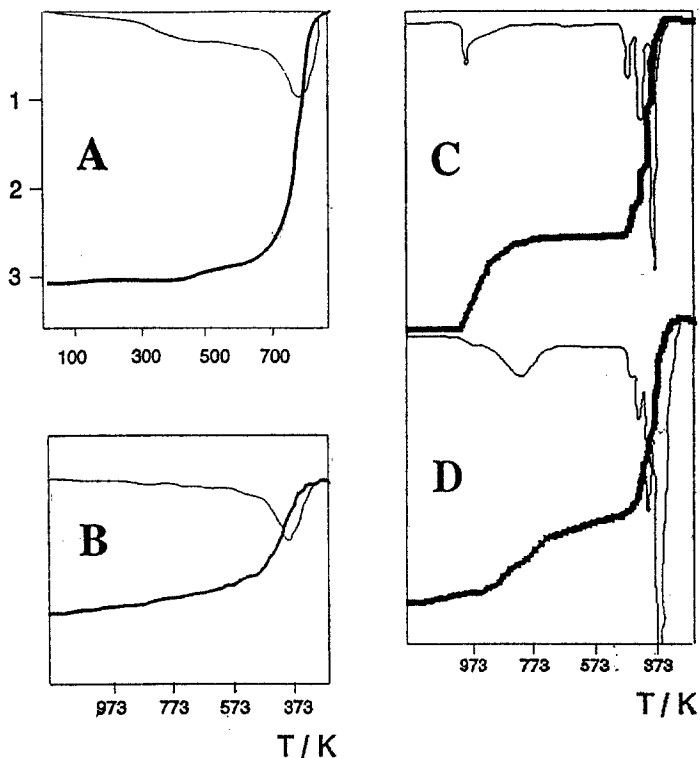


Fig. 2 TG and DTG curves of H-ZSM-5 (A), Co(L)ZSM-5 (B), CoCl<sub>2</sub>·6H<sub>2</sub>O (C), and CoCl<sub>2</sub>·6H<sub>2</sub>O/H-ZSM-5 (D) samples

## Thermogravimetric measurements

The solid-state ion-exchange procedure was controlled for each sample by means of derivatographic measurements. The losses in mass occurring at different temperatures during linear heating of the sample from room temperature to 1270 K were determined. The observed patterns are represented by the CoCl<sub>2</sub>/zeolite system in Fig. 3, where the features for the conventionally exchanged sample are also drawn. The sample exchanged in the conventional way exhibits the usual pattern, with mass loss steps for dehydration at 400 K and dehydroxylation at 723 K. The pattern for the salt/zeolite mixture has several steps, due to processes such as the dehydration of the zeolite, the loss of crystal water, and the release of HCl due to the reaction between metal chloride and the Brønsted acid sites. CoCl<sub>2</sub> gives a similar pattern to that for the solid-state ion-exchanged material. The only difference observable visually is the shift in the last step, at 1000 K for CoCl<sub>2</sub> to 840 K for the zeolite/CoCl<sub>2</sub> mixture, prov-

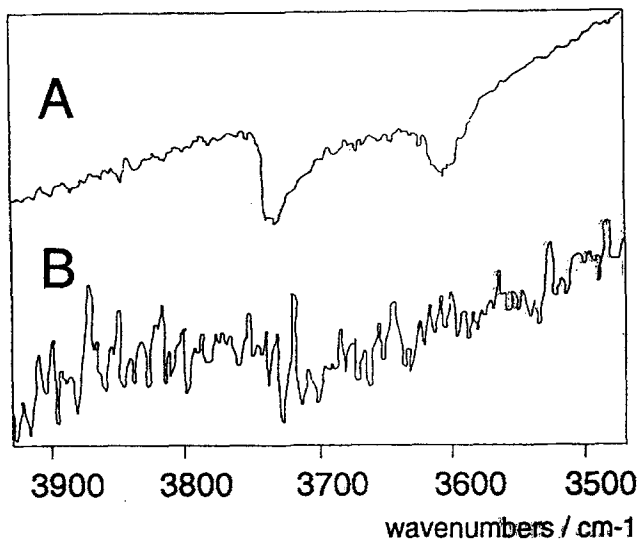


Fig. 3 IR spectra of Fe(L)ZSM-5 (A) and Fe(S)ZSM-5 (B) in the range of OH vibrations

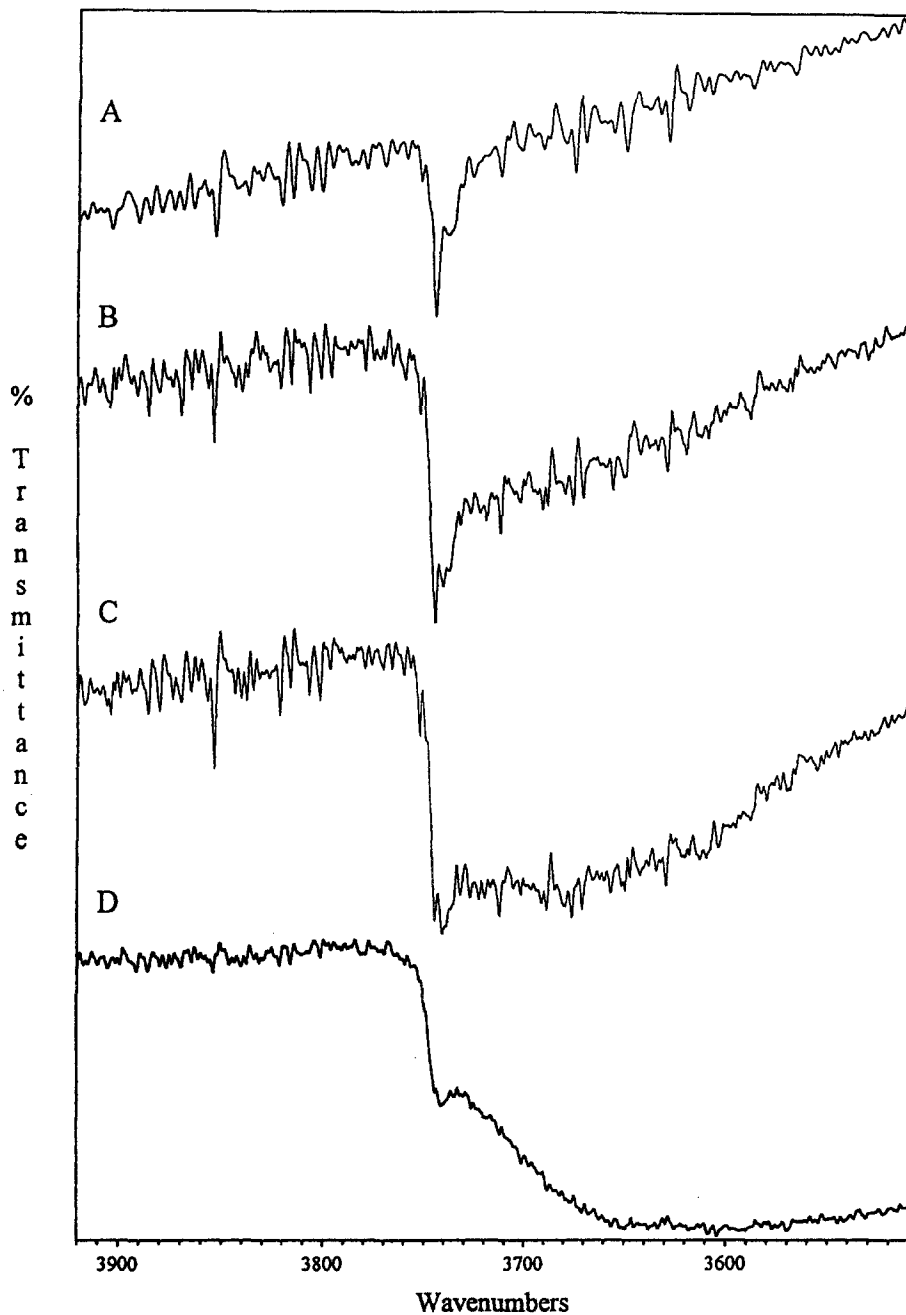
ing that the reaction between the OH groups of the zeolite and the chloride ions of cobalt salt actually occurred. The experimental results and the theoretically calculated mass losses are listed in Table 2.

The spectra taken in the course of acidity measurements yielded information on the concentration of acid sites and the transformation of OH groups originally present in the H-ZSM-5 zeolite. Figure 3 depicts spectra of Fe(L)ZSM-5 (A) and Fe(S)ZSM-5 (B) in the range of OH vibrations. The spectrum of Fe(L)ZSM-5 contains bands characteristic of acidic (at  $3606\text{ cm}^{-1}$ ) and non-acidic (at  $3740\text{ cm}^{-1}$ ) terminal SiOH groups. In contrast, no band can be seen in the spectrum of Fe(S)ZSM-5. Comparison of these spectra reveals that reaction has occurred between the metal chloride and the OH groups. This result is experimental confirmation of the formation of O-Fe-O bonds upon solid-state ion-exchange. Similar changes were found for the other samples.

Table 2 Summary of the thermogravimetric measurements

Starting materials for solid state exchange	$\Delta m_{\text{exp}}/$	$\Delta m_{\text{calc}}$			$\Delta m_{\text{sum}}/$	*
		zeol.dehydr./	crystal water/	HCl/		
						mg
FeCl <sub>2</sub> ·4H <sub>2</sub> O/HZSM-5	15.6	2.5	6.5	6.6	15.6	100
NiCl <sub>2</sub> ·6H <sub>2</sub> O/HZSM-5	18.8	2.4	9.3	6.3	18	96
CoCl <sub>2</sub> ·6H <sub>2</sub> O/HZSM-5	18.5	2.4	9.0	6.1	17.5	95
CuCl <sub>2</sub> ·H <sub>2</sub> O/HZSM-5	9.6	2.5	1.4	5.7	9.6	100

\*Correlation between experimental and theoretical data/%



**Fig. 4** IR spectra of Cu(S)ZSM-5 zeolites. Not steamed (A). Steamed at 773 K followed by evacuation at 773 K (B), 673 K (C) and 573 K (D)

## Effect of steam on zeolites

There is a great difference between the acidity of the solid-, and the liquid phase ion-exchanged zeolites. It seemed to be interesting to try to restore the Brønsted-acid centers of the (S)ZSM-5 zeolites, which were consumed during the ion-exchange procedure, by water vapour treatment. As Fig. 4 demonstrates, IR spectra of zeolites taken on the sample steamed at 773 K after evacuation treated at increasing temperature became similar to that of the (L)ZSM-5 in the range of OH vibrations. This means that Brønsted-acid centre was generated by this treatment.

The ratios of the IR bands at 440–480 and 550–650  $\text{cm}^{-1}$  assure us that no structural destruction occurred during the steam treatment.

## Conclusions

From the results the following main conclusions were drawn:

- ion-exchange in solid-state results in zeolites with high transition metal content assuring a convenient method for preparation catalysts of enhanced active site concentration;
- no crystal destruction took place upon these exchanges;
- on the basis of thermogravimetric results suggestion was given for the occurring elementary reactions.

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