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Dispersion and Solid State Ion Exchange of VCl_3 , $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ onto the Surface of NaY Zeolite Using Microwave Irradiation

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Received April 12, 2004; Revised November 16, 2004

Abstract. Transition metal/Y zeolites have been prepared by solid state ion exchange with microwave irradiation of mechanical mixtures of VCl_3 , $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ or $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ with NaY zeolite at 900 W in 10–20 min. The prepared transition metal/Y zeolites were characterized by X-ray diffraction (XRD), infrared spectroscopy (IR), simultaneous thermal analysis (STA) and surface area measurement (BET). Concentration of dispersed transition metal on zeolite was measured and results revealed that transition metal was dispersed and ion exchanged onto the surface of NaY zeolite.

Keywords: solid-state ion exchange, transition metal, zeolites, microwave irradiation, dispersion

1. Introduction

Metal/zeolites are important class of materials and have many applications such as catalyst for the decomposition of nitrogen oxide to nitrogen and conversion of carbon monoxide to carbon dioxide, the two most important reactions from environmental point of view [1, 2]. In addition to the Si/Al ratio, which affects acid properties of zeolite [3], the exchange of monovalent ions with polyvalent cations creates very strong acidic centers by hydrolysis phenomenon and improves the catalytic properties of it [4]. Introducing transition metal cations into crystalline aluminosilicates and related materials is a well established method for the preparation of metal/zeolites, modification of zeolites

and improvement of their catalytic activity. In majority of studies, metal ions have been introduced into zeolite by aqueous solution, [5, 6] through an ion exchange process. Furthermore, it is well established that the ion exchange process can be carried out in solid state phase between zeolite and metal containing species at elevated temperatures [7, 8] by prolonged heating [9, 10]. However, ion exchange process in solid state is very time consuming but processing time can be reduced significantly by microwave heating [11].

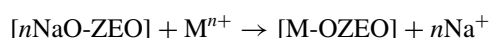
In this work, VCl_3 , $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ /NaY zeolites have been prepared by solid-state ion exchange with the aid of microwave irradiation. Infrared spectroscopy (IR), thermogravimetric analysis (TGA/DTA), X-ray diffraction (XRD) and BET surface area measurements have been used for the evaluation of ion exchanged zeolites.

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2. Experimental

2.1. Preparation of Zeolite

Zeolite NaY was prepared and activated according to the procedure described previously [12]. 2 g of zeolite Y and 2 mmol metal salts [VCl_3 (0.32 g), $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (0.53 g), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.4 g), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.4 g), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.5 g), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.48 g), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.34 g) and ZnCl_2 (0.27 g)] was mechanically mixed by gentle grinding and then heated in a 900 W microwave oven for 10–20 min.



All prepared materials were characterized by a Philips PW-1840 X-ray diffractometer (XRD) with $\text{Cu K}\alpha$ radiation. FT-IR spectra were obtained using KBr pellets on a BOMEM, M.B series spectrophotometer. Simultaneous thermal analysis was performed on a Rheometric Scientific STA-1500 with a heating rate of $10^\circ\text{C}/\text{min}$ in air atmosphere. The BET surface areas were measured by a SIBATA, App. 1100-SA with adsorption of nitrogen at 77 K.

2.2. Measurement of Cation Exchange in Metal/Zeolite

In a typical measurement, 2 g of metal/zeolite was calcined by microwave irradiation and then 100 ml of water was added and stirred for 2 h. Solution was filtered off and solid washed several times with distilled water. The filtered solution was diluted with distilled water to 250 ml and concentration of transition metal was measured by a Perkin Elmer model 2380 atomic absorption unit. The amount of transition metal that was dispersed on zeolite was back calculated from the amount of transition metal that was found in the filtered solution. The results for all measurements are summarized in Table 1.

3. Results and Discussion

Results for the dispersion and ion exchange of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and ZnCl_2 in zeolite are in good agreement with previously reported values [7, 13]. However, there is no report for the solid-state ion exchange of VCl_3 , $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ onto NaY zeolite with mi-

Table 1. Exchange and dispersed amounts of metals in zeolite.

Metal chloride	Exchanged amount	Dispersed amount	Cation exchanged ratio (%)
	from 2 mmol (%)	from 2 mmol (%)	
V(III)	1.65	0.35	82.5
Cr(III)	1.92	0.08	96
Mn(II)	1.79	0.21	89.5
Fe(II)	1.99	0.01	99.5
Co(II)	1.54	0.46	77
Ni(II)	1.42	0.58	71
Cu(II)	1.63	0.37	81.5
Zn(II)	1.84	0.16	92

crowave irradiation and characterization results are discussed in the following sections.

3.1. Infrared Spectra

IR spectrum of NaY zeolite shows three peaks at about 1000, 680 and 435 cm^{-1} , which are due to the internal vibrations of the MO_4 ($\text{M} = \text{Si}, \text{Al}$) tetrahedral moiety of NaY [14]. Apparently, the intensity of these peaks is insensitive to structural variations. However, a slight shift that was observed for the band at 1000 cm^{-1} toward higher frequencies was found to increase with increasing transition metal loading. The structure sensitive NaY bands which appear at about 1200, 741 and 600 cm^{-1} are related to external linkages between tetrahedra and their intensities decrease by loading transition metal into zeolite. In the solid-state ion exchange, which takes place under anhydrous conditions, the metal salts not only can migrate to channels/cages after separation of cations and anions but also react with T-OH ($\text{T} = \text{Si}, \text{Al}$) groups [15]. Recently, these sites have been characterized and measured by FT-IR spectroscopy and authors reported that in the thermal ion exchange method the intensity of stretching vibration of hydroxyl group at 3745 cm^{-1} decreased [16] and metal-oxygen bond appeared about 890 cm^{-1} [17]. Exchange of ions in the solid state ion exchange of VCl_3 , $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ or $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ onto NaY zeolite with microwave irradiation is observed in the FT-IR spectra. The infrared spectrum of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ion exchange sample in a selected region is shown in Fig. 1, as a typical example. The band at 831 cm^{-1} appeared only after solid state ion exchange reaction and results are similar to the previously reported data for

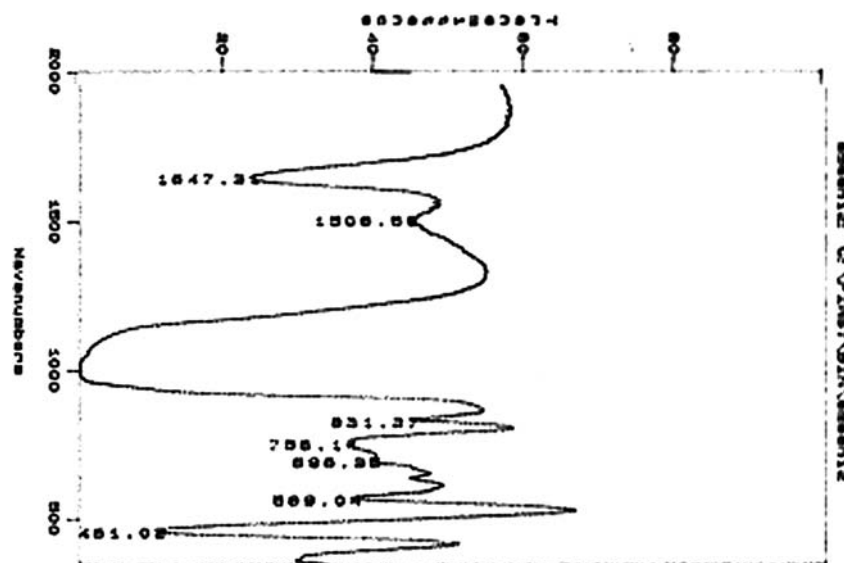


Figure 1. FT-IR for physical mixture of NaY and $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ after heat treatment.

the thermal process [17]. The ion exchanges that are observed in the present study are consistent with the loss of NaY crystallinity in the XRD patterns.

3.2. X-Ray Diffraction

Table 2 shows d values of a mixture of VCl_3 , $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ or $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ with NaY

zeolite before and after heat treatments and Fig. 2 shows XRD pattern of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ before and after heat treatment. The d values of pure NaY zeolite are 14.3, 8.75, 7.51, 5.71, 4.78, 3.8, 2.8 and 2.68. It is interesting to note that the characteristic peaks of crystalline VCl_3 , $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ onto NaY zeolite disappeared completely when the samples were heated for 10–20 min at 900 W.

Table 2. Showing disappears of characteristic peaks assigned to crystalline Metal Chlorids with use of d value.

d value for VCl_3/NaY		d value for $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}/\text{NaY}$		d value for $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}/\text{NaY}$		d value for $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}/\text{NaY}$	
Before heating	After heating	*Before heating	*After (see Fig. 2) heating	Before heating	After heating	Before heating	After heating
14.5	14.6	14.3	14.3	14.3	14.3	14.3	14.3
8.8	8.8	8.8	8.8	8.75	8.75	8.75	8.75
7.4	7.48	7.45	7.45	7.51	7.51	7.51	7.51
5.73	5.75	5.75	5.75	5.71	5.71	5.71	5.71
—	—	—	—	4.94	n.o	5.22	n.o
4.8	4.8	4.75	4.75	4.79	4.79	4.79	4.79
—	—	—	—	—	—	—	—
3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8
2.87	2.89	2.89	2.89	2.9	2.9	2.9	2.9
—	—	2.6	n.o	—	—	—	—
2.68	Decrease intensity	2.68	2.68	2.68	2.68	2.7	2.68
1.67	n.o	1.72	n.o.	2.6	n.o	—	—
—	—	1.45	n.o	—	—	—	—

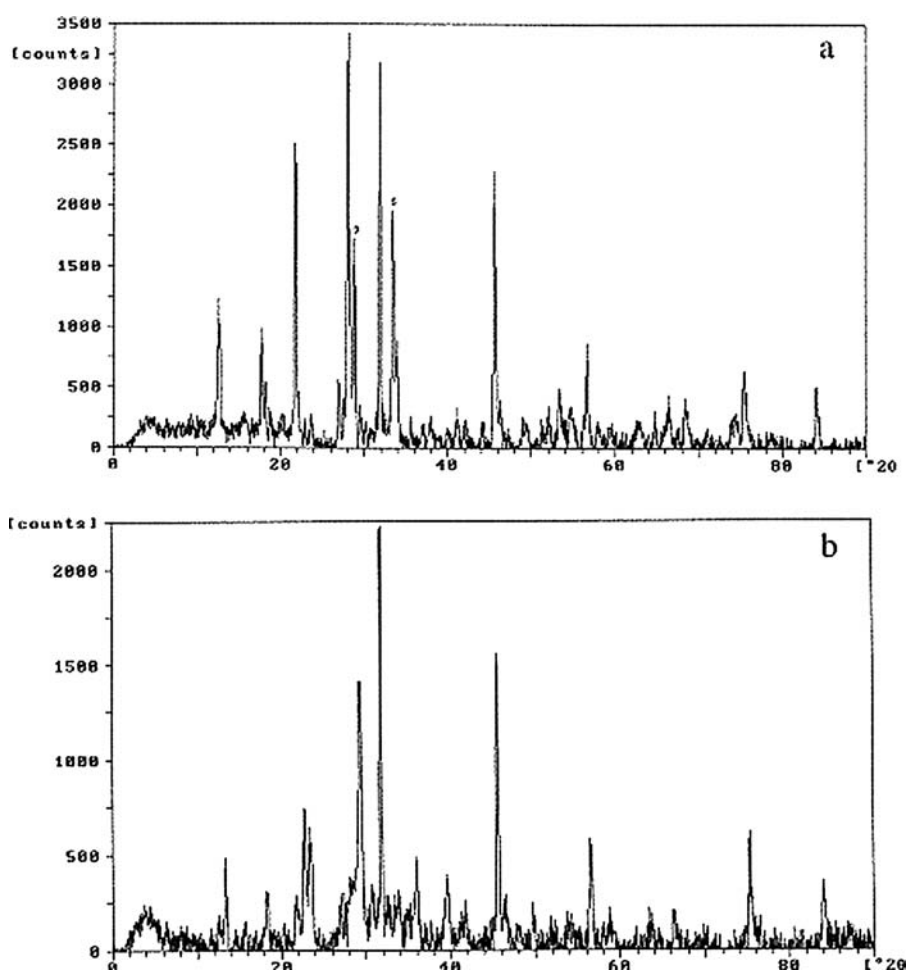


Figure 2. XRD pattern for physical mixture of NaY and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ before (a) and after heat treatment (b).

Generally it has been accepted that the absence of X-ray diffraction peaks of a compound in a mixture is due to the fact that the minor component not detected when present in a very small quantity. However, in a mixture with significant fraction of component, if the minor component is not found to form a stoichiometric compound with the support or dissolution in the support to form a solid solution, the disappearance of peaks is assumed to be due to dispersion of minor component on the surface of support in the form of a monolayer [18]. The disappearance of the XRD peaks of transition metal crystals in the sample might be also explained by high dispersion of transition metal into the channels of NaY zeolite, where the transition metal no longer exists in the crystalline state.

3.3. Thermal Analysis

For clarification of status of dispersed transition metal salts on the surface of NaY zeolite, thermal behavior of pure zeolite and all samples before and after microwave heat treatment have been investigated. Figure 3 shows the DTA and TGA curves of NaY zeolite which is a typical behavior for this compound. The endothermic peaks at 110 and 150°C in DTA curve are assigned to desorption of physical and chemical water in NaY. The DTA curve of pure VCl_3 shows two peaks at 180 and 310°C (Fig. 3(b)), which are attributed to dehydration and melting of VCl_3 , respectively. In contrast, the mechanical mixture of VCl_3 with NaY after heating (Fig. 3(c)) shows only one peak at 90°C in DTA curve

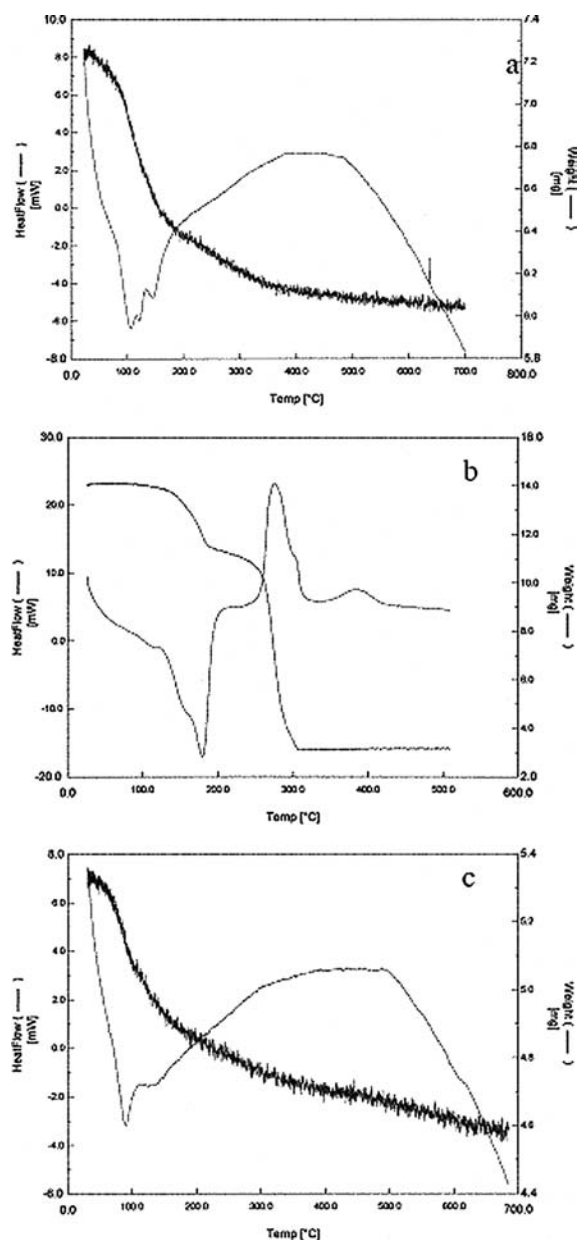


Figure 3. DTA/TGA curves for NaY (a), DTA/TGA curves for VCl_3 (b) and DTA/TGA curves for physical mixture of NaY and VCl_3 after heat treatment (c).

which is assigned to the dehydration of sample. The results suggest that there is no VCl_3 crystalline phase in the sample and VCl_3 is well dispersed into NaY zeolite.

Figure 4(a) shows DTA/TGA curves of pure $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$. The endothermic peaks at 80, 120 and 180°C in DTA curve are assigned to desorption of water

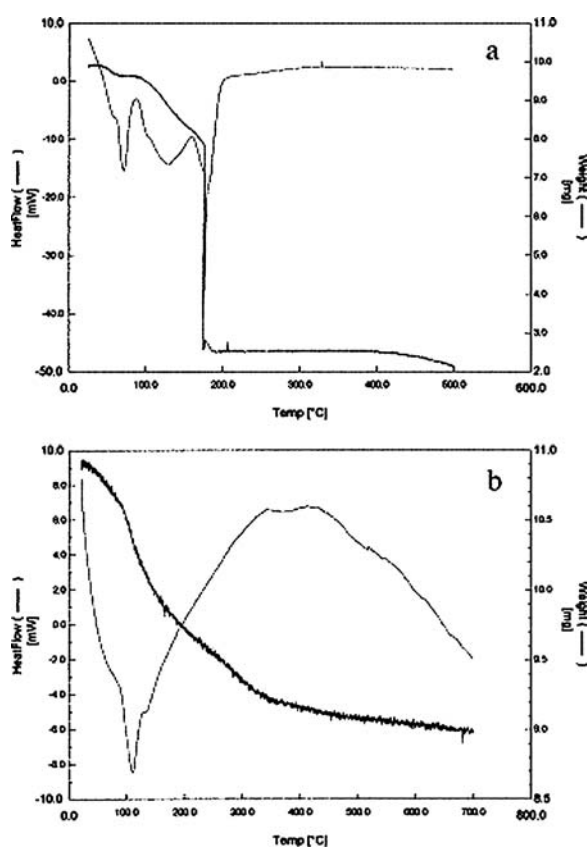


Figure 4. DTA/TGA curves for $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ (a) and DTA/TGA curves for physical mixture of NaY and $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ after heat treatment (b).

and structural change of $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$. Similar to the former case, the DTA curve of a mechanical mixture of $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ with NaY after microwave heating (Fig. 4(b)) shows two peaks at 102°C and 148°C, which are associated to dehydration of physically and chemically bonded water in sample, respectively. These results are consistent with the VCl_3 results and indicate that there is no $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ crystalline phase present in the sample and $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ is well dispersed into NaY zeolite. The TGA/DTA curves of pure $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Fig. 5(a) and (b)) are similar to VCl_3 and $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ with typical endothermic peaks for the dehydration, melting and structural change processes. Thermal behavior of mechanical mixtures of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ /NaY and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ /NaY after heating by microwave, similar to other samples, show only endothermic peaks at 90 and 100°C, respectively, due the dehydration samples. Therefore, it can be concluded that in all of the microwave heat treated samples,

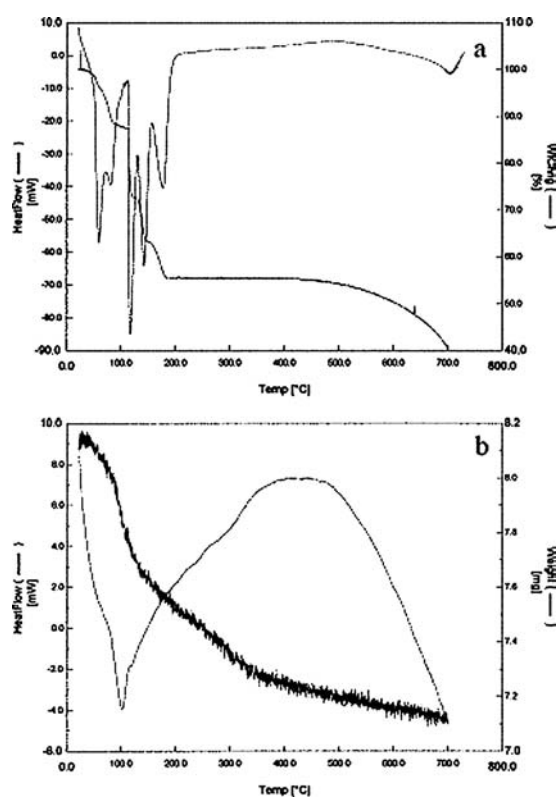


Figure 5. DTA/TGA curves for CoCl₂·6H₂O (a) and DTA/TGA curves for physical mixture of NaY and CoCl₂·6H₂O after heat treatment (b).

transition metal salts are well dispersed into the NaY zeolite and caused a drastic change in their thermal behavior. Ironically, according to the thermal analysis data in all microwave processed samples the zeolitic character still is dominate in spite of quite high concentration, 14–25 wt.%, of transition metal salt in the zeolite.

3.4. Surface Area Measurements

Table 3 shows the surface area measurement results of NaY zeolite, VCl₃/NaY, CrCl₃·6H₂O/NaY,

MnCl₂·2H₂O/NaY and CoCl₂·6H₂O/NaY mixtures after heat treatment. In contrast to the high surface area of NaY zeolite, 933 m²/g, the surface area of transition metal/NaY mixture after microwave heat treatment was reduced significantly. This is a further evidence for the dispersion of transition metal salts in pores of NaY zeolite. It is interesting to note that the surface area of CoCl₂·6H₂O/NaY is the lowest among the various samples. It seems that the higher concentration of transition metal ions in pores and channels of CoCl₂·6H₂O/NaY is the reason for its lower surface area of it.

3.5. Measurement of Amount of Exchanged Cation in Metal/Zeilite

Analysis of transition metal in the metal/zeolite samples showed the present of 82.5, 96.0, 89.5, 99.5, 77.0, 71.0, 81.5 and 92.0 percent of VCl₃, CrCl₃·6H₂O, FeCl₂·4H₂O, MnCl₂·4H₂O, CoCl₂·6H₂O, NiCl₂·6H₂O, CuCl₂·2H₂O and ZnCl₂, respectively after the solid state ion exchange process by dispersion onto the surface, channel and pores of NaY zeolite. This is the first report for the dispersion and solid state ion exchange of transition metals onto the surface of NaY zeolite by microwave irradiation.

4. Conclusion

Various transition metal chlorides can be dispersed and ion exchanged onto the surface of NaY zeolite under microwave irradiation via the solid state interaction of salts and NaY. The appearance of a new band about 820–890 cm⁻¹ in the framework of IR spectra for these salts was considered to be due to the coordination of metal ion to oxygen of the NaY zeolite structure. BET results showed surface area were reduced by dispersion and ion exchange of the transition metal onto zeolite.

Table 3. Surface area for some transition metal/NaY after heating (m²/g).

	NaY	VCl ₃ /NaY	CrCl ₃ ·6H ₂ O/NaY	MnCl ₂ ·2H ₂ O/NaY	CoCl ₂ ·6H ₂ O/NaY
Surface area	933	920	905	896	877

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