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Acidic Properties of $CoCl_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ Microwave Ion Exchanged NaY Zeolite

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The acidity of NaY zeolite was modified with $CoCl_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ by microwave irradiation solid state ion exchange method. The acidity of modified zeolite was investigated by thermal analysis (TGA/DSC) and Fourier transform infrared (FTIR) spectroscopy after pyridine chemisorbed on metal/zeolites. The results showed that in the microwave irradiation solid state ion exchanged zeolites, the Lewis acid sites are dominant acidic sites.

Key Words: Zeolite, Solid state ion exchange, Acid sites.

INTRODUCTION

Zeolites are widely used as solid acid catalysts in many industrial processes. The characterization of their acid sites is critical for evaluation of zeolite performance[1]. The zeolites acidity could be due to Bronsted sites which arise from hydroxyl groups in zeolite pore structure or Lewis sites such as $Al_xO_y^{n+1}$ species on zeolite pore structure[2]. Ion-exchange process has been used to modify catalytic activity of zeolite by introducing wide varieties of ions[3,4]. Ion exchange process in zeolite can be carried out in liquid phase or in solid state[5]. In solid state ion exchange process of zeolite, prolong and high temperature heating is required[6] and recently prolong heating has been reduced by using microwave irradiation[7]. Results show that the exchange of monovalent cation with polyvalent cation in solution can generate very strong Bronsted acid center by hydrolysis phenomenon[8]. The solid-state reaction between zeolite and other crystalline phase appears to be promising process for modification of zeolites catalysts. There is no report on the nature of acid sites for this zeolite. For determination of acidity of zeolite, various methods such as titration with Hammett indicators[9], microcalorimetry[10] and ^{1}H, ^{13}C, ^{15}N and ^{31}P NMR spectroscopy have been developed[11]. FT-IR spectroscopy with different probe molecules, such as ammonia[12], quinoline, pyridine[13] and carbon

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monoxide have been used for the characterization of acid sites. In this work, we report on the nature of acid sites in NaY zeolite that ion-exchanged in solid state by microwave irradiation.

EXPERIMENTAL

Preparation of ion-exchanged Zeolite: Zeolite NaY was prepared and activated according to the procedure described previously[14,15]. In a typical process 2 g of zeolite and 2 mmol of $CoCl_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ were mechanically mixed, ground and heated in microwave oven for 10-20 min with 900 Watt power. The temperature in the solid state ion-exchange is estimated around 700ºC. The XRD pattern showed no metal salt remained and solid state ion-exchange was complete.

Pyridine adsorption: The acidic properties of the ion-exchanged zeolites were studied by Galaxy series FT-IR 5000 spectrometer. The thermal analysis of samples were carried out at heating rate of 10ºC/min up to 700ºC using a Rheometric scientific STA-1500 thermal analyzer in the range of 10-700ºC. One gram of zeolite that ion-exchanged with microwave irradiation was activated under vacuum at 140ºC for 1 h. The samples were cooled down to room temperature under vacuum and then immediately exposed to pyridine vapours for 2 h. Desorption of physically adsorbed pyridine was carried out by evacuation for 1 h at 140ºC. Finally samples were removed and analyzed by FT-IR and DSC.

RESULTS AND DISCUSSION

The metal content and degree of exchanged ions after each ion-exchange process have been reported elsewhere[16].

$CoCl_2 \cdot 6H_2O$/zeolite: FT-IR spectrum of microwave cobalt ion-exchanged zeolite is shown in Fig. 1a. A new band appeared at 831 cm^{-1} and since such a band is absent in the parent NaY Zeolite and physically mixture of NaY + $CoCl_2 \cdot 6H_2O$, it is reasonable to associate it with a T-O-Co (II) (T = Al, Si) vibration[16,17]. Fig. 1b shows the infrared spectra of Co(II)/zeolite after adsorption of pyridine and Fig. 1c shows the infrared spectrum of same sample after desorption of pyridine. The ring variation modes of pyridine are the most sensitive vibrations with regard to nature of intermolecular interactions *via* nitrogen lone pair electrons. In the IR spectra of pyridine adsorbed zeolites, 1800-1200 cm^{-1} region, pyridinium ion and H-bonded pyridine can easily be distinguished[18]. These modes are observed at 1630 and 1547 cm^{-1} for NH_4Y zeolite and at 1625, 1494 and 1454 cm^{-1} for AlHY zeolite[19,20]. In the present work bands appeared at 1647, 1528 and 1426 cm^{-1} with absorption of pyridine (Fig. 1b-c). The band observed at 1646 cm^{-1} can be attributed to deformation vibrations of water which covered two bands at 1630 and 1622 cm^{-1} that related to interaction of pyridine to Bronsted and Lewis sites, respectively. The band at 1528 cm^{-1} can be associated to the interaction of pyridine to Bronsted site which is due to the heavier atomic mass of cobalt in comparison with aluminum shifted to lower frequency. The band at 1426 cm^{-1} can be related to Al(III) Lewis acid sites that shifted to lower frequencies to some extent.

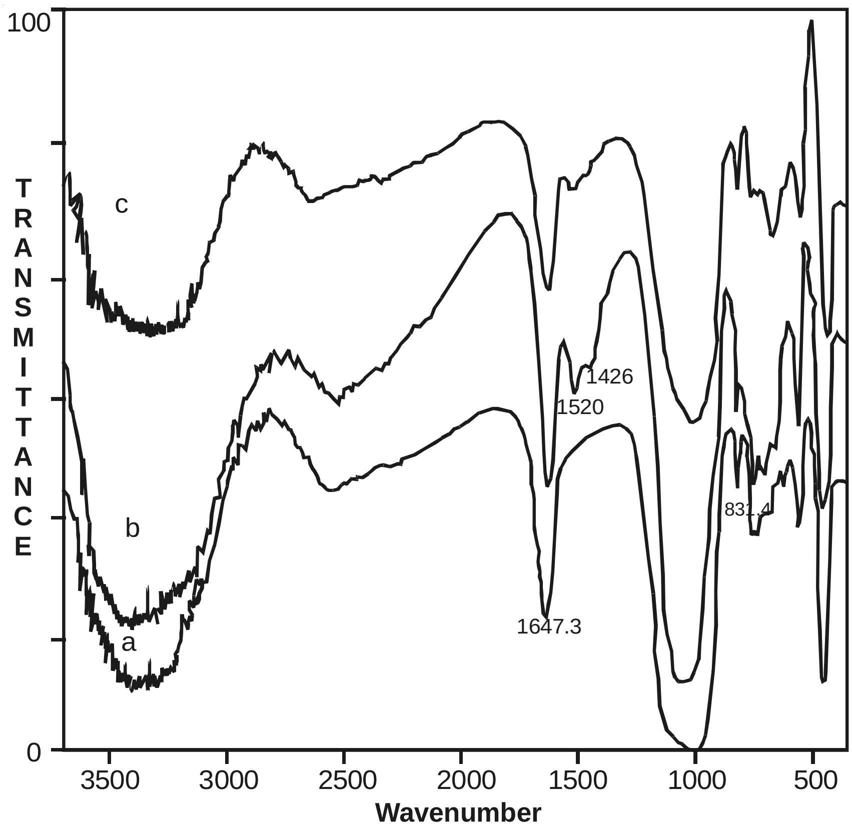

Fig. 1. Infrared spectra (a) activated Co(II)/zeolite (b) pyridine absorbed on Co(II)/zeolite (c) pyridine adsorbed on Co(II)/zeolite

$NiCl_2\cdot6H_2O$/zeolite: In the infrared spectrum of microwave nickel ion-exchanged zeolite a new band appeared at 830 cm^{-1} which can be related to the formation of T-O-Ni (II) (Fig. 2a). Furthermore, the band at 1643 cm^{-1} can be attributed to deformation vibrations of water which covered by two bands at 1630 and 1622 cm^{-1} that related to interaction of pyridine to Bronsted and Lewis sites, respectively. The band at 1520 cm^{-1} corresponds to Bronsted acid sites and bands at 1420 and 1340 cm^{-1} to Al(III) Lewis acid sites. Therefore, it is concluded that the Lewis acidity and a weak Bronsted acidity exist simultaneously in zeolite (Fig. 2b-c).

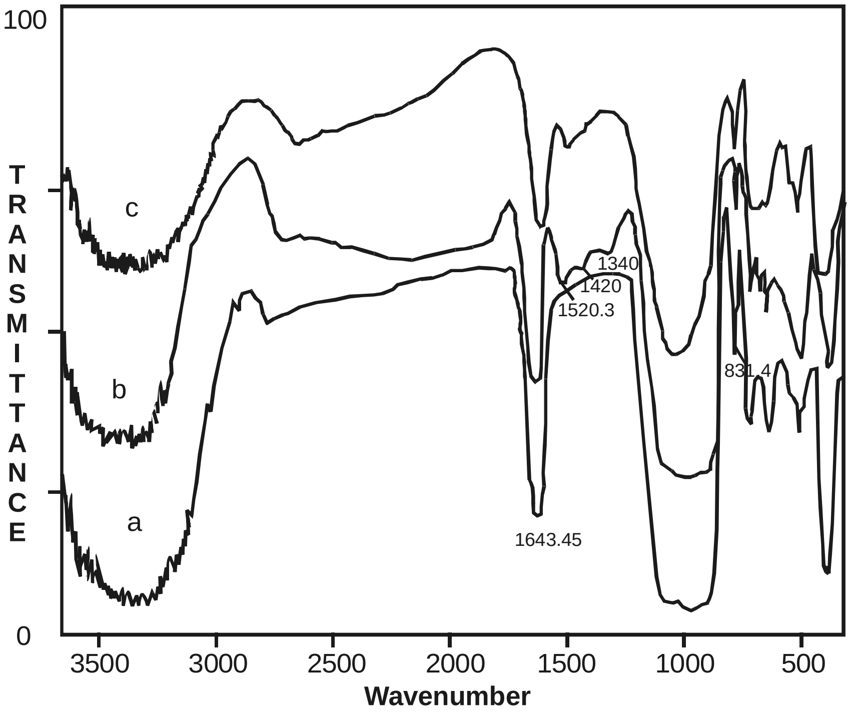

Fig. 2. Infrared spectra (a) activated Ni(II)/zeolite (b) pyridine absorbed on Ni(II)/zeolite (c) pyridine adsorbed on Ni(II)/zeolite

Thermogravimetric analysis

The thermal behaviours of $CoCl_2 \cdot 6H_2O$/Y and $NiCl_2 \cdot 6H_2O$/Y zeolite have been investigated by thermogravimetric analysis. The percentages of weight lose before and after absorption of pyridine are summarized in Table-1. The TG curve of activated Co(II)/Y zeolite shows about 5.1 % weight loss upon heating to 200ºC. This weight loss is accompanied by a broad endothermic peak in the DSC curve in the same temperature range, suggesting that the weight loss is due primarily to the elimination of physically adsorbed and possibly chemically bonded water. Interestingly, same sample after exposure to pyridine and adsorption of it loss about 12.5 % weight in the same temperature range. Apparently, the difference in the weight loss before and after adsorption of pyridine, 7.4 % is associated with the amount of pyridine adsorbed in the acid sites of $CoCl_2 \cdot 6H_2O$/zeolite (Fig. 3a-b). This value for the Ni(II)/Y zeolite (Fig. 4a-b) sample before and after pyridine adsorption is 2.5 %. The higher percentage of pyridine adsorption for the Co(II)/Y zeolite in comparison to Ni sample can be related to the more free sites in Co(II) and Al(III) atoms. This interpretation is consistent with the more tendency of the anhydrous $CoCl_2 \cdot 6H_2O$ for adsorption of pyridine which has been used in this study. Interestingly, the high catalytic activity of above zeolites in the interamolecular acylation reaction which require Lewis acid sites confirms such a claim[3]. Furthermore, when such a catalyst was employed for the esterification and Diels-Alder reactions, the yields significantly was lower than when aqueous solution ion-exchanged metal zeolite was used. Such higher yields are expected from a solid acid with high concentration of Bronsted acid sites[3,4].

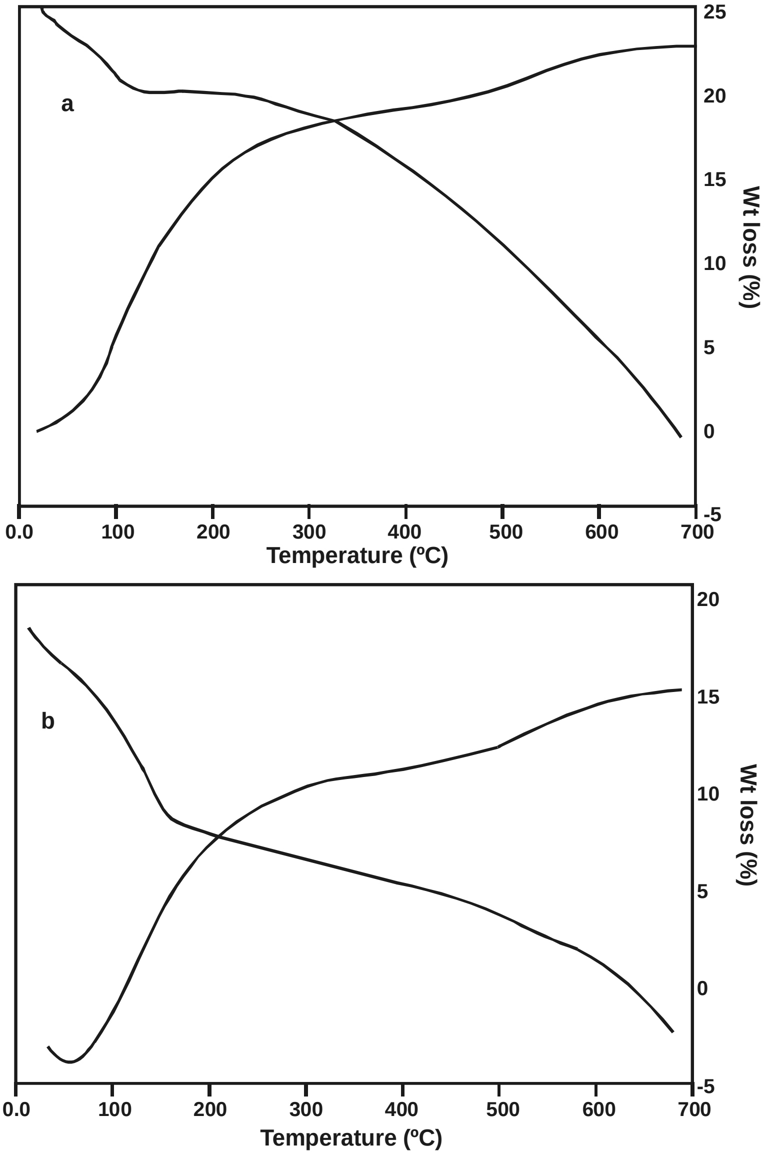

Fig. 3. DSC and TGA for Co(II)/zeolite (a) activated Co(II)/zeolite (b) pyridine adsorbed on Co(II)/zeolite

TABLE-1

Metal/zeolite	Activated zeolite	Zeolite/pyridine after adsorption	Pyridine (%)
$CoCl_2 \cdot 6H_2O$	5.1	12.5	7.4
$NiCl_2 \cdot 6H_2O/Y$	3.5	6.0	2.5

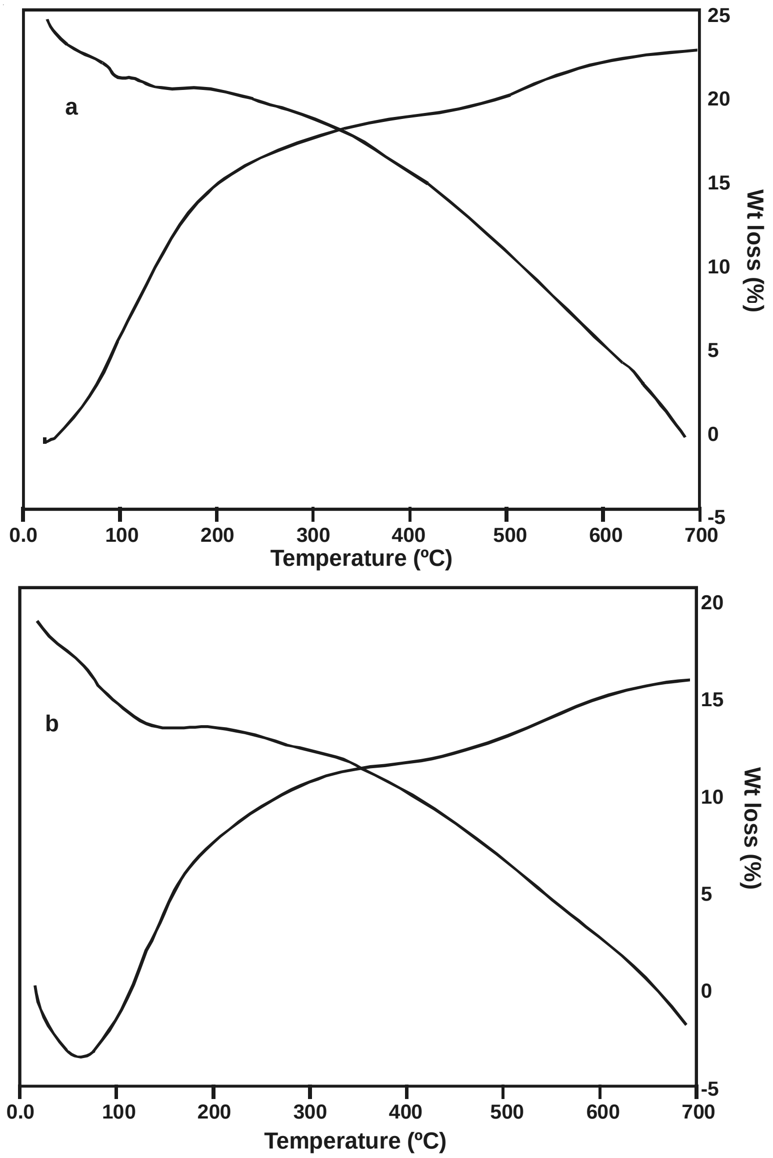

Fig. 4. DSC and TGA for Ni(II)/zeolite (a) activated Ni(II)/zeolite (b) pyridine adsorbed on Ni(II)/zeolite

Conclusion

In the present work, the acidic properties of microwave solid state ion exchanged zeolites of $CoCl_2 \cdot 6H_2O/Y$ and $NiCl_2 \cdot 6H_2 \cdot O/Y$ have been studied. The DSC and FTIR spectra of pyridine adsorbed on the activated metal/zeolite provided evidence for the Lewis acid interaction. The results obtained from this study demonstrate that in the microwave solid state ion exchange method the Lewis acid sites increase and Bronsted acid sites decrease. The increase of Lewis sites can be related to metal bonded to NaY zeolites.

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