

Zinc - Modified Forms of Zeolites by Wet Impregnation Method

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Abstract: Zeolites are crystalline aluminosilicates that possess well-defined pore structures and inner cavities. The framework consists of numerous aluminum and silicon atoms positioned within oxygen tetrahedral sites. Zeolites have been found to possess both Lewis and Brønsted acidity. Solid acid-base catalysts play an extremely important economical and ecological role in chemical and petrochemical industry as well as refinery technology. The range of catalytic transformation has grown steadily in the past two decades as experimental modifications of zeolites were explored. In this work, the various zeolites have been prepared by hydrothermal methods, calcined and ion-exchanged with ammonium nitrate to yield H-zeolites. The catalysts investigated are both medium (H-ZSM-5) and large pore (H-Y) zeolites. These zeolites are modified with zinc by wet impregnation method. FTIR spectroscopy and XRD analysis have been applied to characterize zeolite structures. The results obtained indicate that the introduction of zinc into ZSM-5 and Y samples lead to a series of promising catalysts, with high activity and a good selectivity.

Keywords: HZSM-5 and HY zeolites, zinc, wet impregnation

1. Introduction

Solid acid-base catalysts play a very significant role in chemical and petrochemical industry. Between the solid acid-base catalysts that are used in various industrial processes for the production of fine chemicals, zeolite catalysts represent about 40 % in different processes, from simple drying to complicated catalytic reactions. The use of zeolites as catalysts for organic reactions began in the early 1960s. Initially, zeolite-based catalysts were investigated for applications in the petrochemical industries. In addition to increased use in petrochemical manufacture, zeolite catalysis is expanding into the areas of speciality and fine chemicals synthesis. In the last decade, green chemistry has been recognized as a new approach to scientifically based environmental protection, and catalysis has manifested its role as a fundamental tool in pollution prevention. Zeolites are also well known as environmentally friendly catalysts. Due to the diversification of the application for which these catalysts are employed, considerable research has been focused on the characterization of the active sites, a key property for applications in catalysis [1].

Zeolites are crystalline aluminosilicates from natural or synthetic origin with highly ordered structures. They consisted of TO_4 tetrahedra ($T = Si, Al$), which are linked through common oxygen atoms to give a three-dimensional network through which long channel run. In the interior of these channels are located water molecules and mobile alkali metal ions, which can be exchanged with other cations. These compensate for the excess negative charge in the anionic framework resulting from the aluminum content. The interior of the pore system, with its atomic scale dimensions, is the catalytically active surface of the zeolite. The inner pore structure depends on the composition, zeolite type, and the cations [2].

Zeolites are mainly distinguished according to the geometry of the cavities and channels formed by the rigid framework of SiO_4 and AlO_4^- tetrahedra. The tetrahedra are the smallest structure units into which zeolite can be divided. Linking these primary building units together leads to 16 possible secondary building blocks (polygons), the interconnection of which produces hollow three-dimensional structures. The aluminosilicates structure is ionic, incorporating Si^{4+} , Al^{3+} and O^{2-} . When some of the Si^{4+} ions in the SiO_4 tetrahedra in this framework are replaced by Al^{3+} ions an excess negative charge is generated. A compensating source of positive charge must be added, namely cation, in addition to the framework Si^{4+} and Al^{3+} . These nonframework cations play a central role in determining the catalytic nature of zeolites. Also, the zeolites are ion exchanger. Bringing an aqueous salt solution in contact with the zeolite leads to incorporation of cations from the salt into the zeolite, replacing some of the nonframework cation initially present [3].

Very large areas of catalytic utilization of zeolites are acid-catalyzed reactions in petroleum refining processes, petrochemistry, and organic technology. Proton-donor Brønsted acid sites are generated by isomorphous substitution of tetravalent silicon by trivalent cations and principally by aluminium. Lewis electron acceptor sites are formed by thermal treatment of silicon-rich H-forms of zeolites. The acidity together with shape selectivity of zeolites can be potential in many applications in the processes of fine chemicals and intermediates synthesis. Zeolites can replace unsuitable acid catalysts (e.g. $AlCl_3$, H_2SO_4) which lead to environmentally problematic waste, corrosion and to many other technical problems. Zeolite catalysts can be separated from the reaction mixture and regenerated. The acidity characteristics of the zeolite materials may be modified using a number of methods such

as ion exchange, silicon/aluminium ratio, etc. All involve the removal of Al from the crystal framework [4-10].

The zeolites modified with Zn^{+2} ions are known as active catalysts for aromatization of light paraffins. Therefore, the study of the state of zinc in these materials has been a subject of numerous recent publications [11-13].

In this study, two zeolites (ZSM-5 and Y) have been prepared by hydrothermal methods, calcined and ion-exchanged with ammonium nitrate to yield H-zeolites. The catalysts investigated are both medium (H-ZSM-5) and large pore (H-Y) zeolites. These zeolites are modified with zinc by wet impregnation method. FTIR spectroscopy and XRD analysis have been applied to characterize zeolite structures. The results obtained indicate that the introduction of zinc into ZSM-5 and Y zeolites lead to a series of promising catalysts.

2. Experimental

NaY zeolite, with SiO_2/Al_2O_3 mole ratio of 5.1 and NaZSM-5 zeolite, with SiO_2/Al_2O_3 mole ratio of 23, were synthesized according to the published procedure [14-16]. These zeolites have been initially converted to their protonic forms and after that were modified with zinc by impregnation.

The Zn-modified zeolites (Zn-zeolites) were prepared by mixing hydrogen forms of respective zeolites with an appropriate amount of zinc acetate in distilled water. The mixture was digested at $80\text{ }^\circ\text{C}$ for 5 h, dried $110\text{ }^\circ\text{C}$ for 3 h and calcined at $550\text{ }^\circ\text{C}$ in the presence of air for 12 h.

The zeolites were characterized by several physico-chemical techniques (XRD and FTIR spectroscopy).

X-ray powder diffraction patterns were collected in air at room temperature on a DRON-2.0 equipment, using $CuK\alpha$ radiation of wavelength 0.15404 nm . Diffraction data were recorded from 0.5 to 50° 2-theta, at an interval of 0.01° and scanning speed of $2^\circ/\text{min}$.

Infrared measurements were performed on a JASCO 5300 FTIR spectrometer with a resolution of 4 cm^{-1} and averaging over 250 scans. The potassium bromide (KBr) pellete technique was used to record the FTIR spectra in the region $400 - 4000\text{ cm}^{-1}$ range. For the preparation of KBr pellets, 300 mg of previously dried KBr was mixed thoroughly with 0.5 mg of the sample and pressed in to pellets of 13 mm diameter with a pressure of 7 tons/m^2 .

3. Results and discussion

ZSM-5 is a synthetic high-silica zeolite which has gained vast importance in heterogeneous catalysis. The MFI-type topology shows a three-dimensional 10-membered channel system. Zeolite ZSM-5 is built from the pentasil unit and its unique catalytic performance is attributed to the two-dimensional system of intersecting channels one being strait and one sinusoidal with a diameter of $5.1 \times 5.5\text{ \AA}$ and $5.3 \times 5.6\text{ \AA}$ (Fig. 1) [14,15].

The FAU-type zeolite Y is of highest importance in heterogeneous catalysis. Zeolite Y consists of connected

truncated octahedra (sodalite units), which have a cage of diameter 6.5 \AA (β cage) and accessible through six membered rings of oxygen atoms. These units are linked along two six membered rings giving rise to hexagonal prism. The polyhedra formed in this way enclosed a super cage (α cage) with an internal diameter of 12.5 \AA and accessible through four 12-membered rings of oxygen atoms with a free aperture of 7.4 \AA (Fig. 2) [14,16].

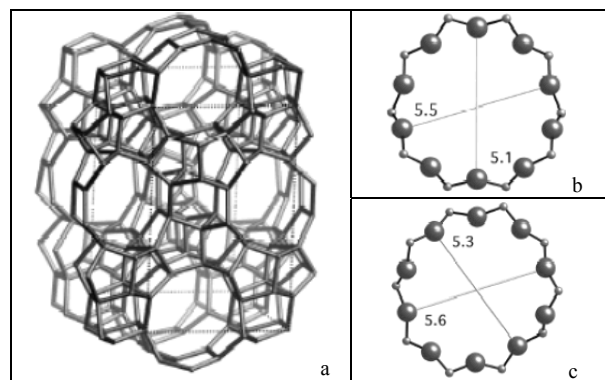


Figure 1. ZSM-5 zeolite: a) framework structure viewed along [010], b) 10-ring viewed along [100], c) 10-ring viewed along [010] [14]

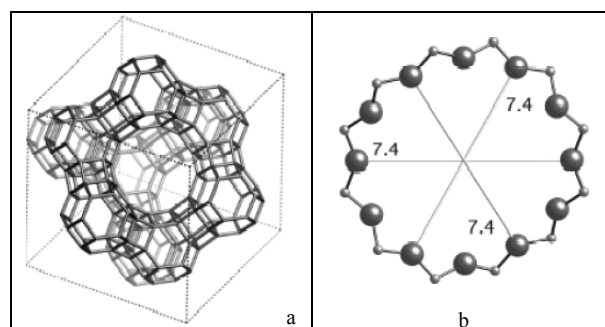


Figure 2. Y zeolite: a) framework structure viewed along [111], b) 12 ring viewed along $\langle 111 \rangle$ [14]

ZSM-5 and Y zeolites have generated considerable interest because of their catalytic properties, in addition to their well-known adsorptive and ion-exchanging capacities. The so-called shape selectivity in zeolites derives from their regular microporous structure. Due to the pore narrowness, zeolites can express an effective sieving effect which allows the passage through their pores of only molecules not bulkier than the pore diameter. With zeolites having an average particle size of a few microns, the internal surface area can represent more than 99 % of the total surface area. Thus, almost all the active sites are located inside the pores. In many zeolites, such as the ZSM-5 and Y zeolites, the size and geometry of the inside of the pores can play a determining role in the catalytic reaction mechanism.

Modifying the reaction sites in zeolites by incorporation of extraneous compounds or ions can lead to a different product distribution. Zn is known to favor the production of aromatic hydrocarbons. The presence of Zn within the zeolite lattice contributes to increase the production of aromatics in the methanol conversion.

Usually, zinc cations are incorporated into a zeolite via ion-exchange or wet impregnation of the zeolite with aqueous solution of the respective metal salt. Biscardi and Iglesias [13] showed that ion exchanged leads directly to intrazeolitic zinc centers, while impregnation leads to exchanged centers and extracrystalline ZnO.

In the common impregnation technique, the zeolite particles are completely immersed in a solution which contain an ionic form of the compound to be impregnated. After several hours of such a wet contact, the suspension is evaporated to dryness. With such a technique known as wet impregnation, the compound is deposited randomly inside and outside the zeolite pores.

In our work, the ZSM-5 and Y zeolites were characterized by several physico-chemical techniques (XRD and FTIR spectroscopy).

The XRD patterns (not presented here) of the zeolite samples ZSM-5 and Y were all very crystalline and analogous with the reported literature [17]. There was no change in the peak intensities of the zeolite samples modified with zinc by impregnation.

Mid-infrared spectroscopy has been applied to identify zeolite structures. The infrared spectrum in the region of 400 - 1200 cm^{-1} is a sensitive tool demonstrating structural features of zeolite frameworks. FTIR spectra in the region of framework vibrations of H- or Zn-zeolite samples are presented in the figures 3 and 4, and the frequencies of vibrations are given in the tables 1 and 2.

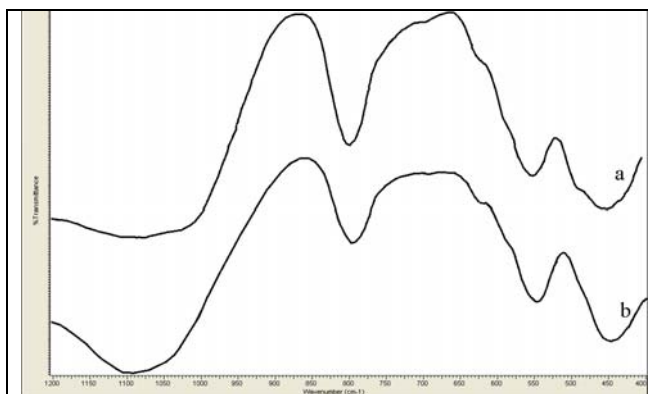


Figure 3. FTIR spectra of ZSM-5 zeolites in the region of framework vibrations: a) H form, b) Zn form.

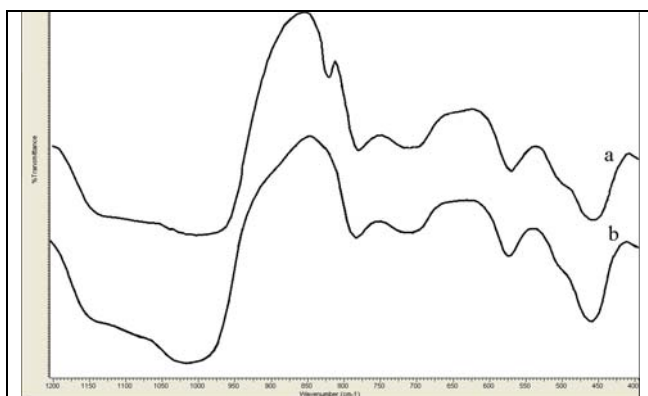


Figure 4. FTIR spectra of Y zeolites in the region of framework vibrations: a) H form, b) Zn form.

The characteristic absorption bands found for H-ZSM-5 (Fig. 3a) are at 1103, 796, 545 and 449 cm^{-1} . The bands around 1103, 796 and 449 cm^{-1} correspond to asymmetric stretching, symmetric stretching and T-O bending vibrations of internal tetrahedra respectively and band around 545 cm^{-1} indicates the presence of double five membered ring in the framework. The absorption bands of HY (Fig. 4a) are in accordance with the published literature [14,16]. Also, in the figures 3 and 4, FTIR spectra in the region of framework vibrations of zinc modified zeolites (Fig. 3b and Fig. 4b) are given in comparison with that of pure H-zeolite (Fig. 3a and Fig. 4a). A very few differences in the structural features of zeolite frameworks should be noted.

TABLE 1. Characteristic absorption bands of framework vibrations for ZSM-5 zeolites in their H or Zn forms

Zeolite					
H-ZSM-5			Zn-ZSM-5		
ν (cm^{-1})*	T (%)	Intensity	ν (cm^{-1})	T (%)	Intensity
1103.28	2.061	VS	1095.56	10.404	VS
867.97	0.201	VW	858.32	1.318	VW
796.60	44.293	M	796.60	65.707	W
659.65	1.098	VW	667.37	95.197	VW
545.85	27.001	S	545.85	40.604	S
514.99	43.124	M	511.14	61.434	M
449.41	12.732	S	447.48	23.954	S

* ν is frequency of vibration (wavenumber).

TABLE 2. Characteristic absorption bands of framework vibrations for Y Zeolites zeolites in their H or Zn forms

Zeolite					
H-Y			Zn-Y		
ν (cm^{-1})*	T (%)	Intensity	ν (cm^{-1})	T (%)	Intensity
1010.70	1.499	VS	1016.48	3.952	VS
856.39	1.658	VW	844.82	0.899	VW
783.10	41.310	M	783.10	57.450	M
754.17	47.531	M	752.24	64.249	W
717.52	41.980	M	715.59	59.373	M
626.86	59.656	M	628.79	73.367	VW
570.07	32.631	S	574.79	49.298	M
540.07	43.415	M	540.07	61.272	M
459.06	10.726	VS	460.99	21.524	S
410.84	39.574	S	410.84	55.368	M

* ν is frequency of vibration (wavenumber).

FTIR spectra of surface hydroxyl groups of H-ZSM-5 and HY samples are presented in figures 5 and 6.

The spectrum of H-ZSM-5 (Fig. 5a) contains two main bands, at 3620 and 3752 cm^{-1} . The band at 3620 cm^{-1} is associated with the acidic OH groups ($-\text{Si}-\text{OH}-\text{Al}-$) and the 3752 cm^{-1} band with external silanol groups. A weak band at 3675 cm^{-1} , are also detected; they are assigned to hydroxyls linked to aluminum atoms dislodged from the framework.

The HY zeolite (Fig. 6a) shows characteristic bridging hydroxyl groups ($\text{Si}-\text{OH}-\text{Al}$) at 3638 (high frequency) and 3555 cm^{-1} (low frequency) and surface silanol ($\text{Si}-\text{OH}$) groups at 3725 cm^{-1} respectively. The high frequency band at 3638 cm^{-1} arises due to $-\text{OH}$ groups situated in the super cages and the low frequency band at 3555 cm^{-1} arises due to $-\text{OH}$ groups in the sodalite cages.

Also, in the figure 5, FTIR spectrum of structural hydroxyl groups of zinc modified H-ZSM-5 sample (Fig. 5b) is given in comparison with that of pure H-ZSM-5 (Fig. 5a). A notable difference in the relative concentration of different kind of -OH groups should be noted. In the spectrum for zinc containing H-ZSM-5 samples, the decrease in concentration of bridging hydroxyl groups due to Zn^{2+} exchange of a H^+ cation is considerably less in zinc impregnated sample. Same compartments are giving at Y samples (Fig. 6).

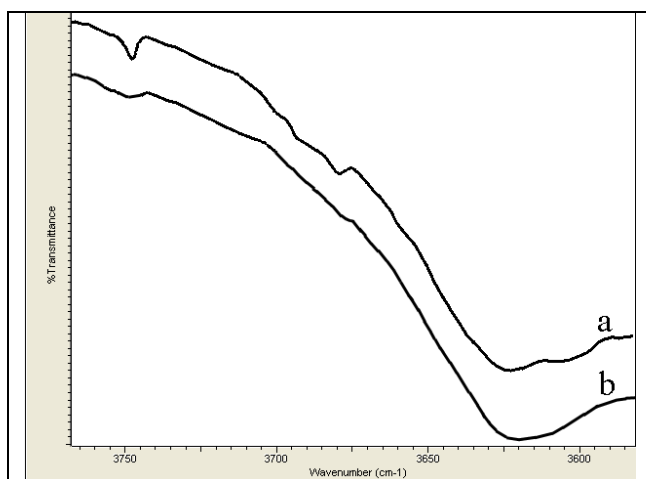


Figure 5. FTIR spectra of ZSM-5 zeolite in structural hydroxyl group vibration: a) H form, b) Zn form.

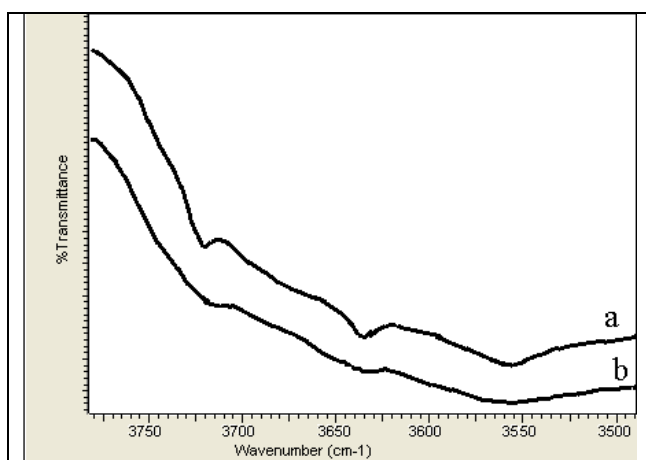


Figure 6. FTIR spectra of Y zeolite in structural hydroxyl group vibration: a) H form, b) Zn form.

This obviously indicates that modification of ZSM-5 and Y zeolites with zinc results in the replacement of a considerable part of the hydroxyl groups by Zn^{+2} ions. Of course, some of the modifying zinc ions could also form small zinc oxide particles inside micropores of the zeolite framework or on the external surface of the zeolite grains. Therefore, the relationship between the amount of the modifying zinc ions and the number of the bridging hydroxyl groups deviates from the linear shape, this deviation being stronger for the higher zinc loadings.

4. Conclusions

The catalysts investigated are both medium (H-ZSM-5) and large pore (HY) zeolites and their modifications with zinc.

The zeolites have been prepared by hydrothermal methods, calcined and ion-exchanged with ammonium nitrate to yield H-zeolites. These zeolites are modified with zinc by wet impregnation method.

All these samples were characterized by XRD for structural purity. All the zeolite showed good crystallinity, and there is no change in the peak intensities of the zeolite samples modified with zinc by impregnation.

From the structural hydroxyl region, for zinc modified ZSM-5 and Y zeolites, a significant difference in the relative concentration of different kind of -OH groups is observed. A decrease in concentration of bridging hydroxyl groups due to Zn^{2+} exchange of a H^+ cation is considerably less in zinc-impregnated sample.

The results obtained indicate that the introduction of zinc into ZSM-5 and Y samples lead to a series of promising catalysts, with high activity and a good selectivity.

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