Supported Metal Zeolites as Environmental Catalysts for Reduction of NOx Molecules
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Abstract
The NOx contamination of air is a major pollutant due to its reaction with the volatile organic compounds, which give rise to ground level (tropospheric) ozone. It is a conventional fact that NOx are one of the major components of car exhaust. In view of that fact, to sustain the tropospheric ozone is to reduce the amount of NOx in the air. Therefore, this paper is concerned with the catalytic activity of Fe-loaded zeolite and Cu-loaded zeolite used to decompose NOx by SCR (selective catalytic reduction) reaction with very high activity have been studied. Their preparations, characterization by XRD, FT-IR and SEM were also studied. Fe and Cu containing zeolites were prepared by solid state ion-exchange method under ambient pressure and at the temperature of 600°C for 4 hours. From this study, selective catalytic reduction reaction was observed, showing about 87% conversion of the NOx molecule with the corresponding optimum amount of catalyst (1.0 ± 0.5) g working under the reactor space volume of 30 cm\textsuperscript{3} at ambient temperature (30-32)°C.

Keywords: catalytic activity, Fe-loaded zeolite, Cu-loaded zeolite, SCR reaction, solid state ion-exchange method

Introduction
Alumino-silicate minerals are the most widespread chemical compounds on earth. They form many different varieties of natural minerals having a defined chemical structure. Among them, the most important are zeolites, clays and pumice [Vasylier & et. al]. In this paper, synthetic zeolites ZSM-5 were investigated by using hydrothermal method. The prepared ZSM-5 were modified by Fe and Cu.

Zeolites have been used as catalyst in many industrial processes, in addition to many other uses due to their microporous structure. Zeolites make extremely active catalyst. Selective reactions can be made to occur over zeolites when certain products, reactants or transition states are kept from forming within the pores because of size or shape.

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Nitrogen containing compounds are key players in any discussion of tropospheric chemistry and in smaller proportion of carbon monoxide and hydrocarbons, originating as much of the transmissions of mobile sources as of fixed sources.

Typical nitrogen containing compounds include nitrous oxide (N$_2$O), nitric oxide (NO), and nitrogen dioxide (NO$_2$). NO and NO$_2$ are collectively known as NOx, where the ‘x’ represents a subscript.

The nitrogen oxide contamination of air is a serious environmental problem nowadays. The natural formation of the NOx (e.g. volcanic activity, lightning) is negligible in comparison with the human sources. These emissions can be industrial processes (e.g. producing of nitric acid), but mainly the combustion of fossil fuel (internal combustion engines, jet engines, heater instruments and power plants), because the reaction between the nitrogen and oxygen takes place at the high temperature of the flame. Moreover in total NOx emission from the radio mobile sources (traffic) is also increasing, and the present engine constructions result in closely perfect burning of the fuel, therefore there is no possibility for the formation of reducing agent necessary for catalytic reduction of NOx. In this field the diversity of conditions causes difficulties in the decomposition of NOx. The most practical, and thermodynamically viable way of neutralizing NOx is the direct decomposition to nitrogen and oxygen. According to the literature it can be carried out over transition metal exchanged ZSM-5 zeolites as catalyst.
These zeolites were proven to be active in selective catalytic reduction reaction (SCR) of NO and NO\textsubscript{2} in the direct decomposition of NO to nitrogen and oxygen.

In the present work iron and copper containing catalyst were investigated in the reaction and decomposition of NO\textsubscript{x} in connection with the method of preparation and reduction characteristics.

Zeolites have been extensively used as catalysts in many industrial processes due to their Brönsted acidity and shape selectively. The incorporation of heteroelements can modify the acidity and the pore structure of zeolites. However XRD cannot distinguish between Si and Al or other metal cations in the framework, and it is therefore necessary to make use of theoretical simulation methods to obtain such information [Wang & et al]. In the present work, the framework of metal supported zeolites catalysts have been investigated. The following Figures show the different kinds of iron sites in zeolite. There are two type of cation exchange are present, isolated exchanged cation and bridged exchanged cation. [Figure 2.a and 2.b].

![Figure 2. (a) Isolated exchanged cations and (b) Bridged exchanged cations](image)

**Experimental**

**Preparation**

Zeolites are crystalline aluminosilicates. The zeolite framework structures have three-dimensional arrangement of SiO\textsubscript{4} and AlO\textsubscript{4} tetrahedra assembled together through sharing of oxygen atoms. The Na form of zeolite starting material was synthesized utilizing the hydrothermal method [Argauer
& et al]. 0.50 g of the sodium hydroxide was placed in a 250 mL beaker, and 2.01 g of silicic acid, followed by 1.01 g of tetrapropylammonium bromide were added. 5.0 mL of distilled water was added to this and mixed thoroughly.

In a separate 50 mL beaker, a solution of 0.25 g of aluminum sulphate was dissolved in 5.0 mL distilled water. Then, 0.05 mL of concentrated sulphuric acid was added via a pipet. The contents of the first beaker were carefully transferred to the second and mixed thoroughly. Distilled water was added to give a total volume of approximately 25 mL, and then allowed to stirring on a magnetic stir plate for approximately ten minutes. This mixture was sealed and transferred to pre-heated oven at 160°C for 44 hours.

The synthesis mixture was removed from the oven and placed in a cold water to room temperature. The white solid was filtered and washed with copious amount of water and suction dry the solid for at least 20 minutes. The dried powder should be very fine and calcined at 500°C for 2 hours.

The ion containing ZSM-5 samples were prepared by the solid state ion exchange procedure described by Karge and Beyer [Szalay & et al]. The solid state method was a 24 hours stirring of 10 g Na-ZSM-5 zeolite in 0.5 dm³ solution of NH₄Cl at 0.5 M concentration. After filtration and washing stirring was repeated. The sample was filtered off, washed, dried and heated at 600°C for 4 hours to decompose the NH₄⁺ ion into gas phase NH₃ and H⁺. The product was H-ZSM-5 form, which was mixed with 5% Fe-equivalent FeCl₃·5H₂O and 5% Cu equivalent Cu-acetate, heated at 600°C for 4 hours.

Characterization

The X-ray diffraction method and IR spectra are essential to describe the crystal structure. The samples were analyzed on X-ray diffractometer and the IR spectra were taken with a FT-IR spectrometer. SEM were also analyzed to describe the morphology of zeolite.

Catalytic Activity of Zeolite

The investigation of catalytic activity was carried out in a flow reactor. The mass of applied catalyst was 1.0 g with 0.35-0.5 mm particle size fraction of granules. After feeding the reactant gases the reaction was followed by a volumetric measurement.
Results and Discussion

This program deals with the preparation of ZSM-5 by using hydrothermal process. The prepared ZSM-5 samples were supported by Fe and Cu and characterized by XRD, FT-IR and SEM techniques.

The color of the prepared ZSM-5 was observed to be white, hard and has a high density between 1.9 to 3.1. The pH value of the prepared zeolites were 4.2 - 4.8. It was found that the prepared zeolites possessed acidic character.

Characterization by X-ray Diffraction Method

The X-ray diffractograms of synthesized samples were taken to confirm its structure, purity and crystallinity. Figure 3(a, b, c) show the X-ray diffraction pattern of catalyst samples. The X-ray diffractograms were compared with the standard data by the help of the computer. The XRD patterns indicated that the solid have sodium-aluminum silicate hydrate structure with high crystallinity. The existence of iron and copper ions in Fe-ZSM-5 and Cu-ZSM-5 was found after supporting of ZSM-5 sample with iron compound and copper compound, which was lately confirmed by SCR with NOx molecules with each samples.

Figure 3.a X-ray diffractogram of H-ZSM-5
Figure 3.b X-ray diffractogram of Fe-ZSM-5

Figure 3.c X-ray diffractogram of Cu-ZSM-5
Characterization by FT-IR Spectroscopy

Figure [4(a, b, c)] show the FT-IR spectra of the products which indicated the presence of zeolites; characteristic bands assigned to internal tetrahedral and external linkages were observed in the region of 400 to 1200 cm$^{-1}$. The peak in the zone 3600-3300 cm$^{-1}$ can be reasonably attributed to the structural water in the zeolitic pore. The main peaks in the 1200-900 cm$^{-1}$ regions are due to absorption by tetrahedral bonds. The Si(Al)-O bond was observed in 440 cm$^{-1}$ and 380 cm$^{-1}$ peak is due to the pore opening.

Before the catalytic conversion reaction of NOx, the examination of the IR spectra of Fe loaded zeolite and Cu loaded zeolite gives the same result. After the reaction in the investigation of catalytic activity, there is an increase of the band assigned between 1648 – 1440 cm$^{-1}$ which indicated that the adsorption as well as selective catalytic reaction occurs between NOx molecule and also catalyst use.

![FT-IR spectrum of H-ZSM-5](image-url)
Figure 4.b FT-IR spectrum of Fe-ZSM-5

Figure 4.c FT-IR spectrum of Cu-ZSM-5
Characterization by SEM

The Scanning Electron Micrograph of synthesized zeolite samples gave different surface conformation. It is evident from the photograph that the surface of the samples are composed of cluster of crystals having numerous voids and pores. The morphology of H-ZSM-5 zeolite crystals are cubic shaped, consisted of sharp edged.

![Figure 5. Scanning Electron Microscope of H-ZSM-5 and Fe-ZSM-5](image)

Catalytic Activity of H-ZSM-5 and Supported Metal ZSM-5

In this research, zeolites and metal supported zeolites were used as catalytic converters to decompose NOx by selective catalytic reduction (SCR) reaction. NOx molecules are passed over the zeolite catalyst bed and reduction reaction takes place inside the pore. NO and NO2 are collectively known as NOx.

The selective catalytic reduction of NOx molecules with each sample was conducted at room temperature in the flow rector and the results of relative percent conversion of NOx molecules was shown in Table (1).

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>% conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>H-ZSM-5</td>
<td>70.83</td>
</tr>
<tr>
<td>2.</td>
<td>Fe-ZSM-5</td>
<td>78.00</td>
</tr>
<tr>
<td>3.</td>
<td>Cu-ZSM-5</td>
<td>87.50</td>
</tr>
</tbody>
</table>

Reaction condition: 1.0 g catalyst, at room temperature, under ambient pressure
From this measurement, Cu-ZSM-5 sample was the best catalytic sorber when compared to Fe-ZSM-5 and H-ZSM-5. All supported metal zeolites were able to show more pronounced catalytic reactivity than the original zeolites in a room temperature.

The FT-IR structural assignment data for zeolites and supported metal zeolites after passing NOx molecules are shown in Table 2. After passing NOx molecules, specific broad band were observed at 3200–3600 cm$^{-1}$ which are due to –OH and N-H stretching. The peaks at 1648, 1629, 1456, 1440 cm$^{-1}$ are due to N=O stretching vibration frequencies. A comparison between the spectra of Fe-ZSM-5 and Cu-ZSM-5, before and after passing NOx molecules, more broad peaks at 3600-3200 cm$^{-1}$ and 1000 cm$^{-1}$ were observed after the pass of NOx molecules, which may indicate the enclosure of NOx molecule inside the pores of the prepared zeolites.

Table 2  Structural assignment data for Fe-BUZ and Cu-BUZ zeolite after passing NOx molecules

<table>
<thead>
<tr>
<th>Wave number (cm$^{-1}$)</th>
<th>Observed</th>
<th>General</th>
<th>Structure vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-BUZ 3200-3600</td>
<td>1648</td>
<td>1600-1400</td>
<td>-OH and N-H stretching</td>
</tr>
<tr>
<td>Cu-BUZ 3200-3600</td>
<td>1642</td>
<td>1600-1400</td>
<td>N=O stretching</td>
</tr>
<tr>
<td></td>
<td>1629</td>
<td>1465</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1456</td>
<td>1384</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1440</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1087</td>
<td>1064</td>
<td>1200-900 (Si(Al)-O) tetrahedral bonds</td>
</tr>
<tr>
<td></td>
<td>1068</td>
<td>933</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>538</td>
<td>516</td>
<td>650-500 Double ring</td>
</tr>
<tr>
<td></td>
<td>518</td>
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<td></td>
</tr>
</tbody>
</table>
Figure 6. a The FT-IR spectrum of Fe-ZSM-5 after passing NOx molecule

Figure 6. b The FT-IR spectrum of Cu-ZSM-5 after passing NOx molecule

Conclusion

From the overall assessment of the present work, it can be concluded that

- Fe-loaded zeolite and Cu-loaded zeolite was prepared by the solid state ion exchange method.

- Supported metal catalyst was characterized by XRD, FT-IR and SEM methods. The XRD data revealed that zeolite is composed of sodium,
aluminum silicate hydrate and the FT-IR spectra assigned that the tetrahedral linkage and pore opening. Supported metal zeolites are totally different from normal zeolite.

- From the selective catalytic reduction of NOx studies, different supported metal zeolite samples contributes the similar character with reaction of NOx molecules.

- Since clay and pumice are natural resources of our country, cost effective depletion of toxic gases such as CO, CO₂, N₂O, NO, NO₂, etc. can be made with the derivated zeolites from these resources.

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