

PREPARATION, CHARACTERIZATION OF OXIDATION-REDUCTION PROPERTIES AND APPLICATION OF Fe-ZSM-5 CATALYSTS

D. Szalay*, G. Horváth**, J. Halász** and I. Kiricsi**
Department of Environmental Engineering, Széchenyi István College,
H-9026 Győr, Hédervári út 3., Hungary
*Department of Applied and Environmental Chemistry,
University of Szeged,
H-6720 Szeged, Rerrich tér 1. Hungary

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Abstract

The removal of nitrogen oxides from mobile and stationary sources remains an important environmental problem. Transition metal exchanged MFI zeolites were proven to be active in catalytic reduction of NO and NO_2 by ammonia or hydrocarbons as well as in the direct decomposition of NO to nitrogen and oxygen. In the present work the role of iron containing catalysts was investigated in the decomposition of NOx and in the reduction of NO by CO in connection with the method of preparation and reduction/oxidation characteristics. The samples were prepared by liquid phase, and solid state ion-exchange methods. The IR spectra, the X-ray diffraction patterns and the BET measurements demonstrated that there was no change in the MFI zeolite structure during the ion-exchange. The iron content determined in the samples proved the higher efficiency of the solid state method in the ion uptake of the zeolite. Acidity measurements showed that the liquid phase method is not favourable for formation of Brønsted acidic sites. The sample prepared by the solid state method was more active in the majority of catalytic reactions, however, it can become oxidized and deactivated easier than the other one. In addition, the investigation showed, that the decomposition of N_2O - in contrast to the other NO and NO_2 reactions - occurs over the oxidized catalyst too, but the reaction is slower.

1 Introduction

The nitrogen oxide contamination of air is a serious environmental problem nowadays. The natural formation of the NO_x (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 NO_x emission from the ratio mobil 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 (CO or hydrocarbons) necessary for catalytic reduction of NO_x . In this field the diversity of conditions causes difficulties in the decomposition of NOx. There is no adequate solution so far for the lean-burn engines.

The most practical, and thermodynamically viable way of neutralizing NO_x is the direct decomposition to nitrogen and oxygen. According to the literature it can be carried out over transition metal exchanged MFI zeolites as catalysts. These zeolites were proven to be active in catalytic reduction of NO and NO_2 by ammonia[?] or hydrocarbons[?] as well as in the direct decomposition of NO[?].

Although much effort was devoted so far to understand the mechanism of these reactions, there is hardly any information available on the role of the metal in forming the active sites. In the present work iron containing catalysts were investigated in the reactions and decomposition of NO_x in connection with the method of preparation and reduction/oxidation characteristics.

2 Experimental

Zeolites are crystalline aluminosilicates. The zeolite framework structures have three dimensional arrangement of SiO_4 and AlO_4 tetrahedra assembled together through sharing of oxygen atoms. The presence of Al^{3+} generates negative charges in the framework, which can be compensated by the presence of cationic species in the voids of the framework, this generating cation-exchange properties.[?]

The Na-ZSM-5 starting material was synthesised in our laboratory utilizing the method described elsewhere.[?] The ratio of Si/Al in our basic zeolite was close to 40, and the Na^+ ions compensating the negative charges was exchanged for Fe^{2+} and Fe^{3+} ions. The iron containing ZSM-5 samples were prepared either by the solid state ion-exchange procedure described by Karge and Beyer[?], and by liquid phase method suggested by Hall and Feng.[?]

The first step of the solid state method was a 24 hour stirring of 10 g Na-ZSM-5 zeolite in $0.5 dm^3$ solution of NH_4Cl at $0.5 mol/dm^3$ concentration. After filtration and washing stirring was repeated. The sample was filtered off, washed, dried and heated at $600^\circ C$ for 4 hours to decompose the NH_4^+ ions into gas phase NH_3 and H^+ . The product was H-ZSM-5 form, which was mixed with 5 % Fe-equivalent $FeCl_3 \cdot 5H_2O$, heated at $600^\circ C$ for 4 hours. This sample is referred to as "S".

The liquid phase ion-exchange method in the case of Fe^{2+} needs nitrogen atmosphere free from oxygen, so we had to use a special apparatus described by Hall. It consisted of two sealed flasks joined at the bottom through a fritted disk sealed into the connecting tube. This allowed ions to pass freely, but prevented the passage of solids. The vessels were filled with distilled water, one of them contained the zeolite, the other contained iron oxalate. The nitrogen atmosphere and the presence of $C_2O_4^{2-}$ ions prevent $Fe^{2+} \rightarrow Fe^{3+}$ oxidation and formation of Brønsted acidic sites during the procedure. The sample prepared by this method is referred to as "H".

3 Methods

To determine the iron content the samples were melted with carbonate, followed by dissolution of the solid formal, and the solutions were titrated by complexometric method. The ion-exchange level was calculated from the results of the measurement.

The X-ray diffraction method and the IR spectra are essential to describe the crystal structure, because they can reveal changes during the ion exchange. The samples were analysed on a DRON3 X-ray diffractometer and the IR-spectra of about 0.5 mg zeolite homogenized in 200 mg KBr were taken with a Mattson-Genesis FTIR spectrometer.

BET surface measurement showed whether any changes happened in the porosity of the zeolite during the exchange. To determine the surface area of the samples a volumetric adsorption apparatus was applied. The adsorption isotherms were taken at 77 K, after pretreatment of the samples in vacuum at 723 K.

To describe the acidity of samples we used the pyridine adsorption method. The feeding of pyridine was followed by temperature programmed desorption followed by derivatographic method. The higher temperature of desorption refers to higher acidity.

The investigation of catalytic activity was carried out in a recirculatory flow reactor. The mass of applied catalysts was 1 g with 0.35-0.5 mm particle size fraction of granules. After feeding the reactant gases the reaction was followed by a volumetric measurements using DATAMETRICS equipment.

4 Results

The iron contents, the ion-exchange levels and the BET surface-areas of the samples are shown in the Table 1. The results throw light on the higher efficiency of solid state method in ion uptake of zeolite. The sample contains more iron than calculated from the theoretical ion exchange capacity is called as "overexchanged" sample. The high ion-exchange level of the "S" sample can be explained by the fact, that the polyvalent iron ions compensate only one negative charge, and iron occupies not only ion-exchange positions, but also the voids of zeolite as iron-oxides. The results of BET-measurements indicate no changes in porosity.

Table 1.: The characteristics of the catalysts

	iron-content (%)	exchange level (%)	BET-surface (m^2/g)
sample S	2.23	316	339
sample H	0.499	47	319

The X-ray diffractograms compared with the literature[?] (Fig. 1) show no changes in the crystal structure of the zeolite. The examination of the IR spectra (Fig. 2) gives the same result. The ratio of the extinctions of the $650 - 550\text{cm}^{-1}$ and $480 - 440\text{cm}^{-1}$ bands (higher than 0.72) confirms that the zeolite structure is intact.[?]

The pyridine thermodesorption measurements (Fig. 3) show low amount of adsorbed pyridine, therefore the amount of acidic sites is low in ZSM-5 structure. In the case of sample "H" no Bronsted acid sites were detected.

The first reaction in the investigation of catalytic activity was the reduction of oxidized samples by hydrogen. Before the measurements the samples were pretreated in oxygen at 400°C for one hour. The change in the pressure of the reactor system in the case of 200°C and 350°C reductions are shown in Fig. 4. For sample "H" there is no considerable change in the pressure at any temperature, the first little fall has not been continued. The sample "S" has been reduced at 350°C .

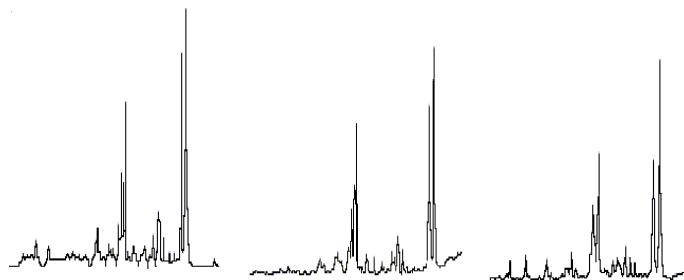


Figure 1: The X-Ray diffractograms of Na-ZSM-5 [8], sample "H" and sample "S"

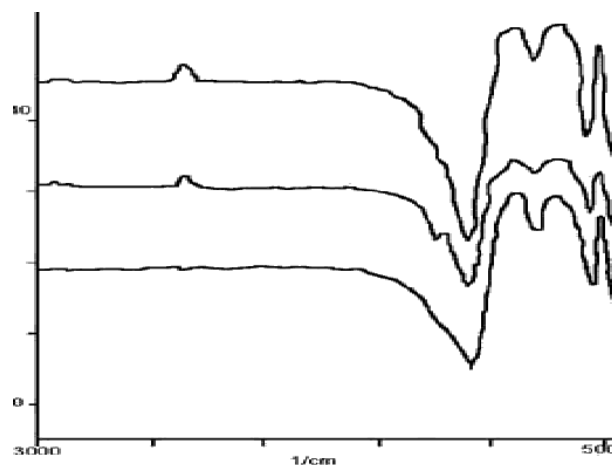


Figure 2: The IR-spectra of H-ZSM-5 (upper), sample "S" (middle) and sample "H" (lower)

Before the decomposition of N_2O the samples were pretreated in hydrogen at 350°C for an hour. The changing in the pressure of the gas phase of reactor for reactions carried out at 400°C and 450°C are shown in Fig. 5. The assumed reaction is: $2N_2O = 2N_2 + O_2$, which causes increase in pressure, has been detected. The curves show, that higher temperature causes faster reaction. The sample "S" gives faster reaction at both temperature.

The role of the catalysts was investigated in $CO + NO$ reaction too. Before the reaction, the samples were pretreated in hydrogen at 350°C for one hour. The changes in the pressure of the reactor are shown in Fig. 6 in the case of 250°C and 350°C reactions. The assumed reaction is: $2CO + 2NO = 2CO_2 + N_2$, which causes decrease in pressure, as has been detected. The sample "S" is more active at 250°C , but after the first reaction it loses its activity. There is no change in pressure at 350°C . However, the sample "H" preserves its activity, and gives higher activity at higher temperature. The $CO + NO$ reaction was carried out over the reduced "S" sample after CO-pretreatment too, and we found that the catalyst preserved its activity. Consequently deactivation can be explained by the result of oxidation by NO or O_2 .

The decomposition of N_2O was carried out over the deactivated, probably oxidized sample "S" as well. The result compared to the reaction over reduced sample "S" is shown in Fig. 7. In the decomposition of N_2O , at

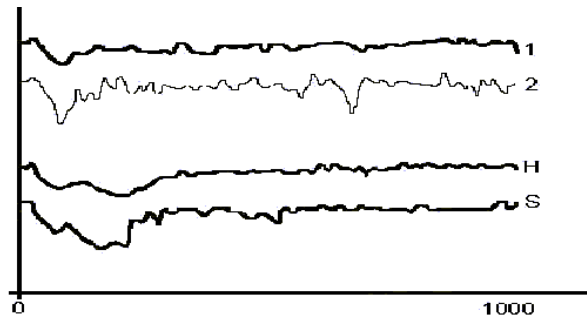


Figure 3: DTG curves of the temperature programmed desorption of pyridine over Na-ZSM-5 (marked 1) H-ZSM-5 (marked 2), sample "H" and sample "S"

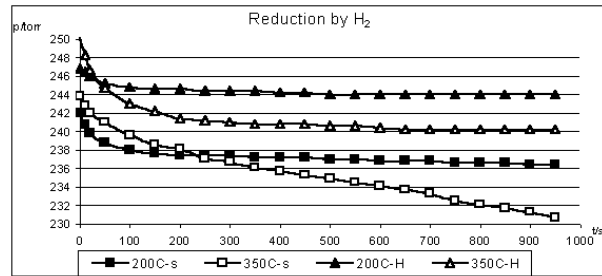


Figure 4: Reduction by H_2

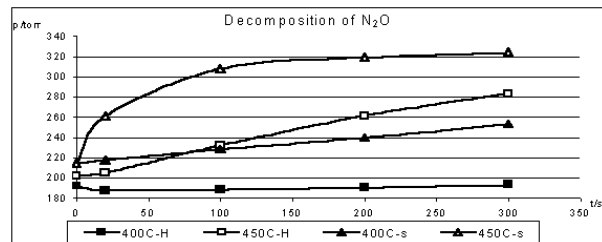


Figure 5: Decomposition of N_2O

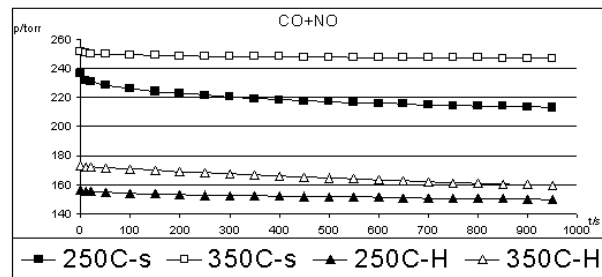


Figure 6: The $CO + NO$ reaction

the same temperature, both the reduced and oxidized catalysts are active, but the reduced sample showed faster reaction.

Finally the $CO + O_2$ reaction was carried out over the samples. Before the reaction the samples were pretreated in hydrogen at $350^\circ C$ for one hour. The change in the pressure of the system are shown in Fig. 8 for reactions

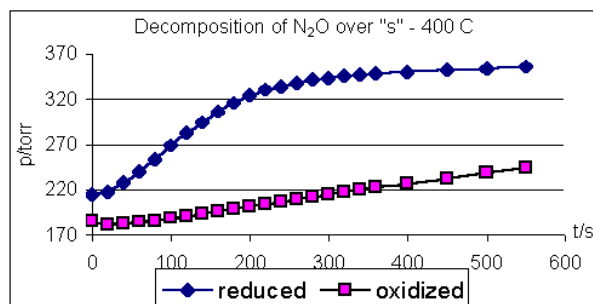


Figure 7: Decomposition of N_2O over sample "S"

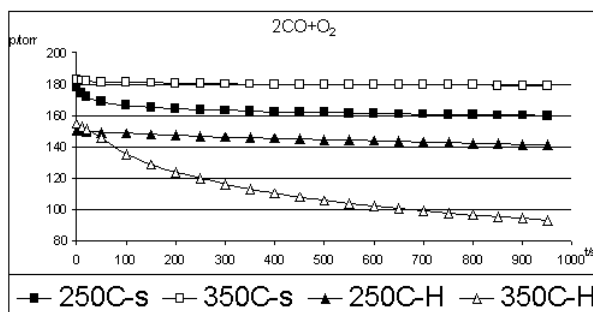


Figure 8: The $CO + O_2$ reaction

250°C and 350°C. The assumed reaction is: $2CO + O_2 = 2CO_2$, which results in decrease in the pressure of the system. The sample "S" has higher activity at 250°C, but after the first reaction it loses the activity, and there is no change has been found in the pressure at 350°C. However, the sample "H" preserves its activity, and gives faster reaction at higher temperature.

5 Conclusions

The results of the investigations proved, that both ion-exchange methods are applicable for catalyst preparation, but the solid state procedure gives more effective catalyst, than the other. The different behaviours of samples during the reduction may be caused by the different oxidation states of iron, mainly Fe(II) in the sample "H", and Fe(III) in the sample "S".

The catalytic activity of the sample "S" in most cases is higher, which is due to the higher iron content, but the sample easily becomes oxidized, leading to the loss of activity in the $CO + O_2$ and $CO + NO$ reactions. The sample "H" preserves the activity in these cases too.

The catalytic decomposition of N_2O occurs probably in different way than the other reactions, because it takes place over oxidized sample "S" too, although the reaction is slower.

6 Acknowledgement

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