

Fe-containing Zeolites as Active and Selective Catalysts for Nitrogen-oxides Reduction

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Abstract: NO has now been revealed to be generating pollutants on a much broader scale due to its reaction with the volatile organic compounds (VOCs) which give rise to ground level (tropospheric) ozone. In this work we described the catalytic activity of Fe-Zeolites, their preparation, characterization by TPD, FTIR and XAFS used to decompose NO_x to N₂ by SCR system with very high activity and low selectivity to non-desired N₂O compound. Fe-containing zeolites obtained by novel sol-gel process with Fe³⁺ and/or Fe²⁺ as counter ion incorporated by reproducible post-synthesis methods are obtained. Fe²⁺ on the framework as counter ions also exist as a Lewis site. We differentiated it from the well-known Lewis sites from Aluminium of the zeolitic framework. Thus, LUMO of above cited metal leading to a coordinatively activity with Brønsted acid sites would be successfully applicable to SCR reaction of NO_x. The catalysts emerge as the preferred choices due to their selectivity, availability, and relatively low cost.

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 (vehicles of transport of combustion to gasoline or diesel engine) as of fixed sources (generating plants of energy, train incinerated chemistries, furnaces). The atmospheric contamination caused by anthropogenic transmissions of originating nitrogen oxides as much of fixed sources as of mobile sources, is considered around 30 million tons per year. These gases come from fuels or the extremely high temperatures to which N₂ and O₂ are warmed up simultaneously. Typical nitrogen containing compounds include nitrous oxide (N₂O), nitric oxide (NO), and nitrogen dioxide (NO₂). NO and NO₂ are collectively known as "NO_x", where the x represents a subscript. The NO_x which they appear in these currents goes of 50-1000 ppm and O₂ 0-21 % [1]. The nitrogen oxides are the main atmospheric polluting agents causing serious impacts on the terrestrial ecosystem, contributing to the formation of acid rain and of photochemistry smog [2].

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The nitric oxide (NO) represents 80% of these transmissions and is produced by three mechanisms different in most of the combustion processes: 1) thermal reaction (to temperatures very elevated) of O₂ and N₂; 2) oxidation of nitrogen compound present in heavy fossil fuel and 3) oxidation of the intermediary HCN, product of the reaction of N radical with hydrocarbons. The nitrogen oxide reduction is a problem that the environmental catalysis still tries to solve. The hydrocarbon use as ammonia substitutes for the nitrogen oxide removal in rich mixtures in oxygen has reached a particular interest in the last years and more indeed the methane use, arising therefore the systems from selective catalytic reduction by hydrocarbons (HC-SCR). Li and Armor [3] were the pioneers in reporting the catalyst of Co-ZSM5 as an effective system for the selective reduction of NO_x in the presence of excess of oxygenate and methane like reducer. Despite the activity one is diminished in the presence of water steam and elevated temperatures [4]. Moreover, perovskite-activated zeolites were successfully used for SCR with low N₂O formation [5]. An over-exchanged Fe-ZSM5 (namely, a zeolite with high Fe/Al ratio has recently been demonstrated to exhibit very promising properties as DeNO_x catalyst [6]. Our main objective is to apply experimental data recently obtained, which show Brønsted acid containing zeolites synthesized by sol-gel method, tuned with lower unoccupied molecular orbital (LUMO) of Fe introduced as counter ion, present a good activity for reduction of NO_x to N₂ in the presence of oxygen with very low N₂O selectivity.

The preparation and comprehensive characterization of Fe-Zeolites, as well as the understanding of the reduction mechanisms are the main goals of this work. Atomic absorption spectroscopy (AAS), X-ray diffractometry (XRD) and XANES are the techniques applied for the physico-chemical characterization of the catalyst. *In situ* infrared spectroscopic studies of pyridine adsorption-desorption and temperature programmed desorption (TPAD) behavior of ammonia from FeNH₄-Z are applied as model experiments to mimic the reaction on a molecular level under well-defined conditions. The results obtained up to now show that the preparation of Fe-ZSM-11 using ion-exchange or impregnation with Fe^{2,3+} nitrate and/or sulphate is reproducible. Iron is found inside the pores of the zeolite in form of homogeneously dispersed on the cation-exchange positions. Fe²⁺-zeolite is the most effective catalyst. However, as Fe²⁺ loading increases from 1 to 3% w/w, Fe³⁺ species are present. This exchange procedure does not inhibit the formation of Brønsted sites.

Fe²⁺ and Fe³⁺-H-ZSM-11 samples were prepared using NH₄-ZSM-11 by ion exchange with FeSO₄·7H₂O or Fe(NO₃)₃·9H₂O solution for 20 h twice, or by wetness impregnation. The final product was dried at 110°C and heated for 10 h under nitrogen flow of 10ml/min and 2°C/min from 100°C to 500°C, then the samples were calcined in air at 500°C for 12 h.

In Figure 1a we show the conversion of NO_x for the different samples. As it can be observed, sample A is the most active reaching conversion levels of NO_x of 70% at low temperatures as 350°C. It is important to observe the very low selectivity to N₂O of samples A, nevertheless sample C reaches 8 % of selectivity to 300°C (see Figure 1b).

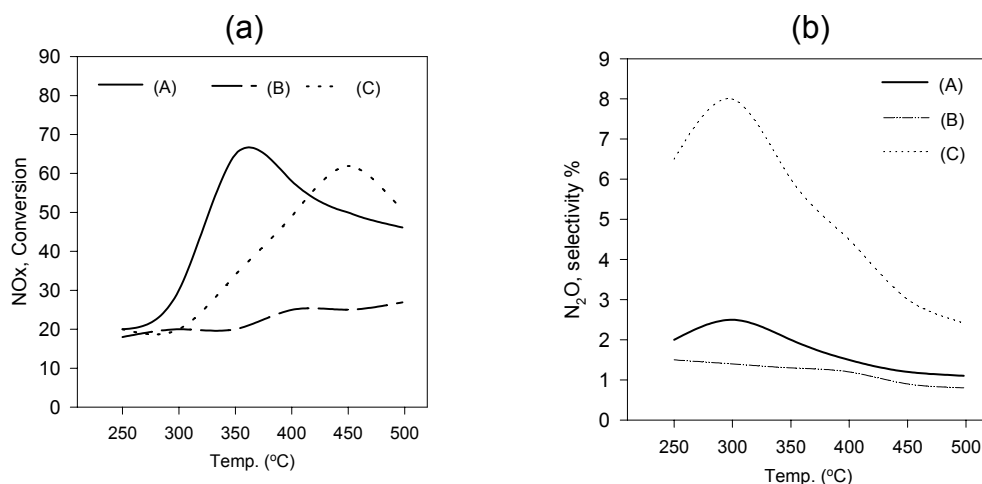
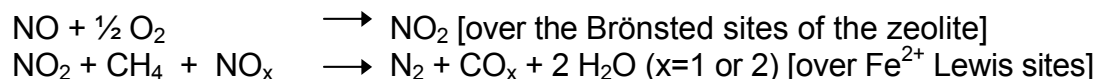


Figure 1. a: Catalytic activity for NO_x SCR; b: Selectivity to N₂O using Fe-Zeolites, A: Fe²⁺-H-ZSM-11(3%) w/w; B: Fe³⁺-H-ZSM-11(3%) w/w; C: Fe²⁺-H-ZSM-11(1%) w/w .

Oxidation number of each sample are determined by Fe K-XANES using Kataby data [7]. Results show that Fe is as Fe³⁺ and as Fe²⁺ in the samples B and C respectively, but as a mixture of Fe²⁺ and Fe³⁺ in Fe²⁺-H-ZSM-11 (3 %) (sample A). Similar results were obtained by FTIR spectra of pyridine-Lewis sites of (Feⁿ⁺-Z). We found that new Lewis bands at 1448 and 1446 cm⁻¹ appear in Feⁿ⁺-Z samples (Py-Fe²⁺ and Py-Fe³⁺ adduct respectively) well differentiate from Lewis sites (1454 cm⁻¹) due to Al in the framework. These bands were used to determine the total number of Lewis sites due to Al³⁺, Fe²⁺ and Fe³⁺ as counter ion on zeolites. In the zeolites with Fe²⁺ appears greater proportion of Lewis sites than Fe³⁺-zeolite. The number of OH sites increases with Fe²⁺ and Fe³⁺ content, due to the fact that Fe²⁺ and Fe³⁺ could lead to the possibility to of interaction only with one exchange site, generating new OH sites. The ratio of Brönsted/Lewis sites is very important; for our samples are: A=1.20; B=3.38 and C=1.48. Thus, the EDA adduct, generated by the LUMO of Fe²⁺ (Lewis sites) and its interaction with intermediate reactive molecules lead to a coordinately effect with Brönsted acid sites would be successfully applicable to NO_x SCR reaction suggesting the following mechanism [8] :



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