Experimental evidence of SCR NO with NH_3 mechanism over FeSiBEA, FeAlBEA and Fe(IE)BEA zeolite catalyst

Stanislaw Dzwigaj[a,*], **Pawel Boron**[a,b], **Malgorzata Rutkowska**[b], **Barbara Gil**[b], **Bartosz Marszalek**[b], **Lucjan Chmielarz**[b,*]

[a]*Sorbonne Universités, UPMC Univ Paris 06, CNRS, UMR 7197, Laboratoire de Réactivité de Surface, Paris, F-75005, France*
[b]*Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, Kraków, 30-387 Poland*
**Stanislaw Dzwigaj: Fax: +33 1 44 27 60 33, stanislaw.dzwigaj@upmc.fr*

Abstract: Various temperature-programmed techniques including: temperature-programmed desorption of chemisorbed reactants, temperature-programmed surface reaction between reactants chemisorbed on catalyst surface and reactants from gas phase as well as stop flow-TPD techniques and FTIR studies of adsorbed NH_3 and NO were used as tools in the studies of mechanism of selective catalytic reduction (SCR) of NO with ammonia in the presence of Fe-containing BEA zeolites obtained by three different methods.
Keywords: iron, BEA zeolite, SCR of NO, TPSR, Stop flow-TPD.

1. Introduction

Selective catalytic reduction (SCR) of NO_x with ammonia, called also DeNOx process, is a widely used technology for diesel engine vehicles to reduce NO_x (NO, NO_2) to N_2. Recently, the studied of SCR are focused on the Fe- and Cu-based zeolite catalysts, which were reported to be very efficient in NO_x reduction at high space velocities [1]. Despite of large number of the studies reported in scientific literature the mechanism of the SCR process and the role of various forms of metallic species in catalytic process are still discussed. This contribution is a continuation of our previous studies [2], which showed high catalytic activity of BEA zeolite modified with iron by different methods (two-step post-synthesis, wet impregnation and ion-exchange) in the SCR process. The main goal of the presented studies is recognition of the mechanism of the SCR process over the Fe-BEA zeolite catalysts. Recently [2], similar studies were reported by authors for BEA zeolite modified with cobalt species.

2. Experimental

Fe-containing zeolites were prepared by the three different methods: two-step post-synthesis (PS), ion exchange (IE) and conventional wet impregnation (Imp).

PS method - TEABEA zeolite, provided by RIPP (China), was treated with concentered solution of HNO_3 at 353 K to remove aluminum ions from the zeolite structure. The resulting SiBEA was dispersed in aqueous solution of $Fe(NO_3)_3{\cdot}9H_2O$ and stirred for 24 h. Then, the obtained suspension was stirred in an evaporator under vacuum of a water pump in air at 353 K until water was evaporated. The solid with the iron content of 1.0 wt % is labeled as FeSiBEA.

IE method- HAlBEA was treated two times with a solution of NH_4NO_3 at 343 K for 3 h to exchange H^+ ions for NH^{4+}. Then, the solid was washed with distilled water, and dried overnight at 363 K. Then, it was dispersed in an aqueous solution of $Fe(NO_3)_3{\cdot}9H_2O$. The obtained sample with the iron content of 1.5 wt % is labelled as Fe(IE)BEA.

Imp method- HAlBEA was dispersed in an aqueous solution of $Fe(NO_3)_3{\cdot}9H_2O$ and stirred for 24 h. Then, the suspension was stirred in evaporator under vacuum of a water pump at 353 K in air until water was evaporated. The solid with iron content of 1.0 wt % is labelled as FeAlBEA.

Before physicochemical characterization and catalytic tests, FeSiBEA, FeAlBEA and Fe(IE)BEA were calcined at 773 K. Details of the catalysts preparation and characterization as well as results of the catalytic tests were presented in our previous paper [2].

Temperature-programmed experiments (NO-TPD, NH_3-TPD, NO+O_2-TPD, (NO+O_2)-NH_3-TPD, NH_3-TPSR, NO-TPSR, Stop-flow TPD) were carried out in a fixed bed continuous flow microreactor system. Gases desorbing from the zeolite samples were continuously analyzed by a quadrupole mass spectrometer (RGA 200 Prevac) connected directly to the reactor outlet. Moreover, FT-IR analyses of zoolites pre-adsorbed with NH_3 and NO were done using Bruker Tensor 27 spectrometer

3. Results and discussion

The modification of BEA zeolite with iron resulted in active and selective catalysts for the SCR process. NH_3-TPD and NO-TPD studies combined with FT-IR analysis of the samples pre-adsorbed with NH_3 and NO showed that deposition of iron on zeolites results in formation of acid sites, which are characterized by lower acid strength in comparison to Al-sites. The amount of ammonia chemisorbed on the catalysts surface is significantly large in comparison to chemisorbed NO. (see Fig. 1). Moreover, NO was adsorbed in the form of nitrates (formed both on the iron and on Si-O-Si sites) and monodentate Fe(ONO) species. NH_3 and NO species, depending of adsorbed form, were characterized by various reactivities.

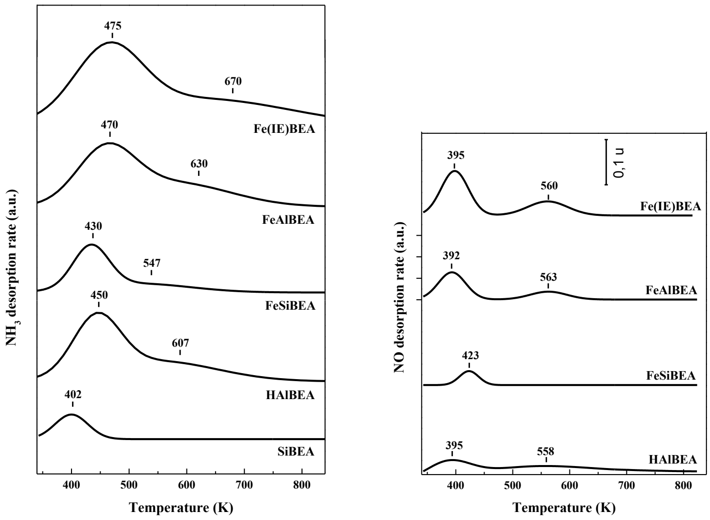

Figure 1. Results of temperature programmed desorption of NH_3- (left) and NO-TPD (right)

4. Conclusions

The temperature-programmed studies and FTIR experiments allowed for the following conclusions: (i) substitution of iron for aluminum in the framework of BEA zeolite results in the formation of weaker acid sites, which are not able to effectively activate ammonium molecules for the SCR process; (ii) iron species in BEA zeolite are able to catalyze oxidation of NO to nitrates, which in the case of the samples containing iron in extra-framework positions can be easy reduced by ammonia to the SCR products. In the case of Al-free BEA zeolite containing iron in framework positons very stable nitrate species, with the limited reactivity in SCR, were formed; (iii) at least two parallel possible SCR reaction pathways can be suggested: (1) reaction between chemisorbed ammonia molecules and NO in gas phase - Eley-Riedel mechanism and (2) reaction of surface nitrates (possibly also NO_2 as Fe-ONO), formed by oxidation of NO, with ammonia (probably in the chemisorbed forms).

References

1. M. Colombo, I. Nova, E. Tronconi, Catal. Today 151 (2010) 223.
2. P. Boroń, L. Chmielarz, J. Gurgul, K. Łątka, B. Gil, J-M. Krafft, S. Dzwigaj, Catal. Today 235(2014) 210.
3. P. Boroń, L. Chmielarz, B. Gil, B. Marszałek, S. Dzwigaj, Appl. Catal. B 198 (2016) 457.