Remarkably enhanced density and specific activity of active sites in Al-rich Cu-, Fe- and Co-beta zeolites for selective catalytic reduction of NO_x

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Abstract

The efficiency of catalysts for abatement of emissions of nitrogen oxides (NO_x) from stationary and especially mobile sources using selective catalytic reduction (SCR) is obviously still not sufficient to meet increasingly more stringent environmental limits. We demonstrate that the conversion of NO_x to nitrogen under the relevant conditions of the SCR-NO_x can be dramatically increased using M/M-oxo Al-rich beta zeolite catalysts (where M = Cu, Co, Fe) with a high concentration of transition metal counter-ions, bearing extra-framework oxygen ligand, particularly in the low-temperature region as well as at high space velocities.

Keywords: SCR-NO_x, zeolites, Fe, Cu, Co

1. Introduction

The negative charge of the zeolite framework originating from the substitution of the framework Si(IV) by Al(III) controls the concentration of the ion-exchanged cations and their electronic properties, i.e. a low and/or versatile redox state depending on the density of the available electrons. Consequently, the maximum concentration of Fe, Cu, Co ions as active centres of appropriate structure and properties relevant for the redox reactions has been limited by the concentration of Al in silica-rich zeolites available.

The aim of this paper is a detailed analysis of the structure of the active sites and evaluation the effect of Al-rich beta zeolite with high content of framework Al (Si/Al~4) on the activity of the M/M-oxo counter-ions (M = Cu, Co, Fe). Al-rich *BEA with Cu, Co and Fe sites were prepared as they are among the most active catalysts for SCR-NO_x using ammonia, methane and propane, respectively, and their activities were quantitatively compared with state-of-the-art Si-rich *BEA zeolites.

2. Experimental

An optimized organotemplate-free hydrothermal synthesis was employed for the preparation of the Al-rich *BEA zeolites (molar Si/Al 4-6). Fe-zeolites with targeted degree of ion-exchange were prepared by ion exchange with aqueous Fe(II) solutions under nitrogen atmosphere. Co-zeolites were prepared by ion exchange with $Co(NO_3)_2$ solutions. Cu-zeolites were prepared by solid-state ion-exchange in the presence of ammonia. The structure and redox properties of the transition metal ion species were analysed by a combination of experimental methods, including FTIR of dehydrated catalysts, UV-Vis-NIR, H_2-TPR, and Mössbauer spectroscopy. Periodic DFT Molecular Dynamics (MD) was used to model the Fe^{3+} and Fe^{2+} transition metal cationic sites employing the VASP program to improve the interpretation of complex results of spectral analysis.

3. Results and discussion

The high concentration of Al in the framework of the template-free synthesized beta zeolites (Si/Al 4-5) provided charge balance for the corresponding high concentration of counter easily reducible M/M-oxo (M = Cu, Fe and Co) species (Figure 1)[1-3]. The study of SCR-NO_x using ammonia, methane and propane as reducing agents over Al-rich beta zeolite with the M/M-oxo counter-ions showed dramatic increases in the conversion of NO to nitrogen compared to Si-rich beta-zeolite-based catalysts, particularly in the low-temperature region as well as at high space velocities[1-3]. Investigation under the relevant conditions of the SCR-NO_x processes in the presence of water vapour in the reaction stream revealed that:

(i) The active Cu centres represented by isolated Cu ions formed after dehydration from monovalent $[Cu(II)(H_2O)_5OH^-]^+$ complexes are populated in a very high concentration in Al-rich Cu-*BEA (Cu/Al 0.78, Si/Al 4.2). The high density and increased specific activity of these atomically dispersed Cu ions lower the activation barrier in the reactions of NH_3-SCR-NO_x and C_3H_8-SCR-NO_x reflected in the 3.5 to 8 times higher reaction rates compared to the Si-rich Cu-*BEA and Cu-ZSM-5 catalysts.[2]

(ii) Al-rich Fe-*BEA (Fe/Al 0.73, Si/Al 4.2) accommodates a very high concentration of polynuclear Fe(III)-oxo complexes and dinuclear or isolated Fe(III)-oxo species without the formation of significant amounts of Fe-oxides. The unprecedentedly high concentration of highly dispersed Fe(III) ions with appropriate redox properties for NH_3-SCR-NO_x and C_3H_8-SCR-NO_x yields a three times higher reaction rate compared to Si-rich Fe-*BEA zeolite (Fe/Al 0.77, Si/Al 11.7) and correspondingly increased conversion of NO_x in the whole temperature region.[2,3]

(iii) The Al-rich Co-*BEA is able to exchange a large amount of a divalent hexaquo complex $[Co(II)(H_2O)_6]^{2+}$ forming after the dehydration a high concentration of Co-oxo sites highly active for CH_4-SCR-NO_x [2] and C_3H_8-SCR-NO_x [1]. Mutually proximate Co-oxo centres in Al-rich Co-*BEA yield 8 to 12 times higher reaction rates per gram of zeolite and up to four times higher TOF per Co.[1,2]

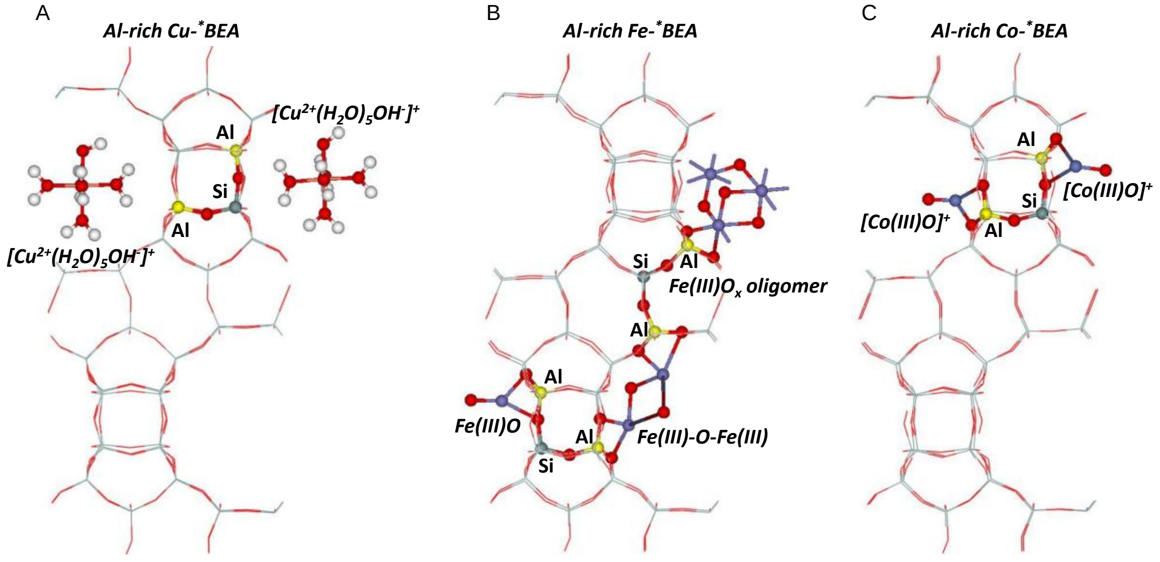

Figure 1. Illustration of main Cu-, Fe- and Co-species present in Al-rich beta zeolites. A) Hydrated Al-rich Cu-*BEA, B) dehydrated Al-rich Fe-*BEA and C) dehydrated Al-rich Co-*BEA. Oxygens and hydrogens in red and white, respectively.

4. Conclusions

The high concentration of framework Al and corresponding high population of AlSiAl sequences in template-free synthesized Al-rich beta zeolite does not result in relative increased binding of bare non-reducible and non-active M(II) ions. To the contrary, the unparalleled high concentration of the atomically dispersed M/M-oxo (where M = Cu, Co, Fe) counter-ions with appropriate redox properties and enhanced specific activities provides 3 to 12 times higher reaction rates for the SCR-NO_x using ammonia, methane and propane as reducing agents compared to state-of-the-art Si-rich zeolite catalysts.

References

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