Enhanced functionality of Al-rich zeolite beta catalysts in industrially relevant acid- and redox-catalysed reactions

Petr Sazama,[a,*] **Radim Pilar,**[a] **Vasile Parvulescu,**[b] **Galina Sadovska,**[a] **Jaroslava Moravkova,**[a] **Dalibor Kaucky,**[a] **Jana Pastvova,**[a] **Stepan Sklenak,**[a] **Alena Vondrova**[a]

[a]*J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejskova 3, 182 23 Prague, Czech*
[b] *University of Bucharest, Department of Organic Chemistry and Catalysis, Romania*
**Corresponding author: petr.sazama@jh-inst.cas.cz*

Abstract

Enhancement of the functionality of zeolitic catalysts represents one of the feasible ways to more efficient handling of natural resources during processing of hydrocarbons and to better emissions control. This study shows that Al-rich beta zeolite based catalysts with significantly increased concentration and functionality of the acid sites (Brønsted OH groups) and ions of transition metals (Fe, Cu and Co) as active sites enhances effectivity in important catalytic processes of hydrocarbon processing and emission control.

Keywords: Al-rich beta zeolite, Acid catalysis, Redox processes.

1. Introduction

The acidic Brønsted OH groups located inside zeolite micropores are exploited in processes with large-scale applications in petroleum refining, petrochemicals and aromatics processing. The catalytic properties of zeolites in hydrocarbons processing are governed by the concentration of the acidic protons charge balanced by negative AlO_4^- in the framework. The standard synthesis procedures for the most important high-silica ZSM-5 and beta zeolites provide maximum content of the framework Al corresponding molar ration $Si/Al \geq 11$. Higher available concentration of Al, e.g. in faujasite or mordenite zeolites, leads to the formation of Al-Si-Al sequences in the zeolite framework yielding a low acid strength of Brønsted OH groups and a significantly lowered catalytic activity. The discovery of hydrothermal synthesis of the Al-rich beta zeolites with a high concentration of Al in the framework[1-3] opened new ways for preparation of zeolite catalysts with extraordinary high concentration of OH with sufficient acidity[4-6].

High and stable catalytic activity of zeolite catalysts in abatement of NO_x emissions are given by the versatile redox state of ions of transition metals (Fe and Cu) as active sites. An increase in the concentration of Al atoms in the framework of silica-rich zeolites (up to Si/Al ~ 11) results in an increased concentration of the ionic species with a proper redox structure and in increased reaction rates in SCR-NO_x reactions. However, a further increase in the Al content attained using faujasite or mordenite zeolites (Si/Al 3-5) provides barely reducible cations without catalytic activity. To the contrary, the versatile redox state and open coordination sphere of Fe, Cu and Co ions in the extra-framework sites of structurally stable Al-rich *BEA zeolite provide high and stable activity in selective catalytic reduction of nitrogen oxides[4,7,8].

The aim of this study is to illustrate the unparalleled potential of Al-rich beta zeolites for obtaining significantly increased concentrations of active centres with enhanced specific activities for industrially relevant acid and redox catalysed reactions.

2. Experimental

Al-rich beta zeolites were hydrothermally synthesized by a procedure based on the reports in Refs.[1,2,4-12] and characterised by XRD, N_2 adsorption at -196 °C, SEM, ^{27}Al and ^{29}Si MAS NMR, XPS and FTIR spectroscopy. Cracking of *n*-decane, hydroisomerization of *n*-hexane, alkylation of benzene and hydroamination of styrene over H-*BEA were investigated regarding the concentration and nature of acid sites. Co, Fe and Cu ions were introduced by the ion-exchange and analysed by UV-Vis and FTIR spectroscopy and H_2-TPR. The kinetics of SCR-NO_x using ammonia, methane and propane as reducing agents was analysed over M/M-oxo Al-rich beta zeolite catalysts (where M = Cu, Co, Fe).

3. Results and discussion

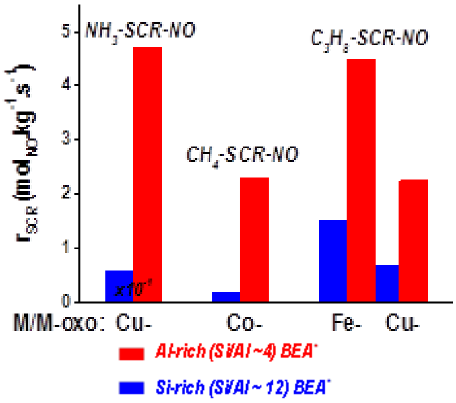
Structural as well as acid, redox and catalytic properties of M/M-oxo Al-rich beta zeolite catalysts (where M = H, Cu, Co, Fe) were examined in detail and compared with the high-silica *BEA zeolites to obtain an insight into the nature and role of the high density of active sites. Less-than-significant differences in the deprotonation energies for OH groups in Al-rich H-*BEA related to the individual Si-Al sequences and the very small shift in the structural OH vibrations indicate that the high concentration of Al atoms in the framework of Al-rich beta zeolites yields H^+ sites like in a Si-rich zeolite but in significantly increased concentrations. High concentration of strongly acidic OH groups is manifested in the increased conversion in *n*-decane cracking, hydroisomerization of pentane and hexane, alkylation of benzene with benzyl alcohol to diphenyl methane and hydroamination of styrene with aniline to phenyl-[2-phenylethyl]amine and phenyl-[1-phenylethyl]amine, correspondingly to the increased concentration of Brønsted acid sites compared to silicon rich beta zeolites (Table 1)[4,6].

High concentration of the atomically dispersed M/M-oxo (M = Cu, Co, Fe) counter-ions with appropriate redox properties and enhanced specific activities provide 3 to 12 times higher reaction rates for the SCR-NOx using ammonia, methane and propane as reducing agents compared to state-of-the-art Si-rich zeolite catalysts (Figure 1)[7,8].

Table 1. Activity of Al-rich H-*BEA in acid-catalysed reactions compared to representative Si-rich H-*BEA zeolite.

Catalytic process	**Si-rich H-BEA Si/Al~12**	**Al-rich H-BEA Si/Al~4.5**
Cracking of n-decane r ($mol_{C10H22}.kg_{cat}^{-1}.h^{-1}$) at 500 °C	650	1200
Hydroisomerization of n-hexane r_{iso} ($mol.g_{cat}^{-1}.s^{-1}$ $*10^8$) at 175 °C	0.51	4.35
Alkylation of benzene with benzyl alcohol $X_{benzyl\ alcohol}$ (%)	15.9	49.0
Hydroamination of styrene with aniline $X_{aniline}$ (%)	14.6	86.8

Figure 1. Illustration of the dramatic enhancement of SCR reactions over Al-rich M/M-oxo-*BEA (M = Cu, Co, Fe) compared to Si-rich M/M-oxo-*BEA analogues.



4. Conclusions

The high concentration of active sites is directly manifested in the enhanced activity compared to conventional Si-rich zeolites in cracking of alkanes, hydroisomerization of pentane and hexane, alkylation of benzene as well as transformation of bulkier molecules over Al-rich H-*BEA, and in SCR-NOx using ammonia or hydrocarbons as reducing agents over Al-rich M/M-oxo-*BEA (M = Cu, Co, Fe). The arrangement of Al atoms in Al-rich beta zeolite providing sites for binding highly active counter-ion H- and M/M-oxo species is not available in other Al-rich zeolites like MOR or faujasites.

References

1.) Majano, G.; Delmotte, L.; Valtchev, V.; Mintova, S. *Chemistry of Materials* **2009**, *21*, 4184.
2.) Kamimura, Y.; Chaikittisilp, W.; Itabashi, K.; Shimojima, A.; Okubo, T. *Chemistry-an Asian Journal* **2010**, *5*, 2182.
3.) Borade, R. B.; Clearfield, A. *Microporous Materials* **1996**, *5*, 289.
4.) Sazama, P.; Wichterlova, B.; Sklenak, S.; Parvulescu, V. I.; Candu, N.; Sadovska, G.; Dedecek, J. et al. *J. Catal.* **2014**, *318*, 22.
5.) Sazama, P.; Tabor, E.; Klein, P.; Wichterlova, B.; Sklenak, S.; Pashkkova, V.; Ogura, M. et al. *J. Catal.* **2016**, *333*, 102.
6.) Sazama, P.; Kaucky, D.; Moravkova, J.; Pilar, R.; Klein, P.; Pastvova, J. et al. *Appl. Catal. A: General* **2017**, *533*, 28.
7.) Sazama, P.; Pilar, R.; Mokrzycki, L.; Vondrova, A.; Kaucky, D.; Plsek, J.; Sklenak, S. et al. *Appl. Catal. B Environ.* **2016**, *189*, 65.
8.) Sazama, P.; Mokrzycki, L.; Wichterlova, B.; Vondrova, A.; Pilar, R.; Dedecek, J.; Sklenak, S.; Tabor, E. *J. Catal.* **2015**, *332*, 201.
9.) Kamimura, Y.; Tanahashi, S.; Itabashi, K.; Sugawara, A.; Wakihara, T. et al. *J. Phys. Chem. C* **2011**, *115*, 744.
10.) De Baerdemaeker, T.; Yilmaz, B.; Muller, U.; Feyen, M.; Xiao, F. S.; Zhang, W.; Tatsumi, T. et al. *J. Catal.* **2013**, *308*, 73.
11.) Yilmaz, B.; Muller, U.; Feyen, M.; Maurer, S.; Zhang, H.; Meng, X. et al. *Catalysis Science and Technology* **2013**, *3*, 2580.
12.) Zhang, H.; Xie, B.; Meng, X.; Mueller, U.; Yilmaz, B.; Feyen, M. et al. *Microporous and Mesoporous Materials* **2013**, *180*, 123.