### 491e In-Situ Studies of [Fe,Al]Mfi Catalyzed Oxidation of Benzene to Phenol

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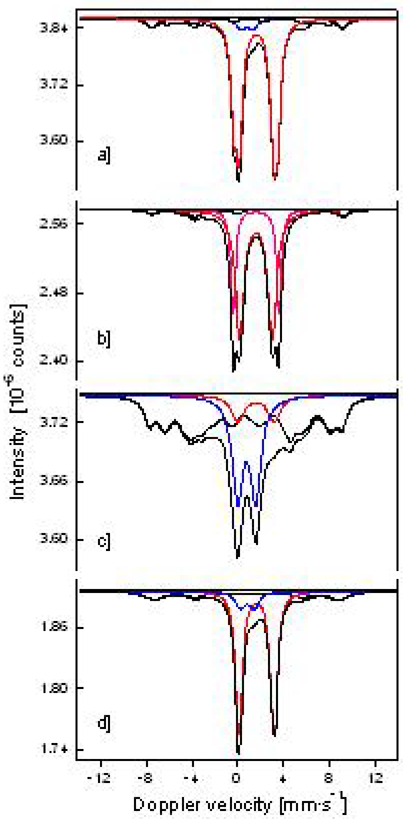
Extra-framework iron species stabilized in the micropore channels of steam-activated isomorphously substituted [Fe,Al]MFI zeolite have been known to catalyze the one-step oxidation of benzene to phenol using N2O as oxidant [1]. However, despite extensive efforts the structure and nuclearity of the active iron sites remain unknown. Much of the uncertainties in determining the nature of the active sites stem from diversities in preparation method, synthesis condition, and elemental composition, leading to a distribution in form of extra-framework iron species. Therefore, to investigate the structure-activity relationships of the [Fe,Al]MFI catalyst in the one-step oxidation of benzene forming phenol, it is essential to start with a relatively homogeneous form of extra-framework iron species. Recently, we reported the formation of extra-framework iron that is predominantly in the high-spin Fe2+ state (ca. 90%) after steam-activation of the isomorphously substituted [Fe,Al]MFI zeolite [2]. Moreover, it was determined that the formation of high-spin Fe2+ species is independent of iron concentration (0.6-0.075 wt% Fe). The presence of the Fe2+ species is significant since it has been linearly correlated [3] to the quantity of the active iron species known as the a-sites, which are able to directly oxidize benzene to phenol in the presence of N2O [1]. Therefore, these samples constitute an excellent basis for the study of structure-activity relationships. In this contribution, we present the structure-activity relationships of the [Fe,Al]MFI catalysts in the direct oxidation of benzene to phenol. Through in-situ studies (i.e. Mössbauer, X-ray absorption near edge, and inelastic neutron scattering spectroscopic studies), we probe the reduction/oxidation properties of the different iron species formed after steam-activation of the samples. The approach is to have a breakdown of the catalytic cycle and then measure the Mössbauer spectrum after every in-situ treatment. That means (1) after pretreatment with He, (2) after N2O loading and finally (3) after reaction with benzene and N2O. For Mössbauer spectroscopy, the reaction was quenched by cooling to room temperature and transferred to a cryostat for low temperature (i.e. 77 and 4.2 K) quasi in-situ Mössbauer measurements. Figure 1 shows the preliminary results of in-situ study and clearly demonstrates that different iron species are oxidized by N2O and are predominantly in the reduced Fe2+ state under steady-state benzene to phenol reaction.

(Figure 1)

Figure 1. 57Fe Mössbauer spectra taken at 4.2 K of a] steam-activated [Fe,Al]MFI (1:8) catalyst, b] after pretreatment in He, c] after loading with N2O, and d] after reaction with benzene and N2O for 1.5 h.

References [1] G.I. Panov, Cattech 4 (2000) 18. [2] J.B. Taboada, A.R. Overweg, P.J. Kooyman, I.W.C.E. Arends, G. Mul, J. Catal. 231 (2005) 56. [3] K.A. Dubkov, N.S. Ovanesyan, A.A. Shteinman, E.V. Starokon, G.I. Panov, J. Catal. 207 (2002) 341.


3.84
3.72
3.60
a]
2.56
2.48
2.40
b]
3.72
3.66
3.60
c]
1.86
1.80
1.74
d]
Intensity [$10^{-6}$ counts]
-12
-8
-4
0
4
8
12
Doppler velocity [mm·s$^{-1}$]