Selective aromatics oxidation by iron-containing ZSM-5 zeolites: on the nature of the active sites

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Introduction

The nitrous-oxide-mediated oxidation of benzene to phenol over iron-containing pentasil zeolite has attracted wide attention (1,2) and presents a potential alternative to the three-step cumene process (3). The extraordinary catalytic properties of Fe/ZSM-5 have been attributed to the presence of small Fe-oxide particles stabilized by the medium-sized pores of the MFI lattice. Moreover, analogies with the dinuclear cluster present in methane monooxygenase (1) have been stressed rendering a biomimetic classification for this catalyst. However, pertinent questions relate to the nature of the active species, the influence of the presence of Al and the effect of the preparation method.

Results and Discussion

We compared two preparation methods for the synthesis of iron-containing ZSM-5. Sublimation of $FeCl_3$ presents a method to disperse iron throughout the zeolite micropore space (Fe/ZSM-5). Despite the initial high dispersion, subsequent pretreatments lead to extensive sintering of Fe-oxide particles. An alternative method is the addition of Fe to the zeolite synthesis mixture ([Fe]ZSM-5). This results in an atomic Fe dispersion, which is also lost during activation of the catalyst. The catalysts were studied by various techniques including IR spectroscopy, ^{57}Fe Mössbauer spectroscopy, ^{27}Al MAS NMR, TEM, Fe K-edge EXAFS, low-temperature nitrous oxide decomposition, *i*-propylamine TPD, and benzene hydroxylation with nitrous oxide.

A combination of Mössbauer and TEM studies clearly shows that in the sublimed catalyst a large fraction of Fe is located on the external surface of the zeolite as Fe-oxide. This fraction hardly depends on the severity of the pretreatment. These observations contrast the values obtained for the Fe-Fe coordination numbers, $N_{\text{Fe-Fe}} \approx 1\text{-}1.5$, from EXAFS. We surmise that disordered Fe-oxide particles result in low Fe-Fe coordination numbers in EXAFS measurements and stress that care has to be taken with interpreting EXAFS data for these catalysts. More relevant are the strong indications that upon high-temperature treatment part of the acidic protons are replaced by charge-compensating Fe-cations (4,5). The decrease in the number of protons with increasing severity of treatment correlates with an increase in the Fe^{2+} fraction (Mössbauer), an increase in the number of active Fe-species (low temperature N_2O decomposition, commonly referred to as α-sites) and an increase in activity and selectivity to phenol in the benzene oxidation. While the selectivity of the steamed Fe/ZSM-5 catalyst is nearly 100%, its stability is quite low. This is attributed to the large number of active species which leads to overoxidation and extensive coke formation.

A peculiar result is that high-temperature steaming is required to provide a catalyst with high selectivity to phenol, whereas high-temperature calcination leads to a catalyst with low phenol selectivity. Although it has been described that the presence of Al in the framework is important for obtaining a good catalyst, we found indications that extra-framework Al species generated by high-temperature steaming are essential for selective catalysts.

This last observation urged us to compare several catalysts obtained from isomorphously substituted zeolites. We prepared three samples, [Fe,Al]ZSM-5, [Fe]ZSM-5 and [Al]ZSM-5 (strictly speaking [Fe]ZSM-5 is an Fe-silicalite). It is important to note that these catalysts were prepared from Fe- and Al-free silica-precursors. DRUV-Vis measurements clearly indicate that after synthesis Fe-species are tetrahedrally coordinated in [Fe,Al]ZSM-5 and [Fe]ZSM-5. Removal of the template already results in partial dislodgement of Fe from framework positions as was also recently reported by Mössbauer spectroscopy (6). Despite the presence of Fe at extra-framework positions in these calcined catalysts, their activities towards nitrous-oxide decomposition are comparably low as for silica-supported Fe-oxide. Subsequent steaming leads to a strong increase in the N_2O decomposition rate for [Fe,Al]ZSM-5 in contrast to [Fe]ZSM-5. [Al]ZSM-5 does not show catalytic activity in any case. These results agree with preliminary results for the selective conversion of benzene-to-phenol, which show that steamed [Fe,Al]ZSM-5 is highly active, whereas steamed [Fe]ZSM-5 and [Al]ZSM-5 exhibit very low activities. The combined results indicate that both extra-framework Fe and Al play an important role in the formation of the active sites.

In the contribution the first results of our high-throughput approach will be presented which include the testing of a larger array of materials with a varying Fe and Al content.

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