Iron-functionalized Al-SBA-15 for benzene hydroxylation†

Ying Li,[ab] Haian Xia,[a] Fengtao Fan,[a] Zhaochi Feng,[a] Rutger A. van Santen,[b] Emiel J. M. Hensen*[b] and Can Li*[a]

Received (in Cambridge, UK) 5th November 2007, Accepted 28th November 2007
First published as an Advance Article on the web 17th December 2007
DOI: 10.1039/b717079c

For the first time an ordered mesoporous silica (Fe–Al-SBA-15) with catalytically active isolated Fe surface species for the hydroxylation of benzene with nitrous oxide is prepared by introduction of Fe^{3+} in the synthesis gel of Al-SBA-15.

Novel catalytic routes for the selective oxidation of hydrocarbons to oxygenates are much desired to replace existing environmentally stressing processes. For this purpose, microporous zeolites have been applied as catalytic hosts for transition metals. Iron-containing ZSM-5 zeolites have received their share of attention because of their unique reactivity in the hydroxylation of benzene to phenol by nitrous oxide.[1] The active sites consist of highly dispersed extra-framework Fe ions with the specific ability to decompose nitrous oxide to an adsorbed atomic oxygen species and molecular nitrogen. This oxygen species can oxidize, amongst others, methane to methoxy groups and benzene to phenol. The catalytic chemistry of FeZSM-5 catalysts for phenol production is a potential alternative for the existing three-step industrial cumene process.[2] The relatively small dimensions of the pores of ZSM-5 impose however strong diffusion limitations to reactants and products and would also limit the conversion of larger reactants. The favourable textural properties of ordered mesoporous silicas (*e.g.*, M41S and SBA-n families) make them in principle more suitable supports for catalytic conversion of reactant molecules[3] that are too bulky to diffuse into the micropores of zeolites. An important scientific question is how the absence of a microporous environment around the active sites affects catalytic reactivity. Up till now, there have been no successful reports of Fe-containing mesoporous materials active in the oxidation of benzene to phenol. FeMCM-41 shows promising selectivity in the oxidation of propylene to propylene oxide by nitrous oxide, however, at very low conversion.[4]

In contrast to the crystalline pore walls of zeolites which afford high chemical reactivity of dispersed extra-framework transition metal cationic clusters,[5] the formation of isolated or at least highly dispersed transition metal oxide clusters on the surface of amorphous mesoporous silicas is much more difficult. A challenge is therefore the surface functionalization of mesoporous silicas. Impregnation of iron salts in mesoporous silicas leads to clustering of iron species upon calcination.[6] In comparison to this, careful calcination allowed to retain the mononuclear nature of a tri(*tert*-butoxy)siloxy iron(III) complex ($Fe[OSi(O{-}tBu)_3]_3(THF)$) grafted to SBA-15.[7] It would be even more attractive to introduce the Fe ions directly during the synthesis of the mesoporous silica. Especially for the SBA-*n* class silicas with their higher hydrothermal stability compared to MCM-type materials, introduction of Fe^{3+} in the final material is not straightforward because of the difficulty to form Fe–O–Si bonds under the strongly acidic synthesis conditions.[8] Herein, we present a simple, hydrothermal method for the preparation of isolated Fe ions at the surface of SBA-15. Incorporation of aluminium in the silica is essential to stabilize such Fe species. The resulting Fe–Al-SBA-15 materials are active for the oxidation of benzene to phenol with selectivity to phenol up to 40% at a benzene conversion of 2.3%. In the absence of Al, an ordered mesoporous Fe-SBA-15 is not active.

Our approach is to add iron and aluminium ions during the synthesis of SBA-15. In a typical synthesis, a suitable amount of block copolymer $EO_{20}PO_{70}EO_{20}$ was added to a HCl solution (pH = 1.5). To this was added dropwise a well-stirred solution of tetramethoxysilane, iron(III) nitrate and aluminium isopropoxide. After vigorous stirring at 313 K for 20 h, the mixture was aged in an autoclave at 373 K for 24 h. The resulting solid was filtered, washed, and dried at 333 K for 15 h and finally calcined at 773 K for 10 h. The synthesis of Fe-SBA-15 and Al-SBA-15 was similar with Fe or Al precursors being added, respectively, to the synthesis gels.[8,9] The typical low-angle XRD (100), (110) and (200) reflections of SBA-15 (space group $P6_3/mm$) were observed. Compared to siliceous SBA-15 higher surface areas are obtained with Fe^{3+} in the synthesis gel (Table 1). As discussed earlier,[8] only limited amounts of Fe can be introduced in the silica walls of SBA-15. With Al^{3+} ions in the synthesis gel, a higher Fe loading is obtained at the same Fe/Si gel ratio.[10]

The iron speciation in Fe–Al-SBA-15 is distinctly different from that in Fe-SBA-15 (Fig. 1). The strong absorption band in the UV region of the electronic spectrum of Fe-SBA-15 indicates the dominance of isolated Fe^{3+} ions in tetrahedral coordination in bulk silica. In accord with this, the Raman spectrum (λ_{exc} = 244 nm) shows two bands at 510 and 1090 cm^{-1} belonging to symmetric and asymmetric stretching modes of Fe–O–Si bonds.[8,10] The coordination of Fe^{3+} ions in Fe–Al-SBA-15 is totally different. Dominant for Fe–Al-SBA-15 is an absorption band around 270 nm (Fig. 1 left). This band is due to isolated octahedrally or pseudotetrahedrally coordinated Fe^{3+} ions[11] and indicates that these ions are located at the surface of SBA-15. By matching the hydrolysis rate of the silicon precursor, *i.e.*, by using tetramethoxysilane rather than tetraethoxysilane, with that of aluminium

---

[a] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Zhongshan Road 457, Dalian, China. E-mail: canli@dicp.ac.cn; Fax: +86-411-84694447; Tel: +86-411-84379070*
[b] *Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB, Eindhoven, The Netherlands. E-mail: e.j.m.hensen@tue.nl; Fax: +31-40-2455054; Tel: +31-40-2475178*

† Electronic supplementary information (ESI) available: Experimental details, UV-Vis spectra and reaction data for steamed SBA-15 supported catalysts. See DOI: 10.1039/b717079c

Table 1 Textural and catalytic properties of SBA-15 and zeolite supported catalysts

Catalyst	Fe (wt.%)	Al (wt.%)	a_0 /Å	S_{BET} /m^2 g^{-1}	V_{pore} /cm^3 g^{-1}	d_{p} /Å[b]	R_{phenol} /mmol g^{-1} h^{-1}[d]	N_{α} /mmol g^{-1}[c]
SBA-15	0.0	0.0	116	752	1.35	71	n.d.	n.d.[e]
Al-SBA-15	0.0	1.54	125	966	1.17	74	0.0	0.0
Fe-SBA-15(A)	0.26	0.0	126	1172	1.31	64	0.0	0.0
Fe-SBA-15(B)	1.97	0.0	125	902	1.28	74	0.0	0.0
Fe–Al-SBA-15(A)	1.63	2.17	124	890	1.23	76	0.13	n.d.
Fe–Al-SBA-15(B)	0.21	3.27	123	780	1.28	82	0.30	0.9×10^{-3}
FeZSM-5	0.45	0.88	—	413[f]	0.15[f]	—	4.9	1.2×10^{-2}

[a] $a_0 = 2 \times d_{100}/\surd 3$. [b] Calculated from desorption branch of isotherm according to the BJH method. [c] Number of α-sites by nitrous oxide decomposition at 523 K. [d] Rate of phenol formation after 0.5 h. [e] Not determined. [f] Calculated according to the Dubinin–Radhovich method.

isopropoxide it is possible to obtain predominantly isolated tetrahedrally coordinated Al^{3+} ions in the silica walls of SBA-15.[9] The role of such tetrahedral Al sites is likely to bring about cationic exchange properties at the SBA-15 surface facilitating the stabilisation of isolated Fe^{3+} ions. The presence of small amounts of isolated tetrahedrally coordinated in the bulk of silica and of more oligomeric and aggregated forms of Fe^{3+} on the surface follows from the shoulder at 250 nm and weak bands around 333 and 430 nm, respectively. The Fe^{3+} species at the surface are identified in the Raman spectrum (λ_{exc} = 325 nm) by a band at 1140 cm^{-1}.[10] Excitation at λ_{exc} = 244 nm results in a lower intensity of this band while the band at 1080 cm^{-1} of the very low fraction of isolated Fe^{3+} ions becomes more intense. The selectivity in these bands' intensities is due to the resonance Raman effect.[12]

Catalyst performance for the hydroxylation of benzene with nitrous oxide was evaluated in an atmospheric single-pass microflow reactor at 623 K. The reactant feed consisted of 1 vol.% benzene and 4 vol.% nitrous oxide in He. There is no conversion of benzene by the Al-SBA-15 and Fe-SBA-15 catalysts. On the contrary, the benzene conversion over Fe–Al-SBA-15(A) after 0.25 h is 3.4% with a phenol selectivity of 23% (Fig. 2). The selectivity to carbon oxides and water is about 5%. The carbon imbalance (72%) implies that a large fraction of the products does not desorb from the catalyst surface. The conversion over Fe–Al-SBA-15(A) decreases strongly with time and after 1 h the conversion is around 1%. Catalyst performance is improved when the Fe content is lowered (Fe–Al-SBA-15(B)). This catalyst was obtained by decreasing the amount of Fe in the synthesis gel. The initial reaction rate to phenol for this catalyst is about two times higher than for Fe–Al-SBA-15(A) (Table 1). The initial phenol selectivity is 16% and the selectivity to full oxidation products is below 1%. The phenol selectivity increases to about 40% with decreasing conversion. Similar to findings for FeZSM-5,[13,14] the phenol selectivity is highest for catalysts with a low Fe loading. The UV-Vis spectra (see Supporting Information†) support the lower degree of agglomeration for Fe–Al-SBA-15 with a lower Fe content. Steam-activated FeZSM-5 exhibits a much higher conversion and the selectivity to phenol is higher. Similar on the other hand is the decrease in benzene conversion with reaction time which corresponds to an increase of the phenol selectivity. Such a behaviour points to a series reaction mechanism in which benzene is first converted to phenol. Initially, the phenol selectivity is lower due to further reaction of phenol to products that do not desorb from the catalyst. These include higher-boiling products such as dihydroxybenzenes and fused aromatic rings that have been hydroxylated more than once.[15] Thus, Fe–Al-SBA-15 exhibits lower phenol selectivities at lower benzene conversions than the zeolite-based catalyst. The difference is due to the shape selectivity brought about by the microporous environment of the active sites in FeZSM-5. The more open surface around the active sites in Fe–Al-SBA-15 does not limit the formation of more bulky reaction products that remain on the catalyst surface.

Typically only a part of the Fe ions are involved in the hydroxylation activity.[16] Hence, we estimated the number of active sites in the most active materials Fe–Al-SBA-15(B) and FeZSM-5 by low-temperature nitrous oxide decomposition. The hydroxylation activity of FeZSM-5 catalysts has been closely linked to their ability to decompose N_2O stoichiometrically at moderate

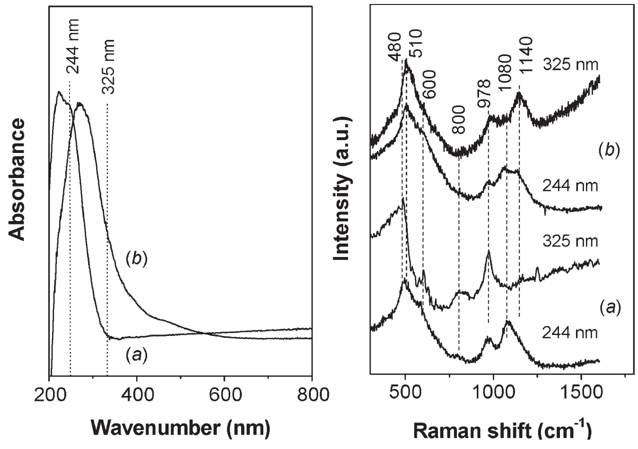

Fig. 1 (left) UV-Vis spectra of (a) Fe-SBA-15(A) and (b) Fe–Al-SBA-15(A) and (right) corresponding Raman spectra.

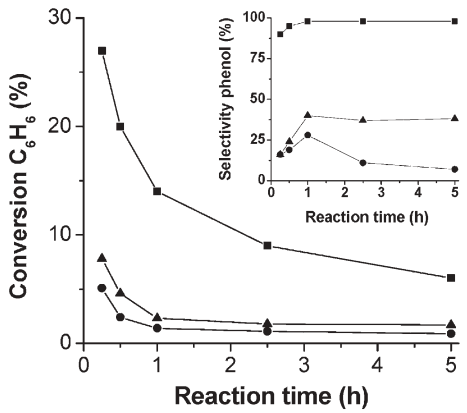

Fig. 2 Benzene conversion and phenol selectivity (inset) as a function of the reaction time for (●) Fe–Al-SBA-15(A), (▲) Fe–Al-SBA-15(B) and (■) FeZSM-5.

temperatures.[16] The latter reaction is thought to oxidize Fe^{2+} centers to Fe^{3+} *via* Fe^{2+}-□ + $N_2O \rightarrow Fe^{3+}$–O + N_2. Such sites are usually called α-sites. Thus, we found that the α-site densities in Fe–Al-SBA-15(B) and FeZSM-5 are 0.9×10^{-3} mmol g^{-1} and 1.2×10^{-2} mmol g^{-1}, respectively. Fe-SBA-15 and Al-SBA-15 did not decompose nitrous oxide under these conditions. This latter result explains the absence of phenol formation for these samples. Similar to findings for zeolite-based oxidation catalysts,[14] it follows that the combination of Fe and Al is required for benzene conversion to phenol. The number of redox-active sites in Fe–Al-SBA-15(B) is one order of magnitude lower than in FeZSM-5 in accordance with the difference in the weight-based activity. This result indicates that the intrinsic reaction rate of the active sites in Fe–Al-SBA-15 is approximately equal to that in FeZSM-5. When charged transition states are involved in the rate-limiting step, one expects a positive stabilizing effect of the oxygen anions of the zeolite cage. The finding that the absence of a microporous environment around the active sites in Fe–Al-SBA-15 does not decrease the intrinsic activity is then in good agreement with the proposal that phenol desorption is rate determining for the selective benzene oxidation.[17] Thus, the only adverse effect of the more spacious reaction environment in the SBA-15 supported catalysts is the increased tendency to produce more bulky by-products. Finally, we checked whether steaming improved the performance of Fe–Al-SBA-15 as it does for FeZSM-5 zeolites.[14,16] In line with the dominance of Fe^{3+} species at the surface in Fe–Al-SBA-15 following calcination, steaming did not improve catalytic performance appreciably (see Supporting Information†). We stress that such a steaming treatment did not deteriorate the activity indicating the good hydrothermal stability of Fe–Al-SBA-15.

In summary, a direct hydrothermal synthesis method for Fe–Al-SBA-15 results in isolated Fe sites at the surface of SBA-15 which exhibit similar catalytic properties as the Fe sites in FeZSM-5 zeolites in the hydroxylation of benzene to phenol with nitrous oxide. Spectroscopic investigations point to the isolated nature of the Fe ions at the surface of Al-SBA-15. Tetrahedrally coordinated aluminium is required to anchor these isolated Fe sites. Compared to shape-selective zeolite-based catalysts the absence of a microporous cage does not limit the formation of undesired, more bulky reaction products. Thus, in spite of the advantageous higher accessibility of the active sites in ordered mesoporous silicas, the absence of a microporous environment may pose some limitations to the efficient use of these materials as catalyst supports. The lower active site density of Fe–Al-SBA-15 compared to FeZSM-5 is related to the absence of crystallinity of the walls of the ordered mesoporous silica. The active sites in Fe–Al-SBA-15 are obtained in a straightforward synthesis procedure not requiring high-temperature steaming as is the case for FeZSM-5.

Notes and references

1 G. I. Panov, *CATTECH*, 2000, **4**, 18.
2 P. P. Notté, *Catal. Today*, 2000, **13**, 387.
3 A. Taguchi and F. Schüth, *Microporous Mesoporous Mater.*, 2005, **77**, 1.
4 Q. H. Zhang, Q. Guo, X. X. Wang, T. Shishido and Y. J. Wang, *J. Catal.*, 2006, **239**, 105.
5 M. H. Groothaert, P. Smeets, B. F. Sels, P. A. Jacobs and R. A. Schoonheydt, *J. Am. Chem. Soc.*, 2005, **127**, 1394.
6 A. S. Kumar, J. Perez-Ramirez, M. N. Debbagh, B. Smarsly, U. Bentrup and A. Bruckner, *Appl. Catal., B*, 2006, **62**, 244.
7 C. Nozaki, C. Lugmair, A. T. Bell and T. D. Tilley, *J. Am. Chem. Soc.*, 2002, **124**, 13194.
8 Y. Li, Z. Feng, Y. Lian, K. Sun, L. Zhang, G. Jia, Q. Yang and C. Li, *Microporous Mesoporous Mater.*, 2005, **84**, 41.
9 Y. Li, W. H. Zhang, L. Zhang, Z. Wei, Q. Yang, Z. Feng and C. Li, *J. Phys. Chem. B*, 2004, **108**, 9739.
10 Y. Li, Z. Feng, H. Xin, F.-T. Fan, P. C. M. M. Magusin, E. J. M. Hensen, R. A. van Santen, Q. Yang and C. Li, *J. Phys. Chem. B*, 2006, **110**, 26114.
11 S. Bordiga, R. Buzzoni, F. Geobaldo, C. Lamberti, E. Giamello, A. Zecchina, G. Leofanti, G. Petrini, G. Tozzola and G. Vlaic, *J. Catal.*, 1996, **158**, 486.
12 C. Li, *J. Catal.*, 2003, **216**, 203.
13 Q. Zhu, R. M. van Teeffelen, R. A. van Santen and E. J. M. Hensen, *J. Catal.*, 2004, **221**, 575.
14 E. J. M. Hensen, Q. Zhu, R. A. J. Janssen, P. C. M. M. Magusin, P. J. Kooyman and R. A. van Santen, *J. Catal.*, 2005, **233**, 123.
15 D. Meloni, R. Monaci, V. Solinas, G. Berlier, S. Bordiga, I. Rossetti, C. Oliva and L. Forni, *J. Catal.*, 2003, **214**, 169.
16 K. A. Dubkov, N. S. Ovanesyan, A. A. Shteinman, E. V. Starokon and G. I. Panov, *J. Catal.*, 2002, **207**, 341.
17 N. A. Kachurovskaya, G. M. Zhidomirov, E. J. M. Hensen and R. A. van Santen, *Catal. Lett.*, 2003, **86**, 25.