

Selective oxidation of benzene to phenol over FeAlPO catalysts using nitrous oxide as oxidant†

N. Raveendran Shiju,^a Steven Fiddy,^b Olivier Sonntag,^c Michael Stockenhuber^c and Gopinathan Sankar^{*ab}

Received (in Cambridge, UK) 26th June 2006, Accepted 20th September 2006

First published as an Advance Article on the web 9th October 2006

DOI: 10.1039/b608982h

A tetrahedrally coordinated iron in framework substituted microporous AlPO-5 catalysts are shown to be active and selective for the hydroxylation of benzene to phenol, using nitrous oxide as the oxidant.

Direct conversion of benzene to phenol has been a topic of interest over the last decade, since the discovery of catalysts that use nitrous oxide as oxidant as opposed to oxygen; use of oxygen is known to be detrimental to the selective conversion to phenol. In 1983 Iwamoto *et al.*¹ reported the use of vanadia catalysts, but interest really stems from the report of ZSM-5 catalysts in 1988, by three separate groups of investigators.^{2–4} Extensive studies of iron containing zeolite catalysts have focussed on the preparation and pretreatment of these materials to achieve the best catalytic results, in addition to the investigation of the nature of the active oxygen species and the structure of the active site;^{5–37} based on the work carried out by Panov and co-workers, Solutia developed a process for the direct oxidation of benzene to phenol using N₂O and FeZSM-5 as catalysts.^{38–40} Several models have been proposed as the active site for the catalytic reaction, which include monomeric FeO_x species, dimeric Fe–O–Fe type species and cubic clusters of FeO_x. It appears that coordinatively unsaturated iron species, present in non-framework positions within the pores of the zeolite facilitate the formation of the α -oxygen species, which Panov *et al.* argued to be responsible for the hydroxylation of benzene to phenol. More recently Ren *et al.*⁴¹ reported that iron phosphate can serve as a catalyst for benzene hydroxylation, with selectivity exceeding 85%, but relatively low conversions, <7%. Using X-ray diffraction, that group identified FePO₄ in the quartz phase as being catalytically active, even though this phase is well known to contain Fe(III) ions in a stable, tetrahedral coordination.⁴¹

Bringing together the results on Fe-ZSM-5^{5–37} and from the Ren group,⁴¹ we have chosen to examine iron-substituted aluminophosphate (AlPO-5 structure) as catalysts for benzene hydroxylation, using nitrous oxide as oxidant, since it has been established recently that Fe(III) ions are present in a tetrahedral coordination in the AlPO-5 structure and they are very good

catalysts for several oxidation reactions with molecular oxygen as oxidant.^{42–44}

Iron containing (0.1, 1 and 4 wt%) AlPO-5 materials were prepared using a well established procedure,⁴⁵ using tetraethylammonium hydroxide as the structure directing agent. The phase purity and stability of the AFI structure was confirmed by both *in situ* and *ex-situ* X-ray diffraction (see ESI).† Catalytic performance was measured in an atmospheric pressure micro-reactor equipped with on-line GC analysis, using 0.5 g of catalyst contained between silica wool plugs. The gas phase was composed of benzene, nitrous oxide and helium diluent, in ratios of 1 : 3.6 : 5.4, and the GHSV was 7200 h⁻¹.

Irrespective of the iron content, all the FeAlPO-5 catalysts typically reached maximum activity during the first hour on stream, with selectivity to phenol always greater than 95%. Other products observed were dihydroxybenzenes (catechol and hydroquinone) and benzoquinone, formed from the oxidation of hydroquinone. The catalyst containing 1 wt% iron was the most active, reaching 13.4% conversion (of benzene) at about 653 K while maintaining high selectivity—its performance is illustrated in Fig. 1. The performances of the catalysts studied are summarised in Table 1; an iron free material (pure AlPO-5) was tested as a reference but found to be inactive under the reaction conditions used in this work. Catalytic activity decreased slowly, by *ca* 20% over a 6-h run, probably due to coke formation. Catalytic activity is completely restored by heating in 10% oxygen–90% helium at 810 K for 2 h. Although the activity of our 1 wt% FeAlPO

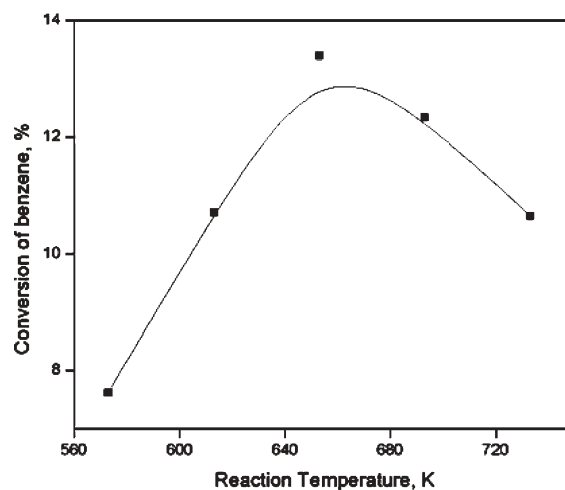


Fig. 1 Catalytic activity of 1 wt% FeAlPO-5 as a function of temperature for the oxidation of benzene to phenol. Benzene : N₂O : He = 1 : 3.6 : 5.4, contact time factor = 0.5 s.

^aDavy Faraday Research Laboratory, The Royal Institution of Great Britain, 21 Albemarle street, London, W1S 4BS, United Kingdom. E-mail: sankar@ri.ac.uk; Fax: +44(0)2076702920; Tel: +44(0)2074092992

^bCCLRC Daresbury Laboratory, Warrington, Cheshire, UK WA4 4AD
^cSchool of Biomedical and Natural Sciences, Nottingham Trent University, Clifton Campus, Nottingham, United Kingdom NG11 8AW
† Electronic supplementary information (ESI) available: X-Ray diffraction patterns of as-synthesised and calcined AlPO-5 and FeAlPO-5 catalysts. See DOI: 10.1039/b608982h

Table 1 Activity of aluminophosphate catalysts for the oxidation of benzene using N₂O as oxidant

Catalyst	Conversion of Benzene (%)	Yield (%)		
		Phenol	Catechol and hydroquinone	<i>p</i> -Benzoquinone
FeAlPO-5(0.1%) ^a	4.4	4.3	—	0.1
FeAlPO-5(1%) ^a	13.4	13.0	0.1	0.3
FeAlPO-5(4%) ^a	11.6	11.4	—	0.2

^a Numbers in parentheses indicate iron content in wt%. ^b Reaction conditions: Temperature: 653 K, benzene : N₂O : He = 1 : 3.6 : 5.4, contact time factor = 0.5 s.

materials are slightly less (but significantly more compared to pure AlPO-5) compared to that reported for FeMFI²³ as well as from our own study (we observed *ca* 23% yield of phenol over FeMFI, well in line with the literature), the creation of an active iron site in FeAlPO-5 involves a one-step process of calcination at temperatures of *ca* 823 K; active FeMFI catalysts are invariably prepared using a two-step process such as calcination of Fe(III) incorporated zeolite and heat treatment at temperatures in excess of 873 K or steaming at high-temperatures. Experimental conditions employed in this work using FeAlPO-5 catalysts were closely similar to the ones reported in ref. 23 which are shown in Table 1 along with the catalytic results.

We have characterised the environment of iron in our aluminophosphate catalysts by X-ray absorption spectroscopy, carried out at station 7.1 of Daresbury Synchrotron Source which operates at 2 GeV; the station was equipped with Si(111) double crystal monochromator and a solid state fluorescence detector. X-Ray absorption near edge structure (XANES) spectra given in Fig. 2 show the presence of a pre-edge feature (marked A), which increases in intensity on heating the sample to 373 K (no further changes in the Fe K-edge XANES studies conducted at temperatures up to *ca* 803 K). This change is indicative of the conversion of octahedrally coordinated Fe(III) to the tetrahedrally coordinated state.^{45,46} Analysis of the Fe–K edge EXAFS spectra of the as-prepared (1 wt% FeAlPO-5) material shows octahedral coordination of oxygen, with an average Fe–O distance of 1.95 ± 0.01 Å. Upon calcination in air at *ca* 773 K, the Fe–O coordination number decreased to 3.9 ± 0.2 , and the iron–oxygen interatomic distance decreases to 1.86 ± 0.02 Å, which is closely similar to the framework substituted Fe(III) ions in FeZSM-5 materials;³⁷ the Fe(III) coordination increased to 6 when exposed to water molecules, which is easily convertible to tetrahedral

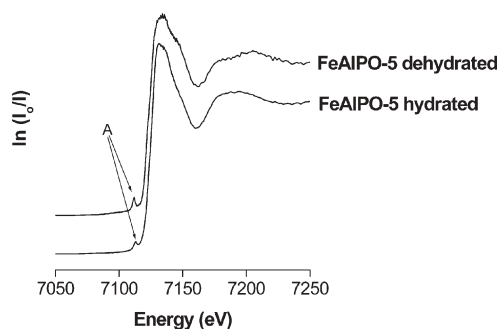


Fig. 2 Fe K-edge XANES of hydrated and dehydrated AlPO-5 catalyst, containing 1 wt% iron. The pre-edge peak is marked as A which increases upon dehydration at *ca* 373 K (and this remains unaltered up to *ca* 803 K) indicating the formation of tetrahedral Fe(III) due to the removal of water molecules bound to framework iron ions in the hydrated state.

coordination by mild heat treatment.⁴⁵ These EXAFS results are consistent with the change in the pre-edge intensity in the XANES data of the as-synthesised and calcined (*in situ*) catalysts.^{43–45} Both EXAFS and XANES measurements thus support the presence of coordinatively unsaturated, tetrahedrally coordinated Fe(III) in the activated catalyst.

In summary, it is found that calcined Fe(III) substituted AlPO-5 material (without additional high-temperature heat treatments which are normally carried out for FeZSM-5 catalysts) is active for the conversion of benzene to phenol in presence of nitrous oxide at *ca* 653 K.

We would like to thank the SRS and CCLRC for provision of beamtime. GS and NRS thank the Royal Society for an incoming fellowship for NRS. We also thank Prof. Richard W. Joyner and Professor C. R. A. Catlow for numerous invaluable discussions.

Notes and references

- 1 M. Iwamoto, K. Matsukami and S. Kagawa, *J. Phys. Chem.*, 1983, **87**, 903.
- 2 E. Suzuki, K. Makashiro and Y. Ono, *Chem. Lett.*, 1988, **17**, 953.
- 3 M. H. Gubelmann and P. J. Tirel, *Fr. Pat.* 2 630 735 (Filed May 2, 1988).
- 4 A. S. Kharitonov, T. N. Aleksandrova, L. A. Vostrikova, V. I. Sobolev, K. G. Ione and G. I. Panov, *USSR Pat.* 1805127 (Filed June 22, 1988).
- 5 G. I. Panov, G. A. Sheveleva, A. S. Kharitonov, V. N. Romannikov and L. A. Vostrikova, *Appl. Catal., A*, 1992, **82**, 31.
- 6 A. S. Kharitonov, G. A. Sheveleva, G. I. Panov, V. I. Sobolev, Ye. A. Paukshtis and V. N. Romannikov, *Appl. Catal., A*, 1993, **98**, 33.
- 7 V. I. Sobolev, G. I. Panov, A. S. Kharitonov, V. N. Romannikov, A. M. Volodin and K. G. Ione, *J. Catal.*, 1993, **139**, 435.
- 8 G. I. Panov, A. S. Kharitonov and V. I. Sobolev, *Appl. Catal., A*, 1993, **98**, 1.
- 9 V. I. Sobolev, A. S. Kharitonov, Ye. A. Paukshtis and G. I. Panov, *J. Mol. Catal.*, 1993, **84**, 117.
- 10 A. M. Volodin, V. A. Bolshov and G. I. Panov, *J. Phys. Chem.*, 1994, **98**, 7548.
- 11 A. S. Kharitonov, V. B. Fenelonov, T. P. Voskresenskaya, N. A. Rudina, V. V. Molchanov, L. M. Plyasova and G. I. Panov, *Zeolites*, 1995, **15**, 253.
- 12 V. I. Sobolev, K. A. Dubkov, E. A. Paukshtis, L. V. Pirutko, M. A. Rodkin, A. S. Kharitonov and G. I. Panov, *Appl. Catal., A*, 1996, **141**, 185.
- 13 K. A. Dubkov, V. I. Sobolev, E. P. Talsi, M. A. Rodkin, N. H. Watkins, A. A. Shteinman and G. I. Panov, *J. Mol. Catal. A: Chem.*, 1997, **123**, 155.
- 14 G. I. Panov, A. K. Uriarte, M. A. Rodkin and V. I. Sobolev, *Catal. Today*, 1998, **41**, 365.
- 15 G. I. Panov, *CATTECH*, 2000, **4**, 18.
- 16 L. V. Pirutko, V. S. Chernyavsky, A. K. Uriarte and G. I. Panov, *Appl. Catal., A*, 2002, **227**, 143.
- 17 K. A. Dubkov, N. S. Ovanesyan, A. A. Shteinman, E. V. Starokon and G. I. Panov, *J. Catal.*, 2002, **207**, 341.
- 18 E. V. Starokon, K. A. Dubkov, L. V. Pirutko and G. I. Panov, *Top. Catal.*, 2003, **23**, 137.
- 19 A. A. Ivanov, V. S. Chernyavsky, M. J. Gross, A. S. Kharitonov, A. K. Uriarte and G. I. Panov, *Appl. Catal., A*, 2003, **249**, 327.

-
- 20 V. N. Parmon, G. I. Panov, A. Uriarte and A. S. Noskov, *Catal. Today*, 2005, **100**, 115.
- 21 J. F. Jia, Q. Sun, B. Wen, L. X. Chen and W. M. H. Sachtler, *Catal. Lett.*, 2002, **82**, 7.
- 22 J. Jia, K. S. Pillai and W. M. H. Sachtler, *J. Catal.*, 2004, **221**, 119.
- 23 K. S. Pillai, J. Jia and W. M. H. Sachtler, *Appl. Catal., A*, 2004, **264**, 133.
- 24 A. A. Battiston, J. H. Bitter, F. M. F. de Groot, A. R. Overweg, O. Stephan, J. A. van Bokhoven, P. J. Kooyman, C. van der Spek, G. Vankó and D. C. Koningsberger, *J. Catal.*, 2003, **213**, 251.
- 25 A. A. Battiston, J. H. Bitter, W. M. Heijboer, F. M. F. de Groot and D. C. Koningsberger, *J. Catal.*, 2003, **215**, 279.
- 26 A. A. Battiston, J. H. Bitter and D. C. Koningsberger, *J. Catal.*, 2003, **218**, 163.
- 27 W. M. Heijboer, P. Glatzel, K. R. Sawant, R. F. Lobo, U. Bergmann, R. A. Barrea, D. C. Koningsberger, B. M. Weckhuysen and F. M. F. de Groot, *J. Phys. Chem. B*, 2004, **108**, 10002.
- 28 W. M. Heijboer, D. C. Koningsberger, B. M. Weckhuysen and F. M. F. de Groot, *Catal. Today*, 2005, **110**, 228.
- 29 P. Marturano, L. Drozdová, A. Kogelbauer and R. Prins, *J. Catal.*, 2000, **192**, 236.
- 30 P. Marturano, A. Kogelbauer and R. Prins, *J. Catal.*, 2000, **190**, 460.
- 31 L. Čapek, V. Kreibich, J. Dědeček, T. Grygar, B. Wichterlová, Z. Sobalík, J. A. Martens, R. Brosius and V. Tokarová, *Microporous Mesoporous Mater.*, 2005, **80**, 279.
- 32 P. Kubánek, B. Wichterlová and Z. Sobalík, *J. Catal.*, 2002, **211**, 109.
- 33 O. Bortnovsky, Z. Melichar, Z. Sobalík and B. Wichterlová, *Microporous Mesoporous Mater.*, 2001, **42**, 97.
- 34 B. Wichterlova, *Top. Catal.*, 2004, **28**, 131.
- 35 R. Joyner and M. Stockenhuber, *J. Phys. Chem. B*, 1999, **103**, 5963.
- 36 R. W. Joyner and M. Stockenhuber, *Catal. Lett.*, 1997, **45**, 15.
- 37 D. W. Lewis, C. R. A. Catlow, G. Sankar, S. W. Carr and J. M. Thomas, *J. Phys. Chem.*, 1995, **99**, 2377.
- 38 A. M. Thayer, *Chem. Eng. News*, 1998, **6**, 21.
- 39 One Step Phenol from Benzene Process Developed. *Chem. Eng. Prog.*, 1997, 16.
- 40 M. McCoy, *Chem. Market Rep.*, 1996, **250**, 1; *Chem. Week*, 1997, Jan. 1/8, 11.
- 41 T. Ren, L. Yan, X. Zhang and J. Suo, *Appl. Catal., A*, 2003, **244**, 11.
- 42 R. Raja, G. Sankar and J. M. Thomas, *J. Am. Chem. Soc.*, 2001, **123**, 8153.
- 43 M. Dugal, G. Sankar, R. Raja and J. M. Thomas, *Angew. Chem., Int. Ed.*, 2000, **39**, 2310.
- 44 R. Raja, G. Sankar and J. M. Thomas, *J. Am. Chem. Soc.*, 1999, **121**, 11926.
- 45 C. Zenonos, G. Sankar, F. Cora, D. W. Lewis, Q. A. Pankhurst, C. R. A. Catlow and J. M. Thomas, *Phys. Chem. Chem. Phys.*, 2002, **4**, 5421.
- 46 A. M. Beale and G. Sankar, *J. Mater. Chem.*, 2002, **12**, 3064.