Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Catalysis Today 112 (2006) 103–106

CATALYSIS TODAY

www.elsevier.com/locate/cattod

# Reactivity of electrophilic oxygen species generated over mesoporous iron-containing catalysts

A. Costine *, T. O'Sullivan, B.K. Hodnett

*Materials and Surface Science Institute, University of Limerick, Limerick, Ireland*

## Abstract

The vapour phase hydroxylation of toluene and epoxidation of propene and 1-butene with nitrous oxide over Fe/SBA-15 catalysts was experimentally investigated. Modification of these mesoporous catalysts by the addition of KCl resulted in a significant transfer from benzylic/allylic oxidation towards aromatic/vinylic oxidation by suppressing the reactivity of nucleophilic oxygen species. Analogous to the Fe/ZSM-5 system, highly dispersed iron species residing within the pore structure are responsible for generating the electrophilic oxygen species upon nitrous oxide decomposition. While substrate conversions are generally low (<4%), the catalysts offer phenolic/epoxide selectivities of ~70% in an environmentally benign one-step reaction.

*Keywords:* SBA-15; Nitrous oxide; Epoxidation; Hydroxylation; Iron oxide

## 1. Introduction

The functionalisation of olefins and alkyl-aromatics to produce more valuable organic compounds such as epoxides and alcohols, requires the selective attack at electron rich double bonds or oxidation of strong C–H bonds. The generation of an oxygen species with a preferential reactivity towards these stronger bonds of a hydrocarbon, in which less stable bonds are also present, remains a formidable challenge. Ideally, for these reactions we need to tailor the electrophilicity of the reacting oxygen species depending on the nature of the C–H bonds present in the starting hydrocarbon, while minimising the reactivity of non-selective oxygen species.

In the liquid phase, the oxidation of toluene with $H_2O_2$ over Fe-grafted SBA-15 produced a mixture of benzaldehyde (32%) and *ortho*- and *para*-cresol (68%) [1], with the active oxygen species favouring ring hydroxylation over side-chain oxidation. Similarly, the oxidation of bulky 2,3,6-trimethylphenol by $H_2O_2$ gave impressive selectivities in ring hydroxylation over iron-containing MFS-9 (91%) and MCM-41 (88%) [2]. It is also known that the epoxidation of propene over TS-1 [3] and Pd/TS-1 [4] proceeds efficiently in the liquid phase with $H_2O_2$ and $O_2$–$H_2$ gas mixture, respectively. Transferring such reactions to the vapour phase would facilitate higher production rates, simpler reactor technology and more convenient catalyst handling.

However, at present, for reactions such as the vapour phase epoxidation of propene, high propylene oxide (PO) selectivity is only achieved at very low propene conversion and with high operating cost. This is particularly evident when a reactant stream containing $H_2$ and $O_2$ is employed [5–7]. The use of $O_2$ or air generally gives low PO yields due to allylic oxidation, though some of the better catalysts offer yields ~14% ([8]; Ag catalyst). The patent literature also describes the addition of different NO/$CO_2$/chlorocarbon combinations to the $O_2$ stream, which acts to moderate activity and enhance PO selectivity [9,10].

The generation of electrophilic oxygen from $N_2O$ has been intensively studied over Fe/ZSM-5, particularly the conversion of benzene to phenol [11–13]. Duma and Honicke [14] described the first successful use of $N_2O$ in propene epoxidation. A PO yield of ~5% was obtained over silica supported iron oxide catalysts promoted with Na ions. Similarly, epoxidation by $N_2O$ over silica supported $FeO_x$ catalysts modified with caesium gave a PO yield of 7.5% [15]. Recently, Wang et al. [16] reported an interesting shift from allylic oxidation to epoxidation during the oxidation of propene with $N_2O$ over alkali impregnated $FeO_x$/SBA-15 catalyst.

---

* Corresponding author. Tel.: +353 61 234159.
*E-mail address:* Allan.Costine@ul.ie (A. Costine).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.11.032

While the release of an oxygen atom from $N_2O$ is energetically more favourable than from the oxygen molecule, and exhibits interesting electrophilic behaviour, only few reports detail the use of $N_2O$ in alkene epoxidation [14–16] and the hydroxylation of alkyl-aromatics [17–19]. This paper describes the creation of well-dispersed iron sites in SBA-15 materials by chemical vapour deposition and their application in olefin/alkyl-aromatic selective oxidation by $N_2O$.

## 2. Experimental

### 2.1. Preparation of Fe/SBA-15 materials

Mesoporous SBA-15 samples were synthesised under acidic conditions, as reported by Zhao et al. [20], using Pluoronic P123 (BASF) as the surfactant. The silica source, tetraethyl orthosilicate, TEOS (Aldrich) was added to an aqueous solution containing HCl and surfactant (initial mole ratio: TEOS/surfactant/HCl/$H_2O$ = 1/0.017/5.7/193). The mixture was magnetically stirred until the TEOS was fully dissolved. Then, the mixture was placed in a closed Teflon vessel and stirred for 20 h at 35 °C, followed by aging at 120 °C for 1 day. The resulting solid product was filtered, washed, air-dried at 50 °C and calcined at 600 °C (2 °C/min) for 8 h. Iron addition was achieved through chemical vapour deposition (CVD) of $FeCl_3$ into the mesopores in a U-shaped quartz reactor. 1.5 g of SBA-15 was loaded onto one leg and flushed overnight under $N_2$ flow, the reactor was isolated and moved to a $N_2$ glove bag, where 0.35–1.0 g of anhydrous $FeCl_3$ was added to the second leg. The reactor was reconnected to the $N_2$ flow and sublimation was performed at 330 °C for 5–30 min. After calcination, the Fe/SBA-15 samples were further modified by KCl impregnation, which typically involved the addition of 5 g of SBA-15 to 200 ml of 0.05 M KCl solution for 6 h under stirring, followed by drying and calcination at 550 °C.

### 2.2. Catalyst characterization

Specific surface areas and porosities were measured by nitrogen adsorption at 77 K using a Micrometrics ASAP 2010 apparatus. Small angle X-ray diffraction patterns were obtained on a Phillips X'Pert X-ray diffractometer operating at 40 kV and 35 mA, using nickel filtered Cu Kα radiation ($\lambda = 0.15406$ nm). Electron micrographs and energy dispersive X-ray (EDX) spectrums were obtained using a Joel JSM-840 scanning electron microscope. Transmission electron micrographs (TEM) were taken using a Jeol JEM2010 Fastem operating at 200 keV. Samples were positioned on a carbon microgrid by placing a few droplets of a suspension of ground sample in ethanol, followed by drying in ambient conditions.

### 2.3. Catalytic testing

A single pass flow reactor was employed. Catalytic tests were carried out in a quartz tube (length 30 cm, i.d. 0.67 cm) using a total gas flow of 60 ml/min. Following pre-treatment of the catalysts with air at 400 °C, reaction runs were conducted for 0.5–8 h. For propene oxidation, reaction runs were usually limited to the temperature range 250–325 °C. Below 250 °C the activity was too low while above 325 °C the selectivity to PO decreased markedly. For toluene oxidation, the hydrocarbon was introduced into the gas stream by means of an evaporator equipped with a thermostat and was oxidised at 350 °C. The temperature of the catalyst bed was measured via an internal thermocouple. An optimum epoxide/cresol yield was observed at a high surplus of $N_2O$ versus hydrocarbon in the reactor feed. For this reason the ratio of hydrocarbon:$N_2O$:nitrogen (carrier gas) was 1:15:84 (mol%), with a total flow of 60 ml/min. Reactants and products were quantitatively analysed by gas chromatography with FID detection (columns: Rtx-5 and PEG-20M). An example of the notation used throughout this paper is given as follows: 1 wt.% Fe/SBA-15 ($K^+$), with the weight loading of iron given first, then the host material, and finally ($K^+$) represents that the samples were impregnated by KCl.

## 3. Results and discussion

X-ray diffraction patterns of Fe/SBA-15 catalysts modified with KCl displayed three reflection peaks (1 0 0), (1 1 0) and (2 0 0) in the low angle region, characteristic of SBA-15 materials [20]. Therefore, the hexagonally ordered structure of SBA-15 was sustained following the introduction of $FeO_x$ and KCl. Wide-angle XRD patterns of Fe/$K^+$/SBA-15 samples registered in the region $2\theta = 10–70°$ showed the broad reflection of the amorphous wall structure of SBA-15, though no diffraction lines corresponding to any crystalline phase of iron oxide or KCl were detected. This suggests that for the Fe/$K^+$/SBA-15 catalysts (Fe, 0–5 wt.%; K/Si, 0–0.1), the chemical vapour deposition of $FeCl_3$ and impregnation of KCl produces highly dispersed species within the mesoporous channels.

The maintenance of the SBA-15 frameworks upon $FeO_x$ and KCl introduction is further supported by nitrogen adsorption/desorption isotherms, which displayed a well-defined step indicating that these materials possess mesoporous structure. Although the incorporation of $FeO_x$ and KCl into SBA-15 led to a continuous decrease in the specific surface area and the cumulative pore volume (Table 1), the pore size is still large by comparison with toluene and propene. SEM analysis revealed that the parent SBA-15 sample consisted of well-defined wheat-like morphology [20] with relatively uniform sizes of about 1 μm, which showed no sign of degradation in its macroscopic structure following $FeO_x$/KCl modification. The well-ordered hexagonal array of mesopores was visualised by means of representative TEM micrographs for SBA-15 catalysts containing different iron loadings (Fig. 1). The combined results of XRD, $N_2$ physisorption, and high-resolution TEM confirm that KCl and iron species are finely dispersed within the mesoporous channels.

Table 1 displays the results for the oxidation of toluene with $N_2O$ over Fe/SBA-15 (with/without KCl) and some physico-chemical characteristics of the catalysts. Unmodified SBA-15 gave only slight toluene conversions with no selectivity to the corresponding cresols, demonstrating that iron was the active phase. Instead, the formation of benzylic products, in particular

Table 1
Selective oxidation of toluene with $N_2O$ over Fe/SBA-15 (with/without KCl modification)

| Catalyst | $S_{BET}$ ($m^2$/g) | $V_p$ ($cm^3$/g) | Conv toluene (%) | Selectivity (%) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | *Ortho*-cresol | *Para*-cresol | *Meta*-cresol | Benzyl alchol | Benz-aldehyde | Other |
| SBA-15 (unmodified) | 952 | 1.14 | 0.8 | 0 | 0 | 0 | 7 | 76 | 17 |
| 1% Fe/SBA-15 | 881 | 1.00 | 1.4 | 5 | 2 | 2 | 10 | 62 | 19 |
| 0.5% Fe/SBA-15 ($K^+$) | 725 | 0.82 | 2.1 | 40 | 9 | 6 | 8 | 32 | 5 |
| 1% Fe/SBA-15 ($K^+$) | 721 | 0.77 | 3 | 53 | 10 | 9 | 6 | 16 | 6 |
| 5% Fe/SBA-15 ($K^+$) | 680 | 0.69 | 3.5 | 22 | 7 | 7 | 13 | 31 | 20 |
| $Fe_2O_3$ | | | 2.4 | 0 | 0 | 0 | 3 | 22 | 75 |
| 0.7% Fe/ZSM-5[a] | 425 | 0.17 | 22 | 2 | 12 | 5 | 0 | 0 | 81 |

Reaction conditions: 1% toluene, 15% $N_2O$, balance $N_2$, TOS = 30 min, total flow = 60 ml/min, temperature = 350 °C, $W_{cat}$ = 0.5 g. For Fe/SBA-15 ($K^+$) catalysts K/Si = 0.05.

[a] Ref. [17].

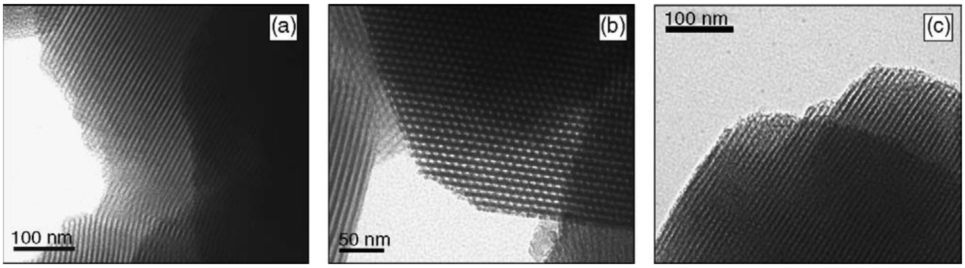

Fig. 1. TEM micrographs of (a) unmodified SBA-15 host, (b) 1 wt.% Fe/K/SBA-15 (K/Si = 0.05) and (c) 5 wt.% Fe/K/SBA-15 (K/Si = 0.05) with views parallel and perpendicular to the pores.

benzaldehyde, along with carbon oxides and benzene was observed. Over Fe/SBA-15 catalyst without KCl impregnation, products of benzylic oxidation and deep oxidation dominated. The addition of KCl suppresses the reactivity of oxygen species towards the weaker benzylic C–H bonds, inducing hydroxylation of the aromatic ring by electrophilic oxygen. Following modification by KCl, *ortho*-cresol became the main product over the catalysts with iron content lower than 1 wt.%. Although toluene conversion increases with additional iron content, the selectivity to phenolic product diminishes markedly with an increase in iron content up to 5 wt.%. Experiments employing only free $Fe_2O_3$ and KCl–$Fe_2O_3$ mixtures gave mostly carbon oxides and some products resulting from benzylic oxidation.

Table 1 also contains results we obtained recently for the oxidation of toluene by $N_2O$ over 0.7 wt.% Fe/ZSM-5 [17]. The active oxygen formed over Fe/ZSM-5 catalysts has similar electrophilic character, though the presence of Brønsted acidity even after iron incorporation facilitates the formation of benzene, xylenes and polyaromatic structures. Interestingly, the change in cresol isomer distribution from predominantly *ortho*-cresol over Fe/SBA-15 catalysts to *para*-cresol over Fe/ZSM-5 catalysts lends credence to the model that the active iron responsible for these reactions is highly dispersed within the pore channels.

The results for the oxidation of propene and 1-butene with $N_2O$ over the Fe/SBA-15 catalysts are presented in Table 2. Similar to toluene oxidation, unmodified SBA-15 gave only

Table 2
Selective oxidation of propene and 1-butene with $N_2O$ over Fe/SBA-15 (with/without KCl modification)

| Catalyst | Conv propene (%) | Selectivity (%) | | | | | Conv 1-butene (%) | Selectivity (%) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | PO | AL | AA | Other | $CO_x$ | | 1,2-BO | Btone | 1-Bol | 1-Bal | Other | $CO_x$ |
| SBA-15 (unmodified) | 0.35 | 0 | 45 | 10 | 8 | 37 | 0.2 | 0 | 4 | 13 | 35 | 20 | 28 |
| 1% Fe/SBA-15 | 1.8 | 4 | 39 | 12 | 4 | 41 | 1.6 | 3 | 2 | 9 | 16 | 22 | 48 |
| 0.5% Fe/SBA-15 ($K^+$) | 1.2 | 55 | 9 | 7 | 5 | 24 | 0.9 | 43 | 11 | 3 | 6 | 12 | 25 |
| 1% Fe/SBA-15 ($K^+$) | 4.0 | 67 | 6 | 3 | 7 | 17 | 3.5 | 64 | 7 | 3 | 4 | 9 | 13 |
| 5% Fe/SBA-15 ($K^+$) | 5.3 | 25 | 11 | 8 | 18 | 38 | 4.8 | 27 | 5 | 5 | 9 | 20 | 34 |
| $Fe_2O_3$ | 0.5 | 0 | 12 | 5 | 3 | 80 | 0.8 | 0 | 0 | 0 | 5 | 12 | 83 |

Reaction conditions: 1% propene/1-butene, 15% $N_2O$, balance $N_2$, TOS = 30 min, total flow = 60 ml/min, temperature = 325 °C, $W_{cat}$ = 0.5 g. For Fe/SBA-15 ($K^+$) catalysts K/Si = 0.05. PO, propylene oxide; AL, acrolein; AA, allyl alcohol; 1,2-BO, 1,2-butylene oxide; Btone, butanone; 1-Bol, 1-butenol; 1-Bal, 1-butenal.

slight olefin conversions with no selectivity to the corresponding epoxides. Over Fe/SBA-15 catalyst without KCl impregnation, products of allylic oxidation and deep oxidation were detected. The addition of KCl to Fe/SBA-15 minimises the interaction of nucleophilic oxygen species with an approaching olefin, thus promoting addition of electrophilic oxygen generated over iron sites upon $N_2O$ decomposition. Although olefin conversion increases steadily with increasing iron content, the selectivity to propylene oxide and butylene oxide diminishes at higher iron loadings (above 1%) where the creation of catalytically inactive iron oxide agglomerates is favoured.

The influence of the K/Fe ratio (1–20) on catalytic performance was investigated for the 1 wt.% Fe/SBA-15 ($K^+$) sample. For both toluene and olefin oxidation, a maximum in conversion was observed at K/Fe = 4, above which substrate conversion began to decline gradually. Product selectivities for both reactions remained relatively unchanged for the range of K/Fe = 1–20. Time-on-stream analysis (0–8 h) showed that the modified Fe/SBA-15 catalysts offer good stability with only a slight reduction in catalytic activity.

## 4. Conclusion

This work shows that the reactivity of electrophilic oxygen formed over surface-modified Fe/SBA-15 catalysts prepared by $FeCl_3$ CVD offer new routes to epoxidation and hydroxylation, reactions in which the starting olefins/alkyl-aromatics often contain labile C–H bonds. The addition of an alkali metal salt following catalyst preparation enhances the selectivity towards products that require an electrophilic form of oxygen, namely addition of oxygen to the benzene ring or π-bond.

## Acknowledgements

The authors would like to thank Enterprise Ireland for financial support and Miroslav Mihov for TEM analysis.

## References

[1] C. Nozaki, C.G. Lugmair, A.T. Bell, T.D. Tilley, J. Am. Chem. Soc. 124 (2002) 13194.
[2] Y. Han, X. Meng, H. Guan, Y. Yu, L. Zhao, X. Xu, X. Yang, S. Wu, N. Li, F.-S. Xiao, Micropor. Mesopor. Mater. 57 (2003) 191.
[3] M.G. Clerici, G. Bellussi, U. Romano, J. Catal. 129 (1991) 159.
[4] R. Meiers, U. Dingerdissen, W.F. Holderich, J. Catal. 176 (1998) 376.
[5] A. Kuperman, R.G. Bowman, H.W. Clark, G.E. Hartwell, G.R. Meima, US Patent 6,821,923 (2004).
[6] N. Yap, R.P. Andres, W.N. Delgass, J. Catal. 226 (2004) 156.
[7] R. Wang, X. Guo, X. Wang, J. Hao, G. Li, J. Xiu, Appl. Catal. A: Gen. 261 (2004) 7.
[8] G. Lu, X. Xuo, Catal. Lett. 58 (1999) 67.
[9] E.M. Thorsteinson, Canadian Patent 1,282,772 (1991).
[10] M. Haruta, Y.A. Kalvachev, S. Tsubota, T. Hayashi, M. Wada, US Patent 6,124,505 (2000).
[11] G.I. Panov, A.K. Uriarte, M.A. Rodkin, V.I. Sobolev, Catal. Today 41 (1998) 365.
[12] A. Reitzmann, E. Klemm, G. Emig, Chem. Eng. J. 90 (2002) 149.
[13] F. Kollmer, H. Hausmann, W.F. Hoelderich, J. Catal. 227 (2004) 408.
[14] V. Duma, D. Honicke, J. Catal. 191 (2000) 93.
[15] E. Ananieva, A. Reitzmann, Chem. Eng. Sci. 59 (2004) 5509.
[16] X. Wang, Q. Zhang, Q. Guo, Y. Lou, L. Yang, Y. Wang, Chem. Commun. 12 (2004) 1396.
[17] A. Costine, T. O'Sullivan, B.K. Hodnett, Catal. Today 99 (2004) 199.
[18] J.L. Motz, H. Heinichen, W.F. Holderich, J. Mol. Catal. A: Chem. 136 (1998) 175.
[19] B. Vogel, C. Scheider, E. Klemm, Catal. Lett. 79 (2002) 107.
[20] D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, G.D. Stucky, J. Am. Chem. Soc. 120 (1998) 6024.