

Preparation of iron oxide nanocatalysts and application in the liquid phase oxidation of benzene

David Lokhat^{1*}, Mike Oliver², Milan Carsky¹

¹ University of KwaZulu-Natal, School of Engineering, Reactor Technology Research Group, Durban 4041, South Africa

² Energy Engineering International, Durban, 3610, South Africa

*Corresponding author: e-mail: lokhat@ukzn.ac.za

A series of iron oxide nanocatalysts were prepared using an ultrasonically assisted co-precipitation technique. Molybdenum promoted Fe₃O₄ and Fe₂O₃ were prepared from the original materials by wet impregnation using a solution of ammonium molybdate. The catalysts were tested in the liquid phase oxidation of benzene at atmospheric pressure and at 60°C using molecular oxygen. Phenol yields between 7% and 14.5% were obtained. The major products were pyrogallol and catechol.

Keywords: Iron oxide nanocatalyst, benzene, oxidation, phenol, liquid phase.

INTRODUCTION

The preparation and application of magnetite nanoparticles as catalysts in organic syntheses is an important area of research and that which has drawn significant attention in recent years. These materials possess interesting chemical and physical properties that are very different from the corresponding bulk phase, which enable them to serve as very effective catalytic agents for a variety of reactions¹. High specific surface area of the particles, efficient dispersion of the catalyst within the reacting medium and the ease of recovery through magnetic separation are some of the benefits of utilizing these materials. Magnetic nanosized transition metal oxides such as Fe₃O₄ and Fe₂O₃ are considered promising catalysts for the oxidation of various organic species².

There are a number of methods available for the synthesis of iron oxide nanocatalysts of this nature, viz. sol-gel processing, solution precipitation and water oil microemulsion method³. Among the various methods reported for the synthesis of Fe₃O₄ the chemical co-precipitation of Fe²⁺ and Fe³⁺ salts by addition of sodium hydroxide is the simplest and cheapest^{1, 3}. Ultrasonic agitation of the reaction medium during co-precipitation can aid in the formation of uniform nanosized particles by preventing agglomeration⁴. Iron oxide nanocatalysts promoted with various transition metal oxides have been shown to have improved chemical and thermal stability². Molybdenum is known to significantly improve the activity of some oxidation catalysts⁵. The metal oxides can be incorporated into the lattice structure through simple wet impregnation using a salt precursor solution⁶.

Phenol is an important intermediate for the production of various antioxidants, agrochemicals and polymers. It is often used as the base compound in the manufacture of Nylon 6. Phenol is predominantly produced commercially via the multistep cumene process. However, high phenol yield is difficult to achieve and the intermediate in the process, cumene hydroperoxide, is explosive. The direct oxidation of benzene to phenol is highly desired^{7, 8}.

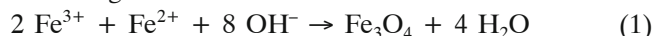
In the present study we examine the catalytic properties of Fe₃O₄ and Fe₂O₃ nanoparticles, prepared from steel fibres using an ultrasonically assisted co-precipitation method, for the liquid phase oxidation of benzene to phenol with molecular oxygen at atmospheric pressure and at 60°C. Both standard iron oxide and molybdenum-

-doped materials were considered. We report on the catalyst synthesis procedures and quantitatively assess the activity in terms of the yield of phenol produced.

EXPERIMENTAL

Preparation of iron oxide nanoparticles

The synthesis of magnetite nanoparticles was based on the classical method of co-precipitation of a stoichiometric mixture (2:1 ratio) of Fe³⁺ and Fe²⁺ salts with NaOH^{1, 9} according to the reaction:



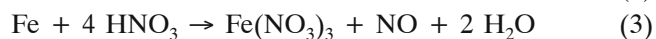
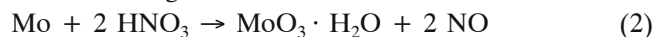
From the literature it was known that to achieve pure magnetite with a uniform size distribution below 50 nm, the synthesis should be carried out between 25–80°C with a Fe²⁺ concentration of 0.5 mol · dm⁻³ (consequently a Fe³⁺ concentration of 1 mol · dm⁻³)¹⁰. A solution of FeCl₂ was prepared by dissolving an appropriate amount of steel wool in dilute HCl under a nitrogen atmosphere (to prevent oxidation during preparation). FeCl₃ was prepared in an open beaker using the same procedure, with the addition of a few drops of hydrogen peroxide to force the transition to the +3 oxidation state. The amount of dilute acid used in each instance was in slight excess to ensure that all the steel wool was digested. The iron salt solutions were combined in a 1:1 ratio and the addition of NaOH was performed dropwise in an open vessel. The mixture was agitated using an ultrasonic bath during the synthesis. A dark green-grey precipitate of Fe(OH)₂ was produced, which according to the literature is a precursor to magnetite⁴. The formation of Fe(OH)₂ and green rust (an intermediate species composed of hydroxide layers interlaced with anions and water molecules) is supposedly favoured at high Cl⁻ ion concentrations and initial low pH^{11, 12}. The Fe(OH)₂ was transferred to a beaker of fresh water and the pH was adjusted to around 13–14 by the addition of NaOH. The vessel was aerated by means of a small pump and the mixture was agitated under the action of the ultrasonic bath. At these conditions the Fe(OH)₂ was oxidized to Fe₃O₄ within two hours¹³.

Magnetite nanoparticles were also produced using a thermal spraying method. Thin steel wire (40 SWG) was continuously introduced into the jet of a high temperature torch (>2500°C) and an incident air stream.

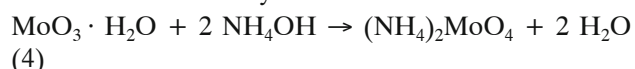
The resulting iron oxide particles emanating from the torch were rapidly quenched in a basin containing distilled water. The basin was drained and the solid particles were filtered and dried.

Preparation of molybdenum-doped iron oxide nanoparticles

A ferromolybdenum alloy having a composition of 80% molybdenum and 20% iron was digested in nitric acid according to:



A slight excess of 60% ammonium hydroxide solution was added to precipitate out the iron as $\text{Fe}(\text{OH})_3$ and form ammonium molybdate:



The magnetite was dried in an oven overnight between 70 and 100°C. The necessary amount of ammonium molybdate solution was added to a weighed amount of dry magnetite (with distilled water if required) to make a slurry. The slurry was stirred gently and then allowed to age overnight. The slurry was centrifuged and the solid material was dried in an oven at 110°C overnight. The dried product was calcined in a furnace at 500°C for three hours only. The ammonium molybdate precursor decomposed to the metal oxide during the drying and calcination steps. After calcinations the iron oxide existed as molybdenum-doped Fe_2O_3 . This reddish brown material was packed into a stainless steel tube and heated under a stream of hydrogen for 6 hours to give molybdenum-doped Fe_3O_4 .

Characterization of iron oxide nanoparticles

The specific surface area of the nanoparticles was measured using a nitrogen adsorption isotherm (BET method) on a Micrometrics ASAP 2020 chemisorption surface area analyzer. Prior to the measurements, all samples were degassed at 200°C under nitrogen for 12 hours to remove moisture and other impurities. The measurements were performed in triplicate and average values are reported here.

The particle size and size distribution of the nanocatalysts were measured with a Shimadzu SALD-3101 laser diffraction particle size analyser. Four samples were processed and average values are reported in this work.

X-ray powder diffraction (XRD) patterns for all materials were recorded using a PANalytical Empyrean X-ray diffractometer with a $\text{Co K}\alpha$ (1.789 Å) radiation source (40 kV, 45 mA). The scans were performed at 25°C in steps of 0.008°, with a recording time of 6.98 s for each step.

Oxidation of Benzene

The liquid phase oxidation of benzene was carried out in a 500 ml glass reaction vessel equipped with a water cooled reflux condenser, gas sparger and thermocouple. The flowrate of oxygen was controlled using a precision rotameter. The reaction vessel was immersed in an ultrasonic heating bath. In a typical experiment approximately 160 g of benzene was combined with 8 g of the

prepared catalyst to give a mixture of 4.7 wt% catalyst. This mixture was charged into the reaction vessel and brought to the operating temperature of 60°C using the sonic heating bath. The flowrate of oxygen gas was then admitted. The reaction was allowed to proceed for 1 hour after which the oxygen flow was terminated and the vessel was removed from the sonic bath.

The iron oxide nanoparticles were separated from the liquid using a neodymium magnet. The liquid product was analyzed via gas-liquid chromatography on a Shimadzu 2014 G.C. equipped with a Chromspec 10% SE30 on Chromosporb packed column, a flame ionization detector and using helium as the carrier gas (30 ml · min⁻¹). The analysis was carried out isothermally at 30°C. n-Hexane was used as an internal standard for quantification purposes. Average relative deviations on FID calibrations were <2%.

RESULTS AND DISCUSSION

In total, five experiments were carried out. Initially, no catalyst was used (blank run). Thereafter experiments with the chemically produced Fe_3O_4 , thermally produced Fe_3O_4 , Mo- Fe_3O_4 and Mo- Fe_2O_3 were performed, respectively. For each of the experiments the conversion of benzene was defined as the ratio of the moles of benzene consumed to the initial moles of benzene. The selectivity of phenol was defined as the ratio of the moles of phenol produced to the moles of benzene consumed. The yield of phenol was defined as the ratio of the moles of phenol produced to the initial moles of benzene.

Figures 1 and 2 show the selectivity and yield of phenol obtained from each of the experiments, respectively. In all instances the conversion of benzene was greater than 90%, even in the absence of catalyst. The predominant products were pyrogallol and catechol, with phenol selectivity not exceeding 15%. These rapid rates of oxidation may in part be due to the application of high energy ultrasonic irradiation during the syntheses. It is known that ultrasonic irradiation improves the rate of oxidation of cyclohexane to cyclohexanone under air in the presence of several transition metal oxide catalysts via several mechanisms, e.g. improved dispersion, possible acoustic cavitation and implosive compression¹⁴. It is possible that a similar enhancement was observed in this study.

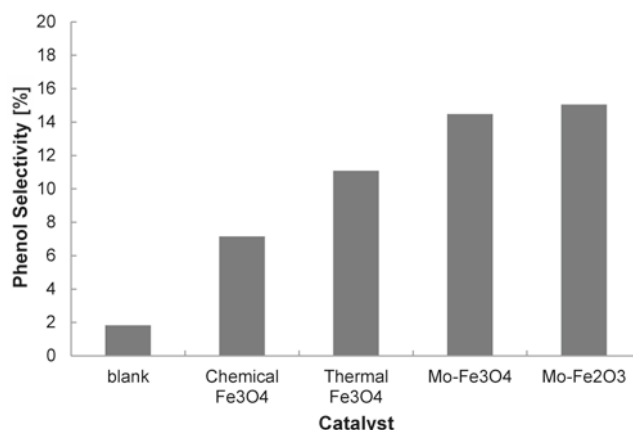


Figure 1. Phenol selectivity in the liquid-phase oxidation of benzene using iron oxide nanocatalysts at 60°C

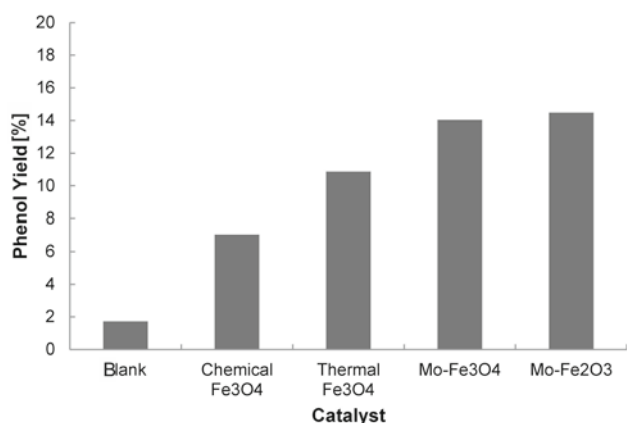


Figure 2. Phenol yield in the liquid-phase oxidation of benzene using iron oxide nanocatalysts at 60°C

The thermally produced catalyst performed slightly better than the chemically produced catalyst in terms of the yield of phenol. However, the molybdenum-doped Fe₃O₄ and Fe₂O₃ (both based on the chemically produced iron oxide) gave the highest selectivity towards phenol. Characterization data for all four prepared catalysts are presented in Table 1. The mean particle diameters of the chemically and thermally produced Fe₃O₄, as determined through the laser diffraction technique, were 80 nm and 800 nm, respectively. The BET specific surface area of the chemically and thermally produced Fe₃O₄ were 9.5 m² · g⁻¹ and 1.2 m² · g⁻¹, respectively. It appears that the smaller diameter particles of the chemical Fe₃O₄ favour the deeper oxidation of benzene to pyrogallol and catechol.

Table 1. Characterization data for the prepared iron oxide catalysts

Catalyst	BET surface [area/m ² · g ⁻¹]	Particle [size ^a /nm]	Crystallite [size ^b /nm]
Thermal Fe ₃ O ₄	1.2	800	86
Chemical Fe ₃ O ₄	9.5	80	34
Mo-Fe ₂ O ₃	9.4	80	37
Mo-Fe ₃ O ₄	9.5	80	21

^a measured using laser diffraction technique.

^b calculated using the Scherrer equation.

Figure 3 shows the recorded XRD patterns of the four different catalysts used in this study. Diffraction peaks corresponding to specific iron oxide phases are indicated. The thermal Fe₃O₄ (pattern a) contained magnetite (ICSD 98-007-7588), wuestite (ICSD 98-008-2232) and magnesioferrite (ICSD 98-015-8431) whilst the chemical Fe₃O₄ (pattern b) contained magnetite, goethite (ICSD 98-015-9970) and maghemite (ICSD 98-008-7121). The average crystallite size for each sample was calculated using the Scherrer equation:¹

$$L = K\lambda / \beta \cos\theta \quad (6)$$

Where L is the crystallite diameter, K is the shape factor, λ is the incident X-ray wavelength, β is the full-width-at-half-maximum (in radians) of the highest intensity powder diffraction reflection, and θ is the corresponding half of a diffraction angle. The reported crystallite sizes for both the chemical and thermal Fe₃O₄ (as determined using the XRD data) were smaller than the particle sizes obtained from the laser diffraction measurements. The

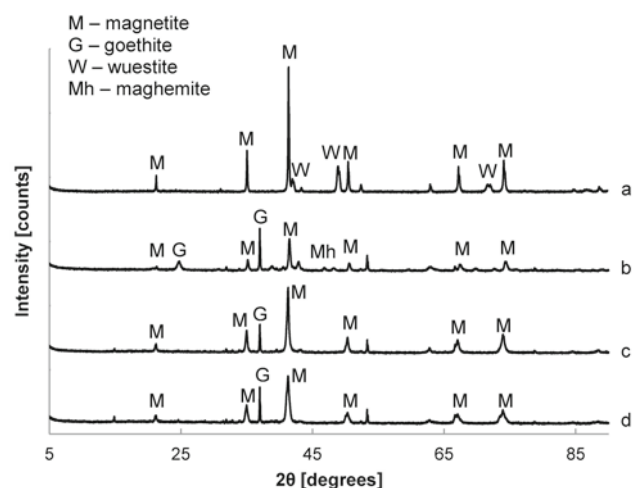


Figure 3. XRD patterns for a) thermal Fe₃O₄, b) chemical Fe₃O₄, c) Mo-Fe₂O₃ and d) Mo-Fe₃O₄

nanoparticles were thus composed of smaller crystallites. The chemical Fe₃O₄ had a smaller crystallite size than the thermal Fe₃O₄. The larger crystallite size of the thermal Fe₃O₄ and the presence of molybdenum in the lattice may promote the partial oxidation of benzene by blocking the route to the deeper oxidation products.

Figure 4 shows the XRD patterns of molybdenum-doped Fe₂O₃ (pattern c), molybdenum-doped Fe₃O₄ (pattern d) and a pure molybdenum oxide phase (molybdate, pattern x). The XRD patterns of the catalyst samples did not show evidence of phase separated oxides of molybdenum and iron. In particular, the diffraction peaks at 13°, 23°, 26° and 27° characteristic of molybdate were distinctly absent from the XRD patterns of the catalyst samples. It is therefore believed that the material exists as a mixed metal oxide with molybdenum incorporated into the lattice. It is possible that the molybdenum present in the lattice is capable of catalysing the oxidation of the substrate via the well-established Mars van Krevelen mechanism, i.e. the benzene takes up oxygen from the surface of the catalyst and the reduced catalyst is re-oxidized by O₂ from the gas phase. The XRD patterns of Mo-Fe₂O₃ and Mo-Fe₃O₄ show evidence of diffraction peak broadening likely caused by a number of surface defects. The peak broadening correlates well with the selectivity towards phenol and it is suggested

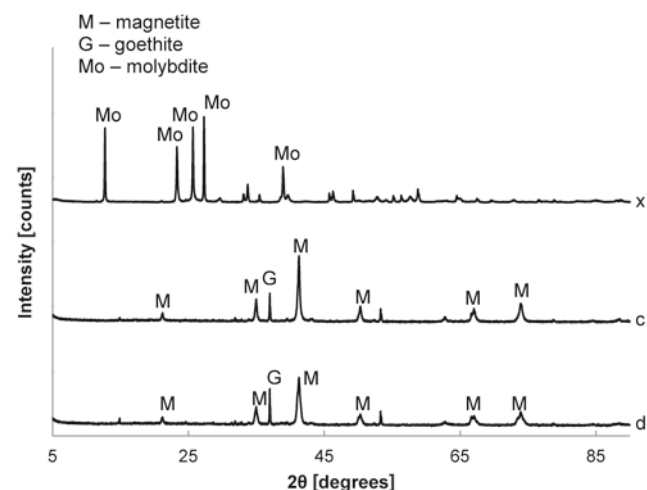


Figure 4. XRD patterns for x) molybdate MoO₃, c) Mo-Fe₂O₃ and d) Mo-Fe₃O₄

that these defects play a pivotal role in the preferential oxidation of the aromatic ring.

A chemical check was performed to determine if molybdenum had effectively been added to the iron nanocatalyst using the wet impregnation technique. An excess of FeCl_3 was added to the supernatant liquid and the filtrate left over after the wet impregnation of the nanoparticles, to form a ferro-molybdenum oxide precipitate. The precipitate was filtered, dried and weighed. The amount of molybdenum left in the liquid after loading was thus determined. In both cases, a practically negligible amount of molybdenum was found to remain in the precursor solution after loading.

CONCLUSIONS

Iron-oxide nanocatalysts, prepared by co-precipitation and thermal spraying methods, were applied for the first time in the liquid phase oxidation of benzene to phenol at atmospheric pressure and at 60°C. These materials were found to be moderately active for the oxidation reaction. The highest yield of phenol obtained was 14.48%. Ultrasonic agitation of the reaction mixture ensured minimal agglomeration of solid material and improved the overall rate of oxidation. The addition of molybdenum to the Fe_3O_4 and Fe_2O_3 was found to be beneficial, with at least a 30% increase in selectivity towards phenol.

ACKNOWLEDGEMENT

The authors thank Mr P. Suthan from the School of Geological Sciences at the University of KwaZulu-Natal for his assistance in the recording of powder X-ray diffraction data. The authors also thank Miss A. Gengiah and Mr V. Sewnarain for their assistance with catalyst preparation and characterization.

LITERATURE CITED

1. Wu, S., Sun, A., Zhai, F., Wang, J., Xu, W., Zhang, Q. & Volinsky, A.A. (2011). Fe_3O_4 magnetic nanoparticles synthesis from tailings by ultrasonic chemical co-precipitation. *Mat. Lett.* 65, 1882–1884. DOI: 10.1016/j.matlet.2011.03.065.
2. Rafiee, H.R., Feyzi, M., Jafari, F. & Safari, B. (2013). Preparation and characterization of promoted Fe-V/SiO₂ nanocatalysts for oxidation of alcohols. *J. Chem.* 2013, 1–10. DOI: 10.1155/2013/412308.
3. Skandan, G. & Singhal, A. (2006). Perspectives on the science and technology of nanoparticle synthesis. In Gogotsi, Y. (Ed.), *Nanomaterials Handbook* (pp. 2.1–2.15). New York: CRC Press.
4. Dang, F., Enomoto, N., Hojo, J. & Enpuku, K. (2009). Sonochemical synthesis of monodispersed magnetite nanoparticles by using an ethanol-water mixed solvent. *Ultra. Sonochem.* 16, 649–654. DOI: 10.1016/j.ultsonch.2008.11.003.
5. Jackson, S.D. & Hargreaves, J.S.J. (2009). *Metal Oxide Catalysis* (Volume 1). New York, John Wiley & Sons.
6. Martos, C., Dufour, J. & Ruiz, A. (2009). Synthesis of Fe_3O_4 -based catalysts for the high temperature water gas shift reaction. *Int. J. Hydro. Energy* 34(10), 4475–4481. DOI: 10.1016/j.ijhydene.2008.08.042.
7. Ichihashi, Y., Taniguchi, T., Amano, H., Atsumi, T., Nishiyama, S. & Tsuruya, S. (2008). Liquid-phase oxidation of benzene to phenol by molecular oxygen over La catalysts supported on HZSM-5. *Top. Catal.* 47, 98–100. DOI: 10.1007/s11244-007-9027-2.

8. Liu, Y., Murata, K. & Inaba, M. (2005). Liquid-phase oxidation of benzene to phenol by molecular oxygen over transition metal substituted polyoxometalate compounds. *Catal. Comm.* 6, 645–698. DOI: 10.1016/j.catcom.2005.06.015.

9. Gupta, A.K. & Gupta, M. (2005). Synthesis and surface engineering of iron oxide nanoparticles for biomedical applications. *Biomat.* 26, 3995–4021. DOI: 10.1016/j.biomaterials.2004.10.012.

10. Kim, D., Kim, K., Kim, K., Shim, I., Lee, M. & Lee, Y. (2006). Tuning of magnetite nanoparticles to hyperthermic thermoseed by controlled spray method. *J. Mat. Sci.* 41(22), 7279–7282. DOI: 10.1007/s10853-006-0952-4.

11. Mackay, A.L. (1961). Some aspects of the topochemistry of the iron oxides and hydroxides. In *Reactivity of solids: Proceedings of the fourth international symposium on the reactivity of solids, 1960* (pp. 571–583), Amsterdam, Netherlands.

12. Refait, P., Benali, O., Abdelmoula, M. & Génin, J.M.R. (2003). Formation of 'ferric green rust' and/or ferrihydrite by fast oxidation of iron (II-III) hydroxychloride green rust. *Corr. Sci.* 45, 2435–2449. DOI: 10.1016/S0010-938X(03)00073-8.

13. Roonasi, P. & Holmgren, A. (2009). A study on the mechanism of magnetite formation based on iron isotope fractionation. In *Proceedings of the Minerals Society Annual Meeting, 15–19 February 2009* (pp. 1–8), San Francisco, USA.

14. Suslick, K.S. & Skrabalak, S.E. (2008). Sonocatalysis. In Ertl, G., Knözinger, H., Schüth F. & Weitkamp, J. (Eds.), *Hand. Heterogen. Catal.*, Vol. 8 (pp. 2007–2017). Weinheim: Wiley-VCH.