



Highly selective and green aqueous–ionic liquid biphasic hydroxylation of benzene to phenol with hydrogen peroxide†

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Received 13th November 2002

First published as an Advance Article on the web 20th March 2003

With equal molar ratio of benzene and hydrogen peroxide and without any additional volatile organic solvent, a green aqueous–ionic liquid biphasic hydroxylation of benzene to phenol with hydrogen peroxide as oxidant and metal dodecanesulfonate salts such as ferric tri(dodecanesulfonate) as catalyst was conducted with excellent selectivity and enhanced conversion.

Introduction

Direct hydroxylation of benzene with hydrogen peroxide to form phenol has attracted much attention and been extensively investigated.^{1–6} The oxidation of benzene and its derivatives by Fenton's reagent (Fe^{2+} – H_2O_2) has been known for a long time.⁷ However, its selectivity is rather poor since phenol is more reactive toward oxidation than benzene itself, and classical Fenton chemistry requires large quantities of iron(II) salts, which are consumed stoichiometrically during the reaction.⁸ Although much effort has been devoted to new processes that produce phenol directly with high yield and selectivity, nevertheless, relatively few catalytic processes have successfully been developed. Very recently, Bianchi *et al.*⁹ reported that water–acetonitrile (1 : 1) biphasic reaction medium, in which the resulting phenol was extracted into the organic phase and the catalyst was soluble in the aqueous phase, dramatically enhanced the selectivity of the benzene hydroxylation by reducing the contact between phenol and the catalyst.

Recently, considerable interest has manifested in the use of room temperature ionic liquids, which have negligible vapor pressure, excellent thermal stability and special physicochemical characteristics in comparison with conventional organic and inorganic solvents, as environmentally benign media for catalytic reaction processes or chemical extractions.^{10,11} In particular, the ionic liquid based biphasic hydroformylation or hydrogenation reactions resulted in the separation and recovery

advantages of catalyst or product. Apart from hydroformylation,¹² hydrogenation,¹³ Friedel–Craft reactions,¹⁴ *etc.*, ionic liquids as reaction media were also successfully used in the selective catalytic oxidation reaction.¹⁵

Herein, an attempt was made to establish an aqueous–ionic liquid biphasic catalytic reaction system for direct oxidation of benzene to phenol with hydrogen peroxide as oxidant and metal dodecanesulfonate salts as catalysts in order to compare or replace traditional aqueous–organic solvent biphasic catalytic reaction systems. In this aqueous–ionic liquid biphasic process, both the catalyst and benzene were dissolved in the ionic liquid, while the oxidant, *i.e.* H_2O_2 was mainly dissolved in the aqueous phase but much less dissolved in the ionic liquid since the water solubility, for example, in the 1-octyl-3-methylimidazolium hexafluorophosphates could be as low as 0.2 g/100 ml¹⁶ and H_2O_2 could be well dissolved in the water. The phenol produced could be extracted into the aqueous phase, thus possible over-oxidation of the resulting phenol could be minimized. The aqueous–ionic liquid biphasic reaction system is schematically shown in Fig. 1. In comparison with the previously reported methods of benzene hydroxylation to phenol, the following advantages were achieved: (1) without any additional volatile organic solvent, (2) low molar ratios of benzene/hydrogen peroxide and catalyst/benzene, (3) highly selective for desired product, and (4) reusable catalyst system. These make such a process not only more environmentally acceptable but also more economically attractive.



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† This work was presented at the Green Solvents for Catalysis Meeting held in Bruchsal, Germany 13–16th October 2002.

Green Context

One of the major difficulties in oxidation chemistry is achieving high selectivity including avoiding over oxidation. In the direct hydroxylation of benzene to phenol, for example – a very important green chemistry target – the product is more reactive under typical hydrogen peroxide conditions, so that over oxidation is commonly observed. One method for overcoming such problems is *via* a biphasic system whereby the desired product is partitioned away from the catalyst or oxidant. Here we see this achieved through novel aqueous–ionic liquid biphasic systems whereby the catalyst and benzene substrate are in the ionic liquid while the oxidant and the desired phenol are concentrated in the water. JHC

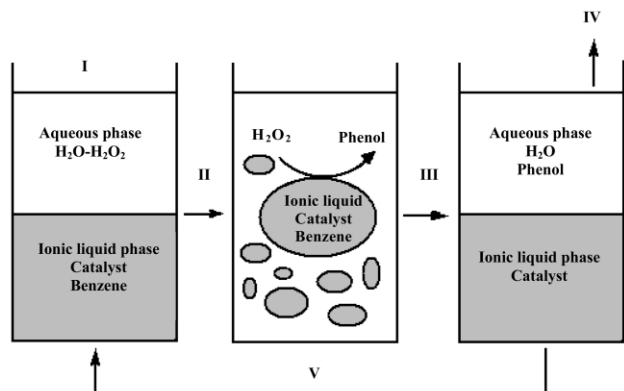


Fig. 1 A schematic representation of the aqueous-ionic liquid biphasic catalytic reaction system for benzene hydroxylation to phenol with H₂O₂. Step I charging; Step II reaction; Step III still; Step IV recovery of phenol via extraction; Step V the ionic liquid and catalyst are reused for another reaction cycle.

Experimental

1-*n*-Butyl-3-methylimidazolium hexafluorophosphate (BMImPF₆), 1-*n*-octyl-3-methylimidazolium hexafluorophosphate (OMImPF₆), 1-*n*-octyl-3-methylimidazolium tetrafluoroborate (OMImBF₄), 1-*n*-decyl-3-methylimidazolium hexafluorophosphate (DMImPF₆) and 1-*n*-decyl-3-methylimidazolium tetrafluoroborate (DMImBF₄), which were insoluble with water, were respectively synthesized according to the procedures reported in previous literature.^{11,17}

Dodecanesulfonate salts with various metal cations, *i.e.* ferric tri(dodecanesulfonate) Fe(DS)₃, ferrous bis(dodecanesulfonate) Fe(DS)₂, cobalt bis(dodecanesulfonate) Co(DS)₂, copper bis(dodecanesulfonate) Cu(DS)₂, and nickel bis(dodecanesulfonate) Ni(DS)₂, were respectively prepared according to the procedures reported in previous literature.¹⁸

Aqueous-ionic liquid biphasic hydroxylation of benzene was carried out in a 100 ml round-bottomed flask equipped with a magnetic stirrer and thermometer. Catalyst (0.05 mmol) was dissolved in the ionic liquid (1.0 ml), then benzene (1.0 ml, 11.25 mmol) and H₂O (25.0 ml) containing 50 mM H₂SO₄ was further added. The mixture was vigorously stirred for 0.5 h at 50 °C, then an aqueous solution of hydrogen peroxide (30%, 1.2 ml, 11.25 mmol) was added. The resulting biphasic system was stirred for 6.0 h at 50 °C. At the end of the reaction, the resulting products and unreacted substrate were extracted from the aqueous and ionic liquid phases with ether (5 ml × 3). The extracted liquid mixture was analyzed on a Hewlett-Packard 6890/5793 GC-MS equipped with a HP 5MS column (30 m long, 0.25 mm i.d., 0.25 μm film thickness). The concentration of organic reactant and products was directly given by the GC/MS chemstation system according to the area of each chromatograph peak. The amount of residual hydrogen peroxide in the aqueous phase was determined by titration with potassium permanganate.

Results and discussion

Firstly, the catalytic activities of the dodecanesulfonate salts with Fe³⁺, Fe²⁺, Cu²⁺, Co²⁺ and Ni²⁺ cations were tested in an aqueous-OMImPF₆ biphasic system, and the results are summarized in Table 1. For all the catalysts used in this work, the only product detected by GC-MS after reaction was phenol, so the selectivities for phenol, based on benzene, were almost 100%. Beside moderately high conversion of benzene, high selectivity of H₂O₂ for benzene conversion was achieved, indicating that such an aqueous-ionic liquid biphasic reaction system for benzene hydroxylation was successfully established.

Table 1 Results of aqueous-ionic liquid biphasic catalytic oxidation of benzene to phenol

Entry	Ionic liquid (ml)	Catalyst (mmol)	Conversion of benzene (%)	Conversion of H ₂ O ₂ (%)	Selectivity of H ₂ O ₂ (%) ^a
1	OMImPF ₆ (1.0)	Fe(DS) ₃ (0.05)	54	60	90
2	OMImPF ₆ (1.0)	Fe(DS) ₂ (0.05)	49	56	88
3	OMImPF ₆ (1.0)	Co(DS) ₂ (0.05)	35	41	85
4	OMImPF ₆ (1.0)	Cu(DS) ₂ (0.05)	38	43	88
5	OMImPF ₆ (1.0)	Ni(DS) ₂ (0.05)	38	44	86
6	OMImPF ₆ (2.0)	Fe(DS) ₃ (0.05)	51	56	91
7	OMImPF ₆ (1.0)	Fe(DS) ₃ (0.04)	52	58	90
8	OMImPF ₆ (1.0)	Fe(DS) ₃ (0.02)	43	48	90
9	BMImPF ₆ (1.0)	Fe(DS) ₃ (0.05)	39	46	85
10	DMImPF ₆ (1.0)	Fe(DS) ₃ (0.05)	51	57	89
11	DMImBF ₄ (1.0)	Fe(DS) ₃ (0.05)	40	46	87
12	OMImBF ₄ (1.0)	Fe(DS) ₃ (0.05)	44	49	90
13	No ionic liquid	Fe(DS) ₃ (0.05)	16 ^b	21	76
14 ^c	OMImPF ₆ (1.0)	Fe(DS) ₃ (0.05)	45	52	87

^a (moles of converted benzene/moles of converted H₂O₂) × 100. ^b Selectivity of phenol based on benzene was 71%. ^c Reused at the 4th times.

Higher activity was observed with the catalyst Fe(DS)₃, and the results of entries 1 and 2 (Table 1) suggested that the chemical state of the iron cation had some impact on the catalytic performance.

The influence of the amounts of ionic liquid and catalyst used on the reaction was then tested, entries 6–8. When the volume of the ionic liquid used was increased from 1.0 to 2.0 ml, the conversions of benzene and H₂O₂ decreased from 54 and 60% to 51 and 56%, respectively, and the selectivity of H₂O₂ was almost unchanged. This may be attributed to different concentrations of benzene or catalysts between the water and ionic liquid, which is dependent upon the volume ratio of water and ionic liquid. If the amount of ionic liquid used was excessive, the benzene or catalyst concentration at the interface of the water and ionic liquid may be lower, thus resulting in a decreased reaction rate between benzene and H₂O₂ over the catalyst. As expected, the reaction rate was decreased with decreasing the amount of catalyst added.

It is well-known that the physicochemical properties of ionic liquids can be varied over a wide range through the selection of a suitable cation and anion.¹⁰ The performance of different ionic liquids in the hydroxylation of benzene was also investigated (entries 1, 9–12). Although a detailed mechanism is not clear at this stage, the experimental results showed that both the length of alkyl chains on the 1-alkyl-3-methylimidazolium cations and the anions had some effect on the conversion and selectivity, and the best results were obtained by using OMImPF₆ as an ionic liquid phase. OMImPF₆, OMImBF₄, DMImPF₆ and DMImBF₄ ionic liquids showed good solubility for the metal dodecanesulfonate salts and formed one phase with benzene, however, these metal dodecanesulfonate salts were only slightly soluble in BMImPF₆ and existed as suspended particles in BMImPF₆ and BMImPF₆ formed two phases with benzene, thus resulting in a poor catalytic performance.

If ionic liquid was not used, lower conversion and selectivity were obtained, entry 13, and some by-products such as hydroquinone and biphenyl were produced. This suggested that the aqueous-ionic liquid biphasic reaction system could not only enhance the selectivity for phenol, but also enhance the benzene conversion.

The possibility of recycling of the aqueous-ionic liquid catalyst system was also examined. After the oxidation products and unreacted substrate were extracted from the aqueous and ionic liquid phase with ether at the end of each reaction, the used aqueous-ionic liquid catalyst system was recharged with benzene and a certain amount of H₂O₂ according to the consumption of H₂O₂ during the previous reaction and the reaction was conducted once again. 45% of benzene conversion

Table 2 Results of aqueous–ionic liquid biphasic catalytic oxidation of toluene

Substrate (ml)	Ionic liquid (ml)	Catalyst (mmol)	Con. of toluene (%)	Product distribution
Toluene (1.0)	OMImPF ₆ (1.0)	Fe(DS) ₃ (0.05)	1	benzaldehyde 100%
Toluene (1.0) + benzene (0.02)	OMImPF ₆ (1.0)	Fe(DS) ₃ (0.05)	3	2-hydroxybenzaldehyde 15.7% <i>o</i> -hydroxytoluene 53.5%, <i>p</i> -hydroxytoluene 30.8%

was maintained after the aqueous–ionic liquid catalyst system was repeatedly used for 4 times. The partial decrease in catalytic activity may mainly be caused by slight leaching of the catalyst to the ether phase during each extraction of the product.

When the substrate was replaced with toluene, Table 2, only 1% toluene conversion was obtained and the resulting product was benzaldehyde with almost 100% selectivity, indicating that toluene as a substrate is much less active than benzene in this aqueous–ionic liquid biphasic reaction system and the active oxygen species have a radical character. Surprisingly, when the substrate was toluene, together with the presence of a small amount of benzene, the toluene conversion was enhanced greatly, and 2-hydroxybenzaldehyde (15.7%), *o*-hydroxytoluene (53.5%) and *p*-hydroxytoluene (30.8%) were produced, suggesting that benzene could promote the oxidation of toluene.

Conclusion

A highly selective and green aqueous–ionic liquid is a promising biphasic catalytic reaction system for direct oxidation of benzene to phenol with hydrogen peroxide as oxidant and a ferric dodecanesulfonate salt as catalysts, and was developed with excellent selectivity and enhanced conversion. In such an aqueous–ionic liquid biphasic catalytic reaction process, the use of volatile organic solvents was avoided. The molar ratio of benzene/hydrogen peroxide and catalyst/benzene could be as low as 1 and 0.002, respectively. The aqueous phase containing the desired product could be separated from the ionic liquid containing the catalyst by simple decantation. Recycling and further optimization of the aqueous–ionic liquid biphasic reaction system were possible.

Acknowledgement

This work was financially supported by National Natural Science Foundation of China (No.20225309).

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