COMMUNICATION

OBC
www.rsc.org/obc

The selective aerobic oxidation of methylaromatics to benzaldehydes using a unique combination of two heterogeneous catalysts

Fatemeh Rajabi,[a] James H Clark,*[b] Babak Karimi*[c,d] and Duncan J Macquarrie*[b]
[a] *Department of Chemistry, Sharif University of Technology, PO Box 11365-9516, Tehran, Iran*
[b] *Clean Technology Centre, Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK*
[c] *Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), PO Box 45195-1159, Gava Zang, Zanjan, Iran*
[d] *Institute for Fundamental Research (IPM), Farmanieh, PO Box 19395-553, Tehran, Iran*

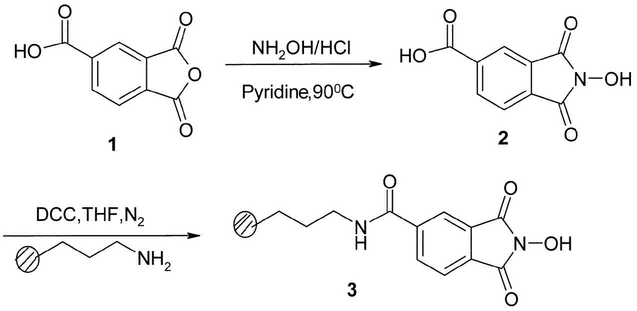
Received 24th December 2004, Accepted 24th December 2004
First published as an Advance Article on the web 21st January 2005

DOI: 10.1039/b419322a

A unique combination of a supported cobalt complex and the first example of supported NHPI in acetic acid gives a surprisingly stable heterogeneous catalytic system for the selective aerobic oxidation of methylaromatics to benzaldehydes at atmospheric pressure.

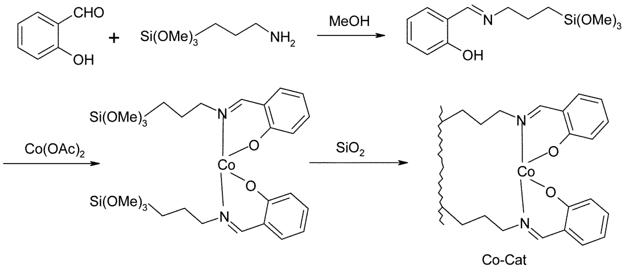
The selective oxidation of methylaromatics is an area of considerable industrial importance and academic interest.[1] Achieving this with only air as the source of oxygen is particularly challenging and environmentally desirable since it avoids the resource-inefficient use of stoichiometric oxidants and the consequential hazardous waste.[2] One of the more recent promising developments in this direction is the use of *N*-hydroxyphthalimide (NHPI) as an oxidation promoter typically alongside a cobalt(II) catalyst.[3] The NHPI has a marked effect on the rate of reactions including the oxidation of methylaromatics but the reactions are rarely selective, give benzoic acids as the major products[4] and the catalyst and promoter are not easily recoverable. We have previously reported cobalt(II) and other redox metal centres immobilised in chemically modified mesoporous silicas as catalysts for reactions including oxidations.[5,6] When used in their normal particulate form in conventional stirred tank reactions, they can easily be recovered (by filtration or decantation) thus simplifying the work-up and reducing waste. In an attempt to extend this logic to the promoter NHPI we have now prepared what we believe to be the first active form of immobilised NHPI also using a mesoporous silica support. More remarkably, these two solids act co-operatively yet also heterogeneously to enhance the rate of, and give excellent selectivity in, the aerial oxidations of methylaromatics when used in acetic acid – a medium which, due to its high polarity, would not normally be considered for supported reagent chemistry.

The supported NHPI is built up from aminopropylsilica (AMPS) which is prepared by our sol-gel method using a mixture of aminopropyl(trimethoxy)silane and tetraethoxysilane in aqueous acetonitrile using *n*-dodecylamine as the neutral templating agent.[7] The NHPI source is prepared by reacting 1,2,4-benzenetricarboxylic anhydride, **1**, (pretreated by refluxing in xylene with a Dean–Stark trap to convert any residual triacid to the anhydride) with $NH_2OH·HCl$ in pyridine to make the phthalimide, **2**.[8] A solution of this in dry THF is then reacted with the AMPS at room temperature to give the supported reagent, **3** (Scheme 1).



Scheme 1

The recovered solid is thoroughly washed with methanol, aqueous oxalic acid, aqueous $NaHCO_3$, water and finally hot methanol in a Soxhlet apparatus.[9] The material was characterised by ^{13}C MAS NMR and DRIFT spectroscopy (characteristic C=O stretching bond at 1710 cm^{-1}). Porosimetry gives a BET surface area of 241 $m^2\ g^{-1}$ and a pore volume of 0.458 $cm^3\ g^{-1}$ (the AMPS precursor shows 287 $m^2\ g^{-1}$ and 0.543 $cm^3\ g^{-1}$). Thermal analysis gives an organic loading of 0.75 mmol g^{-1}. The supported cobalt(II) catalyst is also built up from AMPS using the method we described previously[4] to give a silica–Schiff base–Co(II) complex (Scheme 2).



Scheme 2

We initially screened the activity of the supported NHPI using toluene as the substrate. Using an atmospheric pressure of oxygen, the best conditions proved to be supported Co(II) (0.25 mol%, 0.125 g), supported NHPI (5 mol%, 0.375 g) substrate (5 mmol) in AcOH (15 cm^3) in a baffled flask using a high shear mixer. This reproducibly gave benzaldehyde as the only detectable product (by GC). The yield and selectivity of any reaction in the absence of either of the supported reagents or the AcOH was significantly worse (the supported Co(II) alone gives small amounts of benzoic acid only while the use of MeCN at 80 °C gives only 5% benzaldehyde compared to 12% using AcOH under the same conditions). The product yield increased with increasing temperature up to 100 °C but higher temperatures led to a reduction in rate consistent with O_2 availability being or becoming rate limiting. The catalyst and promoter can be removed together from the reaction mixture by filtration and then washed with hot AcOH and reused with fresh substrate to give only a small reduction in the rate of reaction and no loss in selectivity (Table 1).

The reaction passed the 'hot filtration test' (*i.e.* the reaction stopped after the solids were removed from the hot mixture) and we were unable to detect cobalt in the reaction liquor. We

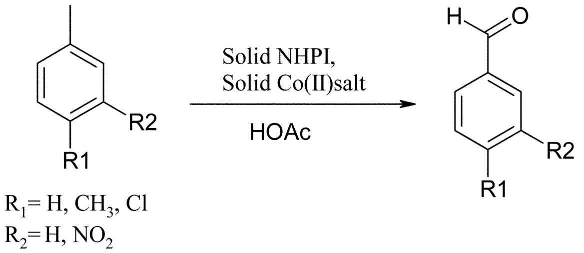
Table 1 Catalytic oxidation of alkylaromatics using supported NHPI and supported Co(II) in acetic acid at atmospheric pressure for 20 h

Substrate	Temp./°C	Isolated yield (%)
Toluene	25	0
	40	4
	60	7
	80	12
	80	10[a]
	100	18
o-Xylene	80	17
	100	22
	120	20
p-Chlorotoluene	80	8
	100	11
	120	10
m-Nitrotoluene	80	8
	100	10
	120	9

[a] Reuse experiment.

have extended the reaction to substituted toluenes – all reacted slowly at atmospheric pressure and with complete selectivity to the benzaldehydes (Scheme 3 and Table 1).

Thus, the use of a novel supported NHPI promoter in combination with a known supported Co(II) catalyst enables higher reactivity and unusual (and more valuable) selectivity, through the surprising use of acetic acid as the reaction medium. The reaction is not only genuinely heterogeneous and multiphasic, but involves communication between two solids!



Scheme 3

References

1 T. Mallat and A. Baiker, *Chem. Rev.*, 2004, **104**, 3037.
2 *Handbook of Green Chemistry and Technology*, ed. J. H. Clark and D. J. Macquarrie, Blackwell, Oxford, 2002.
3 (*a*) Y. Ishii, S. Sakaguchi and T. Iwahama, *Adv. Synth. Catal.*, 2001, **66**, 7889; (*b*) B. Karimi and J. Rajabi, *Org. Lett.*, 2004, **6**, 2841, and the references cited therein.
4 Y. Yoshino, Y. Hayashi, T. Iwahama, S. Sakaguchi and Y. Ishii, *J. Org. Chem.*, 1997, **62**, 6810.
5 I. C. Chisem, J. Rafelt, M. T. Shieh, J. Chisem, J. H. Clark, R. Jachuck, D. Macquarrie, C. Ramshaw and K. Scott, *Chem. Commun.*, 1998, 1949.
6 J. H. Clark, *Pure Appl. Chem.*, 2001, **73**, 103.
7 D. J. Macquarrie, *Chem. Commun.*, 1996, 1961.
8 N. Sawatari, T. Yokota, S. Sakaguchi and Y. Ishii, *J. Org. Chem.*, 2001, **66**, 7889.
9 D. Brunel, F. Fajula, J. B. Nagy, B. Deroide, M. J. Verhoef, L. Veum, J. A. Peters and H. V. Bekkum, *Appl. Catal.*, 2001, **213**, 73.