J. Chem. Research (S), 1999, 674–675†

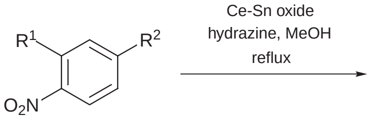
# Reduction of Aromatic Nitro Compounds with Hydrazine Hydrate over a $CeO_2-SnO_2$ Catalyst†

**T. M. Jyothi,*[a] R. Rajagopal,[a] K. Sreekumar,[b] M. B. Talawar,[c] S. Sugunan[b] and B. S. Rao*[a]**

[a] *National Chemical Laboratory, Pune-411 021, India*
[b] *Cochin University of Science & Technology, Cochin-682 022, India*
[c] *High Energy Materials Research Laboratory, Pune-411 021, India*

A $CeO_2$ (10%)-$SnO_2$ catalyst prepared by a co-precipitation method efficiently catalyses the transfer hydrogen reduction of a number of aromatic nitro compounds with hydrazine hydrate under mild conditions.

A wide variety of homogeneous as well as heterogeneous catalyst systems in combination with different hydrogen donors have been employed for selective functional group reductions.[1,2] Transfer hydrogenation requires only mild conditions, offers enhanced selectivity and closed pressure systems involving hazardous hydrogen can be avoided.[3] Reduction of aromatic nitro compounds to the corresponding amines is of immense industrial importance as they are widely used as intermediates for dyes, pharmaceuticals and agrochemicals. Joshi and Mukesh[4] have found that phosphomolybdic acid can efficiently catalyze reduction of nitroaromatics to amines under mild conditions.[4] Recently, Kumbhar *et al.*[5] have employed an $Fe_2O_3$–MgO catalyst, prepared from an Fe–Mg hydrotalcite precursor, for selective reduction of nitroaromatics.



1 2

**a** $R^1 = R^2 = H$
**b** $R^1 = H, R^2 = Me$
**c** $R^1 = Me, R^2 = H$
**d** $R^1 = H, R^2 = Cl$
**e** $R^1 = H, R^2 = OMe$
**f** $R^1 = H, R^2 = NO_2$
**g** $R^1 = H, R^2 = Ac$

**Scheme 1** Reduction of different aromatic nitro compounds with hydrazine hydrate over $CeO_2-SnO_2$ catalyst.

Cerium oxide containing catalysts are well known for their redox properties owing to possible electron transfer process *viz.* $Ce^{4+}$ to $Ce^{3+}$.[6] In the heteropoly acid catalyzed reduction of aromatics, Johnstone *et al.*[3] proposed from *in situ* IR, EPR, NMR and XPS studies, that $Mo^{5+}$ species formed by the reduction of $Mo^{6+}$ species are the active species which coordinate to the electron deficient nitro compounds. Here, we examine the use of a $CeO_2-SnO_2$ catalyst prepared by a coprecipitation method for the reduction of a number of nitroarenes employing hydrazine hydrate as a hydrogen donor.

The important physico-chemical characteristics of the catalyst are presented in Table 1. In the reduction of the nitro compounds no demethylation or dehalogenation was observed and C–Cl, C–$CH_3$ and C–$OCH_3$ bonds were unaffected by reduction. The versatility of this catalyst in this reaction is exemplified by the reduction of a number of aromatic substrates under mild conditions. Results are presented in Table 2. In the reduction of *p*-nitroacetophenone, the keto group is unaffected by reduction, the reaction yielding selectively *p*-aminoacetophenone. Interestingly, *p*-dinitrobenzene is regioselectively reduced to *p*-nitroaniline. The catalyst after filtration was washed several times with dichloromethane followed by thorough washing with distilled water, drying at 383 K and finally calcination in air, with the regenerated catalyst showing the same activity. However, recycling of the catalyst after each reaction did result in a decrease of nitrobenzene conversion.

The basicity as well as the redox properties of this catalyst system must be playing a significant role in this reaction.

In conclusion, we have found that $CeO_2-SnO_2$ is an efficient catalyst for the selective reduction of nitro compounds. Similar metal oxides could be used to effect selective transfer hydrogenation reactions.

## Experimental

*Preparation and Characterization of the Catalyst.*—10 g of $CeO_2$(10%)–$SnO_2$ catalyst was prepared by mixing 2.52 g of cerium nitrate, $Ce(NO_3)_3 \cdot 6H_2O$ and 20.93 g of $SnCl_2 \cdot 5H_2O$ in 150 ml deionised water, followed by adding 30 ml of 1 : 1 aqueous ammonia slowly with continuous stirring to a final pH of 10. The precipitate formed was washed several times with deionised water to remove chloride and nitrate anions. Finally the material was dried at 383 K for 12 h followed by powdering to a mesh size < 100 and calcination in air at 773 K for 6 h. The catalyst was characterized by energy dispersive X-ray analysis, X-ray diffraction, surface area analysis ($N_2$ adsorption), mercury porosimetry and acidity–basicity measurements.[7]

**Table 1** Physico-chemical characteristics of the $CeO_2-SnO_2$[a] catalyst

| | | | Acidity[b]/mmol $g^{-1}$ | | | Basicity[b]/mmol $g^{-1}$ | | |
|---|---|---|---|---|---|---|---|---|
| Surface area/$m^2$ $g^{-1}$ | Pore volume/$m^3$ $g^{-1}$ | XRD phase | W | M | S | W | M | S |
| 107.8 | 0.30 | $SnO_2$ | 0.3 | 0.12 | — | 0.08 | 0.14 | 0.41 |

[a] Catalyst activated at 773 K in air. [b] W, M and S indicate weak, medium and strong acid and basic sites, respectively.

*General Procedure for the Reduction of Different Aromatic Substrates with Hydrazine Hydrate.*—Reduction of different aromatic nitro compounds was carried out in a round bottomed flask fitted with a reflux condenser. In a typical procedure, 100 mg of the catalyst prepared by the above method was suspended in a mixture

---

* To receive any correspondence (*e-mail*: jyothi@cata.ncl.res.in).

† This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

**Table 2** Reduction of various aromatic nitro compounds using hydrazine hydrate as a hydrogen donor over $CeO_2$–$SnO_2$ catalyst[a]

| Substrate | Yield(%) | Mp of product (lit. value[d])/°C |
|---|---|---|
| Nitrobenzene | 100 | 184 (184)(bp) |
| *p*-Nitrotoluene | 92 | 39–44 (41–46) |
| *o*-Nitrotoluene | 85 | 127–131 (128–131) |
| *p*-Chloronitrobenzene | 96 | 69–71 (69–72) |
| *p*-Methoxynitrobenzene | 87 | 57–59 (57–60) |
| *p*-Dinitrobenzene | 85[b] | 146–149 (149–151) |
| *p*-Nitroacetophenone | 79[c] | 103–106 (105–107) |

[a] *Reaction conditions*: substrate = 500 mg, catalyst = 100 mg, methanol = 15 ml and hydrazine hydrate = 4 ml. [b] Mono amino compound (85%) and diamino compound (5%) are formed. [c] The keto group is unaffected. [d] *Dictionary of Organic Compounds,* Chapman & Hall, London, 6th edn., 1996, vol. 1–6.

of 500 mg of nitrobenzene and 15 ml methanol and heated to reflux. To this solution 4 ml of hydrazine hydrate was added dropwise for a period of 30 min. After 4 h, the catalyst was filtered off and the reaction mixture extracted with dichloromethane, and the products were isolated by column chromatography. Product identification was by $^1$H NMR and GC–MS. In some cases gas chromatography (Shimadzu I5A) fitted with a SE30 column and FID was used to measure the product yield.

*Received, 28th June 1999; Accepted, 4th August 1999*
*Paper E/9/05166J*

## References

1 J. R. Kosak, *Catalysis of Organic Reactions*, Marcel Dekker, Inc., New York, 1984.
2 R. L. Augustine, *Heterogeneous Catalysis for the Synthetic Chemist*, Marcel Dekker, Inc., New York, 1996.
3 R. A. W. Johnstone, A. H. Wilby and I.D. Entwistle, *Chem. Rev.*, 1985, **85**, 129.
4 M. V. Joshi and D. Mukesh, *J. Catal.*, 1997, **168**, 273.
5 P. S. Kumbhar, J. Sanchez Valente, J. Lopez and F. Figueras, *Chem. Commun.*, 1998, 535.
6 M. P. Rosynek, *Catal. Rev.-Sci. Eng.*, 1977, **16**, 111.
7 J. C. Wu, C. S. Chung, C. L. Ay and I. Wang, *J. Catal.*, 1984, **87**, 98.