Environmentally friendly hydrogenation of nitrobenzene to *p*-aminophenol using heterogeneous catalysts

Abhay Deshpande [a], F. Figueras [a,*], M. Lakshmi Kantam [b], K. Jeeva Ratnam [b], R. Sudarshan Reddy [b], N.S. Sekhar [b]

[a] *Institut de recherches sur la catalyse et l'environnement, 2 av. A. Einstein, 69626 Villeurbanne Cedex, France*
[b] *Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500 607, India*

ARTICLE INFO

ABSTRACT

Nitrobenzene was converted to *p*-aminophenol at 353 K, using water as solvent and a bi-functional catalyst composed of a mechanical mixture of supported Pt catalyst with zirconium sulphate calcined at 773–923 K. The performance of this system is independent of the support used for Pt, and various supports, such as pure or sulphated zirconia and titania, carbon, MgLa mixed oxide, give similar results. At low Pt content, the reaction rate is first order relative to nitrobenzene, and the slow step is the partial hydrogenation of nitrobenzene to phenylhydroxylamine, which requires only minute amounts of Pt. At higher Pt loadings, the rate of hydrogenation of nitrobenzene to phenylhydroxylamine and consequently to aniline takes over that of the acid-catalysed Bamberger rearrangement of phenylhydroxylamine to *p*-aminophenol. The selectivity of this step depends critically on the solid acid: strong acids such as sulphated zirconia or zeolites give poor selectivities because they tend to decompose the hydroxylamine intermediate. This process does not require sulphuric acid or additives such as DMSO or alkylsulphides, thereby simplifying the downstream processing.

1. Introduction

The selective catalytic hydrogenation of nitrobenzene (NB) to *p*-aminophenol (PAP) is a reaction of industrial importance since PAP is an important pharmaceutical intermediate for the manufacture of paracetamol, a widely used analgesic drug. Two-step processes have been reported for the preparation of PAP, in which nitrobenzene is first partially hydrogenated to phenylhydroxylamine (PHA), followed by the Bamberger rearrangement of PHA to PAP in acidic conditions. Platinum is considered as the best noble metal, and carbon the best support, for the hydrogenation of nitrocompounds [1]. Higher selectivity to PHA has been reported by the addition of sulphur compounds such as dimethylsulphoxide (DMSO) [2], sulphides [3], or basic additives such as pyridine [4], phosphines [5] or phosphates [6]. When basic additives are used, a two-step process has to be used for the synthesis of PAP, involving the isolation of PHA after the partial hydrogenation and addition of sulphuric acid after the hydrogenation step [7] to effect the rearrangement. Using DMSO or sulphides, the process can be converted to one pot synthesis. After 3 h of reaction, a 75% conversion of nitrobenzene has been reported with a PAP selectivity of 79% using 27 mL of concentrated sulphuric acid for 57 mL of nitrobenzene in 406 mL

of water [7]. The PAP thus formed needs to be isolated by neutralising the acid. This leads to the production of salts as effluents, with more complex separations. Most patents also report the addition of surfactants [8] which increase the area of contact between nitrobenzene and water, usually used as solvent.

A few attempts have been made to substitute sulphuric acid by a solid acid. For instance, Chaudhari et al. [9] reported the use of zeolites and acid resins for this reaction. The results were, however, disappointing since starting from 93.4 mmol of nitrobenzene, the conversion was 97% but the yield was only 14%. Very recently, a bi-functional Pt on highly acidic sulphated zirconia was used also with relatively poor results since the PAP yield was below 30% [10]. Indeed, the authors investigated the Bamberger rearrangement separately and observed selectivity lower than 45% at full conversion for this step, using highly acidic solid acids. It is important to note here that as reported by Groscova et al. [11] or Wang et al. [10], the Bamberger rearrangement can yield not only PAP but also aniline and azoxybenzenes. There is therefore an interest for processes, which would be highly selective towards PAP, would not produce salts as effluents, and could avoid complex separation, particularly of the additives required to promote selectivity.

It can be pointed out that this is a difficult task since the coupling of hydrogenation with acid-catalysed rearrangement is rather uncommon in organic synthesis. The formal reaction
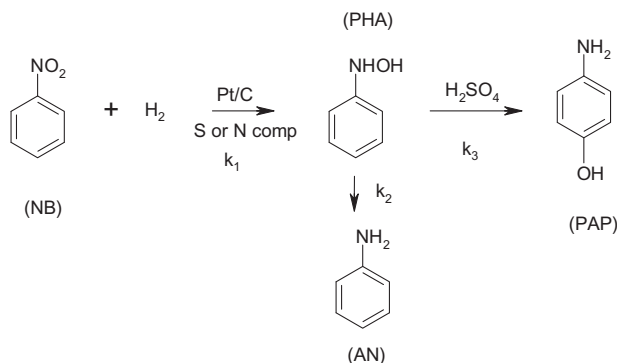
Scheme 1. Simplified reaction scheme.

scheme, reported in Scheme 1, has some common points with the bi-functional isomerisation of paraffins, with the major difference that in paraffin isomerisation, the concentration of the olefin intermediate is governed by the thermodynamic equilibrium of hydrogenation, while here all steps are controlled by kinetics. An obvious conclusion that can be drawn from Scheme 1 is that the rate of rearrangement of PHA to PAP (k_3) and that of the complete hydrogenation of PHA to aniline (AN) (k_2) are the critical factors in determining the selectivity towards the formation of PAP. Thus, for the catalyst system to be highly selective for PAP, k_3 needs to be substantially higher than k_2. On the other hand, AN would be the main product if k_2 is substantially higher than k_3.

We report here a novel reaction system, which permits the substitution of sulphuric acid and selectivity promotors and gives reasonable yields with high selectivity [12].

2. Experimental

2.1. Catalyst preparation

A series of sulphated zirconias were investigated. Two samples (reference numbers 922-1 and 999/1) were supplied by MEL Chemicals, UK, and one was supplied by Loba Chemie (Mumbai, India). These were sulphated with a 1 N solution of sulphuric acid. A laboratory-made zirconia was prepared by hydrolysis of $ZrOCl_2$ (Aldrich) at pH 10. This solid obtained after filtration was sulphated by treatment with a 1 N solution of sulphuric acid (15 mL 1 N sulphuric acid for 1 g zirconia, stirred 15 min), followed by drying at 393 K and calcination at 923 K with a ramp of 1–2 K/min (denoted as ZrSAD-1). The sample 999/1 was received in a sulphated form and used as such.

Another sulphated catalyst, ZrSAD-3, was prepared as follows. Forty-eight grams zirconyl chloride ($ZrOCl_2 \cdot xH_2O$, MW: 322.249) was dissolved in 375 mL water, and Zr hydroxide was precipitated at constant pH = 10 by adding ammonium hydroxide. The precipitate was aged at 353 K for 12 h after which it was separated by centrifugation and washed several times with hot water to remove the excess ammonia and chloride ions. The wet precipitate was transferred to a conical flask. A solution of 21 mL concentrated sulphuric acid in 150 mL water was prepared and added to the conical flask. The slurry was stirred for 1 h at room temperature. Within this time, most of the precipitate dissolved and a turbid solution was obtained. This solution was fed to a rotary evaporator, and water was evaporated at 353 K. At the end, a white precipitate appeared almost instantaneously. The precipitate was then transferred to a glass pan and dried overnight at 393 K. After drying, it was sieved and stored in a bottle. Before use, the sample was calcined at the desired temperature with a ramp of 1–2 K/min.

Table 1
Main characteristics of the acid catalysts.

Catalyst	Supplier	Calcination temperature (K)	Surface area ($m^2 g^{-1}$)	'S' content (wt%)
BEA (Si/Al = 22)	Zeolyst	723	720	–
ZrSAD-3	Home made	Uncalcined	2.7	17.8
ZrSAD-3	Home made	898	11	4.2
ZrSAD-3	Home made	923	15	4.3
ZrSAD-1	Home made	923	122	2.6
MEL-999/1	MEL	898	318	1.4
MEL-922/1	MEL	Uncalcined	309	–
Loba (sulphated)	Loba Chemie	898	20	0.4
Sulphated TiO_2	Home made	773	110	1.9

The zirconium sulphate (ZrSAD-3) was calcined in air at different temperatures between 823 and 923 K. The catalysts, Loba-S and MEL-999/1, were used after calcination in air at 898 K for 2 h. The final calcination temperature was obtained with a linear programming rate of 2 K/min. The BET surface areas and the sulphur contents of these solid acids are reported in Table 1.

Supported Pt catalysts were prepared using zirconia, sulphated zirconia, titania, or a MgLa mixed oxide as carrier. In this series of supports, zirconia and titania are amphoteric oxides, sulphated zirconia is a strong acid, and MgLa mixed oxide has been shown to be a strong solid base [13]. Using aqueous solutions of chloroplatinic acid on the oxide carriers and amine salt for sulphated carriers, 0.1–2% Pt was introduced by the method of impregnation at incipient dryness. After impregnation, the resulting solids were dried overnight at 383 K, calcined in air at 673 K, and finally reduced in H_2 flow at 523 K. A commercial 1% Pt/C was used as received.

2.2. Catalyst characterisation

The structures of the catalysts were checked by powder X-Ray diffraction using a Bruker D5005 instrument. The S content was determined at SCA (Service central de micro analyse du CNRS, Solaise) by infrared spectroscopy analysis of the gases evolved upon oxidation at 1623 K in oxygen. The surface properties of the solid acids were characterised by measuring their surface area and acidity. The surface area was determined from the adsorption isotherm of nitrogen at 77 K on samples activated in N_2 flow for 2 h at 523 K. The acid properties were determined by adsorption of NH_3 at 353 K, using microcalorimetry coupled with volumetry. The solid taken in a sample cell was first evacuated up to 10^{-5} torr at 673 K, then transferred to a Tian–Calvet microcalorimeter. Small increments of NH_3 were then introduced into the cell, and differential heat of adsorption was measured. The differential heat represents the strength of the ammonia interaction with the surface, therefore the acid strength, whereas the amount of NH_3 measures the number of acid sites. The dispersion of Pt on zirconia was estimated from electron micrographs obtained by TEM, using a JEOL 2010 LaB6 instrument, and carbon replicas. The resolution of the apparatus is 0.19 nm and permits the detection of particles 0.5 nm in size. The distribution of particles size was obtained from the micrographs taken from different zones of the sample. A surface average size was calculated from this distribution using the formula $d = \Sigma n_i d_i^3 / \Sigma n_i d_i^2$.

2.3. Catalytic reaction

The hydrogenation of nitrobenzene to *p*-aminophenol was investigated in a 100 mL autoclave from Autoclave Engineers, filled