

Hydrogenation of nitrobenzene to 4-aminophenol in a fully reusable solvent system, by using Pt, Rh, Pd supported on carbon-CF₃COOH catalytic system.

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Introduction

4-Aminophenol is an important raw material for several products in the field of dyes, photographs and pharmaceuticals. For instance, paracetamol (N-acetyl-4-aminophenol) a widely employed analgesic and antipyretic whose production is in continuous growth specially in the far east region. Industrial synthesis of paracetamol is based mainly on 4-aminophenol, which is obtained by three different routes: i) nucleophilic substitution of the Cl of the 4-chloronitrobenzene, ii) reduction of 4-nitro-phenol, iii) selective hydrogenation of nitrobenzene [1]. The selective hydrogenation of nitrobenzene is however, the most convenient from both economical and environmental point of view [1, 2]. The major concern of this process is, however, the presence of H₂SO₄, which is origin of corrosion, safety, environmental and separation problems. The reaction is typically carried out in CSTR in which the biphasic reaction medium is used to accomplish simultaneously the Pt catalyzed hydrogenation of nitrobenzene and the acid catalyzed Bamberger rearrangement of the intermediate N-phenylhydroxylamine. From environmental point of view, the major drawback of the process is the neutralization of the acidic phase, with the consequent by-production of sulfate salts, which are undesired wastes. Starting from recent results obtained in the Beckmann rearrangement of the cyclohexanone oxime in CH₃CN-CF₃COOH system [3], here we show some findings on the hydrogenation of nitrobenzene to 4-aminophenol in a single liquid phase CH₃CN-H₂O-CF₃COOH and in the presence a hydrogenation catalyst. The easy of recovery of solvent and catalysts allows to develop a greener process than that based on the biphasic H₂SO₄-nitrobenzene system

Experimental

The kinetic runs were performed in a well stirred glass reactor thermostatted by circulation bath in the range 323-353 K, containing CH₃CN-H₂O as a solvent, CF₃COOH as an acid catalyst and Pt/C as the hydrogenation catalyst. Hydrogen is fed continuously and maintained constant pressure (*c.a.* 121 kPa) by gum balloon. Small amounts of the solution were drawn at different times and the samples, were analyzed by HPLC using a Perkin Elmer apparatus equipped with a C-8 column with CH₃CN-H₂O as mobile phase.

Results and discussion

Figure 1 shows a typical time concentration profile, of the nitrobenzene hydrogenation to 4-aminophenol catalyzed by Pt/C-CF₃COOH. It can be seen that selectivity in aniline is lower at the initial time of the reaction thus increasing smoothly. In Table 1 the comparison of Pt/C Pd/C and Rh/C are reported. It is noteworthy that the best system is Pt/C-CF₃COOH since the higher yield in 4-aminophenol is achieved. However either Rh/C or Pd/C are able to give 4-

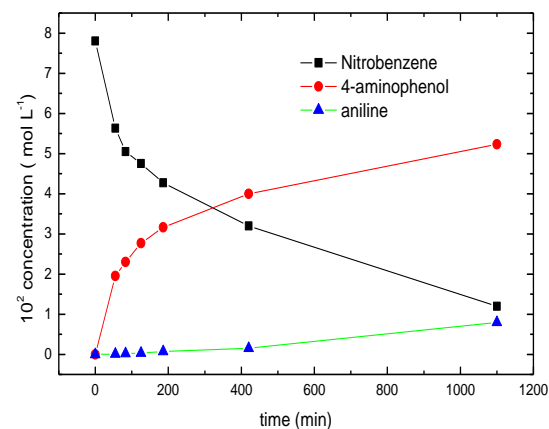


Figure 1. Time concentration profile of nitrobenzene hydrogenation to 4-aminophenol. Run conditions: T 353 K, CH₃CN 22 g, H₂O 2 g, CF₃COOH 0.6 g Pt/C 3% 0.05g.

Table 1. Comparison of activity and selectivity of different hydrogenation catalyst.

Catalyst	Conversion (%)	Yield PAP (%)	Yield AN (%)	Yield other (%)	r ₀ (mol L ⁻¹ min ⁻¹ g _{met} ⁻¹)
Pt/C 3%	41	33	2	6	0.133
Pd/C 5%	42	14	26	1	0.78
Rh/C 5%	46	16	29	1	0.80

PAP = 4-aminophenol, AN = aniline.

References

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2. S. K. Tanielyan, J. J. Nair, N. Marin, G. Alvez, R. J. McNair, D. Wang, R. L. Augustine, *Org. Process Res. Dev.* **11**, 681 (2008).
3. L. Ronchin, A. Vavasori, *J. Mol. Catal. A: Chemical* **313**, 22 (2009).

activity of Pt/C catalyst, is higher than that of the other catalyst. The influence of the operative variables, and of the intermediates concentration shows that the key step is the rearrangement of the phenylhydroxylamine. In addition, the increase of the temperature favors the yield towards 4-aminophenol.