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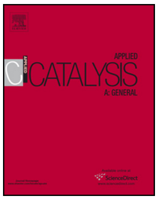

New insight on the mechanism of the catalytic hydrogenation of nitrobenzene to 4-aminophenol in $CH_3CN–H_2O–CF_3COOH$ as a reusable solvent system. Hydrogenation of nitrobenzene catalyzed by precious metals supported on carbon

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Paper dedicated to Prof. Luigi Toniolo for celebrating his long research and teaching activity in the field of Catalysis and Industrial Chemistry after his mandatory retirement.

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ABSTRACT

The preparation of 4-aminophenol via hydrogenation of nitrobenzene in a single liquid phase has been carried in the presence of different precious metal catalysts. The liquid phase is composed of $CH_3CN–H_2O–CF_3COOH$, which can be easily distilled at low temperature, thus avoiding work-up operation. The yield of 4-aminophenol is in the range 45% and in the presence of sulfolane as promoter reaches almost 50%. The best result has been obtained in the presence of Pt/C as hydrogenation catalyst. The role of the solvent is strictly related to the selectivity to 4-aminophenol, since CH_3CN decreases the hydrogenation activity compared to other solvent, CF_3COOH promotes the formation of the desired product both via Bamberger rearrangement in solution as well by a surface catalyzed reaction, while H_2O is responsible for 4-aminophenol formation in both reactions. Even though, nitrosobenzene and phenylhydroxylamine have not been observed, their reactivity suggest a complex pattern of reactions occurring either on the catalyst surface or in the solution. Indeed, formation of 4-aminophenol may occur both in solution, via acid catalyzed Bamberger rearrangement and on the catalyst surface by the formation of a surface Pt-nitrenium complex, which undergoes surface nucleophilic attack by H_2O.

1. Introduction

4-Aminophenol is an important raw material for several products in the field of dyes, polymer and pharmaceutics [1–3]. For instance, paracetamol (*N*-acetyl-4-aminophenol) is a widely employed analgesic and antipyretic whose production is in continuous growth, particularly in the Far East region [4–9]. Industrial synthesis of paracetamol is based on 4-aminophenol, which is obtained through four different routes: (i) nucleophilic substitution of the chlorine of the 4-chloronitrobenzene, (ii) reduction of 4-nitro-phenol, (iii) selective hydrogenation of nitrobenzene, (iv) Beckmann rearrangement of 4-hydroxyacetophenone oxime.

Till now, the selective hydrogenation of nitrobenzene is likely to be the most convenient from both economical and environmental point of view [1,2,4–9]. The major concern of this process is, however, the use of H_2SO_4, which poses corrosion, safety, purification and environmental problems. The reaction is carried out in continuous stirred tank reactor 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 (see Scheme 1) [4–6,8,9]. The aqueous solution of H_2SO_4 is the key for obtaining high selectivity to the 4-aminophenol. The success is due to the easy protonation of the phenylhydroxylamine ($pk_a = 1.9$ [10]), which is extracted from the organic phase. In the acid solution (H_2SO_4 concentration 0.6–1 mol L^{-1}), the sulfate of the *N*-phenylhydroxylamine is formed and it undergoes fast rearrangement to the corresponding 4-aminophenol salt [11]. Moreover, in aqueous phase, the competitive hydrogenation of the phenylhydroxylamine is negligible, being the hydrogenation catalyst hydrophobic. In fact, only the fraction present in the organic phase is hydrogenated to aniline [12].

From an 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 low values products and/or wastes. In addition, diluted sulfuric acid causes huge corrosion concern, with the consequent increased costs [1,2,4–6,8,9].

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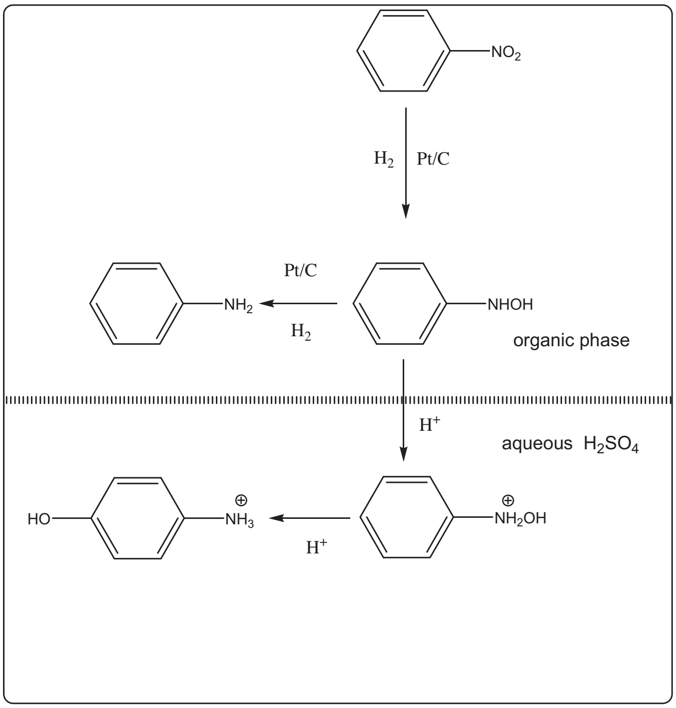

Scheme 1. Hydrogenation of nitrobenzene in biphasic liquid system.

Therefore, removal of H_2SO_4 use is likely to be the most important target for the improvement of the process. Several researchers have recently proposed the use of a biphasic liquid system (water-nitrobenzene) employing Pt supported on solid acid in the presence of surfactant and promoters, which, however, cause problems in the recycle and/or disposal of the aqueous phase [13–15].

Besides, gas phase reaction catalyzed by bifunctional Pt-zeolites catalysts has been proposed. The yields to the 4-aminophenol are interesting for practical purposes, however extensive catalyst deactivation limits its synthetic utility [16].

Starting from these considerations, a single liquid phase process could be a catwalk to a more sustainable process by using easily reusable solvents and catalysts [17–20]. When products are solids or high boiling point liquids the use of a much lower boiling point solvent can be the key to improve the environmental sustainability of the whole process, because of products separation, catalyst and solvents reuse is made easy by filtration and evaporation. In this way, the high cost of CF_3COOH is counter balanced by its recycling, making the process sustainable also from an economical point of view.

The bases of the present research are the results in the Beckmann rearrangement of ketoximes to the corresponding amides in $CH_3CN–CF_3COOH$ as solvent catalytic system [17–20]. The analogy between the Beckmann rearrangement with the process to 4-aminophenol via nitrobenzene hydrogenation originates from the idea that the *N*-phenylhydroxylamine (the intermediate of the process) (see Scheme 1) may undergo acid Bamberger rearrangement very easily in non-aqueous CF_3COOH system.

The rearrangement is well known from long time and the commonly accepted mechanism is via nitrenium ion intermediate followed by nucleophilic attack of a water molecule (Scheme 2) [11,21,22].

Several solvents can be used for the hydrogenation reaction, but those to be considered in this research possess low nucleophilicity in order to avoid side reaction in the Bamberger rearrangement [21,22]. In addition, suitable solvents (for instance CH_3CN and $(CH_3)_2SO$) have to lower the hydrogenation activity of the precious metal catalyst in order to depress the reduction of *N*-phenylhydroxylamine to aniline [23].

Here, we present some new results on the hydrogenation of nitrobenzene to 4-aminophenol in a single liquid phase composed of solvent-$H_2O–CF_3COOH$ and in the presence a precious metal hydrogenation catalyst. Furthermore, we propose a reaction path, which allows an explanation for the several features of this reaction.

2. Experimental

2.1. Materials

Nitrobenzene, aniline, 4-aminophenol, 2-aminophenol, trifluoroacetic acid, sulfolane were all Aldrich products, their purity were checked by the usual methods (melting point, TLC, HPLC, GC and GC–MS) and employed without any purification, acetonitrile HPLC gradient grade was supplied by BDH, 1,4-dioxane, methanol, nitromethane, dimethylformamide and dimethyl sulfoxide are ACS reagent supplied by Aldrich.

Catalysts used were commercial materials supplied by Engelhard (now Basf Catalysts): Pd/C 5%: Escat 10, Pt/C 3%, Ru/C 5% Escat 40 and Rh/C 5%.

2.2. Equipment

Products were identified by gas chromatography (GC), gas chromatography coupled mass spectrometry (GC–MS) and high performance liquid chromatography (HPLC). GC and GC–MS analysis were carried out with a Agilent 7890A equipped with FID or MS detector (Agilent 5975 C and a HP 5 column (I.D. 320 μm 30 m long), helium was employed as carrier under the following conditions: injector 523 K, detector 543 K, flow 1 mL min^{-1}, oven 333 K for 3 min 523 K 15 K min^{-1} and 523 K for 15 min. Due to the thermal instability of the products, routine analysis were carried out by HPLC (PerkinElmer 250 pump, LC 235 diode array detector and a C 8, 5 μm, 4 mm i.d. 25 cm long column) analysis were carried out with $CH_3CN–H_2O$ as mobile phase in isocratic 70% of CH_3CN at 1 mL min^{-1}. Conversion yield and selectivity are calculated by the calibration with standard solutions of the pure products. N_2 physisorption and CO chemisorption has been carried out with a Micromeritics ASAP 2010C automatic adsorption analyzer.

2.3. Catalyst characterization

Chemisorption of carbon monoxide was carried at 308 K with the double isotherm method and 1 min of equilibration time [24]. The chemisorption stoichiometry was set 1 (1 molecule of CO for 1 surface atom of metal) only for comparative purpose. Before the analysis, the catalyst was pretreated in a flow of hydrogen (20 mL min^{-1}) at 473 K for 3 h and for 5 h under vacuum at the same temperature in order to ensure total reduction of the precious metal particles average diameter of catalyst particles (40 μm) and apparent density (0.54 g mL^{-1}) were given by the supplier and are the same for all the catalysts (see Table 1).

2.4. Hydrogenation of nitrobenzene

Some preliminary reactions have been carried out in several solvents (1,4-dioxane CH_3NO_2, $(CH_3)_2NCHO$ and $(CH_3)_2SO$ CH_3OH). The kinetic runs were carried out in a well stirred glass reactor thermostatted by circulation bath in the range 323–353 K, using $CH_3CN–H_2O$ as a solvent, CF_3COOH as an acid catalyst and a precious metal catalyst (Pt, Pd, Rh, Ru) supported on carbon. Hydrogen was fed continuously at constant pressure (*c.a.* 0.12 MPa) by a gum balloon (see supplementary information). Blank reactions in the absence of nitrobenzene have been carried out in order to verify