Journal of Molecular Catalysis A: Chemical 106 (1996) 235–240

Catalytic hydrogenation of aniline in aqueous media

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Received 26 April 1995; accepted 27 September 1995

Abstract

The catalytic hydrogenation of aniline in aqueous media of different acidities was studied. A platinum catalyst supported on graphite was used. The composition of aniline solutions was determined by UV spectroscopy. The characterization of platinum surface and of adsorbed species was performed by cyclic voltammetry. Aniline can be hydrogenated in acid medium, whereas in neutral conditions it acts as a poison. During the hydrogenation of nitrobenzene, the hydrogenation of benzene nucleus is possible in acid medium after a complete conversion of nitrobenzene into aniline.

Keywords: Platinum; Aniline; Nitrobenzene; Hydrogenation

1. Introduction

Although the catalytic hydrogenation of the benzene nucleus is largely studied in the literature, there are few studies concerning the hydrogenation of aniline [1–5]. Generally, in mild conditions, cyclohexylamine is the major product and dicyclohexylamine is formed as a by-product [2–4]. Cyclohexylamine is used as an intermediate for a variety of amine derivatives and also as a sweetening agent, while the dicyclohexylamine is employed in the extraction of natural products and in the medical field.

Different supported metals (platinum, rhodium, ruthenium or palladium) are used as catalysts [1–5], in gas phase or in solution reactions. During the catalytic hydrogenation of nitrobenzene, it was observed that it is possible, under favorable conditions, to obtain further hydrogenation of the aniline produced.

However, the role of experimental conditions (such as the composition of the medium, acidity, temperature) needs to be further investigated, since in some cases no hydrogenation occurs and aniline behaves as a poison [2,3]. This observation led us to carry out a study of the catalytic hydrogenation of aniline, in aqueous media of different acidities, under mild conditions (low temperature and low hydrogen pressure), with platinum catalysts supported on graphite.

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SSDI 1381-1169(95)00267-7

2. Experimental

The platinum catalyst was prepared by impregnation of pure granular graphite (E.G. Carbone Lorraine) with an aqueous solution of chloroplatinic acid and reduction at 573 K. The graphite support was pretreated in an hydrogen stream at 1273 K and in the air at 573 K [6].

The obtained 5% Pt/graphite catalyst was characterized in situ by cyclic voltammetry [6,7] in a glass cell described in previous publications [6,7]. This cell, used also as reactor for the hydrogenation reaction, has five holes allowing to introduce three electrodes (working, counter an reference electrodes) and also the inlet and outlet of gases (N_2 or H_2).

The granular Pt/graphite catalyst was deposited on a glass frit; it was stirred and maintained in suspension, during hydrogenation reaction by a counter current hydrogen flow.

The hydrogenation experiments were carried out in an aqueous solution of different acidities (by a mixture of H_2SO_4 and K_2SO_4), with small aniline concentrations (5×10^{-3} M), $pH_2 = 1$ atm, and generally at 299 K.

The progress of the reaction was followed by HPLC (Waters 486) using a Bondapak C18 column, with a 50:50 MeOH–H_2O eluent and an UV detector, allowing the detection of benzene compounds. In order to analyze the reaction products, in some experiments, gas chromatography was used (with a SE 30 column, 7 ft.) after a continuous extraction with ether.

3. Results

3.1. Consecutive hydrogenation reactions of nitrobenzene

The hydrogenation of nitrobenzene, catalysed by 5% Pt/graphite catalysts, was first studied, in mild conditions (299 K, $pH_2 = 1$ atm) and in aqueous solutions of different acidities.

During these experiments, it was observed that the maximum selectivity in aniline is equal to 100% in a neutral K_2SO_4 solution (pH = 6), while it is equal to about 30% in an acid solution (0.5 M H_2SO_4, pH = 0.5), even when the intermediate product (the phenylhydroxylamine), is completely hydrogenated (Table 1, Figs. 1 and 2).

This last result can be explained by a further hydrogenation of the aniline, which can undergo an hydrogenation of the benzene nucleus, as is obvious from Figs. 1 and 2.

Indeed, the comparison between these two figures shows that in an acid solution there is a decrease of the formed aniline after the nitrobenzene has been completely consumed in the solution, (Fig. 1) when in a neutral solution the produced aniline is not further transformed (Fig. 2).

3.2. Hydrogenation of aniline as a function of the acidity of the solution

The obtained results during the hydrogenation of nitrobenzene led us to a detailed study of

Table 1
effect of acidity on the activity and selectivity of platinum catalysts (5% Pt/graphite), in consecutive hydrogenation reactions of nitrobenzene

Medium	pH	Initial selectivity (%) of		Maximum selectivity of aniline (%)	$a(\Phi NO_2)$ [a]	$a(\Phi NH_2)$ [b]
		Aniline	Phenyl hydroxylamine			
H_2SO_4 0.5 M	0.5	27	73	30	$2 \cdot 10^{-8}$	$1.35 \cdot 10^{-9}$
K_2SO_4 0.25 M	6	67	32	100	$1.5 \cdot 10^{-8}$	0

[a] Activity in hydrogenation of nitrobenzene (mol/min/cm^2).

[b] Activity in hydrogenation of aniline (mol/min/cm^2).

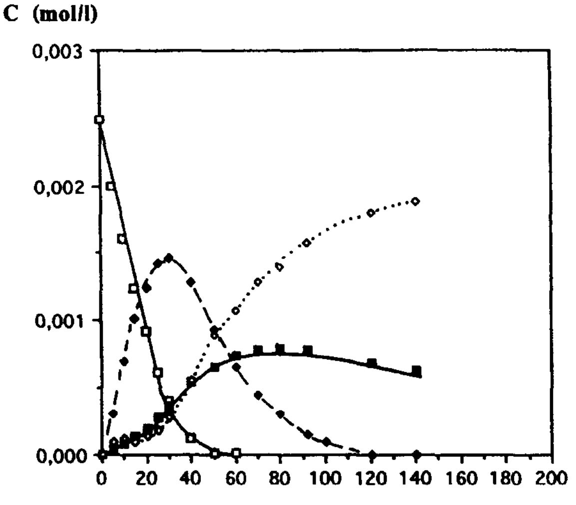

Fig. 1. Evolution of concentration as a function of time in acid aqueous phase catalytic hydrogenation of nitrobenzene (solvent: 0.5 M H_2SO_4, 299 K, $pH_2 = 1$ atm, $C_{\mathrm{nitrobenzene}} = 2.5 \times 10^{-3}$ mol/l). ■ nitrobenzene (mol/l); ◆ phenylhydroxylamine (mol/l); □ aniline (mol/l); ◇ cyclohexylamine + dicyclohexylamine.

the hydrogenation of aniline in different solutions, composed by 0.25 M $K_2SO_4 + x$ M H_2SO_4 (with x equal to 0.5 M, 5×10^{-2} M, 10^{-2} M, 5×10^{-3} M, 5×10^{-4} M, 2×10^{-4} M and 0 M) corresponding to different pH.

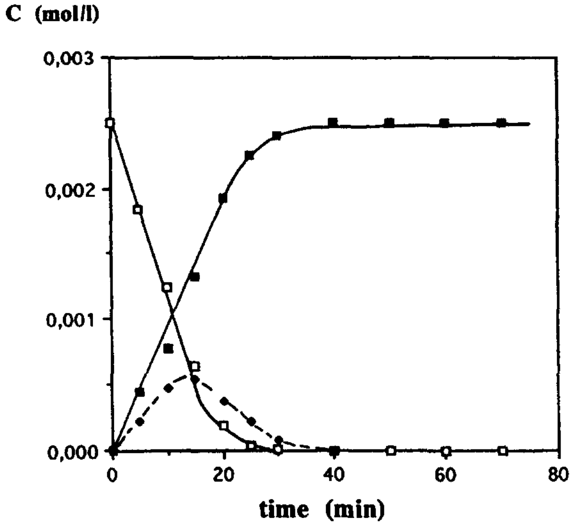

Fig. 2. Evolution of concentration as a function of time in neutral aqueous phase catalytic hydrogenation of nitrobenzene (solvent: 0.25 M K_2SO_4, 299 K, $pH_2 = 1$ atm, $C_{\mathrm{nitrobenzene}} = 2.5 \times 10^{-3}$ mol/l). ■ nitrobenzene (mol/l); ◆ phenylhydroxylamine (mol/l); □ aniline (mol/l).

As a preliminary study, a more concentrated aniline solution (5×10^{-2} M) was hydrogenated (at a pH = 3, at 299 K and $pH_2 = 1$ atm) in order to identify the obtained products.

The obtained mixture of products, after a conversion of 25% and a continuous extraction with ether, under a nitrogen stream, was analyzed by gas phase chromatography (column SE 30, eluent 1.2 bar He, 7 ft., temperature 398 K).

The obtained products were cyclohexylamine (yield 80%) and dicyclohexylamine (yield 20%), in agreement with the literature [2]. The catalytic activity of Pt/graphite decreases with increasing pH, following the curve presented in Fig. 3. Taking into account the value of the pK_a of aniline (pK_a = 4.6), the obtained curve could be explained, in a first approximation, by the presence of two forms of aniline, the protonated from, (ΦNH_3+), which should be active in hydrogenation, and the neutral form, (ΦNH_2), which should be inactive and/or toxic.

Indeed, as indicated in the literature [8], aniline in its neutral form, can act, by the free electron pair in the valency shell ($:NH_2\Phi$), as a poison, in opposition to the anilinium form which is not toxic.

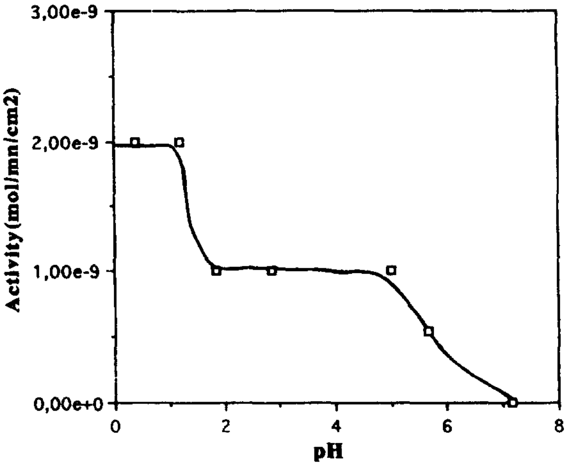

Fig. 3. Catalytic activity of platinum in liquid phase hydrogenation of aniline at different pH of $H_2SO_4 + K_2SO_4$ solution (299 K, $pH_2 = 1$ atm, $C_{\mathrm{aniline}} = 2.5 \times 10^{-3}$ mol/l).

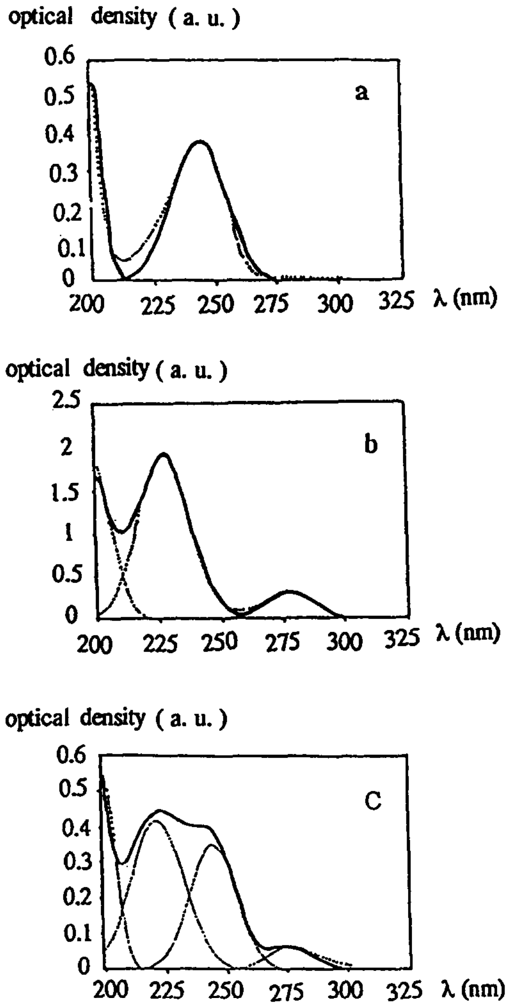

Fig. 4. UV spectra of aniline ($C = 2.5 \times 10^{-3}$ mol/l) in aqueous solutions of different pH: (a) 0.5 M H_2SO_4 (pH = 0.5), (b) 0.25 M K_2SO_4 (pH = 7), and (c) 5×10^{-3} M H_2SO_4 + 0.25 M K_2SO_4 (pH = 3).

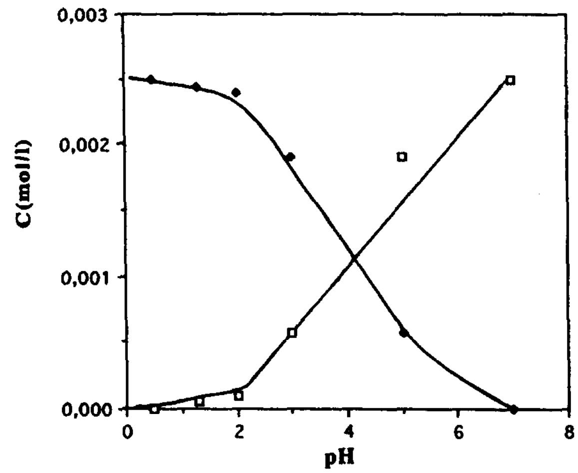

Fig. 5. Evolution of concentration of aniline (ΦNH_2) and of anilinium (ΦNH_3^+) as a function of the pH of the solution (x M H_2SO_4 + 0.25 M K_2SO_4). □ aniline (mol/l); ◆ anilinium (mol/l).

3.3. Composition of the solution of aniline as a function of the acidity

In order to evaluate the composition of a solution of aniline ($C = 2.5 \times 10^{-3}$ M) at different pH, the UV spectra were recorded.

The spectrum of anilinium, recorded in an acid solution (pH = 0.5), displays UV bands at 254 nm (B band) and 203 nm (E2 band), while that of aniline (pH = 6) has bands at 230 nm (E2 band) and 280 nm (B band) (Fig. 4 a,b). The spectra recorded at intermediate values of pH present features of both acid and neutral solution (Fig. 4c). It is possible to calculate the

Table 2

Concentration of aniline and of anilinium in aqueous $2.5 \cdot 10^{-3}$ M solutions of different pH

pH	Experimental concentration [a] (mol/l)		Theoretical concentration [b] (mol/l)	
	aniline	anilinium	aniline	anilinium
0.5	0	$2.5 \cdot 10^{-3}$	$1 \cdot 10^{-6}$	$2.5 \cdot 10^{-3}$
1.3	$5.5 \cdot 10^{-5}$	$2.4 \cdot 10^{-3}$	$1 \cdot 10^{-6}$	$2.5 \cdot 10^{-3}$
2	$9.5 \cdot 10^{-5}$	$2.4 \cdot 10^{-3}$	$1 \cdot 10^{-5}$	$2.5 \cdot 10^{-3}$
3	$5.8 \cdot 10^{-4}$	$1.9 \cdot 10^{-3}$	$6 \cdot 10^{-5}$	$2.44 \cdot 10^{-3}$
5	$1.9 \cdot 10^{-3}$	$5.8 \cdot 10^{-4}$	$1.8 \cdot 10^{-3}$	$7 \cdot 10^{-4}$
7	$2.5 \cdot 10^{-3}$	0	$2.5 \cdot 10^{-3}$	$1 \cdot 10^{-5}$

[a] Determined by UV spectroscopy.

[b] Determined from pK_a.

composition of different aniline solutions at different pH, by deconvolution and measure of the heights of the two characteristic bands at 254 nm and at 230 nm, taking as reference for the anilinium the first one obtained in a solution of pH = 0.5, and for the aniline the second one obtained in a solution of pH = 6 (Table 2, Fig. 5). The obtained values of aniline and anilinium, at different pH, are quite similar to those calculated on the basis of the pK_a of this couple (Table 2). Some discrepancies found at pH equal to 2 and 3 can be due to the deconvolution of peaks (Fig. 4c).

The comparison of Figs. 3 and 5 shows, however, that it is not possible to explain the decrease of the activity at increasing pH only by the decrease of the concentration of ΦNH_3^+ (which is the active species), or by the increase of aniline concentration (which is the toxic species), but probably by the occurrence of these two opposite effects. In order to explain the important decrease of activity in pH 2 and 3 (Fig. 3) it is necessary to assume that the toxicity of a 10^{-4} M ΦNH_2 solution (in the neutral form) is at least as important as the toxicity of a 6×10^{-4} M aniline solution. Indeed, this assumption could be possible, because the benzene compounds with large adsorbabilities can induce saturation coverages at very low concentrations [9,10].

The coverage degrees of platinum by ΦNH_3^+ and by ΦNH_2 were measured in acid (pH = 0.5) and basic (pH = 13) media, respectively, by electrochemical techniques [11]. A basic solution was chosen instead of a neutral one, because the cyclic voltammogram of platinum is not well defined in this medium. The obtained isotherms follow a Langmuir law (Fig. 6 a,b), allowing to obtain the Gibbs free energy of adsorption. This parameter is equal to −29 $kJ \cdot mol^{-1}$ for the acid form (ΦNH_3^+) and −42 $kJ \cdot mol^{-1}$ for the neutral aniline form, indicating that the last one is more strongly adsorbed than the anilinium form. In a first approximation, aniline is 100-fold more strongly bonded than anilinium. This means that for pH values between 0.5 and 3 the ratio of surface coverages between anilinium and aniline, $(\lambda \cdot C)_{anilinium}/(\lambda \cdot C)_{aniline}$, would vary by a factor of about 60; such a large decrease of activity would have also been expected, but in fact the obtained plateau of activity (around pH = 3) is situated at a value half of the initial one at pH = 0.5. Therefore, the stronger adsorption of

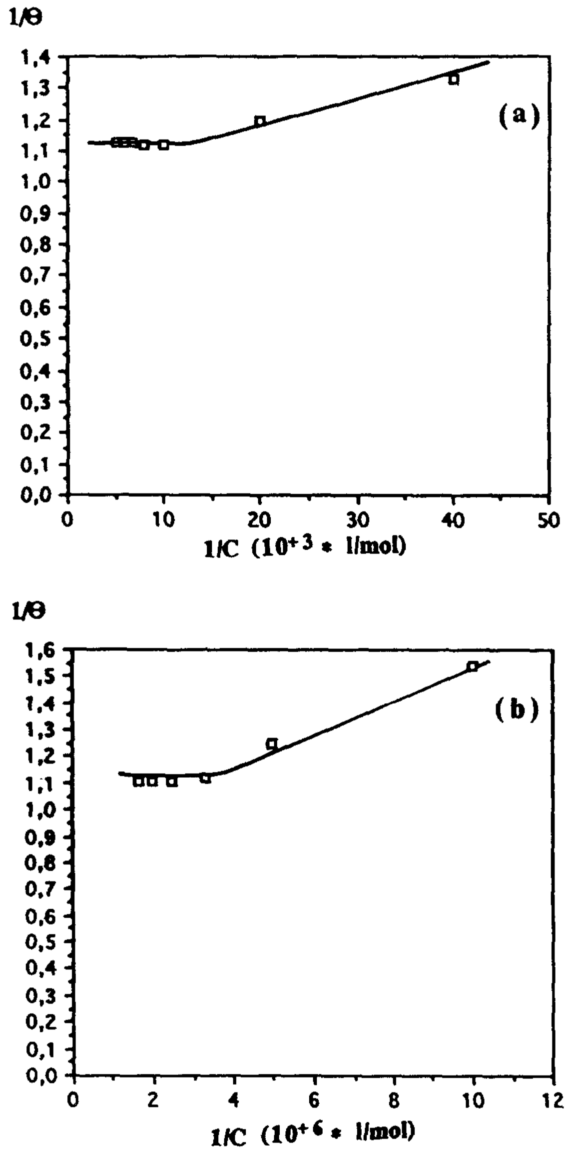

Fig. 6. Langmuir adsorption isotherm of aniline at 299 K: (a) in acid medium (0.5 M H_2SO_4) and (b) in basic medium (0.1 M NaOH).

aniline in comparison to that of anilinium can account only qualitatively for this result.

Otherwise, it could be explained by a displacement of the equilibrium protonation reaction [1]:

$$\Phi NH_2 + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \Phi NH_3^+$$

caused by the consumption of the active species ΦNH_3^+ following the reaction [2]:

$$\Phi NH_{3,ads}^+ + H_{ads} \xrightarrow[k_2]{} \text{hydrogenation products}$$

when $k_2 \gg k_{-1}$.

4. Conclusion

The obtained results prove clearly that the aniline can be hydrogenated only in acid media ($0 < pH < 5$), in its protonated form of anilinium, ΦNH_3^+. The neutral form ΦNH_2 cannot be hydrogenated and behaves as a poison. This can be explained by the different modes of adsorption: ΦNH_3^+ should be adsorbed by the benzene ring allowing its hydrogenation (active adsorbed form), while ΦNH_2 should be adsorbed by the free electron pair on the nitrogen $:NH_2-\Phi$ which acts as a poison (toxic adsorbed form).

These results confirm the important role of the acidity, in the hydrogenation of the aniline, as was reported [3,8].

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