



Liquid phase hydrogenation of nitrobenzene

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ABSTRACT

Hydrogenation of nitrobenzene (NB) was carried out in methanol solutions (initial concentration 0.8 mol l^{-1}) over a Pd/C catalyst (3 wt.% of Pd; reaction mixture contained 2.2 mg Pd l^{-1}) over the pressure range of 2–4 MPa and temperature 30–70 °C in a laboratory scale batch reactor. Zero order kinetics was observed at hydrogen pressures above 2 MPa. Under applied experimental conditions the apparent activation energy was $35 \pm 1 \text{ kJ mol}^{-1}$. A detailed analysis of the reaction mixture inspired the hypothesis that a $\text{C}_6\text{H}_5\text{-NO(H)}$ moiety is formed on the catalyst surface and it undergoes further condensation to azoxybenzene (AOB) releasing water. However, very low concentrations of azobenzene (AB) and hydrazobenzene (HAB) in the reaction mixture indicate that the reaction route to the formation of aniline by hydrogenation of AOB to AB, hydrazobenzene (HAB) and subsequent hydrogenolysis to AN is of low probability. Hydrogenolysis of AOB to $\text{C}_6\text{H}_5\text{-NO(H)}$ and $\text{C}_6\text{H}_5\text{-N(H)}$, where the latter is hydrogenated to AN, is more likely. Based on the experimental observations a new reaction scheme for the heterogeneous catalytic hydrogenation of NB was proposed.

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1. Introduction

Historically, aniline (AN) is one of the most important industrial chemicals. It is the main intermediate for plastics (polyurethanes, more than 75% of world production), pharmaceuticals, herbicides, dyes and pigments as well as production of rubber processing chemicals. AN is produced industrially by hydrogenation of nitrobenzene (NB), which can be performed in the gas or liquid phase. Liquid phase processes are preferred in the case of aromatic nitro compounds that have high boiling points and/or are thermally unstable. Another advantage of the liquid phase hydrogenation is higher volume productivity of a hydrogenation system, and due to fact that the heat transfer coefficient is higher for liquid phase; the capability for utilization of reaction heat is also higher. The latter aspects are the main reasons for carrying out the nitrobenzene hydrogenation in the liquid phase. High yields of aniline (more than

99%) and utilization of the reaction heat (more than 500 kJ mol^{-1}) are essential requirements [1–8].

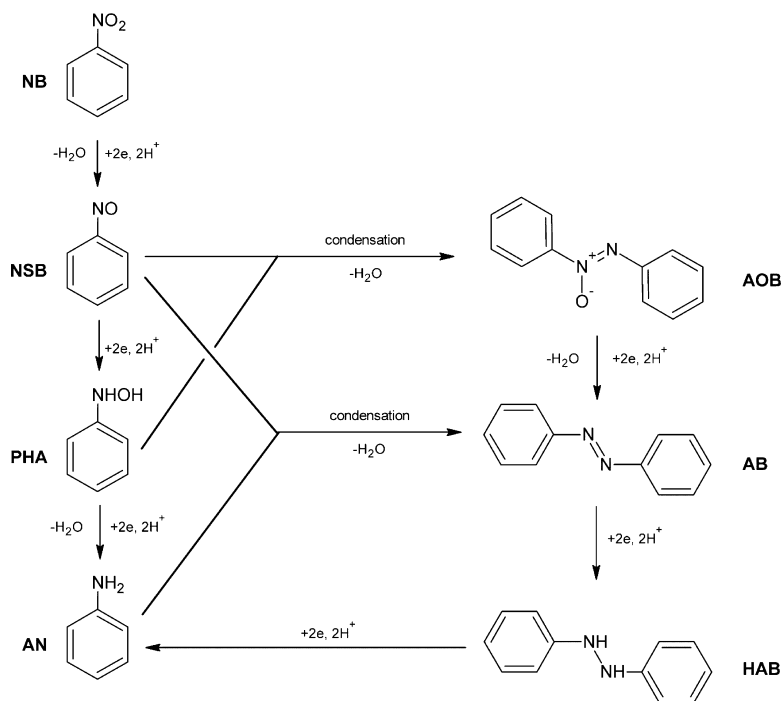
Palladium [9–13], platinum [14] and nickel [6,15–17] catalysts are often used. Although palladium catalysts are most expensive, they are often applied at low and medium temperatures (up to 200 °C), as palladium is highly selective for reduction of functional groups attached directly or onto the side chains of aromatic compounds without touching altering the aromatic ring [18].

Most published papers implement the Haber reaction mechanism [19] which was for a long time the only accepted reaction pathway. According to this reaction scheme, aniline may be formed via two different reaction paths. The first route suggests aniline formation through nitrosobenzene (NSB) and N-phenylhydroxylamine (PHA) intermediates. The second, condensation pathway assumes formation of azoxybenzene (AOB) from NSB and PHA. AOB is subsequently hydrogenated to azobenzene (AB) and hydrazobenzene (HAB). Besides these possibilities condensation of NSB and AN to AB can occur as well as disproportionation of PHA to NSB and AN aniline (Scheme 1) [20,21].

Extents of side condensation and disproportionation reactions strongly depend on the catalyst, concentration of reaction species and hydrogen activity [22]. When the activity of hydrogen is high, hydrogenation and hydrogenolytic reactions are preferred and the

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Scheme 1. Reaction mechanism of nitrobenzene hydrogenation to aniline proposed by Haber [19] and supplemented by Kosak [20] and Dubois [21].

extent of condensation reactions is lower. This is valid especially for catalysts with high affinity to hydrogen, e.g. palladium.

Recently a novel reaction mechanism has been proposed by Gelder et al. [22,23]. These papers claimed that the Haber mechanism was not adequate enough to explain experimental data and therefore some alterations to the typical reaction scheme should be made (Scheme 2).

The authors [22,23] discovered that the initial product of NSB hydrogenation is AOB and that AN is not formed until all the NSB has been converted to AOB. The scheme proposed in [22,23] suggests that in hydrogenation of NB the reaction steps contain different intermediates from those in the Haber mechanism. NSB, or its partially hydrogenated form: Ph–NOH, is not converted to N-phenylhydroxylamine but must undergo condensation.

Scheme 2 is also in accordance with the work of Kochetova et al. [24], where nitrobenzene adsorption on the catalyst surface was supposed to occur directly via the functional nitro group (Scheme 3). In the case of batch hydrogenations the NB concentration is relatively high in comparison with experiments performed in continuous systems. If the NB concentration is low, the concentration of NSB is also low. NSB is very reactive and can be easily converted to PHA and consequently to AN, according to the proposal of Haber. Moreover, hydrogenolysis of the –N=N– group in the AB requires a much higher temperature and a more active (selective to hydrogenolysis) catalyst than in the case of NSB and PHA. Scheme 3 Catalytic steps in the hydrogenation of NB according to Kochetova et al. [24].

In most of the published research the liquid phase hydrogenation of NB has been carried out in the presence of a solvent (methanol [25], isopropanol [14,26,27] or ethanol [6,13,28–30]) at ambient temperatures and pressures below 0.3 MPa. The solvent used in the hydrogenation of NB also helps maintain the reaction temperature at a desired value. This is important, because NB hydrogenations are known for their high exothermicity ($\Delta H_r = -540 \text{ kJ mol}^{-1}$ at 298 K).

In the current work conditions closer to industrial practice were chosen. The reactions were carried out at 2–4 MPa [31]. Industrially temperatures above 150 °C are typically applied to increase

amount of steam produced. However experiments presented in this paper were carried out at 30–70 °C to generate data for the kinetic regime. To enhance hydrogen mass transfer from gas to liquid, methanol was used as a solvent (one of the highest hydrogen solubility among solvents as well as a low cost), although in industry aniline is commonly used. The utilization of methanol and considered temperature range is in agreement with the recommendations of Acres and Bond, who advised methanol and 50 °C for catalyst testing in hydrogenation of nitrobenzene [32].

Slurry reactors with suspended catalyst are still more suitable for liquid phase hydrogenations than fixed bed reactors. Fixed bed reactors have encountered problems with flow maldistribution and energy dissipation as well as the higher possibility of local “heat” centres forming on the catalyst surface. Efficient operation of slurry reactors requires high surface area catalysts with small particles and application of intensive mixing [14]. In the presented work a mechanically stirred reactor with the suspended catalyst was used to evaluate the reaction kinetics.

2. Experimental

2.1. Catalyst preparation

3%Pd/C catalyst was prepared using a simple precipitation–reduction method described in detail in the previous paper [33]. PdCl₂ as a palladium precursor was used. It consequently was dissolved in a HCl solution and precipitated in a slurry of activated carbon (Norit SX Plus) using Na₂CO₃. Reduction with formaldehyde was applied to obtain palladium in an active form. The catalyst contained 3 wt.% of Pd in a dry state.

2.2. Catalyst characterization

Wetness content was determined using IR oven METTLER LP 16 (Mettler Toledo, USA). The catalyst was dried at 105 °C until a stable weight was achieved.

The exact content of Pd in the prepared dry catalysts was measured by ICP-OES method at SPECTROBLUE ICP-OES (Spectro,

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