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Catalyst performance changes induced by palladium phase transformation in the hydrogenation of benzonitrile

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ABSTRACT

The influence of hydrogen pressure on the performance of a γ-alumina-supported palladium catalyst was studied for the multiphase selective hydrogenation of benzonitrile to benzylamine and byproducts. Semi-batch experiments of benzonitrile hydrogenation in 2-propanol were performed with hydrogen pressures between 2.5 and 30 bar, at a constant temperature of 80 °C. The intrinsic property of palladium to absorb hydrogen into its lattice structure has a strong influence on activity and selectivity. The transformation to stable palladium β-hydride above a threshold hydrogen pressure of 10 bar induces a persistent change in turnover frequency and byproduct selectivity. The turnover frequency increases from 0.32 s^{-1} to a maximum of 0.75 s^{-1} at this threshold pressure and decreases to 0.25 s^{-1} with increasing hydrogen pressure. The palladium β-hydride phase suppresses the hydrogenolysis to toluene changing the selectivity from 6.5% to 2.0% and increasing the selectivity of the condensation to dibenzylamine from 1.6% to 2.7%, attributed to modified electronic interactions between catalyst and substrates. The selectivity to the desired product benzylamine is always high and increases with hydrogen pressure from 92.7% to 95.3%. The palladium catalyst state is mainly determined by the activation or operational hydrogen pressure, whichever was the highest, if the activation pressure was above 10 bar.

1. Introduction

The topic of this paper is structure sensitivity of palladium (Pd) catalysts, in particular the effect of structural changes due to Pd β-hydride (β-PdH) formation at higher hydrogen pressure (pH_2). The reaction of interest is the hydrogenation of aromatic nitriles to the corresponding primary amines. Here, controlling the selectivity is a crucial demand and insight into the reaction mechanisms of desired and undesired reactions is very valuable.

Primary aromatic amines are important chemical compounds that have found widespread applications as chemical and pharmaceutical intermediates, solvents, paints, herbicides and synthetic textiles. A major route to produce primary aromatic amines is the heterogeneously catalyzed hydrogenation of aromatic nitriles [1–4]. However, during the hydrogenation of aromatic nitriles toward the aromatic amines, several byproducts are usually formed, resulting in a loss of yield [1–4]. Activity and selectivity are mainly determined by the amount, type and mobility of surface intermediates and transition states which are controlled by the catalyst. Further, it should be noted that the reactant concentration, type of solvent(s), reaction conditions and additives (*e.g.* ammonia) also play an important role [2–4].

A scheme that depicts the reaction pathways during the hydrogenation of benzonitrile (BN) to benzylamine (BA) and the main byproducts can be found in Fig. 1. The reaction network is a combination of hydrogenation, condensation and hydrogenolysis reactions that can yield BA, *N*-benzylidenebenzylamine (DBI), dibenzylamine (DBA), and toluene (TOL), respectively. Ammonia (NH_3) is formed during condensation reactions and hydrogenolysis to TOL. The reaction mechanism is generally explained by the premise of benzylideneimine (BI) or other semi-hydrogenated intermediates and a surface aminal (*i.e.* α-aminodialkylamine (BIBA)).

Several authors contributed to the elucidation of the reaction mechanism since the beginning of the 20th century by proposing that imines (—CH=NH), Schiff bases (—C=N—C), and enamines (—N—C=C—) are the intermediates in the formation of primary, secondary, and tertiary amines [5–10]. However, this mechanism is based on a number of unproven assumptions that are corroborated only by indirect evidence: *e.g.* Schiff bases have been identified in solution, imines were detected on the catalyst surface by IR spectroscopy, and the absence of tertiary amine formation in the hydrogenation of BN has been observed. The inability to detect imine and enamine intermediates is attributed to their high reactivity.

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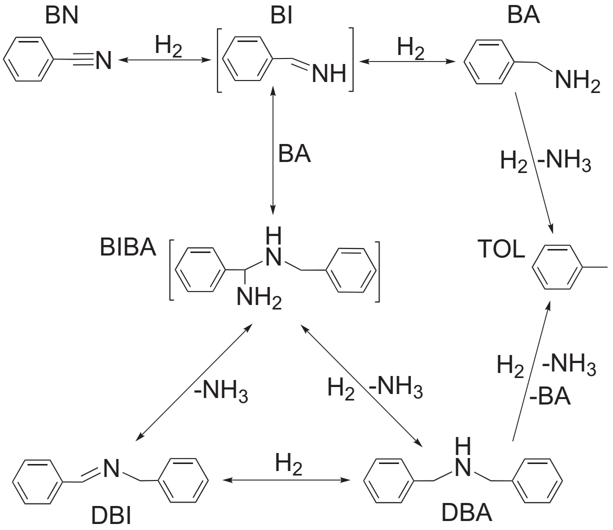

Fig. 1. Reaction pathways to different products in the hydrogenation of benzonitrile (BN): hydrogenation of BN to benzylamine (BA) via benzylideneimine (BI). Condensation of BA and BI via α-aminodialkylamine (BIBA) and *N*-benzylidenebenzylamine (DBI) to dibenzylamine (DBA). Hydrogenolysis to toluene (TOL) of DBA and BA. Direct hydrogenolysis of BIBA to DBA is possible. Species in between straight brackets are surface intermediates never detected in solution.

From several BN hydrogenation studies and our own findings, it can be concluded that the use of supported Pd catalysts results in high activity and, more important, a high selectivity toward BA compared to other platinum-group metal catalysts [11–15]. An overview of different catalysts used under many different conditions in the heterogeneous hydrogenation of BN is shown in Table 1. From our own investigations, it appeared that a commercially available γ-Al_2O_3-supported Pd catalyst exhibited the highest selectivity and was therefore used in this study.

While studying the effect of pH_2 on activity and selectivity over this catalyst, we encountered an unexpected anomaly: we found a maximum in catalyst activity with increasing pH_2, accompanied by a sudden selectivity shift in byproducts leading to an increased yield of BA. The literature does not report such an effect during Pd-catalyzed nitrile hydrogenation. However, in the hydrogenation and hydrogenolysis of hydroxymatairesinol using a Pd catalyst, Bernas et al. also encountered a negative dependence on the pH_2 above a certain pressure [16]. They explained this effect as a result of competitive adsorption of H_2 and the reactant. Dubois et al. studied the hydrogenation combined with hydrogenolysis of 2-methyl-2-nitropropane over a supported Pd catalyst and also encountered an activity maximum; they gave two possible explanations for this effect: more favorable H_2 adsorption for the same active sites or the formation of a new, less active, Pd phase [17]. Skakunova et al. hypothesized that the negative-order effect in the hydrogenolysis of propane over a Pd–Ru catalyst was caused by competitive adsorption of H_2 [18]. In general, hydrogenolysis reactions catalyzed by different supported metals are structure sensitive and often have a negative reaction order with respect to pH_2 up to -2.5 [19–23].

We demonstrate that in BN hydrogenation, competitive adsorption between H_2 and BN is not the explanation of the anomaly observed. Rather, our hypothesis is that structural changes of the Pd crystallites at higher pH_2 explain the observed phenomena. A well-known property of Pd, discovered by Graham in 1866 [24] that differentiates it from all other metals, is the easy absorption of atomic hydrogen in large quantities in the Pd lattice, occupying the octahedral interstices of its face-centered cubic Pd lattice structure already at ambient temperature and low pH_2 [25–27]. Upon absorbing large amounts of hydrogen, the lattice Pd expands (lattice constant increases) when the solid solution phase (α-PdH) transforms into the β-PdH phase [28]. Moreover, the character of the electronic *d*-band of Pd changes [27,29–32]. The amount of H absorption in Pd depends on the H_2 concentration in the liquid, temperature, Pd particle size, surface topography, support interactions, precursor, and pretreatment steps [28,33,34]. Structural changes upon transformation to β-PdH can have a profound effect on the adsorption strength, type, and amount of surface species, and thus on the activity and selectivity [28,35–42].

In this paper, we demonstrate that in γ-Al_2O_3-supported Pd-catalyzed BN hydrogenation, the β-PdH phase formed at increased pH_2 is responsible for the activity and selectivity effects. The pH_2 and the entailing transformation to β-PdH have a profound influence on the catalyst performance. Further, based on analysis of the reaction mixture and characterization of fresh, activated, and spent catalysts, a scheme of the reaction mechanism, modes of surface adsorption, and surface intermediates are presented. By combining *d*-band theory with simple frontier molecular orbital theory, we explain the observed results.

2. Experimental

2.1. Catalyst and materials

Unless explicitly stated, the experiments were carried out using reduced 5 wt% Pd/γ-Al_2O_3 supplied by Alfa Aesar. Blank experiments were performed using γ-Al_2O_3 (99.97%) supplied by Alfa Aesar. The catalysts we studied and reported in Table 1 (5 wt% Pd/C, 5 wt% Pd/$BaCO_3$, 5 wt% Ru/γ-Al_2O_3, 5 wt% Pt/C) were supplied by Aldrich. The other chemicals used in this study were purchased from commercial suppliers and used as received (benzonitrile, 99%, Alfa Aesar; benzylamine, >98%, Alfa Aesar; dibenzylamine, 98%, Alfa Aesar; toluene, 99.5%, J.T. Baker; *n*-isopropylbenzylamine, 98%, Alfa Aesar; 2-propanol, 99%, Aldrich; γ-Al_2O_3, 99.97%, Alfa Aesar).

2.2. Selective hydrogenation

The selective hydrogenation experiments were carried out in a semi-batch mode in a high-pressure stainless steel autoclave (Medimex Reactor CH-2543) equipped with baffles and a gas-induced stirrer. H_2 was continuously fed to the reactor to maintain a constant pH_2 (units: bar gauge further denoted as bar) during a hydrogenation experiment. We used a simple alcoholic solvent, 2-propanol, and did not use any additives.

In a typical experiment, 0.5 g of 5 wt% Pd/γ-Al_2O_3 was added to 150 ml of 2-propanol and subsequently fed to the reactor. Different cycles of pressurizing and depressurizing with N_2 were applied to remove the air from the reactor. Before a hydrogenation experiment, the catalyst was activated in the reactor in 2-propanol under elevated pH_2 at 80 °C for 1 h. The typical pH_2 used for the standard activation was 10 bar. In addition, the influence of activation pH_2 (2.5, 10, and 30 bar) on the catalyst performance was also investigated.

After the *in situ* activation of the catalyst, the reactor was brought to reaction conditions, *i.e.* a temperature (T) of 80 °C and a pH_2 between 2 and 30 bar for the different experiments. Then, 50 ml 2-propanol, adding up to 200 ml, with the appropriate amount of BN, was added to the autoclave via a pressurized filling tank ($C_{BN,0} = 520\ mol/m^3$). Reference hydrogenation experiments ($C_{BN,0} = 520\ mol/m^3$, $T = 80\ °C$, $pH_2 = 10$ and 30 bar) were performed with a γ-Al_2O_3 support without Pd to determine its effect in the hydrogenation of BN. In addition, hydrogenation experiments with