Catalytic Hydrogenation

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A Different Reaction Pathway for the Reduction of Aromatic Nitro Compounds on Gold Catalysts[**]

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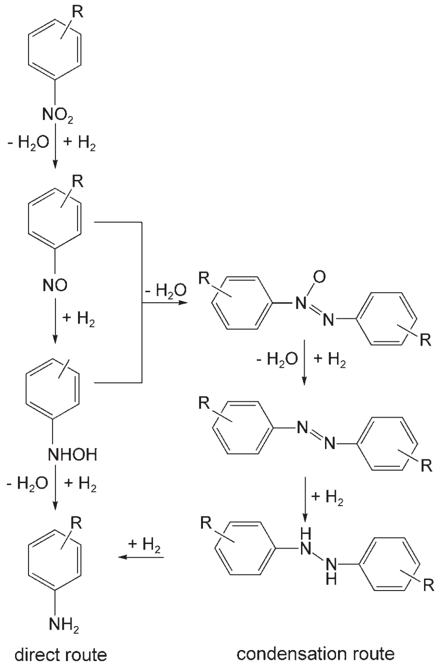
Dedicated to Süd-Chemie on the occasion of its 150th anniversary

Aromatic amines are generally prepared by the reduction of nitro-substituted aromatic compounds, and the mechanism of this reaction has been the focus of a number of publications.[1–6] The selective reduction of a nitro group in an aromatic nitro compound in the presence of other reducible functionalities is generally approached by using a stoichiometric amount of a reducing agent.[7] However, such a process has a high E factor (defined as the ratio by weight of by-products to the desired product)[8] and is not environmentally sustainable. Siegrist et al.[9] showed that a $Pt/CaCO_3$ catalyst in which the surface of the metal is covered by a thin layer of lead and a $Pt/C–H_3PO_4$ catalyst are able to adsorb and dissociate H_2 to promote the selective reduction of a nitro group in the presence of a double bond. However, the reduction of a nitro group with these catalysts leads to the accumulation of the corresponding hydroxylamine and the formation of azoxy and azo compounds. The authors found that the addition of iron (in the case of $Pt/CaCO_3$) or vanadium salts (in the case of $Pt/C–H_3PO_4$) to the solution promotes the reduction of the hydroxylamine and increases the selectivity for the aniline product.

We reported recently that gold on TiO_2 or Fe_2O_3 catalyzes the selective reduction of a nitro group without the need to add metal salts and thus acts as a highly selective and environmentally friendly catalyst.[10] Blaser[11] highlighted these results and raised a relevant question with respect to the reaction pathway with gold catalysts. Herein, we answer that question on the basis of studies in which we combined in situ IR spectroscopy with macrokinetic experiments and determined the reaction intermediates and relative rates of the elementary steps during gold catalysis.

The generally accepted reaction network for the catalytic reduction of aromatic nitro compounds is based on the electrochemical model presented by Haber.[12] In this reaction scheme, two different routes are proposed. In the more direct route, the aromatic nitro compound is reduced to the nitroso compound and then further to the corresponding hydroxylamine in two very fast consecutive steps. Finally, the hydroxylamine is reduced to the aniline derivative in the slowest reaction step (direct route, left pathway in Scheme 1). The second route proposed involves the condensation of one molecule of the nitroso compound with a molecule of the hydroxylamine to give the azoxy compound, which is reduced in a series of consecutive steps to the azo, hydrazo, and aniline compounds (condensation route, right pathway in Scheme 1).



Scheme 1. Proposed reaction pathways for the reduction of an aromatic nitro compound to the corresponding aniline.

On the basis of the products observed by Siegrist et al. during the reduction of aromatic nitro compounds on $Pt/CaCO_3$ or $Pt/C–H_3PO_4$[9] and the postulates of Blaser,[11] it was possible to conclude that the aniline derivatives were formed on such catalysts through both routes. Thus, the reaction network presented in Scheme 1 appears to be valid for this transformation.

Upon the use of Ir, Pt, and Pd supported on carbon as catalysts, Makaryan and Savchenko[6] reached a completely different conclusion. In fact, they propose that the transformation of N-aryl hydroxylamines into amine products

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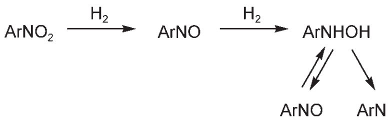
Supporting information for this article, including experimental details of the synthesis of Au/TiO_2, catalytic reactions, and FTIR measurements, is available on the WWW under http://www.angewandte.org or from the author.



Scheme 2. Reaction pathway proposed by Makaryan and Savchenko[6] for the transformation of an aromatic nitro compound into an aniline through disproportionation of the corresponding hydroxylamine.

proceeds as a result of disproportionation of the N-aryl hydroxylamine on the catalyst rather than through hydrogenation (Scheme 2).

Studer et al.[3] took this disproportionation mechanism into account and cleverly added a second catalytic function (iron or vanadium salts in solution) to avoid the accumulation of the hydroxylamine by catalyzing the disproportionation of the hydroxylamine with the nitroso intermediate to give the corresponding aniline. On the other hand, Visentin et al.[1] concluded on the basis of a combination of calorimetric, FTIR-ATR (attenuated total reflectance), and gas-uptake signals with Pd/C as catalyst that the results of Makaryan and Savchenko would be consistent with a direct hydrogenation route in which hydroxylamine is accumulated (Scheme 3).

Scheme 3. Direct hydrogenation route proposed by Visentin et al.[1]

Finally, a fourth potential mechanism for the reduction of aromatic nitro compounds to anilines has been proposed on the basis of isotopic results with a nickel catalyst. In this case a direct route from the nitro compound to the hydroxyamine is also included in the reaction scheme: nitro compound→hydroxylamine→aniline derivative.[13]

Thus, there is no general consensus, but a number of different proposals with respect to the mechanism of reduction of aromatic nitro compounds to anilines. In the case of gold, which has unique catalytic properties, as it is chemoselective but does not accumulate hydroxylamine, the question becomes: How does the reaction occur on this unique catalyst?

To establish the reaction pathway for gold on TiO$_2$, we first carried out hydrogenation experiments in a batch reactor by feeding nitrostyrene or nitrobenzene and following the reaction with time (see Figure 1 and experimental details in the Supporting Information). The yields of the different products were then plotted against the total conversion (Figure 1). The results showed that the gold catalyst is highly chemoselective for the reduction of the nitro functionality (Figure 1 b). From a chemical point of view, aniline must be a secondary product, as we indeed observed subsequently by in situ IR spectroscopy. However, remarkably, it appears in Figure 1 a as if aniline were a primary product. One explanation, if one accepts that aniline must be a secondary product, is that under the reaction conditions the nitroso and hydroxylamine compounds formed react before desorbing. This explanation is consistent with the fact that the nitroso and hydroxylamine derivatives are not detected in the reaction media. However, we can not conclude from these results whether the reaction occurs mainly through the direct route, the condensation route, or both routes described in Scheme 1.

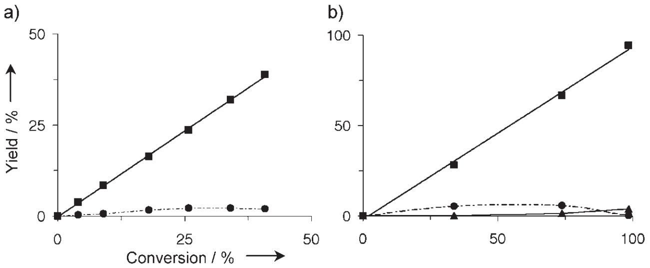


Figure 1. Distribution of products during the hydrogenation of a) nitrobenzene and b) nitrostyrene (■ aniline or aminostyrene, ● azobenzene or azostyrene, ▲ aminoethylbenzene).

As azobenzene was observed among the reaction products, if only in small amounts, we studied the reactivity of the gold catalyst in the sequence of reactions in the condensation route (Scheme 1). First, the reaction of azoxybenzene on Au/TiO$_2$ was investigated (see the Supporting Information). The results in Figure 2 a show clearly that azobenzene is an unstable primary product, whereas aniline is a secondary product, although the yield of aniline is very low even at high conversion. When azobenzene was used as the reactant, hydrazobenzene appeared as an unstable primary product, and aniline was formed rapidly as secondary product (Figure 2 b).

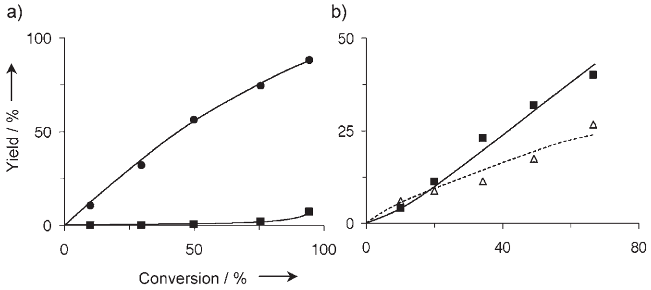


Figure 2. Distribution of products during the hydrogenation of a) azoxybenzene and b) azobenzene (■ aniline, ● azobenzene, △ hydrazobenzene).

These results on the kinetics and selectivity of the reaction (see Figures 1 and 2 and the Supporting Information) indicate clearly that the main route for the reduction on Au/TiO$_2$ of a nitro group is not the condensation route in Scheme 1, that is, reduction via an azoxybenzene. Unlike with Pt/CO$_3$Ca or Pt/C–H$_3$PO$_4$ catalysts, the reduction of the nitro group appears to occur very predominantly through the direct route given in Scheme 1, that is, nitro compound→nitroso compound→hydroxylamine→aniline.

Nevertheless, since the nitroso compound is a common intermediate in the direct route and the condensation route in Scheme 1, we also fed nitrosobenzene as a reactant. The results in Figure 3 show that azoxybenzene was formed with practically 100 % selectivity, although a trace amount of

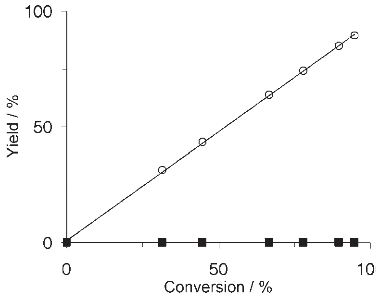
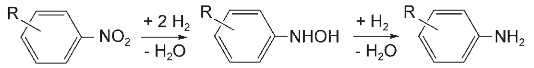


Figure 3. Distribution of products during the hydrogenation of nitrosobenzene (■ aniline, ○ azoxybenzene).

aniline was observed, whereas phenylhydroxylamine was not detected.

These results also confirm that in the reduction of nitrobenzene, reaction through the condensation route in Scheme 1 must be negligible when the gold catalyst is used. On the other hand, if one accepts that the reaction occurs through the direct route in Scheme 1, one has to assume on the basis of the results in Figure 3 that in the sequence nitro→nitroso→hydroxylamine→aniline the hydrogenation of the nitroso compound is much faster than the reduction of the nitro group to the nitroso group, as the nitroso compound was not detected among the reaction products and azoxybenzene was formed in very small amounts. However, another possibility, which involves the direct reduction of nitrobenzene to phenylhydroxylamine without the intermediacy of nitrosobenzene, would also be consistent with the experimental observations (Scheme 4).



Scheme 4. Possible reaction pathway for the reduction of an aromatic nitro compound to an aniline without the intermediacy of a nitroso compound.

At this point, we studied the hydrogenation of nitrobenzene and the reaction intermediates by in situ FTIR spectroscopy to further investigate the validity of the direct route in Scheme 1 and to find out if the reaction pathway in Scheme 4 is operative. When nitrobenzene was brought into contact with Au/TiO_2 in the IR cell (see the Supporting Information), it was adsorbed strongly on TiO_2 and Au/TiO_2. The two resulting intense IR bands at 1526 and 1350 cm^{-1} were assigned to the asymmetric and symmetric stretching vibrations of the nitro group. Detailed analysis of the IR spectra of nitrobenzene adsorbed on TiO_2 and Au/TiO_2 showed that the maximum for the asymmetric stretching vibration $\nu_{as}(NO_2)$ is shifted slightly to a lower frequency with Au/TiO_2 relative to that observed with TiO_2. Moreover, upon deconvolution of the IR band for the Au/TiO_2 sample, two contributions were detected clearly: one band at 1526 cm^{-1}, which was also observed with TiO_2, and a new band at 1520 cm^{-1}. The band at 1526 cm^{-1} is due to the interaction of nitrobenzene with the support (with Ti–OH, as deduced from the shift observed for the OH band, and with Ti^{4+} Lewis acid sites), whereas the lower-frequency band at 1520 cm^{-1} is related to a stronger molecular interaction. As this band is absent for the sample on pure TiO_2, we propose that gold-metal particles (at interface sites or as metal atoms) are responsible for the activation of the nitro group.

Time-resolved IR spectra were recorded after nitrobenzene/H_2 coadsorption at 120 °C on the Au/TiO_2 catalyst to determine the intermediate species in the reaction (see the Supporting Information). Three main IR bands were observed in the 1750–1400-cm^{-1} region, at 1502, 1493, and 1476 cm^{-1}. Upon comparison with our reference IR spectra, we were able to deduce that in the reduction with hydrogen of nitrobenzene adsorbed on the Au/TiO_2 catalyst, nitrosobenzene (IR band at 1476 cm^{-1}), phenylhydroxylamine (IR band at 1493 cm^{-1}), and aniline (IR band at 1502 cm^{-1}) are present on the catalyst surface. We observed no evidence of the presence of other products (azoxybenzene or azobenzene).

The variation in the intermediate species with time during the hydrogenation of nitrobenzene was investigated by deconvolution of the FTIR spectra (Figure 4). As a result of experimental limitations and limitations in the post-treatment "processing" of the spectra, product concentrations at reaction times lower than 5 min were not determined.

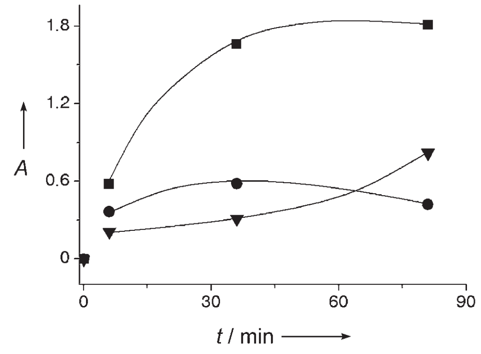


Figure 4. Evolution with time of the concentration of intermediate species in the hydrogenation of nitrobenzene on Au/TiO_2, as deduced from in situ IR experiments (▼ aniline, ■ phenylhydroxylamine, ● nitrosobenzene).

After a reaction time of 5 min, the formation of nitrosobenzene, phenylhydroxylamine, and aniline was observed. In a first approximation, the kinetic curves appear to indicate a sequential transformation: nitrobenzene→nitrosobenzene→phenylhydroxylamine→aniline, whereby the rate of reduction of nitrosobenzene is greater than the rate of reduction of phenylhydroxylamine. Interestingly, nitrosobenzene was not observed among the reaction products during the batch-reaction study (see Figure 1). Its absence indicates the existence of a strong interaction between this compound and the catalyst surface, so that nitrosobenzene reacts on the catalyst surface prior to its desorption. Moreover, the reduction of phenylhydroxylamine appears to be the rate-determining step in the sequence.

The hydrogenation of nitrosobenzene was also studied by time-resolved FTIR spectroscopy of the Au/TiO_2 sample at

120 °C (see the Supporting Information). Three bands, at 1476, 1492, and 1503 cm^{-1}, were clearly visible and were assigned to nitrosobenzene, phenylhydroxylamine, and aniline. No other bands due to intermediate compounds in the condensation pathway were detected. Figure 5 shows the evolution of the intermediate species in the hydrogenation of nitrosobenzene with time, as determined by deconvolution of the FTIR spectra. The concentration of nitrosobenzene was found to decrease rapidly, whereas the concentration of both phenylhydroxylamine and aniline increased over the same period.

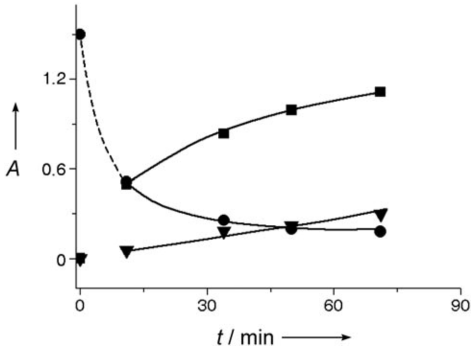
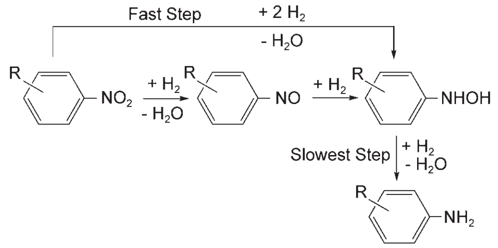


Figure 5. Evolution with time of the concentration of intermediate species in the hydrogenation of nitrosobenzene on Au/TiO_2, as deduced from in situ IR experiments (▼ aniline, ■ phenylhydroxylamine, ● nitrosobenzene).

A reaction pathway in which the aromatic nitro compound is first reduced to the nitroso compound, then to the corresponding hydroxylamine, and finally to aniline can be inferred from the in situ FTIR experiments with nitrobenzene and nitrosobenzene (direct route in Scheme 1). However, the amount of phenylhydroxylamine formed when nitrobenzene was used as the reactant (see Figure 4) was significantly higher than the amount produced when nitrosobenzene was used (see Figure 5). This result indicates that a direct route from nitrobenzene to phenylhydroxylamine also contributes to the production of aniline, in agreement with the results presented by Gelder et al.,[13] who showed that it is possible to reduce nitrobenzene to phenylhydroxylamine directly.

Thus, on Au/TiO_2 catalysts, phenylhydroxylamine is formed as both a primary product (from nitrobenzene) and a secondary product (via nitrosobenzene) at the Au/TiO_2 active sites. The gradual accumulation of this intermediate on the catalyst surface shows that the transformation of phenylhydroxylamine into aniline is the rate-determining step of the whole process. Furthermore, the fact that only very small amounts of azoxybenzene were observed in the liquid-phase batch experiments suggests strongly that the inhibition of the condensation of hydroxylamine and nitroso intermediates during the hydrogenation of aromatic nitro compounds on Au/TiO_2 catalysts is predominantly a result of the low concentration of nitrosobenzene present, together with the strong adsorption of nitrosobenzene and phenylhydroxylamine to the Au/TiO_2 active sites. Because of the strength of the adsorption, these compounds do not desorb from the catalyst/support surface and condensate to form azoxybenzene, but instead are hydrogenated to produce aniline.

On the basis of the results presented herein, we conclude that aromatic nitro compounds are hydrogenated on Au/TiO_2 by the reaction route shown in Scheme 5. This reaction pathway differs from that reported for Pt/$CaCO_3$ and Pt/C–H_3PO_4 and explains why the presence of iron or vanadium salts is not required for the reaction with the gold catalyst to proceed with high selectivity for the aniline products.



Scheme 5. Proposed reaction pathway for the hydrogenation of aromatic nitro compounds to aniline derivatives in the presence of the Au/TiO_2 catalyst.

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