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Organic Thiol Modified Pt/TiO_2 Catalysts to Control Chemoselective Hydrogenation of Substituted Nitroarenes

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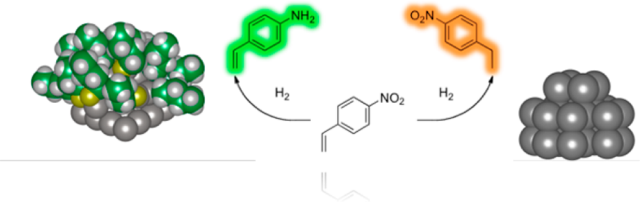
Supporting Information

ABSTRACT: The quest for selective heterogeneous hydrogenation catalysts is state of the art research. We present a simple surface modification method for Pt/TiO_2 catalysts employing organic thiols for the liquid phase selective hydrogenation of 4-nitrostyrene. Our modified catalyst shows a 100% switch of selectivity to 4-aminostyrene at conversion levels close to 100%.



KEYWORDS: *supported Pt, selective hydrogenation, nitrobenzene, TiO_2, surface modification*

Hydrogenation reactions over heterogeneous catalysts are of industrial as well as of scientific interest.[1] An optimal hydrogenation catalyst combines high activity, selectivity, and stability. For generally employed supported metals in hydrogenation catalysts such as Pt and Pd, selectivity control is an issue when more reducible groups are present in the same molecule. An example for such a reduction is the hydrogenation of substituted nitroarenes to the corresponding anilines which are important substrates for pharmaceuticals, dyes, and pigments.[2] The conventional Pt and Pd catalysts simultaneously reduce the nitro- and all other reducible groups in the molecule. A way to circumvent this problem is to use less active metals, such as gold[3−5] or to modify the more active catalysts.[6−8] There are various surface modifications reported in the literature for a variety of catalytic challenges.[9−13] Modification via ligands is a well established method to tune the performance of catalysts. Recently PVP stabilized Rh nanoparticles were modified via phosphine ligands to tune the performance during the hydrogenation of substituted aromatics.[13] Upon modification with several different spacious phosphine ligands, the selectivity toward ring hydrogenation could be increased to values greater than 90% during the liquid phase hydrogenation of phenylacetone. In this study, we report a new simple surface modification procedure for supported Pt particles on TiO_2 employing organic thiols to selectively hydrogenate 4-nitro to 4-aminostyrene in the liquid phase. Scheme 1 summarizes the effect of our modification.

Performing the hydrogenation over an unmodified Pt/TiO_2 catalyst yields 4-ethylnitrobenzene and 4-ethylaniline simultaneously. Upon modification with organic thiols the selectivity of the catalyst can be switched so that the primary product of the hydrogenation reaction is exclusively 4-aminostyrene. The supported Pt nanoparticles, prepared by incipient wetness impregnation, were modified by mixing the Pt/TiO_2 catalyst with the organic thiol. All experimental details can be found in the Supporting Information. Briefly, an appropriate amount of Pt/TiO_2 was suspended in 100 mL of degassed (with N_2) ethanol and mixed with the corresponding organic thiol in a Pt/thiol ratio 1:100 under N_2 purging for 16 h at room temperature. The modified catalyst was filtered and washed with ethanol and analyzed by transmission electron microscopy (TEM) and Fourier transform infrared (FT-IR) spectroscopy. TEM analysis showed that the unmodified Pt nanoparticles were present in small clusters of 1 nm size which slightly grew upon modification with the organic thiols to around 1.4 nm. The size of the thiol modified Pt nanoparticles remained more or less constant after the reaction (1.2 nm). FT-IR measurements revealed characteristic vibrational features of the organic thiols with loss of an S−H stretching mode, thus confirming that the thiols were adsorbed via the sulfur on the Pt nanoparticles (Supporting Information). The so modified catalyst was used in the liquid phase hydrogenation of 4-nitrostyrene. Mesitylene, the internal standard, and toluene, the solvent, were filled into an autoclave with an appropriate amount of modified catalyst. After purging, the autoclave was pressurized to 10 bar, heated under stirring to 80 °C, and samples were taken after certain time intervals and analyzed by GC.

Figure 1 shows the result of our kinetic measurements of the liquid phase hydrogenation of 4-nitrostyrene over (a) the Pt/TiO_2 catalyst and (b) the 1,6-dithiolhexane-modified Pt/TiO_2 catalyst.

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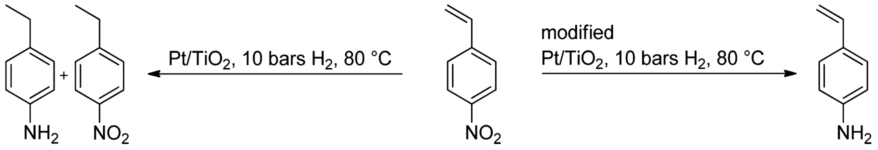
Scheme 1. **Products Observed during the Liquid Phase Hydrogenation of 4-Nitrostyrene at 80 °C under 10 bar H_2 in Toluene over an Unmodified Pt/TiO_2 (Left) and an Organic Thiol Modified Pt/TiO_2 Catalyst (Right)**



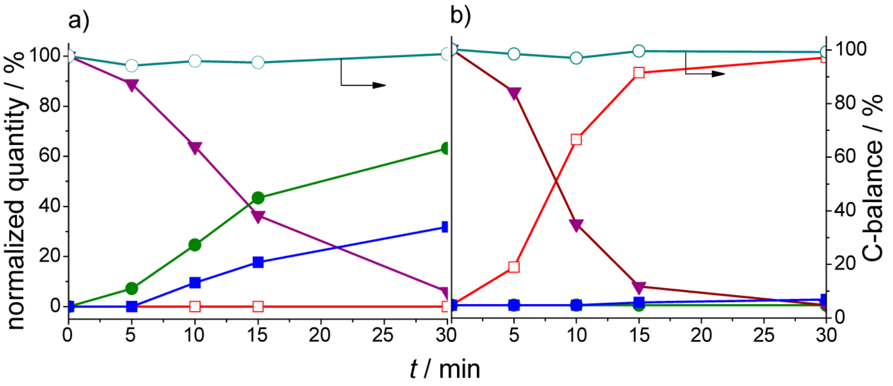


Figure 1. Evolution of substrate, intermediates, products, and C-balance in the liquid phase hydrogenation of 4-nitrostyrene: (purple solid triangle) 4-nitrostyrene, (green solid circle) 4-ethylnitrobenzene, (blue solid square) 4-ethylaniline, (red open square) 4-aminostyrene, and (light blue open circle) C-balance over (a) Pt/TiO_2 and (b) 1,6-dithiolhexane-modified Pt/TiO_2. Reaction at 80 °C with 50 mg catalyst under 10 bar H_2 in 25 mL of toluene.

Over Pt/TiO_2, the concentration of 4-nitrostyrene decreased exponentially over the reaction time and was fully converted within about 30 min. The primary product was 4-ethylnitrobenzene. After 10 min 4-ethylaniline was observed among the products. The concentration of both compounds increased with time; the 4-ethylnitrobenzene concentration increased stronger than that of 4-ethylaniline. After longer reaction times (not shown) 4-ethylnitrobenzene was fully converted to the final product 4-ethylaniline. The carbon balance was always in excess of 95% and thus no side reactions occurred to a significant extent. A completely different behavior was observed for all thiol-modified catalysts, of which 1,6-dithiolhexane is shown as example. The modified catalyst converted 4-nitrostyrene to 4-aminostyrene as the exclusive product. Thus, a complete switch of selectivity was achieved by the surface modification. This high selectivity could be maintained at all conversion levels. The yield of 4-aminostyrene was close to 100%. The evolution of the 4-aminostyrene proceeded almost as mirror image of the 4-nitrostyrene concentration. At 100% conversion traces of 4-ethylaniline were observed among the products. After longer reaction times, (not shown) 4-aminostyrene fully converted to the completely hydrogenated product 4-ethylaniline. No phenylhydroxyl amine derivates were observed at any point of the reaction, also indicated by a carbon balance in excess of 95% during the whole reaction.

We determined the effect of different organic thiols on selectivity and activity during the liquid phase hydrogenation of 4-nitrosytrene. Table 1 summarizes the selectivity and rate at ~40% conversion (a) of 4-nitrostyrene as well as the selectivity at conversion levels close to 100% (b) for the different modifiers. All rates reported in Table 1 were obtained at 40% conversion of 4-nitrostyrene which lies in the linear regime of the 4-nitrostyrene conversion for all unmodified and modified catalysts. This resembles a 0 order reaction as generally reported in the literature and is thus concentration independent. The rates reported are therefore in the absence of mass-transfer limitation as it is concentration dependent.[14]

Table 1. **Selectivity and Rate of Reaction at ~40% Conversion of 4-Nitrostyrene during the Liquid Phase Hydrogenation of 4-Nitrostyrene before and after Surface Modification with Different Surface Modifiers and Selectivity at Conversion Levels Close to 100%**[a]

Pt/TiO_2	selectivity to 4-aminostyrene (%)[b]	rate (mmol g_{cat}^{-1} s^{-1})[c]	selectivity to 4-aminostyrene (%)[c]
no modifier	0%	0.0647	0%
thioglycerol	100%	0.0027	97%
1,6-dithiolhexane	100%	0.0100	98%
α-lipoic acid	100%	0.0033	100%
1-dodecanethiol	88%	0.0096	64%

[a] Reaction at 80 °C with 50 mg catalyst under 10 bar H_2 in 25 mL of toluene. [b] About 40% conversion. [c] Near full conversion.

4-aminostyrene was never observed among the products over the unmodified Pt/TiO_2 catalyst (Figure 1a). The rate at 40% conversion for the unmodified Pt/TiO_2 catalyst was the highest observed for all the catalysts in Table 1. This is not surprising as the thiols block part of the surface of the Pt nanoparticles and thus also active sites.[15] The modifier structure affected the selectivity: the modifiers containing polar groups (thioglycerol, 1,6-hexanedithiol and α-lipoic acid) yielded 100% selectivity toward 4-aminostyrene whereas an unpolar modifier (1-dodecanethiol) yielded only 88% selectivity. This trend was obviously also observed at conversion levels close to 100%. The best results gave the catalyst modified with α-lipoic acid (100% yield) followed by 1,6-hexanedithiol (98%) and thioglycerol (97%). Compared to other modified catalysts at high conversion levels these selectivities are outstanding.[1] The different modifiers showed an influence on rates for 4-nitrostyrene conversion. The lowest rates were observed for the thioglycerol modified catalyst (0.0027 mmol g_{cat}^{-1} s^{-1}) and the α-lipoic acid modified catalyst (0.0033 mmol g_{cat}^{-1} s^{-1}). Higher rates were observed for 1-dodencanethiol (0.0096 mmol g_{cat}^{-1} s^{-1}) and 1,6-hexanedithiol (0.0100 mmol g_{cat}^{-1} s^{-1}). Thus the best result regarding selectivity and activity was obtained for the modification with 1,6-dithiolhexane. In general the lack of selectivity of unmodified Pt catalysts for the hydrogenation of substituted aromatics is ascribed to the flat adsorption via the benzene ring and thus to a simultaneous exposure of the reducible groups toward the active sites.[16] As all modified Pt/TiO_2 catalysts were treated with a molar 100-fold thiol modifier excess, likely, maximum coverage was achieved for all catalysts.[17] Thus the adsorbed thiol modifiers prevent the flat adsorption of the substrate 4-nitrostyrene. A preferential interaction of the nitro-group with the TiO_2 support thus leads to the observed switch in selectivity. The difference between the polar and the unpolar modifiers could originate from the intermolecular interaction of the functional groups with the neighboring modifier leading to a denser coverage compared to the unpolar modifier. An outstanding hydrogenation catalyst should yield excellent activity, selectivity, and stability. Therefore we tested the 1,6-dithiolhexane modified catalyst in recycle experiments, where we topped up the substrate and followed selectivity and conversion after 1 h. Figure 2 shows the conversion of 4-nitrostyrene (red column) selectivity toward 4-aminostyrene (blue column), 4-ethylnitrobenzene (green column), and 4-ethylaniline (orange column) after 3 cycles of reaction.

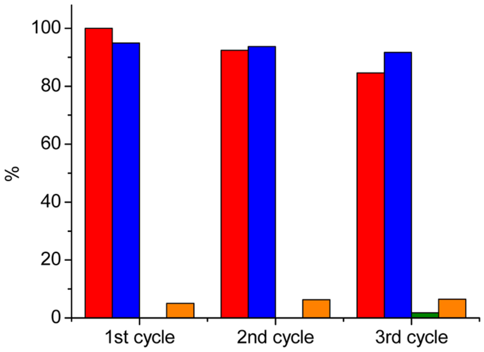


Figure 2. Top-up recycle experiments over the 1,6-dithiolhexane modified Pt/TiO_2 catalyst. Conversion of 4-nitrostyrene (red column), selectivity toward 4-aminostyrene (blue column), 4-ethylnitrobenzene (green column), and 4-ethylaniline (orange column) after 1 h of reaction at 80 °C with 50 mg of catalyst under 10 bar H_2 in 25 mL of toluene.

For the first cycle 100% conversion of 4-nitrostyrene was achieved with a selectivity of 95% toward 4-aminostyrene and 5% 4-ethylaniline. In the second cycle, the catalyst converted 4-nitrostyrene to 92% conversion with selectivity toward 4-aminostyrene of 94% and 6% toward 4-ethylaniline. In the third cycle conversion and selectivity after 1 h decreased, and 4-ethylnitrobenzene were observed among the reaction products. Conversion and selectivities toward 4-aminostyrene, 4-ethylnitrobenzene, and 4-ethylaniline of 85%, 92%, 2%, and 6% were achieved. Performing more cycles showed a continuous loss in catalyst performance. This compares favorably to industrial applied catalysts for this reaction as they are often "one-shot" catalysts. The loss in selectivity toward 4-aminostyrene might be due a degradation of the thiol-coverage on the Pt nanoparticles, and the loss of activity could be due to leaching or competition of the product with the substrate.

To summarize, we showed a simple modification procedure to control the chemoselectivity over supported Pt nanoparticles on TiO_2 employing organic thiols as surface modifiers. A 100% switch in selectivity toward 4-aminostyrene was achieved. The variation of the modifier showed that a polar group adjacent to the chain of the organic thiol revealed higher selectivities. The best result was achieved with 1,6-dithiolhexane modified Pt/TiO_2. This new system adds to the "heterogeneous tool box" and may find application in other selective hydrogenation challenges.

ASSOCIATED CONTENT

Supporting Information

Further details about catalyst preparation and modification, kinetic measurements, TEM measurements, and FT-IR spectroscopy measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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