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Functionalization of Platinum Nanoparticles with L-Proline: Simultaneous Enhancements of Catalytic Activity and Selectivity

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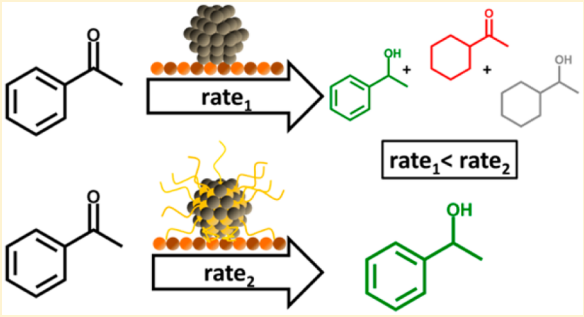
Supporting Information

ABSTRACT: In this work we present the successful application of functionalizing Pt nanoparticles (NPs) with hydrophilic organic ligands as a strategy for enhancing their catalytic activity and selectivity. In the first step, Pt NPs were prepared by a colloidal approach and subsequently functionalized in a separate synthesis step with L-proline (PRO). The functionalized NPs were supported onto Al_2O_3 and investigated as heterogeneous catalysts for the selective hydrogenation of acetophenone. Whereas significant amounts of side products are formed by supported, "unprotected" (ligand-free) NPs, the PRO-functionalized Pt NPs are highly chemoselective even at 100% conversion. Experiments under kinetically controlled conditions reveal that this high chemoselectivity is not accompanied by a loss of catalytic activity. In contrast, an enhanced rate toward the desired product was found for PRO-Pt in comparison to the "unprotected" Pt NPs. This finding demonstrates that the use of ligands in heterogeneous catalysis allows for simultaneous enhancements of activity and selectivity.



1. INTRODUCTION

In organometallic, homogeneous catalysis, the use of ligands is essential for the stabilization of the catalytically active metal in solution. If a coordinating species desorbs from the metal center a free adsorption site is generated, which may become occupied by a reactant to undergo a reaction catalyzed by the metal. Alternatively a reactant may also become adsorbed by insertion. From homogeneous catalysis research it is known that the ligand can positively contribute to catalytic reactions and enable for the control of selectivity by interacting with the adsorbed reactant.[1] Furthermore, examples are known in which ligands enhance reaction rates by changing and participating within the catalytic cycle.[2]

For nanoparticles (NPs) applied in heterogeneous catalysis, only the surface atoms contribute to the reaction. Most of the coordination sites of the surface atoms are however blocked by adjacent metal atoms. If ligands are bound to the remaining free coordination sites of the surface atoms, their ability to adsorb and catalytically convert reactants may eventually become inhibited. In heterogeneous catalysis ligands are hence considered as catalyst poisons. They are usually only applied for the preparation of model catalysts by means of colloidal methods (to control, e.g., size, shape, or composition) and removed after particle deposition. This can be achieved by, e.g., ex situ or in situ O_3 treatments under ambient conditions[3,4] or using specific heating cycles under reductive and oxidative conditions.[5] The relevance of controlling selectivity as one of the major research goals in catalysis for the next decades however requires new and sophisticated strategies to modify the catalytic properties.[6] As a result, the use of ligands has recently started to attract significant attention within the field of heterogeneous catalysis and their ability for the control of chemo- and stereoselectivity was demonstrated.[7−9]

So far most studies in heterogeneous catalysis that focus on selectivity were performed with thiol ligands.[7,8,10,11] Sulfur is known to bind strongly to catalytically active metals so that the ligand can be tightly anchored to the particle surface. As a result partial blocking of the surface occurs that leads to the above-mentioned decrease of the catalytic activity.[8,11] This seems to be a general issue when functionalizing NPs with ligands that may not be avoidable.

In the present study colloidally prepared Pt NPs functionalized with L-proline (PRO) were investigated as heterogeneous catalysts for the selective hydrogenation of acetophenone. It was found that in contrast to bare Pt particles the PRO-Pt NPs are highly chemoselective. This enhanced selectivity is not—as observed in previous cases—accompanied by inhibition of the catalytic activity. Instead we show that the reaction rate toward the desired product on PRO-Pt is enhanced in comparison to the bare Pt NPs. Our results therefore demonstrate that PRO cannot be considered as a catalyst poison but to act as a promoter with positive effects on the activity and selectivity.

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2. EXPERIMENTAL SECTION

2.1. Material Synthesis. *2.1.1. Syntheses of "Unprotected" (EG-Stabilized) Pt Nanoparticles.* "Unprotected" Pt NPs were prepared by a slightly modified protocol of the original recipe established by Wang et al.[12] First, 0.25 g of $H_2PtCl_6 \cdot H_2O$ (40% metal, ChemPur) was dissolved in 25 mL of ethylene glycol (EG) (99.8%, Sigma-Aldrich) in a 250 mL glass flask. A solution of 0.50 g of NaOH (98.9%, Fisher Chemical) dissolved in 25 mL of EG was added and the mixture vigorously stirred at 500 rpm (stir bar length = 2.5 cm) to ensure proper mixing. The flask was equipped with a reflux condenser, and the precursor solution was heated to 150 °C using a preheated oil bath while the stirring rate was maintained at 500 rpm. The yellow solution turned black after about 5 min, indicating the formation of Pt NPs. The reaction mixture was kept at 150 °C for 1.5 h to ensure complete reduction of the Pt precursor followed by cooling to ambient temperature. The particles were precipitated by adding 50 mL of 1 M HCl (VWR) and separated from the supernatant solvent by centrifugation. The precipitated particles were washed once with 1 M HCl and then redispersed in 100 mL of cyclohexanone (≥99.0%, Sigma-Aldrich) for all further preparation steps.

2.1.2. Synthesis of PRO-Functionalized NPs. The preparation of PRO-functionalized NPs followed a previously established route for the functionalization of "unprotected" Pt NPs with hydrophilic ligands[8] and was the same for all other amine ligands investigated within the present study. First a ligand solution was prepared with deionized water, resulting in a L-proline (≥99%, Sigma-Aldrich) concentration of 8.3 mM, and 12.5 mM NaOH. In order to functionalize the NPs four aliquots of this ligand solution were added to the previously prepared dispersion of Pt NPs in cyclohexanone (see section 2.1.1). This corresponds to a ligand-to-Pt ratio of 6.4 to achieve saturation of the particle surface with ligands. The resulting emulsion was vigorously stirred for 30 min. During this mixing the particles are transferred from the organic phase into the aqueous phase, indicated by a color change of both phases. The organic phase turned clear, while the aqueous phase became black indicating the successful functionalization of the particles. The PRO-Pt NPs were then filled in a separation funnel and separated from the supernatant organic solvent after proper phase separation was achieved.

2.1.3. Purification and Cleaning of PRO-Functionalized NPs. For the characterization of functionalized NPs it is essential to clean them from residual nonbinding ligands. Therefore, the aqueous dispersion of PRO-functionalized NPs was concentrated by removing the solvent at a rotary evaporator (P = 20 mbar; T = 50 °C) until a very thick, tarry looking dispersion is obtained. Next, an excess of acetone (99.9%, VWR) was added that initiates precipitation of the functionalized NPs. After centrifugation the supernatant solvent is removed and the precipitate washed twice with ethanol (99.9%, VWR) and once with acetone (99.9%, VWR).

2.2. Characterization. *2.2.1. Transmission Electron Microscopic Investigations of "Unprotected" and Ligand-Functionalized Pt NPs.* Samples were prepared by drop-casting of the particle dispersion onto the transmission electron microscopy (TEM) grid (ultrathin carbon film, Quantifoil, Cu 200 mesh). The grids were then dried in an oven for 30 min at 80 °C. For "unprotected" NPs the cyclohexanone Pt stock solution was used for TEM grid preparation (see section 2.1.1). PRO-functionalized NPs prepared and purified as described in sections 2.1.2 and 2.1.3 were redispersed in an alkaline solution with a concentration of 0.01 M NaOH (98.9%, Fisher Chemical), followed by drop-casting onto the TEM grid. A Tecnai F20 S-TWIN microscope (FEI) was used at an acceleration voltage of 200 kV and a magnification of 150k. Particle sizes were determined using ImageJ and counting at least 200 particles. From the average size, the dispersion (ratio of surface atoms to total number of atoms within the particle) was estimated according to a model calculation previously described in detail.[8]

2.2.2. NMR Spectroscopic Characterization of PRO-Functionalized NPs. Residual H_2O is a significant issue for NMR spectroscopic studies, as water protons lead to a huge background in the spectrum. In order to remove residual H_2O from PRO-Pt NPs, the samples were cleaned as described in 2.1.3 and then redispersed in D_2O (99.9%, Deutero). Afterward the solvent was removed at a rotary evaporator (T = 50 °C; P = 20 mbar) until the sample appeared to be dry. The dried particles were redispersed in D_2O for a second time followed by solvent removal at a rotary evaporator (T = 50 °C; P = 20 mbar). After these purification steps the particles were again redispersed in alkaline D_2O and subsequently investigated by means of NMR spectroscopy (Bruker AVANCE NB-360). ^{1}H NMR spectra were recorded with standard methods; see reference for applied pulse sequence of HH-COSY (with gradients, not phase sensitive).[13]

2.2.3. Determination of Ligand Coverage. In order to estimate the ligand coverage, the nitrogen-to-Pt ratio was determined. Therefore, elemental analysis (EA) was applied to measure the nitrogen content of PRO-functionalized NPs and atomic absorption spectroscopy (AAS) to determine the Pt content. Preparation and cleaning of PRO-functionalized NPs was performed as described in section 2.1 followed by drying for 12 h in a desiccator under reduced pressure. For AAS measurements the samples were digested in freshly prepared aqua regia. EA measurements were performed using a Euro ES elemental analyzer with chromatographic separation and a TCD. AAS was conducted on a Varian AA 280 FS spectrometer. To obtain the ligand coverage the N:Pt ratio was corrected by taking the dispersion of the particle (ratio of surface atoms to total number of atoms of a particle; see section 2.2.1 for determination) into account.

2.3. Deposition of "Unprotected" and Functionalized Particles. For catalytic investigations the "unprotected" and functionalized NPs were deposited onto Al_2O_3 (PURALOX SCCa 150/200; Sasol, grain size = 200−500 μm) to give nominal metal loadings of 2 wt% with respect to the initially used amount of Pt precursor. The support material was added to the particle dispersions and the solvent removed using a rotary evaporator (P = 20 mbar; T = 50 °C). In order to clean the supported, functionalized Pt NPs from residual ligands that do not bind to the particle surface, the samples were twice rinsed with ethanol (99.9%, VWR). Supported "unprotected" Pt NPs were rinsed twice with acetone (99.9%, VWR). The cleaned catalysts were kept under vacuum in a desiccator for 30 min prior to their application in catalytic experiments. Accurate determination of catalytic activities requires the actual metal loading of the supported particle catalysts. Therefore, the metal loading of every catalyst was measured by AAS (Carl Zeiss Technology AAS 5 FL) and used for normalization of the reaction rates. Digestion of the particles was achieved with freshly prepared aqua regia. The typical loadings for supported "unprotected" and functionalized NPs are around 1.6 and 1.3 wt%, respectively.

2.4. Catalytic Investigations. *2.4.1. Catalytic Hydrogenation of Acetophenone.* Two custom-designed autoclaves (Parr Instrument Company) were used for catalytic studies, both connected to the same H_2 gas line and the same thermostat in order to perform two catalysis experiments in parallel under identical experimental conditions. In a typical experiment each autoclave was loaded with 1 mL of acetophenone (99%, Sigma-Aldrich), 9 mL of cyclohexane (99.99%, Acros), and 200 mg of catalyst. After purging with H_2 (Linde 5.0), the reaction pressure in the autoclaves was set to 20 bar H_2, and the experiments were performed at a temperature of 293 K. In order to determine reaction rates, the conversion was kept below 10% to achieve differential operation conditions. The conversion was tested to scale linearly with the amount of catalyst used within the experiment. Furthermore, the stirring rate was varied as well as the catalyst pellet size by grinding the support particles, but no effect on the conversion was obtained. The presence of diffusion limitations can hence be excluded and the requirements to determine turnover rates from conversions below 10% are fulfilled.[14] The experimental errors of the selectivities and activities were determined from the standard deviation of five catalysis experiments, each performed with a separately prepared catalyst of individually synthesized particles. The presented errors do thus not merely reflect the error of the catalytic experiments, but also deviations that may appear from the catalyst preparation.

2.4.2. Product Analysis of Catalytic Experiments. The reaction mixtures of the catalytic experiments were analyzed by gas chromatography (Shimdazu GC-2010plus AF IVD) using a Lipodex E (Macherey-Nagel, 27 m length, 0.25 mm inner diameter, 0.25 μm

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film thickness) column and a flame ionization detector (FID). A column flow of 0.86 mL min^{-1} was applied with He (Linde, 5.0) as carrier gas and a linear velocity of 25.1 cm s^{-1}. Prior to analysis the samples were diluted with acetone (VWR, 99.9%) to a solvent-to-sample ratio of 5:1. Injection was performed at 200 °C and a split ratio of 50:1. The oven temperature was held at 90 °C for 1 min, then heated to 120 °C at a rate of 2 °C min^{-1} and kept for 1 min. After further heating to 180 °C at a rate of 5 °C min^{-1} the temperature program was stopped. The activity and selectivity were determined from the total amount of detected products and reactant and by taking the corresponding response factors into account.[15] Representative chromatograms of catalysis experiments performed with "unprotected" and PRO-functionalized NPs are shown in Figure S1.

GC-MS (Agilent Technologies 5975 C) and Agilent ChemStation Software were applied in order to achieve assignment of the different side products. Samples were injected at 200 °C with a split ratio of 20:1 and separated under isothermal conditions (120 °C for 30 min) using a Innopeg 1000 column (50 m).

3. RESULTS AND DISCUSSION

A unique approach for investigating the effect of ligands on the properties of NPs is the use of so-called "unprotected" NPs.[12,16] Such particles are only weakly stabilized by ethylene glycol and CO, which are removed upon functionalization with, e.g., amine or thiol ligands, while the particle size is maintained.[12,17] As this allows the separation of particle preparation and their functionalization into two independent steps, changes in the material properties can be related exclusively to the influence of the ligand.[18] Based on this strategy, we recently presented a synthesis route for the functionalization of Pt NPs with hydrophilic ligands.[8] This recipe was applied in the present study to prepare Pt NPs functionalized with L-proline (PRO, see Figure 1 for structure). Particle size analysis performed for

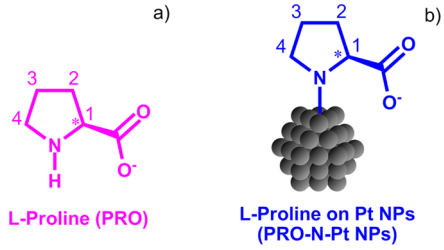

Figure 1. Structures of unbound (magenta) and Pt-bound PRO (blue) under alkaline conditions.

"unprotected" and PRO-functionalized NPs confirms that the particle size is maintained during functionalization (see Figure S2).

NMR spectroscopic studies were performed on PRO-functionalized Pt NPs dispersed in alkaline D_2O to demonstrate that PRO is successfully bound to the particle surface and cleaned from residual nonbinding ligands. The cleaned particles give only one set of ^1H signals that can be related to the structure of PRO (see Figure S4). In order to demonstrate that these signals originate from Pt-bound PRO and not from desorbed ligand molecules, a small amount of the pure ligand was added (see Figure 2). This leads to the appearance of a second set of ^1H signals which can be assigned to free PRO in alkaline D_2O.[19] Identification of the signals that belong to the same molecule can be verified by correlations in the HH-COSY spectrum (Figure 2). The correlations are identical confirming that the Pt-bound ligand is indeed PRO. It can thus be distinguished between unbound (magenta, see also Figure 1) and Pt-bound PRO (blue, see also Figure 1). Complete removal of organic impurities from functionalized NPs for NMR spectroscopic investigations is a hardly achievable preparation task.[20,21] In the present case some organic residues are visible (black). The most significant residues that appear reproducibly but to varying extent were identified as ethanol and acetic acid. Addition of both of these molecules led to increase of the assigned signals demonstrating they are not bound to the particle surface. All other residues were not found to appear reproducibly.

Only carbon-bound hydrogen was detected, because H/D exchange of oxygen- and nitrogen-bound protons in D_2O occurs too fast. Due to the stereogenic carbon atom of PRO (1 in Figure 1, labeled with *), the ^1H NMR signals of CH_2 groups are not chemically equivalent. This effect is most pronounced for the CH_2 group (2 in Figure 1) that is adjacent to the chiral carbon atom (1). The ^1H signals of the two inequivalent protons are labeled with 2a and 2b in Figure 2. Comparison of the same protons in free and Pt-bound PRO shows that the signals of 1 and 4 are considerably more shifted than the 2 and 3 protons (numbering according to Figure 1). This effect may be related to the fact that these protons are in closer proximity to the nitrogen atom which is chemically altered due to the binding to Pt. A further suitable effect may be the closer proximity of 1 and 4 to the particle surface compared to 2 and 3.

It has been demonstrated that "unprotected" Pt NP cannot be functionalized with carboxyl ligands.[22] We hence conclude that PRO binds only via the amine group to the particle surface. This assumption is further supported by correlations in HMBC spectra of the hydrogen of 1 (label according to Figure 1) with the carboxyl carbon in free and Pt-bound PRO (Figure S5). The ^{13}C chemical shifts are very similar suggesting that the carboxyl group in the Pt-bound state does not differ considerably from the free PRO. We therefore use the abbreviation PRO-N-Pt NPs for Pt NPs functionalized with PRO to indicate the binding mode.

Hydrogenation of acetophenone was performed in order to investigate and compare the catalytic properties of PRO-N-Pt NPs to "unprotected" Pt. This reaction represents a typical chemoselectivity challenge in heterogeneous catalysis. Chemoselective hydrogenation of the carbonyl group to phenylethanol (see structure 3B in Figure 3, green) is the desired reaction but simultaneously hydrogenation of the aromatic moiety to form methylcyclohexylketone (3C, red) can occur. This is a particular problem for practical hydrogenation catalysts like supported Ni, Pd, or Pt particles, which usually exhibit selectivities for phenylethanol (3B) around 60−80%.[23−26] Both these products (3B and 3C) may serve as intermediates that become eventually fully hydrogenated to yield the saturated alcohol cyclohexylethanol (3D, gray). Besides, a stereogenic center is generated by formation of the desired product (3B, the stereogenic C atom is labeled with *). The reaction thus enables to investigate the ability to control chemoselectivity with ligands and furthermore to probe the presence of stereoselectivity that may appear when using chiral ligands such as PRO.

Table 1 shows the selectivities of supported, "unprotected" Pt NPs and PRO-N-Pt NPs at 100% conversion. A total amount of 35% of the undesired saturated alcohol (cyclohexylethanol, 3D) was obtained for the "unprotected" Pt NP catalyst demonstrating the above-mentioned limitations of Pt for this reaction.[25,26] In contrast, PRO-N-Pt NPs are highly

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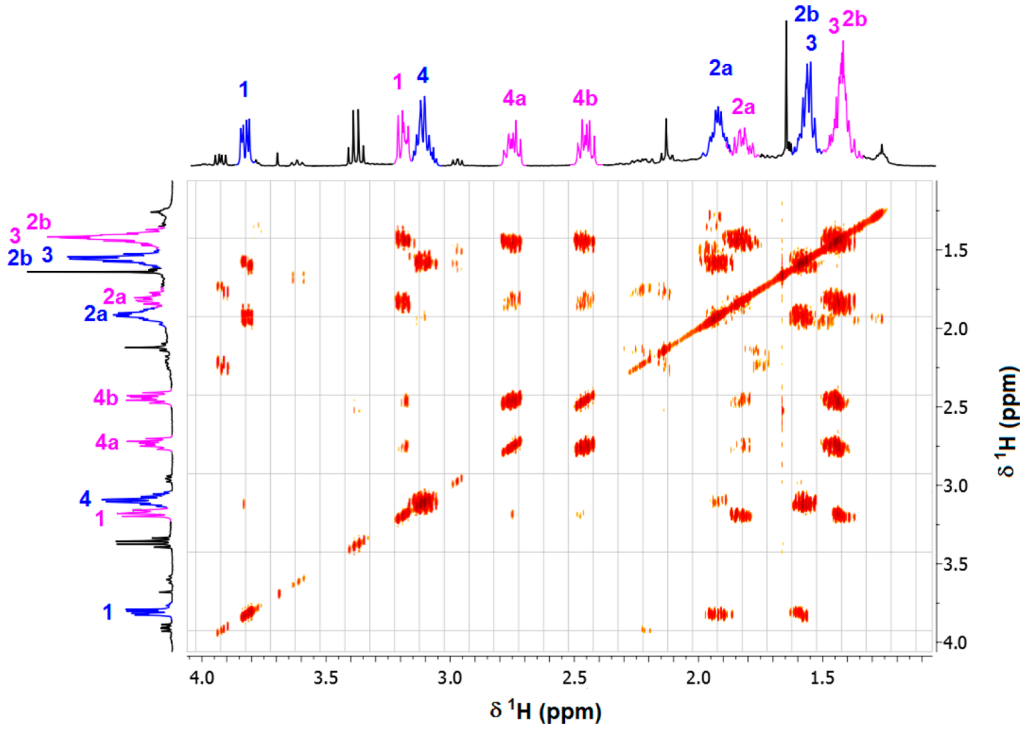

Figure 2. ^{1}H and HH-COSY spectrum (360 MHz, 8.4 T, D_2O) of a mixture of free PRO (magenta) and Pt bound PRO (blue). Signals of contaminations are black.

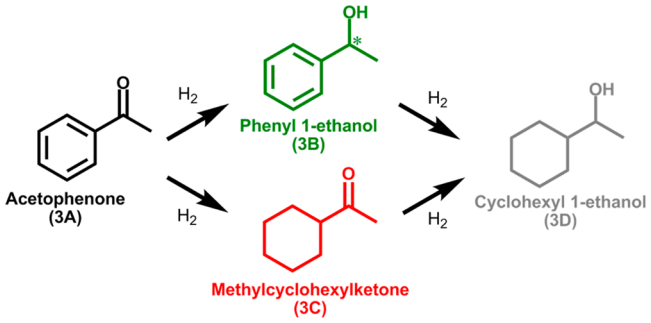

Figure 3. Reaction scheme for the catalytic hydrogenation of acetophenone (3A, black). The desired reaction product is the aromatic alcohol (3B, green), but hydrogenation of the aromatic moiety occurs as a competitive reaction path leading to the saturated carbonyl (3C, red). 3B and 3C may both further react to give the saturated alcohol (3D, gray).

Table 1. Catalytic Experiments Performed in Cyclohexane at T = 293 K, P_{H_2} = 20 bar, t = 24 h

	ligand coverage	conversion (%)	3B	3C	3D	ee (%)
Pt NPs	0	100	65	0	35	0
PRO-N-Pt NPs	0.85	100	≥99	0	0	14 ± 1

chemoselective toward the desired aromatic alcohol with some modest stereoselectivitiy (14% enantiomeric excess (ee)). This exclusive chemoselectivity at full conversion is not specific for PRO but was also obtained for other hydrophilic primary and secondary amine ligands (see Figure S6a,b for further ligand structures tested). In contrast, a thiol-bound ligand (N-acetyl-cysteine (NAC), Figure S6c) led to complete inhibition of the catalytic activity (see reference for synthesis and characterization of NAC-S-Pt)[27]

A selectivity enhancement by using additives like ligands or adsorbates is usually accomplished at the expense of activity.[28] The additive binds to the particle surface which may lead to poisoning of unselective sites.[29] Simultaneously the catalytically active surface becomes at least partially blocked which causes a decrease in activity.[30,31] In order to determine if the activity of the Pt NPs is reduced due to the functionalization with PRO, the formation rates on "unprotected" Pt NPs and PRO-N-Pt NPs for the individual products (3B, 3C, and 3D) were determined (see Figure 4, color code for reaction products is the same as in Figure 3).

Even though the ligands bind to surface atoms we surprisingly found that the catalytic activity normalized to the total number of surface atoms (Figure 4a) is not negatively affected by the presence of PRO. Instead the formation rate toward the desired product phenylethanol (3B) is enhanced. This finding seems to be inconsistent with the explanation that the ligands merely poison the unselective sites. For this scenario the rate of formation for phenylethanol (3B) over PRO-N-Pt should be either the same or lower than that of "unprotected" Pt NPs.[32] It has been shown that the "unprotected" Pt NPs used by us are in the metallic state after preparation and that binding amines does not significantly alter the electronic properties of Pt.[16] Furthermore, if electronic effects are of significance for the catalytic properties of amine-functionalized Pt NPs, the presence of ligands should lead to changes of activation energies.[33] However, it has been previously shown for various amines on Pt that they do not alter activation energies of reactions that strongly depend on the electronic properties of the catalytic metals like CO oxidation.[30] If an electronic effect would be the determining factor for the enhanced rate, one should be able to achieve the same effect with other amines. However, the use of, e.g., *N*-methyl-proline

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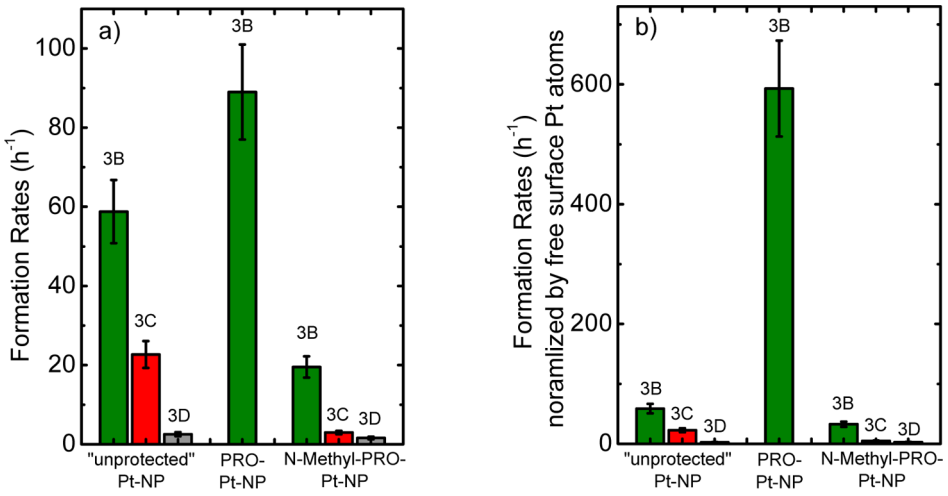

Figure 4. Formation rates normalized to the total number of surface atoms for each product (see panel a) on "unprotected", PRO-N-Pt, and *N*-methyl-PRO Pt NPs. The color code reflects the structures shown in Figure 3. A significantly enhanced rate toward the desired product phenylethanol (3B) is obtained for PRO-N-Pt in comparison to the "unprotected" Pt NPs. In contrast *N*-methyl-PRO inhibits the activity while showing a selectivity improvement. All hydrogenation rates normalized to the total number of free surface Pt atoms for "unprotected", PRO-N-Pt, and *N*-methyl-PRO-Pt NPs are shown in panel b). The phenylethanol (3B) formation rate on PRO-Pt NPs is significantly higher than that on "unprotected" Pt NPs, whereas it is inhibited on *N*-methyl-PRO-functionalized Pt NPs. A differently scaled form of panel b is shown in Figure S7, that allows for a better comparison of "unprotected" and *N*-methyl-PRO-functionalized particles.

(N-Me-PRO), as discussed in further detail below, led to a significant inhibition of the activity (see Figure 4). Therefore, we can exclude that electronic effects induced by the amine ligands are the reason for the enhanced catalytic activity. So far we only discussed rates normalized to the total number of surface atom. It should however be taken into account that only ligand free surface sites can contribute to the reaction. With respect to the ligand coverage of PRO-N-Pt NPs (see Table 1) only 15% of all surface atoms are free of ligands. If this value is applied in order to normalize the rate to the total number of free surface atoms (Figure 4b), the formation rate for the desired product on PRO-N-Pt NPs exceeds that of the "unprotected" NPs by a factor of 10. Based on this finding and the fact that an electronic effect can be excluded, we conclude that the reaction on PRO-N-Pt NPs does not proceed via the same mechanism as on "unprotected" Pt NPs. Thus, different mechanistic scenarios are discussed in the following that may account for simultaneous enhancements of activity and selectivity.

First it is considered if homogeneous catalytic species are formed by metal leaching that may contribute to the reaction. Catalytic reactions with supported metal particles in liquid media can cause formation of homogeneous species through metal leaching. This is a typical problem for heterogeneous catalysis under strongly oxidizing conditions.[34] In hydrogenation reactions the opposite reaction is favored (particle formation from homogeneous catalysts), as reduced metallic species nucleate to minimize their free surface energy.[35] The formation of homogeneous species thus seems unlikely to account for the obtained rate enhancement. To demonstrate that in the present case no homogeneous species are formed that lead to the obtained activity and selectivity enhancements, a filtration test was performed. For this purpose a catalysis experiment was run to about 50% conversion and then stopped. The heterogeneous catalyst removed by filtration and the reaction mixture again exposed to reaction conditions. No further conversion was obtained. We hence conclude that the obtained activity and selectivity enhancements are not related to leaching of the catalytically active metal.

A further suitable explanation may be the presence of a ligand acceleration effect, which describes the ability of a ligand not to just merely act as a spectator but to contribute to the reaction.[2] The participation of the ligand leads to alternative activation and reaction mechanisms that may exhibit enhanced reaction rates in comparison to the purely metal-catalyzed reaction path. The appearance of acceleration effects are known from homogeneous as well as heterogeneous catalysis.[2] In heterogeneous catalysis the use of cinchona alkaloids as so-called modifiers has been reported to accelerate hydrogenation rates for ketones.[36] The modifier is dissolved in the reaction medium and can coordinate C═O groups to form a highly activated complex.[37] If such a reactant−modifier complex adsorbs on a Pt particle that activates H_2 via dissociative adsorption, chemo- and stereoselective hydrogenation of the carbonyl occurs at rates that are enhanced in comparison to catalytic hydrogenation of the carbonyls by Pt. The acceleration effect of cinchona alkaloids is, however, limited to specific ketones. For the reaction investigated in the present study (Figure 3) modifiers were actually found to reduce the reaction rate toward the desired product by 84%.[38] The difference between the modifier approach and the concept of functionalizing particles with ligands for applications in heterogeneous catalysis is that the latter is based on the strategy that the ligand is not soluble in the reaction medium and strongly bound to the particle.[8] Otherwise the particles would desorb from the support and simultaneously the ligands from the particle surface leading to a loss of the functionalization. To demonstrate that ligands indeed do not act like modifiers two tests were performed. First, an experiment was performed in exactly the same way modifiers are applied. The heterogeneous catalyst (supported "unprotected" Pt NPs) was added to the reaction mixture together with the ligand and then the reaction was started. As expected, the selectivity of this experiment reflects exactly the results obtained for "unprotected" Pt NPs, because the ligand is not soluble in the reaction medium. Second, a

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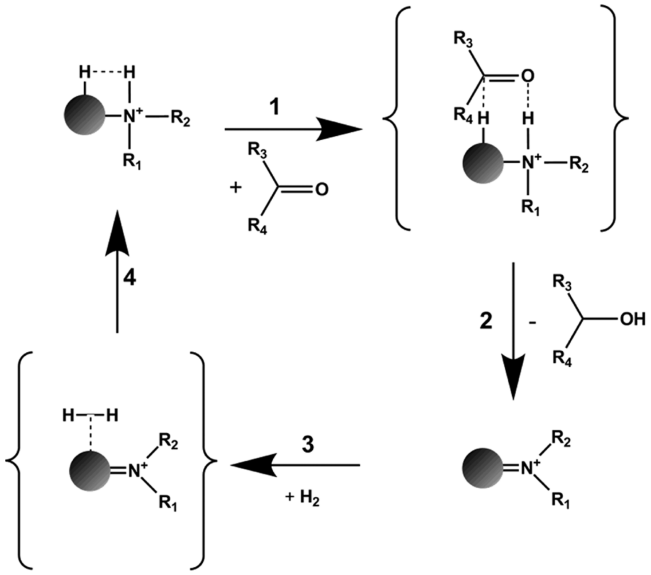
supported PRO-N-Pt sample was applied as catalyst under the same conditions used for all other experiments (see section 2.4), but using ethanol as solvent instead of cyclohexane. PRO is slightly soluble in ethanol. It can hence desorb from the particle surface to act like a modifier, which is soluble in the reaction medium.[39] In addition, the functionalized NPs can also desorb from the support and act as "quasi-homogeneous" catalysts when the ligand is soluble in the reaction medium. This effect was indeed observed. After catalytic experiments the reaction mixture showed a pale dark color, which indicates the presence of colloidal particles. The result of this catalytic experiment shows that neither full conversion nor full chemoselectivity was obtained (see Table S1). Furthermore, the stereoselectivity was found to decrease from 14% to 3% in comparison to the experiments performed under the same conditions but in cyclohexane (see Table 1). We can thus conclude that the selectivity controlling ability of PRO is not fully utilized when being applied as a modifier. Instead it has to be kept in the surface-bound state similar to a ligand in homogeneous catalysis which can only enhance the selectivity when being coordinated to the metal center.

In homogeneous catalysis the use of primary and secondary amines as ligands to accelerate the hydrogenation of ketones is a well-established strategy.[40] The key for this effect is that amine-bound hydrogen atoms become acidic upon coordination of the amine to a late transition D-metal like Ru or Pt.[40] In comparison to aromatic moieties, the electronic structure of carbonyl groups makes them suitable for attractive interactions with protons. The acidic amine protons can coordinate to the oxygen of the C═O group and activate it (see step 1 in Scheme 1). The amine hydrogen protonates the C═O group oxygen while a hydride is transferred from the metal to the carbon atom (Scheme 1, step 2).[41] Afterward, the catalyst adsorbs H_2 (Scheme 1, step 3), which is dissociated (Scheme 1, step 4) to re-form the catalytically active species.

Scheme 1. Ligand-Accelerated Hydrogenation of Carbonyls via N−H Effect[a]



[a]Amine-bound hydrogen atoms become acidic through coordination to late transition D-metals (gray sphere). Such protons can interact with carbonyl oxygen (step 1) and participate within the reaction, leading to an enhanced hydrogenation rate (step 2). After reaction the catalyst adsorbs (step 3) and dissociates H_2 (step 4) by which the initial catalyst is re-formed.

A catalytic experiment to test for the presence of a N−H effect can be performed by using tertiary amines as ligands. As illustrated in Scheme 1 the N−H guided reaction path can only proceed when amine protons are available.[40] If however tertiary amines are applied as ligands no amine proton is present and hence no N−H effect can occur (compare Scheme 1).[41] In order to perform this test, a catalyst was prepared by using Pt NPs that were functionalized with N-Me-PRO (see Figure S6d for structure), the simplest tertiary amine derivative of PRO. An increasing steric demand of ligands leads to a decreasing ligand coverage.[8,42] As a result a decrease of the ligand coverage from 0.85, as determined for PRO-N-Pt NPs, to 0.4 was obtained when using a N-methylated derivative, which was taken into account when normalizing the rates to the total number of free surface atoms (Figure 4b). Comparison of the N-Me-PRO NPs with the "unprotected" Pt NPs shows that the formation rates of all three products are reduced by the presence of this ligand. However, as the rates for the side products (3C and 3D) are even stronger inhibited than that of the desired product (3B) a selectivity enhancement (from 70% to 81%) is obtained by functionalizing with N-Me-PRO (Figure S7 shows a zoom into the part of Figure 4b being relevant for this discussion). This finding can be explained by a dilution effect that is also known from the field of bimetallic catalysis.[43] In order to react an aromatic ring has to adsorb in a "laying down" geometry, which requires larger ensembles of adjacent free surface sites than the adsorption and hydrogenation of the carbonyl group.[32,44,45] Ligands, however, dilute adjacent surface atoms and hence decrease the size of Pt ensembles on the particle surface.[10,42] As a result the probability of reactions of aromatic moieties decreases with an increasing ligand density on the surface.[32] Because hydrogenation of the carbonyl group requires less adjacent surface atoms than adsorption and reactions of the phenyl moiety, one may question if for this reaction the dilution effect could also lead to a simultaneous increase in the number of sites available for carbonyl hydrogenation. If this assumption holds the formation rate of phenylethanol (3B) on N-Me-PRO-Pt NPs, normalized by the number of free surface atom, should be enhanced compared that on "unprotected" Pt NPs, which is however not the case (see Figure 4b and Figure S7). Instead the rate is reduced by almost a factor of 2. We thus conclude that N-Me-PRO leads to a selective poisoning of unselective sites by diluting larger surface ensembles, which is not accompanied by the formation of additional sites for carbonyl hydrogenation. Comparison of N-Me-PRO- with PRO-functionalized NPs shows that for the latter no considerable reaction rates for the undesired hydrogenation of the aromatic moiety are obtained. This effect could be explained by the higher ligand coverage of PRO that may ultimately lead to complete inhibition of phenyl hydrogenation on PRO-N-Pt NPs. While the presence of a dilution effect can be concluded to occur on PRO-N-Pt NPs, it does not, however, account for the fact that the rate for the desired product (3B) is about 18 times higher on PRO-N-Pt NPs (see Figure 4b). Instead a second effect must be considered in order to explain the enhanced catalytic activity. With respect to the homogeneous catalysis literature and the above-described testing strategy we conclude that our findings evidence that for PRO the amine proton plays an essential role for obtaining high catalytic activity, by participating within the reaction.[40,41] The enhanced selectivity and catalytic activity may thus be described

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as an interplay of two effects: (i) the high coverage of PRO leads to inhibition of undesired reactions of the phenyl group (ii) the presence of a ligand acceleration effect leads to an enhanced activity toward the desired carbonyl hydrogenation.

Finally, we investigated the stability of the PRO-N Pt NPs under different conditions as the stability of the ligand shell is a crucial aspect of such materials. In order to avoid suitable changes or degradation during catalysis, very mild reaction conditions are chosen (T = 293 K; P = 20 bar H_2). No change in the catalytic performance was obtained after 850 catalytic turnovers per ligand. Doubling of the number of turnovers to 1700 still led to more than 99% chemoselectivity. However, the stereoselectivity decreased to an 2% ee. We thus conclude that after 1700 turnovers changes have started to occur within the ligand shell. For thiol-functionalized Pd NPs it has been shown that storage at air led to altering of the catalytic properties.[46] We thus tested the stability of the PRO-functionalized Pt NPs at ambient conditions. Therefore, supported, PRO-functionalized Pt NPs were stored at ambient conditions and then applied as catalysts. After exposure for 1 week in air at room temperature the enhanced selectivity was completely lost and the catalytic properties revealed those of the "unprotected" Pt NPs. We thus conclude that similar as thiol-functionalized Pd NPs also PRO-N-Pt NPs are not stable over long periods under ambient conditions. Finally, we tested the ability of recycle the catalyst. Therefore, a supported PRO-N-Pt NP catalyst with full chemoselectivity and a stereoselectivity of 14% ee was separated from the reaction mixture after the catalysis experiment. The sample was then washed and dried under vacuum using the same procedure as for the freshly prepared catalysts (see section 2.3). While the chemoselectivity after recycling was still higher than 99%, the stereoselectivity decreased to an ee of 3%, which shows that recycling leads to changes of the ligand shell.

The current view on the use of ligands in heterogeneous catalysis is that they enable for the control of selectivity but at the expense of activity. The presented results however demonstrate that this conclusion is not general. Instead both activity and selectivity can also be enhanced simultaneously, revealing a so far unknown potential of ligands for their application in heterogeneous catalysis that needs to be explored.

4. CONCLUSION

A recently introduced preparation route for the functionalization of "unprotected" Pt nanoparticles with hydrophilic ligands was applied to synthesize Pt NPs functionalized with L-proline. Characterization by NMR spectroscopy was performed, which confirms binding of PRO to the particles and the successful removal of residual nonbinding ligands from the samples. PRO-functionalized NPs were supported on Al_2O_3, investigated as heterogeneous catalysts for the hydrogenation of acetophenone and compared to "unprotected" and *N*-methyl-PRO functionalized Pt NPs. While a considerable amount of side products is formed by the "unprotected" Pt NPs, the PRO-functionalized particles were found to be highly chemoselective. Surprisingly this enhanced selectivity induced by PRO was not achieved at the expense of activity, as in the case of *N*-methyl-PRO functionalized Pt NPs, but led to an increase of the formation rate toward the desired product. This finding evidence that the amine proton of PRO plays an essential role for these activity enhancements. Based on our results we conclude that the effect of PRO is twofold. The high coverage of PRO leads to inhibition of undesired reactions of the phenyl group, by diluting Pt ensembles. In addition PRO exhibits a ligand acceleration effect that can be related to a N−H effect, which leads to an enhanced activity toward the desired carbonyl hydrogenation.

The presented results demonstrate that ligands can at the same time positively affect the catalytic activity and selectivity of NPs. If this finding is indeed related to a N−H effect it should be feasible to mimic ligand acceleration effects, known from homogeneous catalysis, on supported NPs thus making them applicable to heterogeneous catalysts. As next step, we will aim at using our strategy of functionalizing NPs with hydrophilic ligands in order to develop heterogeneous catalysts that are not just very active and chemoselective, but also highly stereoselective.

■ ASSOCIATED CONTENT

Supporting Information

Representative chromatograms of catalytic experiments, representative TEM images and particle size analysis, NMR spectra of PRO-N-functionalized Pt NPs, structures of additionally tested ligands, results of catalysis experiments with PRO-Pt NPs in ethanol, and a differently scaled version of the graph in Figure 4b. 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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