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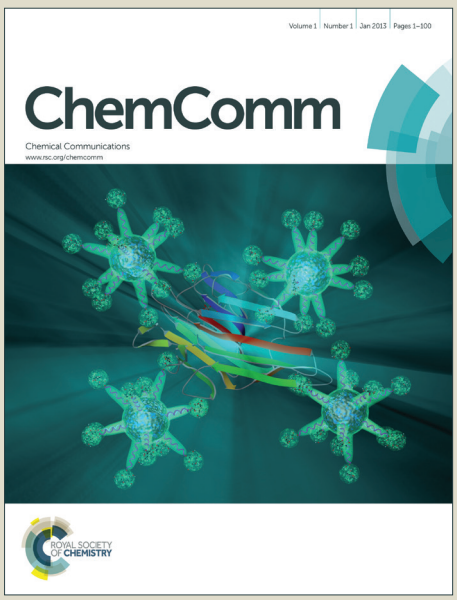

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The Effect of Particle Size and Ligand Configuration on the Asymmetric Catalytic Properties of Proline-functionalized Pt-Nanoparticles

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The effect of particle size on the asymmetric catalytic properties of supported ligand-functionalized nanoparticles (NPs) was investigated for the first time and found to alter significantly the activity but surprisingly not the stereoselectivity. These results suggest that the stereoselectivity of these complex systems is primarily determined by the ligand-reactant interaction, whereas the activity is determined by the particle size.

Understanding and the development of new strategies for the control of selectivity is one of the major research aims for this century's catalysis research.[1] Even though the use of ligands for this task is a well-established strategy in homogeneous catalysis their exploration in heterogeneous catalysis has just begun revealing a so far unknown potential. By binding ligands to a nanoparticle (NP), the surface becomes electronically and geometrically modified. As a result the reactant activation may be affected which in turn leads to a change in selectivity.[2-4] It has furthermore been shown that the use of chiral ligands enables for the induction of asymmetry and hence to achieve stereoselectivity.[5] This evidences that beyond the potential of ligands to modify the surface properties it is possible to achieve ligand-reactant interactions as known from homogeneous catalysis. Ligands may hence be applicable as a selectivity controlling element perpendicular to the surface of a NP.

A metalorganic catalyst consists of a single metal atom with a geometrically well-defined ligand sphere. In contrast, a particle exhibits a surface composed of atoms that are geometrically and electronically different and its properties depend furthermore on the particle size. Therefore, it has to be considered that the ligands on a particle surface may be chemically different. As a result rather unpredictable effects of particle size on the activity and stereoselectivity may be expected. Especially the influence of the surface on the asymmetric induction, which has so far not been studied, is of fundamental importance in order to determine guidance for achieving high stereoselectivities with ligand-functionalized NPs.

As the potential of ligands for asymmetric catalysis with supported NPs has just recently been discovered, only a few systems are known yet, and reported enantiomeric excesses (ee) are quite low (max. 14 % ee).[6] The finding of highly stereoselective systems will hence be an important and time consuming research task for the next decade, just like in the beginning of asymmetric metalorganic catalysis.[7]

In the present study, we show the first step towards high stereoselectivities (34 % ee for 1C in Fig.1) by hydrogenating ethylacetoacetate (EAA) over Pt NPs (1.2 nm in size) functionalized with L-proline (PRO). Using this system, which is right now the actual benchmark for stereoselectivity with supported ligand-functionalized NPs, we performed a study on the effect of particle size and ligand configuration that enables to gain some fundamental insights into what determines the catalytic properties of these materials.

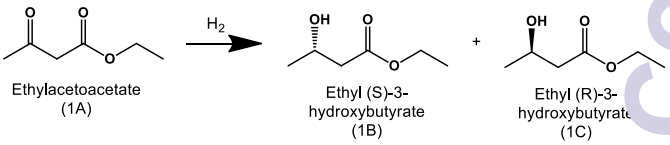

Figure 1. Investigated reaction: Hydrogenation of ethylacetoacetate (EAA, 1A) leads to the formation of (S)- and (R)-Ethyl-3-hydroxybutyrate (1B and 1C, respectively).

For the material preparation we followed a specific strategy established and presented in detail previously (see Section 1 in ESI for detailed syntheses protocols).[5] Briefly, so-called "unprotected"

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Electronic Supplementary Information (ESI) available: Experimental details, representative chromatograms of catalytic experiments, representative TEM images and particle size analysis, IR spectra of PRO-N-functionalized Pt NPs before and after exposure to catalytic conditions, scheme of N-H assisted reaction pathway, formation rates of "unprotected", PRO-, and N-methyl-PRO-functionalized Pt NPs, all formation rates normalized to the number of ligand-free surface atoms, long-term stability tests. See DOI: 10.1039/x0xx00000x

NPs are first synthesized and functionalized with the desired ligand in a separate step. The particles are then deposited by adding the support material to the colloidal dispersion, followed by solvent removal. As the particle size is preserved in each preparation step, the approach enables for the independent control of particle, ligand, and support and hence to study their influence systematically.[5] The size of "unprotected" Pt NPs can be controlled to some extend by varying the pH value of the reaction mixture.[8] In the present study we used this approach and prepared Pt NPs of 1.2 nm (± 0.3) and 2.1 nm (± 0.5) that were subsequently functionalized with L- and D-proline (see Fig. S1 – S2 in ESI for size distributions and TEM images). The two particle sizes are within the mitohedrical region (0.8 to 4 nm) where the ratio of low to highly coordinated surface atoms changes distinctively with size. Above 6 nm atoms with high coordination numbers (in low-index planes) predominate and particle size has approximately no influence.[9, 10] On the basis of the model of van Hardeveld and Hertog the ratio of low to highly coordinated surface atoms changes from 2 to 0.7 when increasing the particle size from 1.2 to 2.1 nm (see ESI Section 3 for further details). Thus, significant changes in the catalytic properties can be expected for these two types of particles if size effects are of importance for PRO-functionalized NPs.

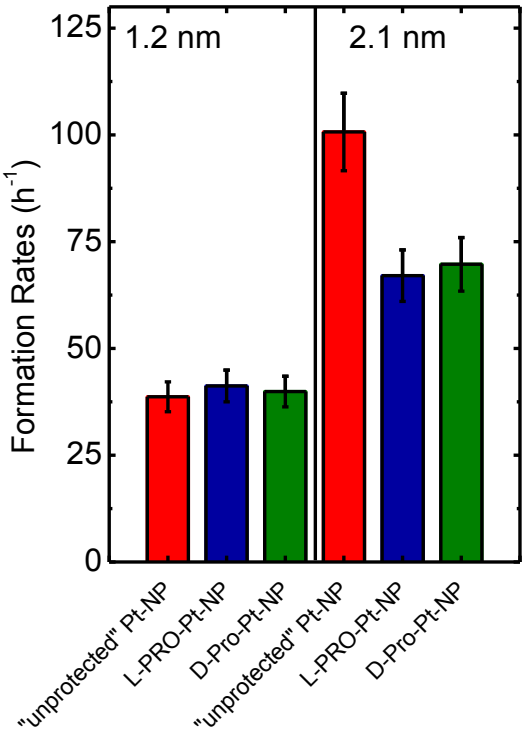


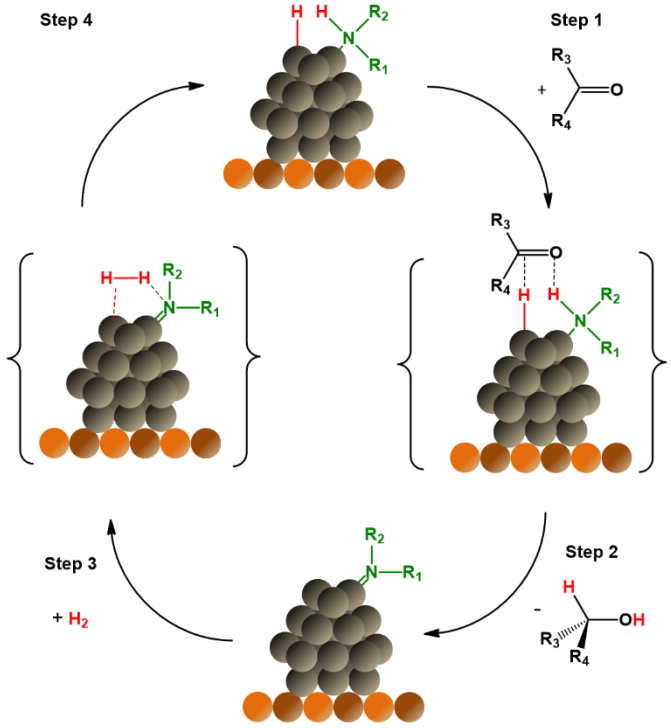
Figure 2. Formation rates normalized to the total number of surface atoms on "unprotected" (red), L-PRO-Pt (blue), and D-PRO-Pt NPs (green). Particles of 1.2 nm size are shown on the left, 2.1 nm particles on the right.

Catalytic activities for the hydrogenation of EAA over "unprotected" Pt NPs of 1.2 and 2.1 nm and the same particles functionalized with L- and D-proline (PRO) are shown in Figure 2 and Table 1, as steady state formation rates. In order to allow a representative discussion, the formation rates were normalized to the total number of surface atoms, determined from the average particle size of the TEM size distributions given in Figure S1 (see reference for details on dispersion estimation).[5]

When comparing the steady state formation rates, it is found that for both, "unprotected" and PRO-functionalized Pt NPs, the rates change with particle size. Over larger particles the activities are generally higher. Especially the "unprotected" Pt NPs show a strong size dependence with an increase by a factor of 2.7 as the particle size is increased from 1.2 to 2.1 nm. PRO-functionalized NPs still show a 1.7 fold enhancement. For Pt clusters electronic structure induced changes of the catalytic properties already start to vanish at cluster size of 20 atoms.[11] As the number of atoms for the small particles (1.2 nm) investigated here is already around 64 (see ESI Section 3 for further details), a change of the electronic structure that is of catalytic relevance can be excluded for the two investigated sizes. The obtained increase of the steady state formation rates with particle size is however a known phenomenon for the hydrogenation of C=O compounds over supported Pt NPs and has been related to decarbonylation of carbonlys by low coordinated Pt surface atoms.[12] The CO formed by this reaction then poisons these highly reactive surface atoms so that they cannot further contribute to the catalytic reaction. In order to demonstrate the presence of CO on the particles, PRO-functionalized particles were investigated by IR spectroscopy before and after exposure to catalytic conditions (see Section 4 in ESI). The resulting spectra do not reveal any characteristic feature for CO on Pt before exposure to reaction conditions, but a distinctive band appears above 2000 cm^{-1} after exposure that is characteristic for CO linearly adsorbed on Pt.[13]

For the small size the rates normalized to total number of surface atoms are almost the same over "unprotected" and PRO-functionalized particles, even though ligands are expected to block catalytic sites. Activation energies for reactions over Pt have been demonstrated to be not affect by amine ligands.[14] An electronic effect of amine ligands on the catalytic properties of Pt can hence be excluded.[15] Primary and secondary amines are however known to induce an alternative reaction pathway compared to the pure metal catalyzed reaction that may be related to the so-called N-H effect that is known from homogeneous catalysis (see Scheme S1 in ESI).[16] This effect can also proceed on ligand-functionalized Pt NPs as recently discussed and superpose the blocking of active surface.[6] An appropriate test for the presence of this effect is the use of a tertiary amine as ligand.[17] Because a tertiary amine does not exhibit any hydrogen substituents, such ligands are not able to induce a N-H assisted reaction path, but must cause an activity inhibition. Performance of this test for a N-H effect using N-methyl-L-proline (N-Me-PRO) as the simplest tertiary amine derivative of PRO was indeed found to be positive for the investigated reaction (see Section 6 in ESI). A N-H induced acceleration for the investigated reaction over PRO-functionalized NPs is hence concluded to occur that is making up the losses in activity through blocking of catalytic surface atoms by ligand binding.

On 2.1 nm particles the presence of PRO leads to a slight reduction of the rate normalized the total number of surface atoms of around 30 % (see Fig. 2), when compared to "unprotected" NPs of the same size. Hydrogenation of EAA over a bare metal surface is expected to require adjacent surface atoms as both, EAA and hydrogen, have to be activated and to be adjacent to each other in order to react.[18] For all PRO-functionalized samples the ligand coverages are so high (0.8 to 0.96, see Table 1) that the remaining ligand-free surface atoms can be considered as being isolated sites. We therefore propose that a purely metal-catalyzed reaction cannot occur on PRO-Pt NPs, but the N-H assisted reaction path. For the N-H mechanism the carbonyl does not have to adsorb directly on a bare metal atom but H_2 (see Scheme S1 in ESI). This coordinated molecular hydrogen is then activated via heterogeneous dissociation, induced by interaction with the nitrogen atom of the adjacent ligand that acts as a base.[16] This means that a free adsorption site on the metal has to be available close enough to the ligand for H_2 activation to proceed, which leads to formation of the active species that adsorbs and hydrogenates the carbonyl reactant.



Scheme 1. N-H assisted reaction path with a ligand-free surface atom adjacent to a ligand-blocked as active site. The C=O reactant can interact with Pt bound hydrogen and an amine bound proton, to become activated (Step 1) and hydrogenated (Step 2). The catalyst is reformed by coordinating molecular hydrogen (Step 3) that is heterogeneously dissociated by interacting with a ligand-free surface atom and the ligand nitrogen (Step 4).

The ligand sphere of a metalorganic catalyst is flexible and coordinated solvent molecules can desorb to leave open sites for H_2 adsorption. In contrast, a surface atom exhibits a rigid ligand sphere. It seems thus very unlikely that a single surface atom to which a ligand is bound is able to adsorb a further molecule such as H_2. [illegible] oxygen covered Pt surfaces it has been reported that dissociativ[e] hydrogen activation can occur on a site pair formed from a free [P]t surface atom and an adjacent oxygen binding Pt atom.[19] H_2 [ca]n adsorb molecularly on the free surface atom and then dissociate b[y] interaction with the adjacent oxygen binding Pt atom. We therefore propose that for the N-H assisted reaction pathway over a Pt NP, [a] ligand-free surface atom has to be available, adjacent to a ligand-blocked surface atom. Such a site pair is then suitable facilitate H[2] activation via dissociation. Due to the high ligand coverages of PRO-Pt NPs their activity has then to be considered as being limited by the availability of ligand-free surface atoms to form the proposed active site. This reasoning enables for explaining why on large particles [in] contrast to the small ones a slight decrease in activity is obtained by binding PRO, as the ligand coverage on the larger particles is higher than on small (Table 1).

Table 1. Catalytic experiments performed in THF at T = 25°C, P_{H_2} [= 3] bar. A negative ee corresponds to an excess of (S)-Ethyl-3-hydroxybutyrate (1B in Fig.1) a positive ee to an excess of (R)-Ethyl-3-hydroxybutyrate (1C in Fig.1).

Sample	NP size (nm)	Ligand cover-age	Rate per surface atom (h^{-1})	Rate per free surface atom (h^{-1})	ee (%)
Pt NPs	1.2	0	39	39	0
Pt NPs	2.2	0	101	101	0
L-PRO-Pt	1.2	0.85	41	273	34
L-PRO-Pt	2.2	0.96	67	1675	30
D-PRO-Pt	1.2	0.8	40	200	-30
D-PRO-Pt	2.2	0.93	70	1000	-33

In order to illustrate the effect of ligand acceleration, when considering that the availability of ligand-free surface at[oms] determines the actual activity, the formation rates were normalized to the total number of ligand-free surface atoms (see Figure S5 in ESI and Table 1). A 5 to 7 fold increase in activity can be obtained f[or] small and a 10 to 17-fold increase for the large NPs b[y] functionalization with PRO (see Section 5 in ESI for further details and discussions).

Comparison of the stereoselectivies reveals that even thoug[h] the ratio of low to highly coordinated surface atoms change[s] significantly from 1.2 to 2.1 nm, there is no distinctive change [in] selectivity, by taking the experimental error into account (± 2%). T[his] differentiates these systems from the use of chiral modifiers for supported Pt NPs, for which particle size dependent stereoselectivities have been reported.[20] The absence of an[y] significant particle size effect on the stereoselectivity may b[e] explained in two ways. The ligand-reactant interaction is not strongly influence by the structure of the underlying metal surface, becaus[e] according to the N-H assisted reaction pathway (Scheme 1) the organic reactant is not directly adsorbed on the metal surface for i[ts] activation. Alternatively, all low coordinated Pt atoms may [be]

poisoned by CO due to decarbonylation of the reactant and the reaction proceeds only over highly coordinated surface atoms that are similar for the two particle sizes.

Finally, the effect of ligand configuration on the stereoselectivity was probed. From homogeneous catalysis it is known that the product configuration can be inverted while maintaining the ee when using the opposite enantiomer of a metalorganic complex.[21] Similar results have been reported for the use of chiral modifiers for supported Pt NPs.[22] Comparison of the stereoselectivities obtained for different particle sizes and the two PRO enantiomers shows that with regard to the experimental error the absolute value of the enantiomeric excess does not change, while the product configuration is inverted. It is hence concluded that with ligand-functionalized NP catalysts the stereochemistry of the product can be controlled by using the appropriate ligand configuration.

The fact that the absolute value of the ee neither depends on the particle size nor on the ligand configuration suggests that for ligand-functionalized NPs the surface morphology is not of significant importance for the stereoselectivity. Instead, it is primarily determined by the ligand-reactant choice similar as in homogeneous catalysis,[17] whereas the activity is a matter of particle size. If this finding does not merely hold for the present case but in general the search for ligand-functionalized Pt NP catalysts with higher stereoselectivities can be reduced to the search for appropriate ligand-reactant combinations while the activity can be optimized via tuning the particle size. We next aim to perform a broader study with PRO derivatives as ligands and different reactants in order to further validate this hypothesis.

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Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.
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