Heterogeneous Catalysis

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Observation of Parahydrogen-Induced Polarization in Heterogeneous Hydrogenation on Supported Metal Catalysts**

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For homogeneous hydrogenation reactions catalyzed by transition-metal complexes in solution, utilization of the nuclear spin isomers of molecular hydrogen has become an established tool for studies on reaction mechanisms and kinetics.[1] Parahydrogen-induced polarization[2] (PHIP) can enhance the NMR spectroscopy signals of reaction intermediates and products by several orders of magnitude and provides the high sensitivity essential for such studies. It was demonstrated recently[3,4] that PHIP effects can also be observed in hydrogenation reactions catalyzed by metal complexes immobilized on a solid support. Industrial hydrogenation processes are predominantly heterogeneous and utilize supported metal catalysts. Such catalysts are not expected to produce PHIP effects,[5] since the reaction mechanism involved should destroy the original correlation of the two nuclear spins of parahydrogen. Herein we demonstrate for the first time that, contrary to these expectations, supported metal catalysts such as Pt/Al_2O_3 and Pd/Al_2O_3 do exhibit PHIP effects. This fact can be used for the production of spin-polarized fluids for MRI applications and for developing new research tools for mechanistic and kinetic studies on heterogeneous hydrogenation processes.

Homogeneous hydrogenation of unsaturated compounds in solution is often performed with transition metal complexes (e.g., Wilkinson's catalyst, $[RhCl(PPh_3)_3]$).[6] The detailed mechanism of the reaction is fairly well understood. The catalytic cycle (Scheme S1 in the Supporting Information) starts with oxidative addition of an H_2 molecule to the metal center to give a metal dihydride species and ends with reductive elimination of the product. Molecular hydrogen is known to be a mixture of two nuclear spin isomers: orthohydrogen with a total nuclear spin of $I=1$, and parahydrogen with $I=0$. If one of them (usually para-H_2) is used in the hydrogenation reaction, pairwise addition of the two hydrogen atoms from the same H_2 molecule, ensured by the reaction mechanism, preserves their correlated nuclear spin state.[2] Furthermore, this correlation can strongly enhance NMR signals of the reaction intermediates and products.

If hydrogenation is performed in the probe of an NMR spectrometer (i.e., in the high magnetic field of the NMR instrument), two strongly enhanced antiphase multiplets are commonly observed in the ^1H NMR spectrum of the reaction product (Figure S1a). This experimental scheme is known as PASADENA (parahydrogen and synthesis allow dramatic enhancement of nuclear alignment).[2,7] If hydrogenation is carried out in a low magnetic field and the reaction products are then adiabatically transferred to the NMR magnet for detection, the two multiplets show net signal enhancement of the opposite sign (Figure S1b). This experimental scheme is termed ALTADENA (adiabatic longitudinal transport after dissociation engenders net alignment).[8] The observation of both ALTADENA and PASADENA requires that the two H atoms from the same para-H_2 molecule travel as a pair throughout the entire catalytic cycle all the way to the product, and that the time elapsed between initial dissociation of the H_2 molecule and formation of the product molecule is not much longer than the nuclear spin relaxation time of the intermediates involved. All this is favored by the fact that all processes take place on a single metal atom of the complex in solution. Since the NMR spectroscopy signal-enhancement factors observed can be as large as several orders of magnitude, hydrogenation with parahydrogen has become a powerful tool for studying the mechanisms and kinetics of homogeneous hydrogenation reactions.[1]

Heterogeneous hydrogenation processes often use highly dispersed supported metals (e.g., Pt/Al_2O_3, Pd/Al_2O_3) as catalysts. Unlike homogeneous hydrogenation, which takes place on a well-defined single metal center, heterogeneous hydrogenation proceeds over a vast surface of a metal cluster. This gives rise to a large number of interaction possibilities and a variety of relevant and irrelevant species present on the surface during the reaction. As a result, despite a great deal of effort devoted to studying the mechanisms of heterogeneous hydrogenation of simple alkenes such as ethylene, conclusions regarding the reaction mechanism are still controversial.[9]

By combining the use of parahydrogen with heterogeneous hydrogenation processes, it may be possible to develop new fundamental and practical applications which rely on the substantial amplification of the NMR signals, such as mechanistic studies of heterogeneous hydrogenation and production of polarized fluids for advanced MRI studies. However, the use of parahydrogen in combination with supported metal catalysts has been postulated to be pointless,

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since the reaction mechanism apparently does not sustain pairwise addition of hydrogen to a substrate on multiatomic metal crystallites,[5] which is one of the main prerequisites for such applications. We now show that, contrary to expectation, utilization of parahydrogen in the hydrogenation of propylene catalyzed by highly dispersed supported metal catalysts (Pt/Al_2O_3 and Pd/Al_2O_3) does produce nuclear spin polarization of the reaction product propane, that is, pairwise addition of hydrogen does take place to a measurable extent.

To this end, four Pt/Al_2O_3 catalysts with different sizes of Pt metal particles (0.6, 1.1, 3.5, and 8.5 nm, denoted as Pt(6), Pt(11), Pt(35), and Pt(85), respectively) and a Pd/Al_2O_3 catalyst with 10–11-nm Pd particles were used for heterogeneous gas-phase hydrogenation of propylene to propane. The Pt catalysts with the smallest metal particles, Pt(6) and Pt(11), produce clear PASADENA polarization patterns (Figure 1).

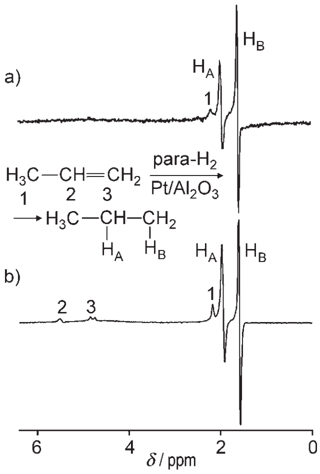

Figure 1. ^1H NMR spectra detected in the PASADENA experiments during in situ hydrogenation of propylene over Pt/Al_2O_3 catalysts with a) 1.1-nm Pt particles (number of NMR signal accumulations (NA) = 1) and b) 0.6-nm Pt particles (NA = 8). The two hydrogen atoms in the product which originate from the para-H_2 molecule are labeled A and B. The residual NMR signals of the reactant (propylene) are labeled 1–3.

Strongly polarized peaks were observed for the 0.6-nm Pt particles, despite the fact that this catalyst was noticeably less active in the hydrogenation of propylene than the other three Pt catalysts with larger metal particles.[10] This catalyst showed parahydrogen-induced polarization even at low flow rates of the reactant mixture, and the magnitude of the enhanced NMR signals was constant over a wide range of flow rates. The two Pt catalysts with the largest Pt particles (3.5 and 8.5 nm) produce only weak polarization of the product lines in the NMR spectrum. When hydrogenation is carried out in a low magnetic field outside the NMR magnet, all five supported metal catalysts exhibited ALTADENA polarized signals. Among the four Pt/Al_2O_3 catalysts, the Pt(6) catalyst again exhibited the strongest polarization (Figure 2). The Pd/Al_2O_3 catalyst produces weak (but observable) ALTADENA polarization (Figure 3).

The accepted general reaction mechanism of heterogeneous hydrogenation involves dissociative chemisorption of

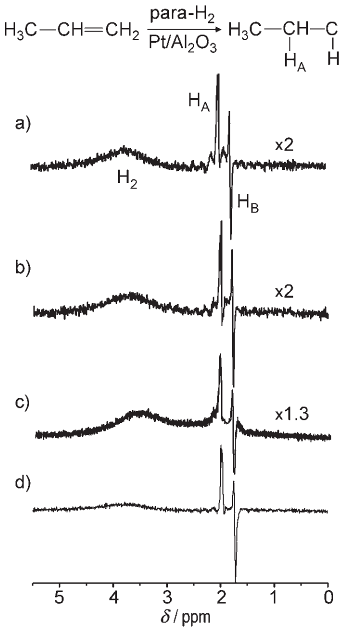

Figure 2. ^1H NMR spectra detected in the ALTADENA experiments during hydrogenation of propylene in the Earth's magnetic field over Pt/Al_2O_3 catalysts with a) 8.5-, b) 3.5-, c) 1.1-, and d) 0.6-nm metal particles. The spectra are scaled relative to each other as indicated in the figure. The two hydrogen atoms in the product which originate from the para-H_2 molecule are labeled A and B. A broad feature in the low-field part of the spectrum corresponds to H_2.

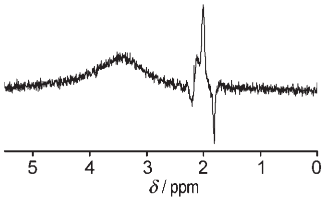

Figure 3. Same as Figure 2, but for the Pd/Al_2O_3 catalyst.

hydrogen on the metal surface, which creates a pool of surface H atoms available for the reaction.[11] These H atoms can move over the surface, spill over onto the support, and dissolve into the metal lattice. An alkene (e.g., $CH_3CH{=}CH_2$) is then physisorbed or chemisorbed on the metal surface, harvests a hydrogen atom from the surface pool to form a surface alkyl moiety (($(CH_3)_2CH{-}M$ or $CH_3CH_2CH_2{-}M$), and then another H atom to yield the final alkane product ($CH_3CH_2CH_3$).[11–13] In some studies, however, it is argued that mostly the H atoms dissolved in the metal lattice and emerging at the surface are reactive enough to hydrogenate surface alkenes.[14,15]

Observation of PHIP effects is commonly regarded as evidence that addition of the two H atoms occurs pairwise. At the same time, mechanisms which involve addition of random H atoms from the surface pool or those emerging at the metal surface are clearly inconsistent with the pairwise addition mechanism. Furthermore, dissociative chemisorption of hydrogen on the metal surface initiates relaxation processes which gradually destroy the original spin correlation. Therefore, even if two H atoms accidentally happen to come from the same H_2 molecule, nuclear spin relaxation will make this pairwise addition inefficient for generating polarized products.

A plausible explanation of the experimental observations relies on the fact that hydrogenation rarely proceeds on a clean metal surface. Under realistic hydrogenation reaction conditions, carbonaceous deposit is formed on the metal surface.[9,15,16] This can lead to isolation or localization of catalytic sites, for example, by partitioning the vast metal surface into isolated islands of bare metal,[16] which hinders migration of the H atoms of the surface pool to the localized reaction sites and at the same time forces the H_2 molecules being chemisorbed at the localized centers to react with nearby substrate molecules. It is also feasible that catalytic-site localization can take place even in the absence of a significant amount of carbonaceous deposit, since a variety of species are present on the metal surface during the reaction, such as π-bonded and di-σ-bonded propylene, propylidyne, and so on.[11,13] While all these species are highly mobile, their presence can still partition the surface into smaller areas and thus lead to "dynamic localization" of a catalytic site. The influence of metal particle size on the magnitude of polarization observed in the experiments seems to support the hypothesis of reaction-site localization. Indeed, despite the fact that the hydrogenation efficiency of Pt(6) is lower than that of the other Pt catalysts, it produces stronger NMR signal enhancements. We believe that it is reasonable to assume that partitioning of smaller surfaces by various adsorbates should be more efficient and thus should lead to better site localization and higher yields of the pairwise addition route.

Pairwise hydrogen addition, while definitely present, is not necessarily the main reaction mechanism. For the catalysts used herein, predominant quantities of the product are likely to be formed in processes which involve random H atoms. For 100% pairwise addition, the maximum enhancement factor (relative to the external line of the CH_2 multiplet)[2a] expected under our experimental conditions would be about 3470. The value observed experimentally for the Pt(6) catalyst was about 100. Therefore, the contribution of the pairwise addition route can be estimated as about 3% if nuclear spin relaxation is neglected. However, many spin relaxation mechanisms can reduce the observed polarization. These include relaxation of the chemisorbed hydrogen and other reaction intermediates such as metal-bound 2-propyl or 1-propyl groups. The relaxation of the product molecule itself is dramatically accelerated by collisions with the pore walls of the alumina support. Therefore, the estimated value of 3% is the lower boundary for the contribution of the pairwise addition route, and the true value must be larger. Unfortunately, a more accurate estimate is impossible at present, since it would require detailed knowledge of all reaction intermediates, their lifetimes, and nuclear spin relaxation rates. Nevertheless, the results demonstrate that pairwise hydrogen addition is not an insignificant reaction path that can be safely ignored. If the hypothesis of site localization is reasonable, it is then obvious that the degree of polarization observed should depend on the pretreatment and state of the metal surface, which will be checked in future experiments.

The observation of parahydrogen-induced polarization with supported metal catalysts should not be limited to the Pt and Pd catalysts only. Our preliminary results demonstrate that other supported metals can produce parahydrogen-induced polarization as well. The PHIP phenomenon can thus be potentially employed to develop highly sensitive approaches for advancing mechanistic and kinetic studies of reactions catalyzed by supported metal catalysts. It appears that the commonly accepted assumption that heterogeneous hydrogenation with supported metal catalysts is not expected to produce any parahydrogen-induced polarization has discouraged any activity in this research field. The data obtained here disprove, without doubt, this assumption. Furthermore, many applications of the NMR spectroscopy and MRI techniques suffer from low intrinsic sensitivity, and therefore significant efforts are devoted to the development of various nuclear spin polarization schemes. In particular, approaches based on the homogeneous hydrogenation with parahydrogen are now being extensively developed for producing hyperpolarized contrast agents for biomedical and other MRI studies.[4,17] In the context of MRI applications, heterogeneous catalytic processes can have definite advantages. In particular, heterogeneous catalysts are easy to separate from the reaction products to produce catalyst-free polarized fluids and can be used to produce polarized gases.

In summary, we have demonstrated for the first time that heterogeneous hydrogenation of an alkene (propylene) with supported metal catalysts (Pt/Al_2O_3, Pd/Al_2O_3) leads to an observation of enhanced signals in the ^1H NMR spectra of the reaction product (propane) when hydrogen enriched in the para-H_2 spin isomer is used in the reaction. This observation indicates that hydrogen addition occurs pairwise to a measurable extent. A plausible explanation of the experimental results relies on the concept of static or dynamic isolation or localization of catalytic sites by various adsorbates which partition the metal surface into smaller regions.

Experimental Section

Four Pt/Al_2O_3 catalysts with different sizes of Pt metal particles (0.6, 1.1, 3.5, and 8.5 nm) and a Pd/Al_2O_3 catalyst with 10–11-nm Pd particles were used. All supported catalysts contained 1 wt% of the metal and were prepared by incipient wetness impregnation of the alumina support (γ-Al_2O_3, specific surface area ca. 200 $m^2 g^{-1}$; 0.25–0.5-mm granules for Pt/Al_2O_3 and 1-mm granules for Pd/Al_2O_3). Aqueous solutions of oligomeric μ-hydroxo Pt^{IV} complexes with different acidity were used as active-component precursors in the preparation of Pt/Al_2O_3 catalysts. The size of Pt particles after calcination in air at 400°C (Pt(6), Pt(11), Pt(35)) or 600°C (Pt(85)) was evaluated from high-resolution transmission electron microscopy data. The elemental composition of the surface (Al, O, Pt) was the same for all samples, as established by energy-dispersive X-ray microanalysis. The Pt/Al_2O_3 catalysts were activated before reaction, either in a stream of hydrogen at 70°C for 2 h, or under a mixture of hydrogen and propylene at room temperature for over 1 h. The Pd/Al_2O_3 catalyst was prepared by impregnating alumina granules with an aqueous solution of $PdCl_2$, which were subsequently dried at 120°C under nitrogen, and then reduced at 350°C for 1 h in a nitrogen/hydrogen mixture containing 15% of hydrogen.

The mixture of gaseous reactants was prepared as follows. First, an evacuated aluminum cylinder was filled with 1 atm propylene, and then 2 atm hydrogen enriched to ca. 50% of para-H_2 was added. The apparatus for producing ca. 50% para-H_2 and the flow setup were similar to those described elsewhere.[3,4]

All NMR experiments were carried out on a Bruker AV300 SB 300 MHz NMR spectrometer. For PASADENA experiments, ca. 0.03 g of the catalyst was placed on the bottom of a 10-mm NMR tube purged with H_2 to avoid catalyst deactivation. An initial delay of 5 min was used for the sample to reach 70°C. The experiments were then performed at the highest possible gas flow rate, with the gas supplied through a capillary inserted into the NMR tube from the top.[3] The NMR spectra were acquired while the flowing gas was agitating the solid catalyst particles within the sample tube. 45° rf pulses were used to maximize the observed PASADENA polarization.[7] For the ALTADENA experiments, a U-shaped reaction cell made from 1/4“ copper tubing was used. The catalysts were packed between two plugs of glass cloth and the reaction cell was heated to 90°C while the mixture of propylene and H_2 flowed through the cell and then into the NMR tube positioned in the NMR probe.

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