



Strong Metal–Support Interactions for Palladium Supported on TiO₂ Catalysts in the Heterogeneous Hydrogenation with Parahydrogen

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Parahydrogen-induced polarization (PHIP) was successfully utilized to demonstrate the strong metal–support interaction (SMSI) effect for palladium supported on titania catalysts. Heterogeneous hydrogenation of 1,3-butadiene over Pd/TiO₂ catalysts led to the formation of 1- and 2-butenes and butane, and hyperpolarized products were obtained if parahydrogen was used in the reaction. However, if the catalysts were reduced in H₂ flow at 500 °C before the hydrogenation reaction, the observed polarization levels were significantly lower or even zero, which was indicative of the suppression of the pairwise addition of hydrogen route. This observation indicated the possibility to detect the SMSI effect by the PHIP technique. Moreover, by using X-ray photoelectron spectroscopy it was shown that Pd is partially present as Pd^{δ+} after reduction under a hydrogen atmosphere at 500 °C. These results were confirmed by transmission electron microscopy, which revealed the formation of Pd^{δ+} and the dissolution of Pd in the titania lattice.

The hydrogenation of unsaturated compounds with parahydrogen leads to the observation of the parahydrogen-induced polarization (PHIP) phenomenon.^[1,2] This results in a significant enhancement in the NMR signals of the corresponding reaction products or intermediates. In the case of homogeneous catalytic hydrogenation, a single metal center often plays the role of the active site for hydrogen activation, and therefore, the pairwise hydrogen addition route is the major mechanism for such processes.^[3,4] In contrast, heterogeneous pairwise addition of hydrogen is uncommon. Nevertheless, it can be suc-

cessfully observed by the PHIP technique,^[5–7] contrary to the implications of the Horiuti–Polanyi mechanism^[8] widely accepted for a broad range of supported metal nanoparticles. Therefore, understanding the nature of active sites that can add two hydrogen atoms from the same hydrogen molecule as a pair to a substrate molecule is a highly important task.^[9–11]

Recently, it was shown that the nature of the catalyst support can have a significant impact on the rate of the pairwise addition of hydrogen.^[12,13] Remarkably, titania-supported metal catalysts were shown to exhibit much higher levels of the pairwise addition of hydrogen (and larger PHIP effects) relative to that exhibited by metals on other supports.^[9,14] Therefore, examination of the nature of the active sites for titania-supported nanoparticles in the context of the pairwise addition of hydrogen may open up new possibilities for the rational preparation of catalysts that are able to maximize the observed PHIP effects and for the production of hyperpolarized molecular contrast agents potentially suitable for in vivo magnetic resonance imaging investigations.^[14–16]

In catalysis, it is well known that metals supported on titania exhibit the strong metal–support interaction (SMSI) effect.^[17,18] This phenomenon is known to modify the selectivity and activity of a catalyst.^[19,20] Therefore, significant alteration in the selectivity of the pairwise addition of hydrogen for titania-supported catalysts described above is not surprising.^[11–13] One plausible explanation for the nature of the SMSI effect is the electronic interaction between the metal and the support, which leads to the formation of an electron-rich metal.^[21,22] Another possible explanation is migration of the support material and encapsulation of metal nanoparticles. Importantly, titania is able to rapidly migrate over considerable distances and to appear on initially pristine metal surfaces.^[23] However, the first observation and evidence for the SMSI effect was related to a significant loss in chemisorption ability for noble metal catalysts supported on titania after hydrogen treatment at high temperatures.^[17] Such dramatic changes in the chemisorption properties are closely linked to the catalytic activity and selectivity of supported nanoparticles. Therefore, the SMSI effect plays a very important role in many heterogeneous catalytic processes.

The major differences in the PHIP effects observed for metal nanoparticles supported on titania relative to those previously observed for metals on other supports^[11–13] were tentatively attributed to low-temperature SMSI effects. Therefore, in this communication the behavior of titania-supported catalysts is

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explored over a much broader temperature range to systematically address the SMSI effect and its influence on the efficiency of the pairwise addition of hydrogen in hydrogenation reactions with parahydrogen. The decrease in the overall catalytic activity of Pd/TiO₂ catalysts under SMSI conditions (H₂ treatment at 500 °C) and significant (down to zero) loss of PHIP levels during heterogeneous hydrogenation of 1,3-butadiene with parahydrogen were observed, and the Pd^{δ+} state was detected as confirmation of the presence of the SMSI effect.

Two series of Pd/TiO₂ supported catalysts reduced under an atmosphere of H₂ at 100 and 500 °C were used in the heterogeneous hydrogenation of 1,3-butadiene (Figure 1). Strong PHIP signals were observed if the Pd/TiO₂ catalyst reduced at

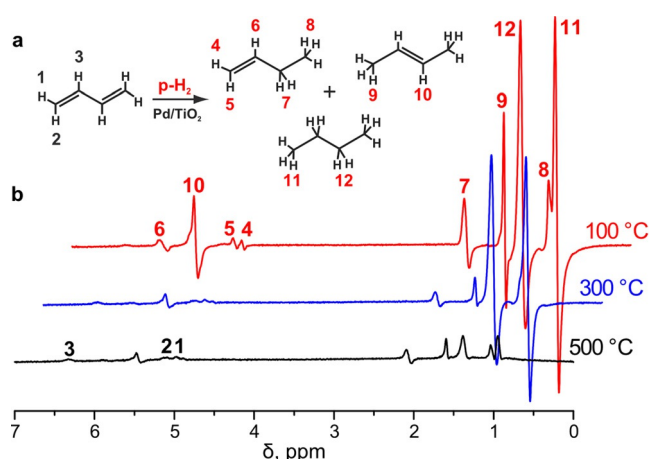


Figure 1. ¹H PHIP NMR spectra for the heterogeneous hydrogenation of 1,3-butadiene at 100 °C over Pd/TiO₂ with a 4.5 nm average particle size previously reduced under an atmosphere of H₂ at various temperatures (100, 300, and 500 °C).

100 °C was used. Remarkably, for the Pd/TiO₂ catalyst reduced under a H₂ atmosphere at 500 °C, the observed polarization levels diminished dramatically: the polarization dropped to almost zero for butane, and for 1-butene and 2-butene it became more than one order of magnitude lower than that observed with the Pd/TiO₂ catalyst reduced at 100 °C. Such a dramatic decrease in polarization intensity may be explained in terms of the SMSI effect. With the aim to investigate the influence of the reduction temperature on the intensities of the PHIP signals and the underlying SMSI effect, the samples of the Pd/TiO₂ catalyst were reduced at various temperatures in the range of 100 to 500 °C at 100 °C increments. As a result, it was established that the intensities of the PHIP signals decreased progressively and significantly with an increase in the reduction temperature (Figure 1).

Importantly, the decrease in intensities of the polarized signals was also accompanied by a decrease in the overall hydrogenation activity of the Pd/TiO₂ catalysts. This demonstrates the presence of the SMSI effect, as defined in the context of catalytic research. At the same time, the overall activity of the Pd/TiO₂ catalyst in the heterogeneous hydrogenation of 1,3-butadiene decreased by only 20–30% if the reduction temperature was increased to 500 °C. This is in stark contrast to the

fact that PHIP effects were not detected for butane if the Pd/TiO₂ catalyst reduced at 500 °C was used (see Figure S1 in the Supporting Information).

There are two possible reasons for these observations. First, the significant loss in polarization may be caused by agglomeration of metal nanoparticles, which without doubt occurs during reduction at high temperatures. Second, the decrease in the polarization levels may be directly related to the nature of the active sites responsible for the pairwise addition of hydrogen. To determine the particle-size distributions for the Pd/TiO₂ catalysts reduced at various temperatures, transmission electron microscopy (TEM) was utilized. For the Pd/TiO₂ catalyst reduced at 100 °C, the average particle size was found to be approximately 4.5 nm, whereas for the catalyst reduced at 500 °C it was approximately 5.5 nm (see Figure S2). This insignificant particle size increase is not expected to have such a dramatic impact on the rate of the pairwise addition of hydrogen. Moreover, for the Pd/TiO₂ catalyst with a 9.4 nm metal particle size reduced at 100 °C, PHIP effects in the heterogeneous hydrogenation of 1,3-butadiene with parahydrogen were successfully detected, whereas the same catalyst reduced at 500 °C under a hydrogen atmosphere did not produce significant PHIP effects (see Figure S3). All of these observations imply that the change in the metal particle size has an insignificant influence on the levels of the observed PHIP effects and that the main mechanism of polarization loss is blockage of the catalytically active sites responsible for the pairwise addition of hydrogen.

The origin of the SMSI effect for palladium catalysts supported on titania upon reduction under a hydrogen atmosphere at temperatures of approximately 500 °C, which leads to a moderate loss in the overall catalytic activity along with a significant decrease in polarization levels, was further studied by using TEM. Importantly, for the Pd/TiO₂ catalyst reduced at 500 °C, unique TEM images were obtained that provided an opportunity to observe the SMSI between TiO₂ and Pd directly (Figure 2).

It was found by TEM that a thin (≈2 nm) layer of Pd is formed on the support surface, and the interplanar distances of Pd metal change from 2.25 to 2.17 Å. Moreover, Pd signals are observed in the energy-dispersive X-ray (EDX) spectrum for catalyst areas in which no palladium particles are visible by

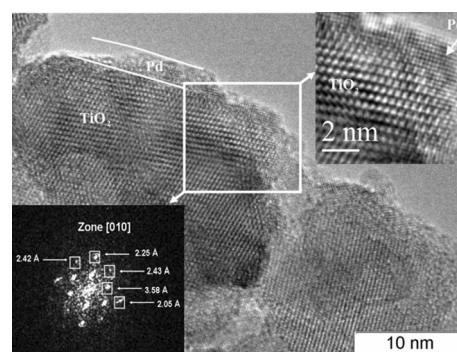


Figure 2. TEM image of the Pd/TiO₂ catalyst reduced at 500 °C under a hydrogen atmosphere, visualizing the formation of a thin layer of Pd.

TEM (see Figure S4). Consequently, some part of Pd is present in the catalyst sample as small atomic clusters. These observations confirm that some interaction between Pd and TiO_2 during high-temperature reduction occurs. One plausible explanation for this effect is the partial oxidation of Pd^0 caused by its interaction with the surface of TiO_2 .

To verify the electronic state of palladium, X-ray photoelectron spectroscopy (XPS) was utilized. Ex situ XPS studies for which reduction of the Pd/TiO_2 catalyst samples occurred outside the XPS setup were performed (see the Supporting Information). Figure 3a shows the $\text{Pd}3\text{d}$ photoelectron spectra measured for Pd/TiO_2 after sample reduction and/or oxidation at various temperatures.

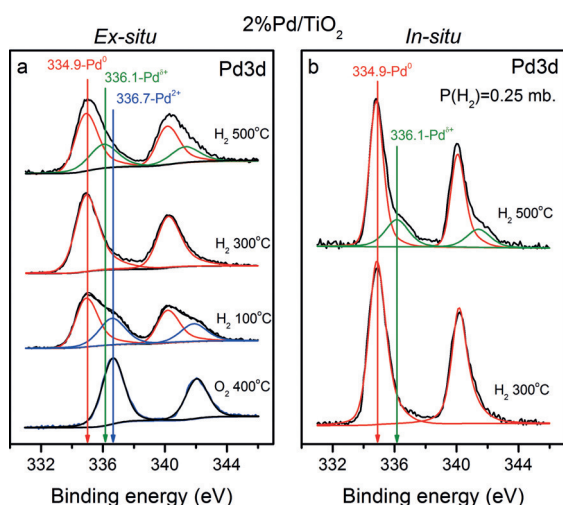


Figure 3. XPS spectra of the Pd/TiO_2 catalyst obtained during the a) ex situ and b) in situ experimental protocols.

Three different electronic states of Pd are detected depending on the sample treatment procedure. The state with a binding energy of 336.7 eV, which is common for palladium(II) oxide (PdO), was obtained after treatment of the catalyst sample under an oxygen atmosphere at 400 °C.^[24–26] Further treatment at 100 °C under an atmosphere of H_2 led to the appearance of a second state with a $\text{Pd}3\text{d}_{5/2}$ binding energy of 334.9 eV, which can be attributed to the metallic Pd^0 form.^[24–27] After heating Pd/TiO_2 at 300 °C under a H_2 atmosphere, only the metallic Pd^0 state was present at the surface of titania. Finally, hydrogen treatment at 500 °C (SMSI conditions) allowed us to observe an additional Pd state (binding energy of 336.1 eV), assigned to $\text{Pd}^{\delta+}$, which was formed as a result of the interaction between Pd and TiO_2 .

Further confirmation of the formation of the $\text{Pd}^{\delta+}$ state for the Pd/TiO_2 catalyst was obtained by using an in situ H_2 treatment at 500 °C along with XPS detection (Figure 3b). A clearly visible $\text{Pd}^{\delta+}$ state was found to form during reduction at 500 °C. To the best of our knowledge, this is the first direct observation of the formation of $\text{Pd}^{\delta+}$ for a catalytic metal system supported on titania (see the Supporting Information). We note that under such conditions any possibility for the presence of PdO is completely excluded. Low concentrations of Pd

(2%) and therefore an insignificant contribution of Ti^{3+} species to the total intensity of the $\text{Ti}2\text{p}$ photoelectron spectra leads to the absence of the Ti^{3+} characteristic line in the $\text{Ti}2\text{p}$ photoelectron spectrum (see the Supporting Information). Moreover, it is not possible to detect the Ti atoms located under Pd particles. On the basis of these results, most $\text{Pd}^{\delta+}$ species detected by XPS are located at the interface between the Pd nanoparticles and titania.

Therefore, we may suggest that the formation of the $\text{Pd}^{\delta+}$ state, as confirmed by TEM and ex situ and in situ XPS, may prevent the pairwise addition of hydrogen. We note that the amount of the $\text{Pd}^{\delta+}$ state is approximately 25%, and the overall catalytic activity decreased by 20–30%. Therefore, dissolution (encapsulation) of Pd metal in the lattice of TiO_2 , which was successfully detected by TEM (Figure 2), leads to the formation of the $\text{Pd}^{\delta+}$ state, as detected by XPS. During encapsulation of Pd nanoparticles, an entirely new state of palladium is formed. Given that the overall activity of the catalyst decreased proportionally to the amount of $\text{Pd}^{\delta+}$ states produced, whereas the activity in the pairwise addition of hydrogen decreased dramatically, the formation of the $\text{Pd}^{\delta+}$ state on titania correlates with the disappearance of catalytically active sites responsible for the pairwise addition of hydrogen and the observation of PHIP effects. The combination of the results obtained by TEM and XPS allows us to suggest that $\text{Pd}^{\delta+}$ sites are formed at the metal–support interfaces, which provides direct confirmation of the presence of the SMSI effect. The combination of the XPS data with the NMR spectroscopy results obtained during heterogeneous hydrogenation with parahydrogen (Figures 1 and 3a) also allows us to conclude that maximum levels of polarization were achieved for the partially reduced catalyst for which the total amount of metal–support or metal–oxide interfaces was maximized.

In conclusion, the strong metal–support interaction (SMSI) effect for palladium supported on titania catalysts is associated with the formation of the $\text{Pd}^{\delta+}$ state during high-temperature (500 °C) hydrogen treatment. In the context of the observed parahydrogen-induced polarization (PHIP) effect, the high-temperature SMSI effect dramatically decreases the activity of the Pd/TiO_2 catalyst in terms of the pairwise addition of hydrogen. Therefore, utilization of the catalyst reduced at 500 °C in the heterogeneous hydrogenation of 1,3-butadiene with parahydrogen leads to a dramatic (more than one order of magnitude) loss in polarization. Formation of the $\text{Pd}^{\delta+}$ state by encapsulation of palladium metal nanoparticles, as confirmed by X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM), correlated with the decrease in the number of active sites responsible for the pairwise addition of hydrogen. Utilization of the PHIP technique to investigate SMSI effects along with TEM and XPS analysis was demonstrated here for the first time and demonstrates that PHIP effects are much more sensitive to the onset of SMSI effects than the catalytic activity or chemisorption measurements. The reported results also imply that the true origin of the much larger PHIP effects observed for titania-supported metal catalysts reduced at low temperatures relative to those observed for metals on other supports needs to be explored further.

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