



# The effect of oxidative and reductive treatments of titania-supported metal catalysts on the pairwise hydrogen addition to unsaturated hydrocarbons



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## ARTICLE INFO

### Article history:

Received 5 October 2015

Accepted 5 February 2016

Available online 17 March 2016

### Keywords:

Parahydrogen-induced polarization (PHIP)

Hydrogenation

Heterogeneous catalysis

X-ray photoelectron spectroscopy (XPS)

Transmission electron microscopy (TEM)

## ABSTRACT

Heterogeneous hydrogenation of unsaturated compounds with parahydrogen is a highly promising technique for boosting the sensitivity of magnetic resonance spectroscopy and imaging by hyperpolarizing reaction products in gaseous and liquid phases, and potentially reaction intermediates as well. This demands an efficient heterogeneous catalyst providing both the high selectivity toward pairwise hydrogen addition (i.e., ability to incorporate both H atoms of H<sub>2</sub> molecule in the same product molecule) as well as sufficient overall hydrogenation activity. In this work, we studied the influence of oxidative and reductive treatments of the supported metal catalysts on the NMR signal enhancements provided by parahydrogen-induced polarization (PHIP) effects in hydrogenation of propene, propyne, 1,3-butadiene and 1-butyne. The 5 wt% titania-supported Pt, Pd, Rh and Ir catalysts used here were characterized by X-ray photoelectron spectroscopy (XPS) and high-resolution transmission electron microscopy (HRTEM). Generally, the preliminarily reduced catalysts were found to be more efficient than the oxidized ones. For instance, while the reduced Ir/TiO<sub>2</sub> catalyst provided the intense PHIP NMR signals, its oxidized counterpart showed almost no activity in hydrogenation. For the oxidized Pd/TiO<sub>2</sub> catalyst, HRTEM revealed the formation of titania pedestals under large (ca. 5–7 nm) PdO nanoparticles. At the same time, the small (ca. 1 nm) partially reduced Pd<sup>δ+</sup> particles were observed on the facets of TiO<sub>2</sub> support. These changes in catalyst structure led to a significant decrease in pairwise hydrogen addition selectivity.

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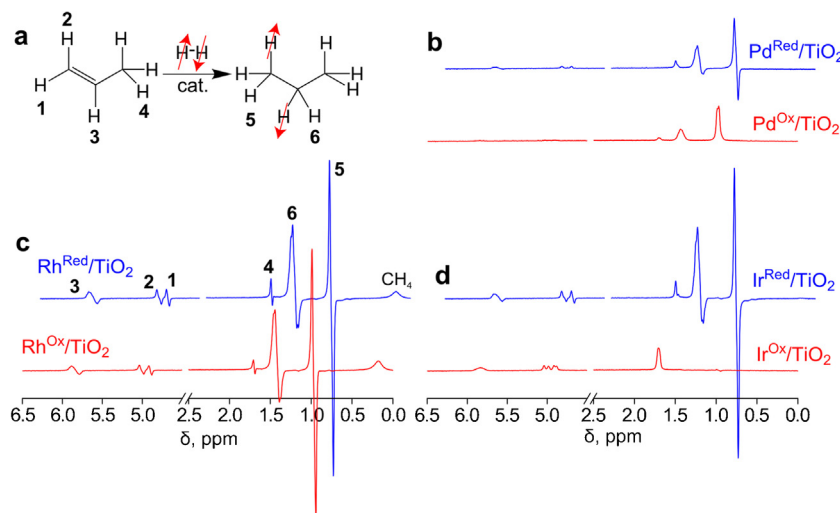
## 1. Introduction

Nowadays, methods based on nuclear magnetic resonance (NMR), such as magnetic resonance spectroscopy (MRS) and magnetic resonance imaging (MRI), are unique analytical tools which are widely and routinely used in chemistry, medicine, and many other areas of research and practice. In the context of *operando* studies in catalysis [1–5], the MRI/MRS toolkit can be useful for

conducting mechanistic studies of catalytic processes and for characterizing the behavior of operating model catalytic reactors. In particular, this toolkit allows one to map in situ the distribution of the liquid phase within the catalyst bed, to directly visualize various dynamic processes, and to evaluate local reactant-to-product conversion [6–8]. However, the NMR-based techniques have a significant drawback of low intrinsic sensitivity. One of the efficient ways to overcome this problem is the use of nuclear spin hyperpolarization techniques [9,10], e.g., dynamic nuclear polarization (DNP) [11] for hyperpolarization of solids, liquids or solutions, spin-exchange optical pumping (SEOP) [12] for hyperpolarization of gases, and parahydrogen-induced polarization (PHIP) [13,14] which can be successfully utilized for hyperpolarization of both

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**Fig. 1.** (a) The reaction scheme of propene hydrogenation; (b–d) <sup>1</sup>H NMR spectra acquired during propene hydrogenation with p-H<sub>2</sub> at 100 °C over Pd<sup>Red</sup>/TiO<sub>2</sub> and Pd<sup>Ox</sup>/TiO<sub>2</sub> catalysts (b), over Rh<sup>Red</sup>/TiO<sub>2</sub> and Rh<sup>Ox</sup>/TiO<sub>2</sub> catalysts (c); and over Ir<sup>Red</sup>/TiO<sub>2</sub> and Ir<sup>Ox</sup>/TiO<sub>2</sub> catalysts (d). All spectra were acquired while the gas was flowing (4.1 mL/s) with 8 signal accumulations and are presented on the same vertical scale.

liquids and gases. The basis of PHIP is the exploitation of the singlet nuclear spin order of a parahydrogen molecule (p-H<sub>2</sub>). However, because p-H<sub>2</sub> molecule has zero nuclear spin and therefore is NMR silent, the equivalence of the two H atoms of a p-H<sub>2</sub> molecule needs to be broken in order to get an enhanced NMR signal. This can be achieved via incorporation of p-H<sub>2</sub> in a product of a hydrogenation reaction [15]. Two major requirements for such hydrogenation reaction should be pointed out: (i) the reaction should proceed in a pairwise manner of hydrogen addition, meaning that two H atoms from the same p-H<sub>2</sub> molecule should be added to the same unsaturated substrate molecule; and (ii) the two nascent protons of p-H<sub>2</sub> molecule should end up in magnetically non-equivalent positions in the product molecule [16]. If both these requirements are met, the corresponding <sup>1</sup>H NMR signals of reaction products or intermediates can be significantly enhanced (up to 4–5 orders of magnitude in the case of standard NMR instruments) [16]. Moreover, the NMR lines get a characteristic line shape which makes it easy to detect PHIP phenomena and therefore the existence of pairwise hydrogen addition route [17].

Originally, PHIP effects were observed for the first time in homogeneous hydrogenations catalyzed by transition metal complexes, e.g. Wilkinson's catalyst [Rh(PPh<sub>3</sub>)<sub>3</sub>Cl] [13,18], due to a well-defined nature of an isolated catalytic center responsible for pairwise hydrogen addition. Later on, the PHIP technique was extensively utilized for mechanistic and kinetic studies of homogeneous hydrogenations catalyzed by transition metal complexes and clusters [17,19]. However, utilization of homogeneous PHIP to produce hyperpolarized fluids suitable for biomedical MRI studies is significantly complicated because of the presence of a toxic homogeneous catalyst in the reaction mixture, which cannot be easily removed from the solution after the reaction [20]. At first sight, this problem can be solved by the use of heterogeneous hydrogenation. However, the conventional catalysts for heterogeneous hydrogenation reaction are noble metal nanoparticles supported on porous oxides or carbon. For this type of catalysts, it is generally assumed that H<sub>2</sub> molecules adsorb dissociatively on the metal surface according to the established Horiuti-Polanyi mechanism [21]. Therefore, the complete randomization of H atoms involved in hydrogenation over the catalyst surface is expected, which should lead to a complete loss of spin correlation between the parahydrogen-derived protons and, consequently, to the absence of any PHIP effects in the NMR spectra of the products. Nevertheless, PHIP effects were observed in heterogeneous hydrogenation

of unsaturated hydrocarbons over supported metal nanoparticles, meaning that the pairwise addition of hydrogen is possible with such catalysts [22]. Subsequent studies showed that PHIP effects can be observed in heterogeneous gas phase hydrogenations of various hydrocarbons such as propene [23,24], propyne [25], 1,3-butadiene and 1-butyne [26] as well as α,β-unsaturated carbonyl compounds [27] over several Pt, Pd, Rh and Ir [28] catalysts supported on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and TiO<sub>2</sub> as well as over bulk metals and bulk metal oxides [29] (Pt, Rh, CaO, Cr<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> [30], PtO<sub>2</sub>, PdO and Rh<sub>2</sub>O<sub>3</sub>). Moreover, polarization was also successfully observed in liquid phase heterogeneous hydrogenations over supported metal nanoparticles [31–33]. Generally, the highest intensities of PHIP NMR signals were obtained in heterogeneous hydrogenations catalyzed by catalysts supported on TiO<sub>2</sub> [26]. The attempts to explain this fact led to an investigation of the influence of strong metal-support interaction (SMSI) effect on the pairwise hydrogen addition and PHIP [34]. However, in spite of all these studies the nature of active sites of supported metal catalysts which, contrary to the dissociative Horiuti-Polanyi mechanism, can add molecular hydrogen to the unsaturated substrates in a pairwise manner is still unclear [26]. Despite the fact that the contribution of pairwise hydrogen addition route is often not very high (ca. 1–3%) [26], finding an answer to this question is surely of great interest for chemical science as well as for possible practical applications. For instance, the production of hyperpolarized propane gas, which can be used as an efficient contrast agent for MRI of lungs, by heterogeneous hydrogenation of propene with p-H<sub>2</sub> was recently demonstrated with the use of titania-supported rhodium catalysts [23,35]. And without doubt, the fundamental understanding of the mechanism of pairwise hydrogen addition and the nature of active sites of supported metal catalysts responsible for pairwise hydrogen addition can help to design an efficient catalytic system with the largest contribution of the pairwise addition route to provide the maximum NMR signal enhancement suitable for comprehensive MRI studies.

It was mentioned above that TiO<sub>2</sub>-supported metal catalysts exhibit higher contribution of pairwise hydrogen addition route and higher levels of PHIP NMR effects intensities compared to the metal catalysts on other supports. Therefore, the goal of this paper is to get some insight into the heterogeneous pairwise hydrogen addition phenomenon over titania-supported catalysts. The influence of metal oxidation state on the intensities of PHIP effects was investigated. For this purpose, a series of preliminary oxidized or reduced titania-supported Pt, Pd, Rh and Ir catalysts were prepared,

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