

Subtle Surface Processes in Heterogeneous Hydrogenation Catalysis Revealed by Parahydrogen-Enhanced NMR

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ABSTRACT: Pairwise and random addition processes are ordinarily indistinguishable in hydrogenation reactions. The distinction becomes important only when the fate of nuclear spin correlation matters, such as in parahydrogen-induced polarization (PHIP). An important indicator of the mechanism is its stereoselectivity, which is revealed with the aid of density matrix spectral simulations. With rationally designed heterogeneous catalysts, PHIP has the potential to provide insights into fundamental catalytic hydrogenation reaction mechanism and produce metal-free hyperpolarized substrates for biomedical utilization.

REACTION MONITORING

Reaction monitoring using HPLC or LC-MS is a routine practice in organic chemistry to determine the reaction progress and kinetics. While off-line monitoring with manual sampling limits the number of data points in the reaction profile, hence the accuracy of kinetic interpretation, on-line/*in-situ* reaction monitoring produces a complete and real-time picture under actual process conditions. On-line reaction monitoring using Nuclear Magnetic Resonance (NMR) spectroscopy represents an invaluable process analytical technique, providing structural information which facilitates both qualitative and quantitative analysis.

PARAHYDROGEN-ENHANCED NMR

NMR is a unique tool for obtaining structural and dynamical information of molecules. However, this method suffers from poor sensitivity compared to most other types of spectroscopy. It is often a considerable challenge to capture sparse reaction intermediates, let alone transient species. It is even worse in gas phase where the nuclear spin density is rather sparse, roughly three orders of magnitude lower than that in liquids. The intrinsic low sensitivity, due to the small population difference between nuclear spin states determined by the Boltzmann distribution, can be solved, to some extent, by various hyperpolarization techniques.

Parahydrogen-Induced Polarization (PHIP, Figure 1) utilizes the ability of the singlet state nuclear spin order of *para*-H₂ to be converted into observable nuclear spin magnetization by the addition of the *para*-H₂ molecule to an unsaturated substrate. This technique converts the highly-ordered nuclear spin singlet into enhanced NMR signals (up to 4 orders of magnitude) through catalytic hydrogenation reactions or reversible interactions with the metal center of inorganic complexes such as Crabtree's catalyst. It is thus directly related with catalytic hydrogenation reactions and finding wide applications in kinetic and mechanistic exploration of both homogeneous and heterogeneous catalysis.

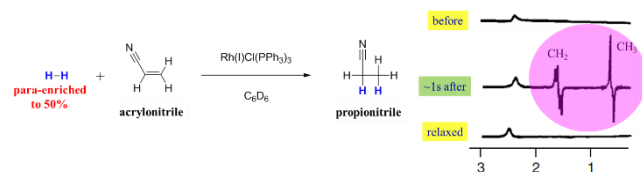


Figure 1. The original discovery of parahydrogen-induced polarization (PHIP) in the homogeneous hydrogenation of acrylonitrile to propionitrile with 50% enriched *para*-H₂. Propionitrile signals were dramatically en-

hanced for a short period of time. Reference: Bowers, C. R., Weitekamp, D. P. *J. Am. Chem. Soc.* **1987**, *109*, 5541

KINETICS & MECHANISM OF HETEROGENEOUS HYDROGENATION CATALYSIS

Surface processes involved in heterogeneous catalysis can be effectively studied by *in-situ*/operando techniques. In heterogeneous hydrogenation reactions, molecular hydrogen dissociates into atomic hydrogen upon chemisorption on metal surfaces followed by migration, spillover and even dissolution into the lattice, leading to random addition. Pairwise addition, where the two hydrogen atoms come from a single molecule and retain their nuclear spin correlation through the complete reaction cycle, is not typically considered as a distinct process. Nevertheless, surface reaction activities and pathways have been shown to be affected by the presence of reactants, intermediates, products and by-products such as carbonaceous deposits. Other factors affecting heterogeneous catalysis include the nature of the catalyst, such as metal type, particle size, shape, facet, morphology, dispersion, as well as the properties of supports, especially those with strong metal-support interactions (SMSI). Such factors are also important in determining the favorability of pairwise addition. While it would be extremely difficult to distinguish between these two pathways using conventional methods such as gas chromatography, parahydrogen-enhanced NMR provides a unique tool to study pairwise hydrogen addition, since only this pathway leads to dramatically enhanced (up to 10⁴) NMR signals.

EXPERIMENTAL

In this work, a variety of catalysts were prepared. Nanoparticles (Pt, Ir, etc.) supported on different oxides (Al₂O₃, TiO₂, etc.) were prepared through precipitation of metal salts onto supports from an aqueous solution by controlling solution pH followed by aging and calcination. Shaped CeO₂ nanocrystals with surfactant-free surfaces were synthesized by the hydrothermal method. Catalysts were characterized by ICP-AES, STEM, BET, CO and H₂ chemisorption. Para-enriched H₂ (50% *para*-H₂) was prepared on-site by passing normal-H₂ (containing 25% *para*-H₂ based on Boltzmann thermodynamics) through a copper coil filled with activated carbon (spin catalyst) and immersed in liquid nitrogen (77 K).

For PHIP experiments, an on-line reaction monitoring system comprised of a home-built micro-reactor with heating unit was installed on the top of the magnet (Figure 2). The precise delivery and stability of gas mixture (propyne/propene, normal-/*para*-H₂ and carrier gas N₂) is facilitated with Mass Flow Controllers (MFCs). The whole system is under LabVIEW control, allowing precise timing manipulation of reaction and NMR detection. The resultant hyperpolarized propene/propane stream flows down to the NMR probe for detection. Kinetic parameters, such as reaction temperature, gas composition and flow rate, can be varied to optimize PHIP enhancement. By comparing resultant NMR spectra from reactions with normal-H₂ or *para*-H₂, contribution from pairwise addition is possible to be derived.

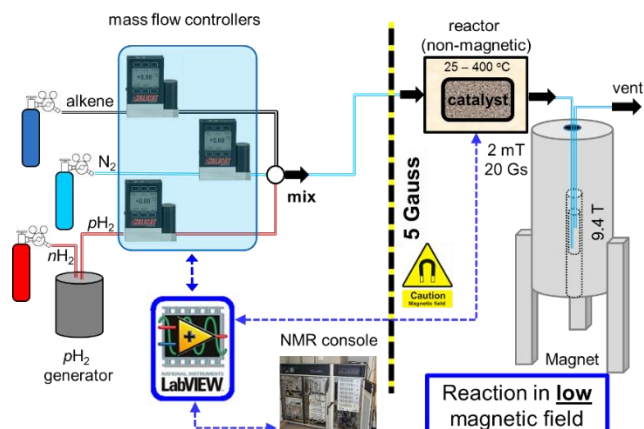


Figure 2. On-line reaction monitoring system for heterogeneous catalysis. Alkene, N_2 and $para\text{-}H_2$ (prepared on-site from normal- H_2) are delivered through the precise control of mass flow controllers. The reactor is mounted on top of the NMR magnet and the product stream is directed to the detection region inside the magnet through a stainless-steel tubing and vented to the exhaust. The reaction takes place in low magnetic field.

For hydrogenation reactions, *in-situ* reaction monitoring using parahydrogen-enhanced NMR offers dramatically increased sensitivity and unique mechanistic insights. This is because hyperpolarization with unmistakable patterns only happens in the case of pairwise addition, where the two hydrogen atoms from the same $para\text{-}H_2$ molecule are added onto the substrate in a concerted syn-pathway. It is thus possible to unravel the stereoselectivity in the alkyne semi-hydrogenation reaction where surface isomerization from *cis*-propene renders hyperpolarized *trans*-propene (Figure 3). It also provides an extraordinary window to peek at the subtle surface processes in the heterogeneous propene hydrogenation catalysis which produced hyperpolarized propene with significant signal enhancement through pairwise reversible exchange catalysis with no net chemical change (Figure 4). The effects of catalysts, such as metal type, support, nanoparticle shape/facet, on the reaction kinetics were also exploited, consistent with the well-established role of surface oxygen vacancy densities in conventional heterogeneous catalysis (Figure 5). Gained insights facilitated optimization of catalysts with enhanced reactivity and/or selectivity.

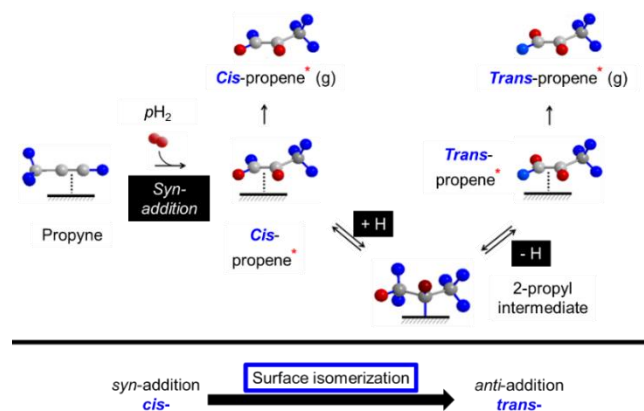


Figure 3. Propyne partial reduction pathways revealed by PHIP. Due to the *syn*-addition requirement of PHIP, hyperpolarized *trans*-propene is not expected but formed through surface isomerization of *cis*-propene. See Publication No. 1.

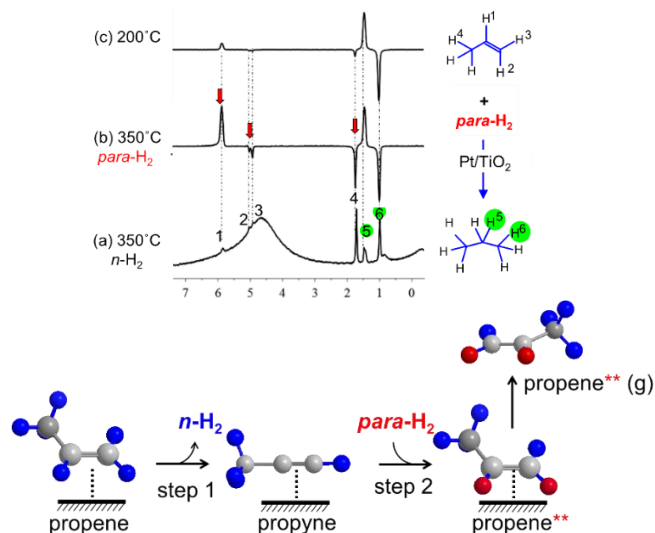


Figure 4. Hyperpolarized propene through heterogeneous reversible exchange catalysis. The subtle surface process of propene dehydrogenation to propyne and re-hydrogenation with $para\text{-}H_2$ to form hyperpolarized propene was observed thanks to the dramatic signal enhancement of PHIP. See Publication No. 2.

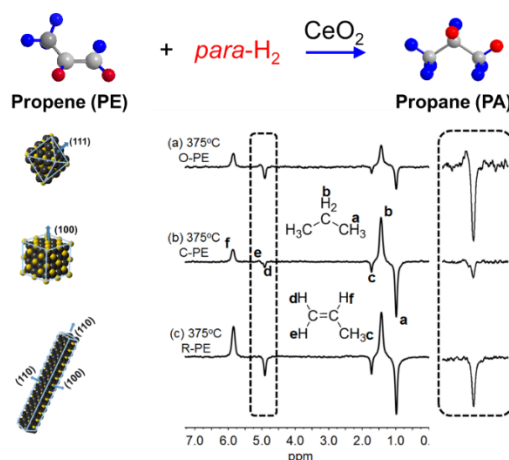


Figure 5. Shape/facet dependent hyperpolarization enhancement. PHIP efficiency and the extent of signal enhancements are significantly different for catalysts with different shapes or facets. Oxygen vacancy density was believed to make a strong contribution to this difference. See Publication No. 3.

While in the non-hydrogenation mode, signal amplification by reversible exchange (SABRE) enables the detection of suitable substrates at nanomolar scale without net chemical reactions, thanks to the strong signal enhancement as a result of polarization transfer from $para\text{-}H_2$.

PERSPECTIVE

Parahydrogen-enhanced NMR has been serving as a crucial tool in the exploration of catalytic reaction mechanisms and intermediates. Its application towards generating metal-free hyperpolarized molecular probes employing heterogeneous catalysis for *in-vivo* imaging further boosts this research area. Dissociative chemisorption followed by rapid diffusion and tumbling is normally expected for hydrogen molecules on metal surfaces, which leads to a loss of the high spin order of singlet $para\text{-}H_2$. Thus, systematic studies with a great variety of particle size, shape, morphology, and support are very meaningful in search of optimal conditions for pairwise selectivity on surfaces.

Novel catalysts such as metal-embedded metal-organic frameworks (MOFs) and zeolites are showing promising hydrogenation activities. The use of MOFs/zeolites in heterogeneous catalysis has numerous unique and outstanding advantages. In addition to extraordinarily high surface areas, their crystal structures, compositions and nanoporosity properties can be well controlled in a systematic way to enhance catalytic activity and selectivity. Together with computational material design and DFT calculations, PHIP-oriented studies using such catalysts may open new opportunities of achieving high pairwise selectivity and gaining invaluable insights which may guide the rational design of catalysts.

Quoting the ‘Sabatier principle’, for the optimum catalyst, the energy of interaction between metal surfaces and *para*-H₂ molecules should be strong enough for activation but not too strong to permit the retention of singlet nuclear spin orders and thus pairwise selectivity.

POTENTIAL RESEARCH DIRECTIONS

1. Synthesis of novel catalysts with well-controlled physical/chemical properties: well-defined metal/metal oxide nanoparticles, Zeolites, MOFs, etc.
2. Material characterization/imaging using advanced NMR techniques: solid-state NMR, MRI, DNP, dynamics & chemical exchange, diffusion by hyperpolarized Xe, hyperpolarized hydrocarbon from PHIP, etc.
3. Reaction kinetics and mechanisms of heterogeneous catalysis using *in-situ*/operando spectroscopy
4. DFT reaction modeling and computational design of catalysts with enhanced activity/selectivity

PUBLICATIONS

1. **Zhou, R.**, Cheng, W., Neal, L. M., Zhao, E. W., Ludden, K., Hagelin-Weaver, H. E., Bowers, C. R., “Parahydrogen Enhanced NMR Reveals Correlations in Selective Hydrogenation of Triple Bonds over Supported Pt Catalyst”, *Phys. Chem. Chem. Phys.*, **2015**, *17*, 26121-26129
2. **Zhou, R.**, Zhao, E. W., Cheng, W., Neal, L. M., Zheng, H., Quinones, R. E., Hagelin-Weaver, H. E., Bowers, C. R., “Parahydrogen Induced Polarization by Pairwise Replacement Catalysis on Pt and Ir Nanoparticles”, *J. Am. Chem. Soc.* **2015**, *137*, 1938-1946
3. Zhao, E. W., Zheng, H., **Zhou, R.**, Hagelin-Weaver, H. E., Bowers, C. R., “Shaped Ceria Nanocrystals Catalyze Efficient and Selective Parahydrogen Enhanced Polarization”, *Angew. Chem. Int. Ed.*, **2015**, *54*, 14270-14275 (rated as Very Important, top 10%)

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