

# Neutron Scattering Investigations of Hydride Species in Heterogeneous Catalysis

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**Abstract:** In heterogeneous catalysis, hydrides on the surface or in the bulk play a critical role as either active components or reaction intermediates in many hydrogen-involved reactions. Yet characterization of the nature and structure of these hydride species remains challenging. Neutron scattering, extremely sensitive to light elements such as hydrogen, has shown great potential in meeting this challenge. In this review, we surveyed recent advances in neutron studies of hydride species mainly over two most typical classes of catalysts, metals and oxides. Findings on catalysts outside these categories are brought up when we consider them relevant for contextualizing the present review. The adsorption, dissociation, spillover and reactivity of hydrogen, especially hydride species over supported metal and oxide catalysts have been successfully investigated mostly via neutron vibrational spectroscopy. The insights from these neutron studies, otherwise not possible with other techniques, shed light on the interaction mechanism of hydrogen with solid surfaces and reaction mechanisms where hydrogen is involved. Future research challenges on neutron scattering studies of hydrides, and catalysis in general, are also highlighted and more *operando*-type neutron studies need be conducted to advance the field.

## 1. Introduction

Hydride is a compound with one or more anionic hydrogens, H<sup>-</sup>, bound to a more electropositive element, normally a cation. Hydride species are common catalysts and catalytic intermediates in a variety of homogeneous and heterogeneous catalytic cycles.<sup>[1-2]</sup> Molecular hydrides have been well studied in great detail in homogeneous catalysis as they are involved in several important H-involved reactions such as hydrogenation, hydroformylation, and hydrosilylation. In heterogeneous catalysis, hydrides on the surface or in the bulk also play a critical role as either active components or reaction intermediates from H<sub>2</sub> storage<sup>[3]</sup> to catalytic processes including hydrogenation/dehydrogenation, hydrodesulfurization, ammonia synthesis, hydrogenolysis (cracking), reforming, electrocatalysis and photocatalysis.<sup>[1, 4-5]</sup> However, hydrides in heterogeneous catalysis are much less understood regarding their structure and catalytic functions compared to the molecular counterparts in homogeneous catalysis, mostly due to difficulty in revealing the molecular structure of hydrides on/in solid catalysts whose structures are complex.

Hydrides on the surface and in the bulk of a catalyst can be formed from heterolytic dissociation of H<sub>2</sub> or the dissociation of organic molecules. Common spectroscopy approaches including <sup>1</sup>H-NMR, infrared and Raman spectroscopy<sup>[1]</sup> have been

employed to characterize the structure of surface and bulk hydrides over a variety of catalysts including metals, oxides and sulfides etc. Neutron scattering is uniquely suited for characterizing hydride species because the incoherent neutron cross-section of hydrogen is much larger than any other element in hydrogen-containing materials and thus the neutron scattering will be dominated by hydrogen. Neutron vibrational spectroscopy (NVS), e.g., inelastic neutron scattering (INS), is powerful in identifying the chemical nature of hydrogen species and has several advantages over the traditional optical spectroscopy such as IR and Raman. First, INS is not limited to selection rules as in IR and Raman and therefore all molecular motion modes can be observed. This is especially advantageous for modes at low frequency (<1000 cm<sup>-1</sup>) over IR and Raman where the lattice modes can dominate the spectra. Second, INS is straightforward in quantification of hydrogen content in hydrogen-containing materials, both as surface and bulk hydrides. This is not possible for IR spectroscopy because the interaction in NVS only involves nucleus while that in IR/Raman involves electrons. Since the electronic structure of each molecule and species is unique, it is not possible to transfer IR absorption coefficient between molecules. For adsorbed species on surfaces this is rarely possible and is meaningless when there is a mixture of species present and thus quantification is very challenging. Last but not least, INS results can be relatively easy to compare to first-principles calculations,<sup>[6]</sup> allowing atomistic level understanding of the chemical structure of hydrogen species. In addition, neutrons are suitable for the observation of the dynamic behavior of hydrogen species via neutron diffraction and quasi-elastic neutron scattering approaches.

Due to the scarcity of neutron sources, neutron scattering was much less utilized than the more available techniques such as NMR, IR and Raman in the study of hydride species in solid catalysts. Thanks to the advantages of neutron scattering including NVS as mentioned above, some unique insights have been obtained on the chemistry of hydrides over a wide class of catalysts including supported metals, oxides, sulfides, zeolites and metal organic frameworks (MOFs).

In this contribution, we will exclusively focus on advances in neutron studies related to hydride species over two most typical classes of catalysts, metals and oxides. Due to the concise scope of this minireview, we refer the readers to some comprehensive reviews on neutron applications for heterogeneous catalysis in general,<sup>[6-13]</sup> and to the special issue of Physical Chemistry Chemical Physics vol 18, issue 26 in 2016.<sup>[14]</sup>

## 2. Hydrogen Interaction with Supported Metal Catalysts

Supported metal particles are the most commonly used catalysts for hydrogen-involved reactions due to their excellent ability to activate and convert H<sub>2</sub> and hydrogenous species. Unveiling the structure of the surface hydrogen species, including hydrides, is a prerequisite for understanding the reaction mechanism of these hydrogen-involved reactions over metal catalysts. Neutron scattering has shown to be a suitable analytical tool for the observation of dynamic phenomena that involve

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hydrogen such as hydrogen adsorption, hydrogen *spillover*, and the generation/consumption of hydrogenous surface species under catalytic conditions.

## 2.1 Hydrogen Adsorption and Spillover

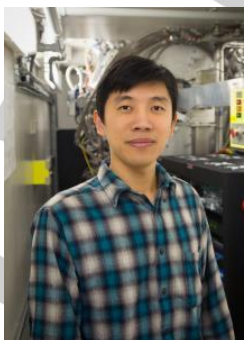
Felipe Polo-Garzon received his PhD in Chemical Engineering from Clemson University under the advice of Dr. David A. Bruce. His doctoral work consisted of a combined experimental and computational description of the reaction mechanism for dry reforming of methane (DRM) over pyrochlore catalysts. Currently, he is a Postdoctoral Research Associate in the Surface Chemistry and Catalysis Group in the Chemical Science Division at Oak Ridge National Laboratory (ORNL). His research interests deal with the development of reactivity descriptors for heterogeneous catalysis, as well as the elucidation of governing reaction mechanisms through in-situ and operando characterization techniques, kinetic analysis and computational tools. His research experience includes acid-base catalysis, methane conversion, water-gas shift reaction, among others.



Si Luo received her PhD in Physical Chemistry from Stony Brook University and Brook Haven National Lab under the advice of Dr. Jose A. Rodriguez. Her PhD research focused on the characterization and development of nano catalysts and model catalysts related to hydrogen production reactions. Currently, she is a postdoctoral research associate in the Surface Chemistry and Catalysis Group in the Chemical Science Division at ORNL. Her research interest includes synthesis, characterization of energy related catalysts to reveal surface chemistry during heterogeneous catalysis through operando spectroscopy techniques, and the relationship between catalytic activity and morphological, structural properties. Her research experience involves photocatalytic water splitting, water gas shift and acid gas conversion, et al.



Yongqiang Cheng is a neutron scattering scientist at the Spallation Neutron Source, Oak Ridge National Laboratory. He received his PhD from Johns Hopkins University in 2010. He is interested in developing and applying computation and simulation methods to interpret neutron scattering data, and to bridge theory and experiment by establishing structure-dynamics-property correlations.



Katharine Page is a Diffraction Instrument Scientist in the Neutron Scattering Division at Oak Ridge National Laboratory (ORNL). She received her PhD in 2008 from the Materials Department at the University of California, Santa Barbara, under the direction of Ram Seshadri and Anthony K. Cheetham. She was a Director's Postdoctoral Fellow and an Instrument Scientist at the Lujan Neutron Scattering Center, Los Alamos National Laboratory, prior to joining ORNL in 2014. Her research is focused on garnering new insights into complex functional materials, both bulk and nano, through advances in structural characterization techniques. Her research includes efforts to understand and exploit local to long-range ordering in ferroelectric oxides, energy conversion materials, and nanoscale catalysts, among others. She is a 2015 recipient of the Department of Energy (DOE) Early Career Award and she participates in the UNCAGE-ME and IDREAM Centers, both Energy Frontier Research Centers of the DOE.



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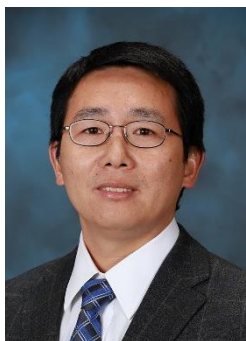


Dr. Phillip Britt is the Director of the Chemical Sciences Division at Oak Ridge National Laboratory (ORNL) and ORNL program manager for United States Department of Energy, Office of Sciences, Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences programs. His research has primarily focused on gaining mechanistic insights into the complex mix of free-radical, ionic and concerted reaction paths of oxygen functional groups in organic energy resources, which is crucial to devising improved methods for converting fossil and biomass resources into fuels and chemicals. He has over 150 scientific publications and reprints and has organized 12 symposiums at National American Chemical Society (ACS) Meetings. He received the 2016 Henry H. Storch Award in Fuels Science from the Energy and Fuels Division, the 2015 Secretary of Energy's Achievement Award for his work on the Waste Isolation Pilot Plant Technical Assessment Team, the Distinguished Service Award from the ACS Division of Fuel Chemistry, and he is a Fellow of the ACS (2011).



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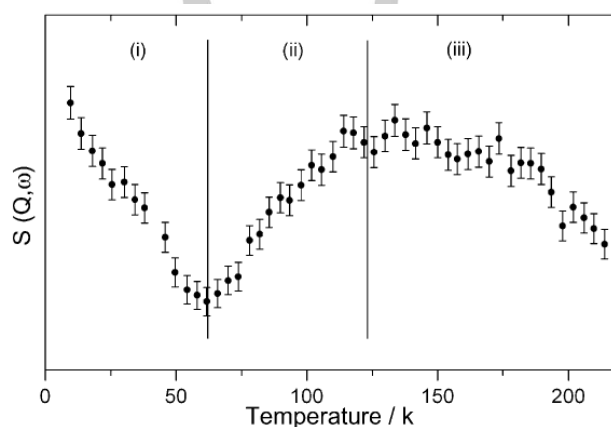
The excellent neutron scattering cross-section of hydrogen makes it possible to discriminate different adsorption sites of hydrogen, and indirectly determine the surface termination of catalysts. Such information is of utmost importance for the computational description of reaction mechanisms. Although neutron scattering has been extensively used to study the interactions of hydrogen-containing species with bulk metallic materials, such as Raney nickel, Raney palladium, palladium black, and platinum black,<sup>[15-19]</sup> many catalysts of practical interest consist of an active metal (typically a noble metal) deposited on a support. These *supported-metal catalysts* aim to expose as many active sites as possible, thus reducing the cost of the catalyst. Further, supported nanoparticles may possess catalytic properties that are absent in their bulk counterparts.

Pt is probably one of the most used catalysts in hydrogen-involving reactions and has been the subject of early neutron studies. For instance, an early work by Renouprez and Jobic,<sup>[20]</sup> INS was used to characterize hydrogen adsorption on three platinum samples (Pt supported on silica, Pt encaged in Y-zeolite and Raney Pt). It was concluded that hydrogen adsorbs mainly on sites of  $C_{4v}$  symmetry on the Pt/SiO<sub>2</sub> and Raney Pt samples, and in a lesser extent on sites of  $C_{3v}$  symmetry. This ratio of exposed facets corresponds to a cubic shape with (111) truncations. Pt encaged in Y-zeolite (Pt-Z) showed a similar proportion of  $C_{4v}$  and  $C_{3v}$  sites, suggesting cuboctahedra shape. Adsorption of hydrogen at high temperature over Pt-Z also suggested subsurface adsorption and surface reconstruction.

As promising fuel cell catalysts,<sup>[21]</sup> Pt and Pt-Ru supported catalysts on carbon have been the subject of neutron studies on their interaction with hydrogen. Although Pt has shown generally the best performance for fuel cell operation, the addition of Ru aims to improve the tolerance of the catalyst against CO and CO<sub>2</sub> impurities present in hydrogen feeds.<sup>[22-23]</sup> For instance, Albers and co-workers<sup>[24]</sup> studied the interaction of hydrogen with Pt supported on commercial carbon black. The shape of the particles was identified to be intermediate between cubic and cuboctahedral, after estimating the percentage of hydrogen species (on-top, twofold bridge, threefold bridge, fourfold bridge) present on the catalysts through an in situ INS study of hydrogen adsorption at different pressures. This work shows the unique capability of INS in obtaining surface species information which is not possible via other optical spectroscopy due the strong absorption of electromagnetic radiation by the black carbon.

The same group<sup>[25]</sup> further studied platinum and platinum/ruthenium particles supported on carbon black with neutron spectroscopy. They found that as the particle size increases the vibrational mode of atomic hydrogen at  $C_{3v}$  sites

was narrowed and the peak maximum shifted to lower energies. The hydrogen atom occupied more the (111) sites of Pt particles, and the contribution from  $C_{4v}$  sites decreased. Vibrational modes for Pt-OH, Pt/Ru-OH and water were also discriminated. In a study published two years later (2006), by some of the same authors,<sup>[26]</sup> on-top adsorption of H was observed on nanoparticles of Pt supported on high surface area carbon black. The authors also described three chemical phenomena in the elastic window scan of hydrogen on Pt(50%)/C (see Figure 1); namely, (i) desorption of physisorbed H<sub>2</sub>, (ii) H<sub>2</sub> dissociation to produce an adsorbed layer of atomic H, and, (iii) decreasing of the response due to the Debye-Waller factor (associated with the noise of the signal at higher temperatures).



**Figure 1** Elastic window scan of hydrogen on Pt(50%)/C. Reprinted with permission from ref <sup>[26]</sup>. Copyright 2006 Elsevier.

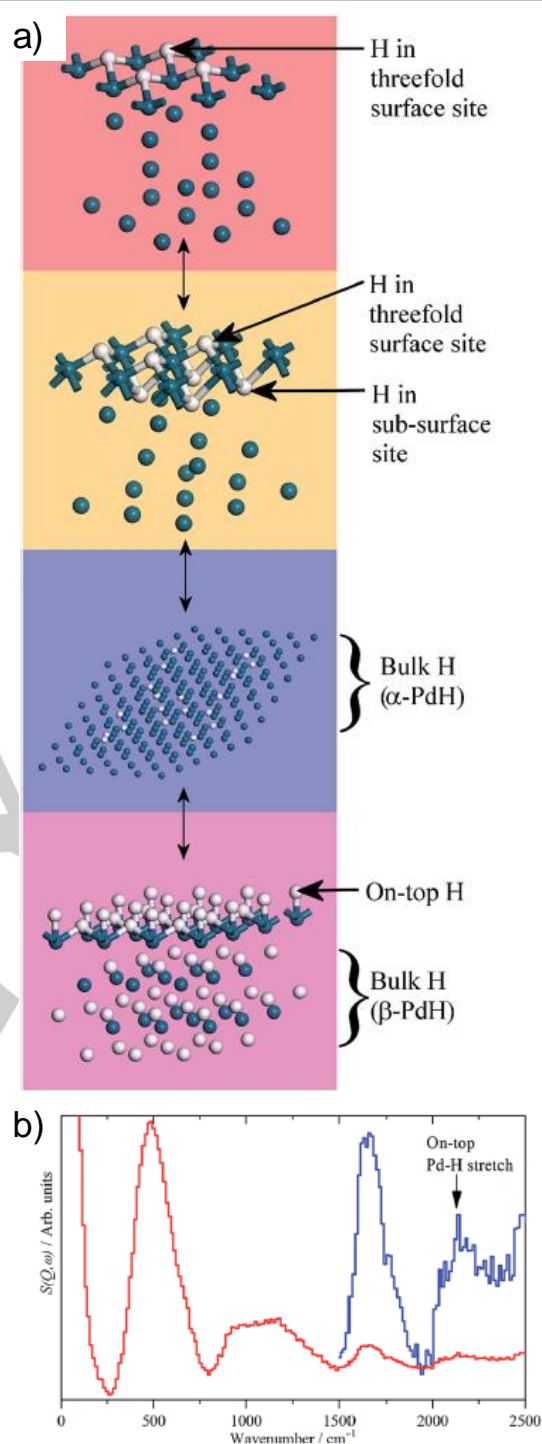
In another follow-up INS study of hydrogen adsorption on alloyed particles of Pt-Ru supported on carbon black,<sup>[27]</sup> The authors concluded that the larger the particle size the larger the Pt/Ru ratio, suggesting that Ru prevents the agglomeration of Pt nanoparticles. INS spectra showed that hydrogen occupies the threefold sites on the alloyed catalysts. There was no evidence of on-top adsorption, despite this adsorption site is observed for the single metal catalysts.<sup>[26]</sup>

Pd is another frequently used and studied hydrogenation catalyst.<sup>[28-31]</sup> A study by Albers et al.<sup>[32]</sup> on supported-Pd catalysts revealed, via INS, that the level of aggregation of the supported particles affects the storage capabilities of  $\beta$ -palladium hydride. Further, the addition of Pb in Lindlar-type catalysts (5%Pd/CaCO<sub>3</sub> and 5%Pd+3.5%Pb/CaCO<sub>3</sub>) was shown to lower by a factor of ~2 the  $\beta$ -palladium hydride formed. García-Mota et al.<sup>[33]</sup> showed via DFT simulations that Pb hinders the formation of hydrides. Such findings are relevant for the selective hydrogenation of triple-bonds to double-bonds, as it has been reported that the  $\beta$ -palladium hydride has higher activity and lower selectivity than the  $\alpha$ -phase.<sup>[34]</sup> Along the same lines, it has been reported that alloying of Pd/C catalysts with Pt and Fe promoted the disaggregation down to isolated primary particles, which is shown to be correlated with reduced availability of  $\beta$ -phase hydride species, and enhanced activity for the hydrogenation of nitrobenzene.<sup>[35]</sup>

In a very recent work, Parker et al.<sup>[36]</sup> studied Pd nanoparticles supported on activated carbon, carbon black, and other supports, to unveil the effect of particle size, morphology and support on the formation of palladium hydride with both INS and computational approaches. They found that the particle size and state of aggregation influenced the hydride formation. Also, the support affects the hydrogen-storage capacity of the catalyst and the rate

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of release. The rate of dehydrogenation of the Pd/activated-carbon (porous support) is slower than for Pd/carbon-black (non-porous support). The type of support also influences the type of hydrogen found in the Pd nanoparticles (Figure 2a). For the sample shown in Figure 2b, the modes at 485, 1100 and 1640  $\text{cm}^{-1}$  were assigned to  $\beta$ -PdH; whereas the weak peak at 2150  $\text{cm}^{-1}$  is assigned to the on-top Pd-H which is observed for the first time. Other assignments are (spectra not shown):  $\sim 560 \text{ cm}^{-1}$  presumably corresponds to  $\alpha$ -PdH, 470  $\text{cm}^{-1}$  corresponds to subsurface hydrogen, and the modes at 760, 820 and 980  $\text{cm}^{-1}$  correspond to hydrogen in the threefold surface site on (111) facets. These different types of hydride species and their evolution on Pd surface are nicely illustrated in Figure 2a. This work enables the estimation of relative proportion of bulk- to surface-H occupation in calculated model and in industrial nanoparticles.

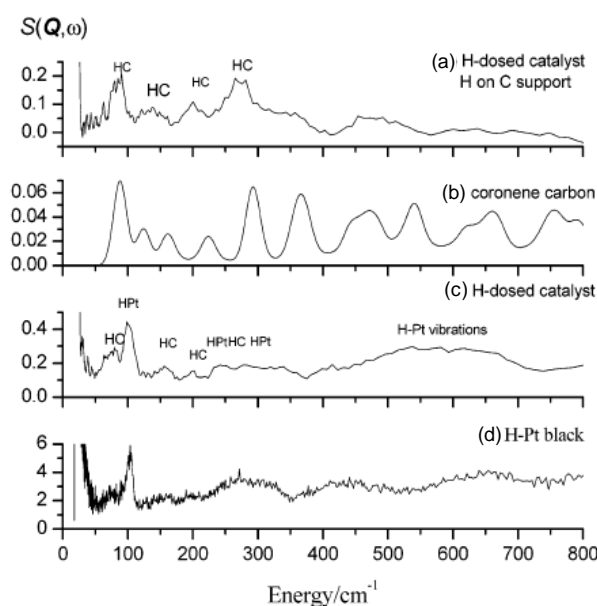


**Figure 2 (a)** Summary of the evolution of hydrogen on palladium. Top to bottom: the threefold sites are initially occupied, with subsequent occupation of the threefold and subsurface sites. This leads to  $\alpha$ -PdH and finally to  $\beta$ -PdH with the on-top sites occupied. The sequence is fully reversible. Pd = dark blue, H = white. **(b)** INS difference spectrum of 20%Pd/carbon-black-60 ppm H ([catalyst + 700 mbar  $\text{H}_2$ ] – [dehydrogenated catalyst]). The blue trace is a x10 ordinate expansion of the 1500–2500  $\text{cm}^{-1}$  region. Reprinted with permission from ref [36]. Published by The Royal Society of Chemistry.

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When metal nanoparticles are dispersed on the supports, adsorbed species such as hydrogen can migrate from the metal sites to the support, the so-called spillover. The concept of *spillover effect* in catalysis has bridged the gap between experimental results and traditional catalysis concepts that did not appear to be in complete communion.<sup>[37]</sup> Neutron scattering has undoubtedly showed the existence of spillover of hydrogen; and therefore, it has been crucial to achieve atomistic understanding of catalytic process which should strengthen the predictive capabilities of micro-kinetic modelling. Hydrogen spillover on supported-metal catalysts consists of the dissociation of molecular hydrogen on active metal particles, followed by diffusion of atomic hydrogen to the support. Besides heterogeneous catalysis, this phenomenon has captured great attention for hydrogen storage, since it has been shown that the hydrogen storage capabilities of high surface area materials increases considerably when even small amounts of metals, with hydrogen dissociation capabilities, are deposited on the surface.<sup>[6]</sup>

Hydrogen spillover on carbon supported Pt (Pt/C), Ru (Ru/C) and PtRu (PtRu/C) has been detected by means of INS and reported in various publications.<sup>[22-23, 25, 38-40]</sup> In the work of Mitchell et al.<sup>[22]</sup> on a Ru/C catalyst, they reported that at 23 K H<sub>2</sub> adsorbs as a strongly adsorbed monolayer and also as a weakly adsorbed second layer. Starting at 80 K, H<sub>2</sub> dissociates and H-atoms spillover to the support. Spillover is concluded due to the failure to observe significant INS intensity from the Ru-H species at a ratio of H/Ru of 3. Ratios greater than unity are suggested as a consequence of spillover. In follow-up publications by Mitchell et al., when comparing a series of Pt and Ru supported catalysts on carbon, spillover was found greater for Ru containing catalysts.<sup>[23, 39]</sup> The authors used an unconventional set-up for the cell containing the sample to be studied with the neutron beam. An annular cell was used, with the carbon support (only) in the center of the cell and exposed to the neutron beam; whereas, the catalyst pellets surrounded the central part of the cell. In other words, when only the catalysts were dosed with hydrogen, and the temperature was increased to ~500 K, hydrogen spillover to the carbon support was detected by the neutron beam in the 'annular cell' set-up (see Figure 3). The INS spectra showed *riding modes* of H on C, Pt and Ru, further supporting hydrogen spillover. A *riding mode* refers to the movement of H atoms in phase with the vibrations of the surface atoms. The authors identified two types of spillover hydrogen: H at the edge sites of a graphite layer (293 K), and weakly bound mobile H atoms diffusing through the support (~500 K).<sup>[23, 39]</sup> Tsao et al.<sup>[40]</sup> showed hydrogen spillover on Pt-doped activated carbon (Pt/AC) using INS. Since INS can detect molecular rotation of H<sub>2</sub>, a decrease in the intensity associated with this rotation signifies the dissociation of H<sub>2</sub> molecules into atomic H, followed by spillover. Such decrease in the intensity was obtained after increasing the temperature of the system (H<sub>2</sub> on Pt/AC). The estimated H/Pt ratio up to 25 showed that a large amount of H must have bonded to the carbon support.



**Figure 3** INS spectra of (a) slow-H-dosed Pt/C in the annular cell, that is, with only carbon and H thereon in the neutron beam; (b) calculated carbon-only coronene spectrum, that is, H modes suppressed; (c) fast H-dosed catalysts in the standard cell, that is, with the catalyst and H thereon in the neutron beam; and (d) Pt black reduced, evacuated, and dosed with hydrogen. Peaks labeled HC are due to riding modes of H on carbon, and those labeled HPt are due to riding modes of H on Pt (peaks additional to those observed for carbon and H on carbon). Note that the H-Pt peak of the catalyst at ~100 cm<sup>-1</sup> corresponds to the strong peak in the Pt black spectrum. Reprinted with permission from ref <sup>[39]</sup>. Copyright 2003 American Chemical Society.

Spillover over Palladium supported catalysts has also been subject of study with INS. In the work of Contescu et al.,<sup>[41]</sup> hydrogen spillover to the carbon support in Palladium-modified activated carbon fibers (Pd-ACF) was confirmed via INS. Irreversible hydrogen storage was seen when a second adsorption cycle was performed on Pd-ACF. In a work by Albers et al.,<sup>[42]</sup> they studied palladium catalysts supported on powder and pelletized activated carbon, carbon black, and graphitized carbon black. The catalysts were treated with HCl, which derived in various improvements: better metal dispersion, narrowing of the particles size distribution, higher concentration of Pd at the surface, and higher catalytic activity towards hydrogenation. It is suggested that the HCl treatment removed ash and adsorbed species. INS spectra of the HCl-treated samples showed the formation of molecular-like polyaromatic structures (hydrogasification), which is attributed to enhanced hydrogen spillover from the palladium particles.

Another aspect of hydrogen interaction with surfaces is the catalytic conversion of ortho- to parahydrogen. Molecular hydrogen may be parahydrogen or orthohydrogen, depending upon the coupled spin state of the two protons. The relative concentration between these two types of molecular hydrogen depends on temperature, with parahydrogen being the dominant species at low temperatures. Conversion of ortho- to parahydrogen is an exothermic process that causes evaporation of liquid hydrogen, which is detrimental for safe storage and handling of liquid hydrogen. This undesired evaporation can be avoided through fast catalytic conversion of ortho- to parahydrogen during the liquefaction process.<sup>[43]</sup> Hartl et al.<sup>[43]</sup> studied the adsorption of hydrogen via INS on two catalysts that promote the ortho- to parahydrogen conversion, Cr-doped silica

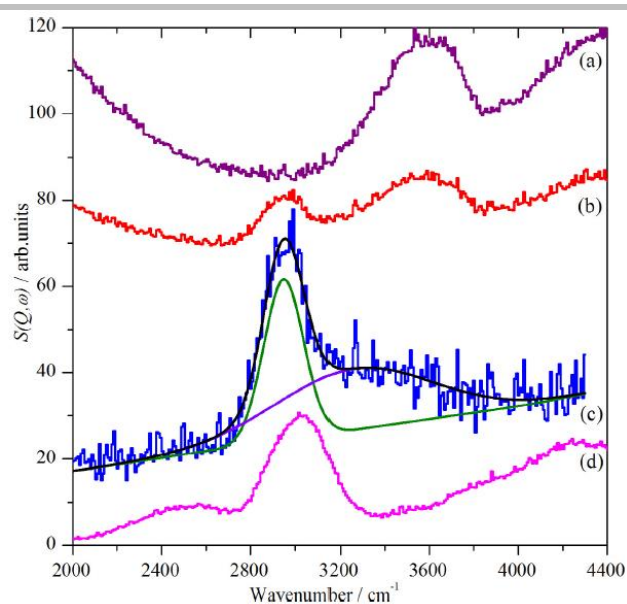
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(CrO-SiO<sub>2</sub>) and ferric oxide gel (Fe<sub>2</sub>O<sub>3</sub>). The first catalyst, CrO-SiO<sub>2</sub>, is a magnetically dilute catalyst since the magnetic centers weakly interact with each other; the second catalyst, Fe<sub>2</sub>O<sub>3</sub>, is a magnetically dense catalyst. INS spectra following the conversion of hydrogen showed that the adsorption of hydrogen in the two catalysts is very different. Hydrogen adsorption was weaker on CrO-SiO<sub>2</sub> than on Fe<sub>2</sub>O<sub>3</sub>; therefore, adsorption/desorption/migration processes occur more easily. In addition, CrO-SiO<sub>2</sub> takes up more hydrogen per surface area than on Fe<sub>2</sub>O<sub>3</sub>. These insights provide fundamental understanding of factors that may affect the performance of ortho- to parahydrogen conversion catalysts, despite complete conversion was reached within the time it takes to load hydrogen on the sample under the experimental conditions chosen.

## 2.2 Hydrogenous Species Relevant for Catalysis

Hydrogen-containing species are common intermediates for catalytic processes of interest. As reviewed by Parker, Lennon and Albers,<sup>[8-9]</sup> since neutron scattering can probe the interaction of hydrogen with catalysts, one can perform unique characterization, such as the observation of C-H/N-H/O-H stretch region, and the quantification of adsorbed hydrogen.<sup>[44-46]</sup> Advances in neutron spectroscopy also allow characterizing the interaction of species with a catalyst under operando conditions.<sup>[47-48]</sup>

INS spectra of Ni/Al<sub>2</sub>O<sub>3</sub> catalysts tested for dry reforming and steam reforming of methane showed vast differences in the concentration of surface hydroxyls, and the type of hydrocarbonaceous overlayers. Dry reforming of two differently treated Ni/Al<sub>2</sub>O<sub>3</sub> catalysts showed mostly aliphatic carbon on one sample, while the other sample presented mostly aromatic carbon. Quantification of hydrogen in the hydrocarbonaceous overlayers of the Ni/Al<sub>2</sub>O<sub>3</sub> catalysts showed C:H ratios range from 160:1 to 11690:1, highlighting the good hydrogen cycling capabilities of the catalysts, but the poor (and different) carbon cycling capabilities.<sup>[44-46]</sup> In a follow-up study within the same group,<sup>[49]</sup> INS was used to characterize a Pd(5%)/Al<sub>2</sub>O<sub>3</sub> catalyst after propyne hydrogenation. Opposite to what the authors found on the Ni/Al<sub>2</sub>O<sub>3</sub> catalysts after dry reforming of methane, the C:H ratio was much smaller (1:1.8) and typical of aliphatic species. This is in agreement with the C-H stretching mode ranging from 2850-3063 cm<sup>-1</sup> (see Figure 4). Strongly hydrogen-bonded hydroxyls were also observed, indicating some functionality of the overlayer deposited on the catalyst. β-PdH was observed as well as a broad feature around ~ 500 cm<sup>-1</sup>.



**Figure 4** INS spectra (recorded on MERLIN with  $E_i = 4840 \text{ cm}^{-1}$ ) of (a) the Pd(5%)/Al<sub>2</sub>O<sub>3</sub> catalyst after activation, (b) the catalyst after carrying out six hours of the propyne hydrogenation reaction, (c) the scaled difference spectrum (4x ordinate expanded relative to (a) and (b)) with curve resolved components and the total fit and (d) 0.5933 g of polystyrene (0.5x ordinate expanded relative to (a) and (b)). Reprinted with permission from ref <sup>[49]</sup>. Copyright 2013 Elsevier.

The INS study performed by Albers et al.<sup>[50]</sup> on Pd nanoparticles supported on activated carbon showed that hydrogenation/dehydrogenation cycles can eliminate subsurface hydrides due to the restructuring of dislocations and lattice defects. It was also shown that high temperature and pressure favored hydrogen spillover leading to the formation of surface amorphous hydrogenated carbon. Analysis of a spent 5% Pd/C catalyst, used in the reaction of bromobenzene and styrene to trans and cis-stilbene, revealed surface deposition of cis-stilbene, despite most of the product was trans-stilbene. The identification of this surface species via INS sheds light on the role that adsorption sites of the catalyst may have on the product selectivity.

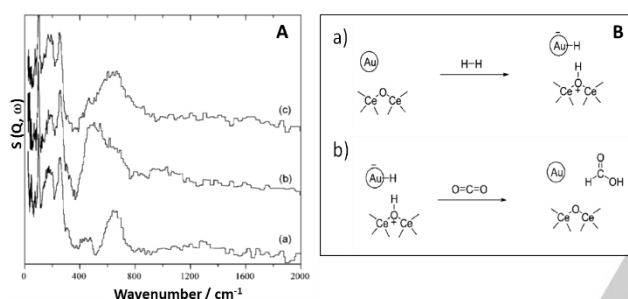
INS vibrational spectroscopy allowed to identify methylidyne, ethylidyne and vinylidene (C<sub>x</sub>H<sub>y</sub>) surface intermediates after CH<sub>4</sub> decomposition on two metal-supported catalysts: Ru/Al<sub>2</sub>O<sub>3</sub> and Ni/SiO<sub>2</sub>.<sup>[51]</sup> Upon temperature increase, the intensity of the bands corresponding to ethylidyne decreased, and the intensities of those corresponding to vinylidene species increased. This suggests that the vinylidene species was more stable than ethylidyne at higher temperatures (598 K).

Palladium catalysts used for hydrogenation of C=C and C=O groups at industrial scale were studied by INS.<sup>[52]</sup> After trial with different spectroscopy tools including NMR, IR, Raman etc., only INS was able to clearly show that the surface sites were blocked by the methyl group adsorbed on on-top configurations. These strongly adsorbed methyl groups were responsible for reducing the catalyst performance. In another publication,<sup>[53]</sup> within the same group, coke build-up on Pd/SiO<sub>2</sub> catalysts after hydrogenation of acetylene to ethylene was studied by means of INS. Neutron scattering revealed characteristics of the carbonaceous formations through the dynamics of the protons, which contribute to the understanding of the mechanisms of coke formation.

Bulk gold is generally considered an inert material for catalysis. However, gold nanoparticles have shown remarkable performance catalyzing various reactions.<sup>[54]</sup> Supports are used

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for the dispersion and stabilization of gold nanoparticles; nevertheless, supports have shown to play a role in the catalytic performance of the nanosized Au centers. The existence of hydrogen peroxide and hydroperoxy radicals on Au/TiO<sub>2</sub> after the reaction of H<sub>2</sub> and O<sub>2</sub> had been previously postulated as an intermediate in the epoxidation of propylene over Au clusters using molecular oxygen and hydrogen.<sup>[55-56]</sup> The work of Sivadinarayana et al.<sup>[57]</sup> experimentally confirmed for the first time, via INS, the existence of these intermediates. Juárez et al.<sup>[58]</sup> studied the interaction of H<sub>2</sub>, CO<sub>2</sub> and O<sub>2</sub> with Au supported on ceria (Au/CeO<sub>2</sub>). The authors identified bridging hydroxyl groups at 400–600 cm<sup>-1</sup> upon the hydrogen treatment via INS (Figure 5A). FTIR was useful in identifying the existence of the hydride species Au-H which can go undetected by INS due to the small percentage of Au in the catalyst sample. Therefore, the work of Juárez et al. showed evidence for heterolytic dissociation of molecular hydrogen, with H<sup>+</sup> attached to the support and H<sup>-</sup> attached to Au (see Figure 5B). This work shows clear evidence of the combined role of Au and the support for low temperature hydrogen chemisorption, which can hydrogenate CO<sub>2</sub> as shown in Figure 5A and B.



**Figure 5 A.** INS spectra recorded at 20K for the Au/CeO<sub>2</sub> after outgassing at 423 K for 1 h under vacuum (a), subsequent exposure to H<sub>2</sub> at 423 K for 1 h (b), and exposing the sample to CO<sub>2</sub> at 423 K for 1 h (c). **B.** Heterolytic dissociation of molecular hydrogen on Au/CeO<sub>2</sub> (a) and CO<sub>2</sub> hydrogenation on Au/CeO<sub>2</sub> (b). Reprinted with permission from ref.<sup>[58]</sup>. Published by The Royal Society of Chemistry.

In a paper recently published by Silverwood et al.,<sup>[59]</sup> the authors also suggest the existence of the hydride species bonded to gold (Au-H) on an Au/CeO<sub>2</sub> catalyst, after reduction with hydrogen. Both INS and IR spectroscopy were used to assign a peak at 2125 cm<sup>-1</sup> to Au-H, whereas in the past this peak had been assigned to Ce<sup>3+</sup> by other authors.<sup>[60-61]</sup> Experiments with H<sub>2</sub> and D<sub>2</sub> allowed the authors to suggest hydrogen spillover occurs upon exposure of the catalyst to H<sub>2</sub>, but then, upon exposure to D<sub>2</sub>, reverse hydrogen spillover (from OH species on the ceria surface) onto the gold may occur. Alternatively, it is suggested that gas phase HD may be formed and then chemisorbed onto the surface.

INS studies were also performed by Silverwood et al.<sup>[62]</sup> to study the CO<sub>2</sub> reforming of methane over Ni/Al<sub>2</sub>O<sub>3</sub> and Ni-Au/Al<sub>2</sub>O<sub>3</sub>. The two catalysts presented similar catalytic performance, although the addition of gold to the alumina-supported catalyst slightly increased deactivation. Neutron characterization showed that hydrogen is retained on the surface in much smaller quantities than carbon (coke formation), which indicates that association of atomic hydrogen to form H<sub>2</sub> and the following desorption are processes that occur relatively fast in the reaction mechanism for dry reforming over these catalysts. INS spectra also allowed quantifying the density of hydroxyls on the surface of the catalysts. Despite the density of hydroxyls on Ni/Al<sub>2</sub>O<sub>3</sub> is roughly 4 times the density on Ni-Au/Al<sub>2</sub>O<sub>3</sub>, the

performance of these catalysts is similar, suggesting that the hydroxyl groups do not belong to the main reaction pathway.

Apart from the extensively used neutron spectroscopy, neutron diffraction (ND) was also found powerful in characterizing surface chemistry and catalyst structures in hydrogen-involved reactions. Youngs et al.<sup>[63]</sup> studied the hydrogenation of benzene to cyclohexane over Pt/SiO<sub>2</sub> by means of ND. They successfully monitored the pore size of the catalyst under reaction conditions, as well as the bond lengths associated with the species involved in the reaction. The evolution of differential cross scattering data (F(Q)) with time allowed to calculate rate constants for deuterium dissociation, deuteration of benzene-d<sub>6</sub>, and pore diffusion. From these values, the authors concluded that the reaction is mass transfer limited. Such conclusion is crucial for tailored improvement of reactive systems.

A recent publication showed that characterization with ND can provide information about supported catalysts used industrially. By means of neutron diffraction (ND), Kandemir et al.<sup>[64]</sup> studied the transformation of a catalysts used in the industrial synthesis of methanol from syngas (H<sub>2</sub>/CO/CO<sub>2</sub>), Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>. Studies performed at reaction conditions allowed to conclude that, during reaction, there is no inclusion of C or H species into the bulk, brass is not formed, and the nature of the supported Cu is relatively stable during reaction. In their study, they suggest that the interactions between Cu and ZnO are rather of fixed Cu particles and mobile ZnO<sub>x</sub>, since the catalyst under study has large Cu nanoparticles and poorly crystalline ZnO. Mobile Cu phase and static ZnO were reported previously for a highly crystalline ZnO with small Cu particles.<sup>[65-67]</sup>

In summary, neutron scattering has become one of very few experimental techniques capable of providing detailed information about adsorption mechanisms of hydrogen (and their transient nature), and how they are related to the catalyst performance and product selectivity over a range of catalytic materials. Atomistic experimental description of the reaction mechanism for any hydrogen-containing molecule on metal-supported catalysts appears to benefit greatly from characterization via neutron scattering.

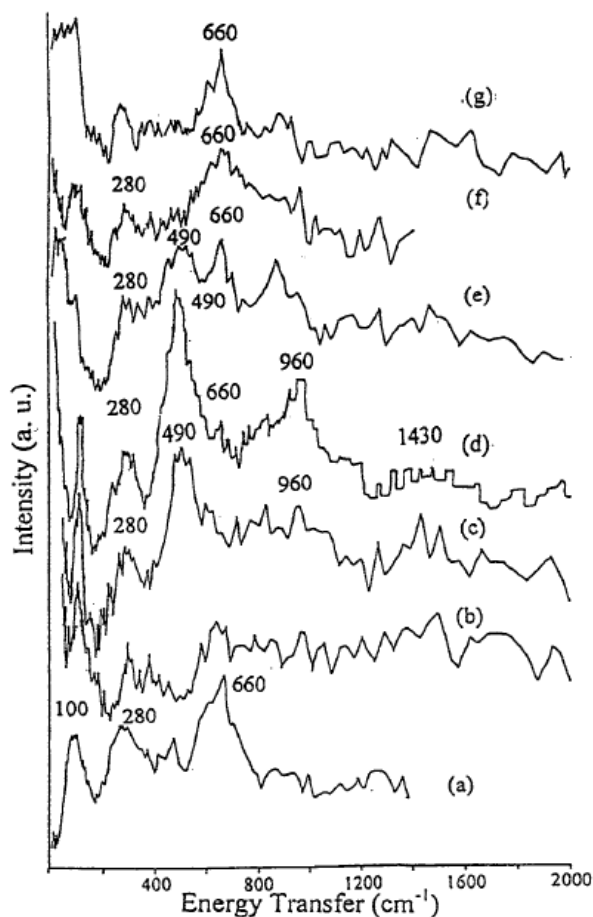
### 3. Hydrogen Interaction with Oxide Catalysts

Oxide surfaces can react with H<sub>2</sub> either homolytically (forming two new OH groups) or heterolytically (forming one new OH and one metal hydride species, M-H). The presence of the M-H vibrational bands is diagnostic of heterolytic dissociation on oxide surfaces and can be further confirmed from the isotopic shift from D<sub>2</sub> adsorption. Metal hydrides were experimentally observed on many oxide surfaces including MgO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub>, ZnO, ZrO<sub>2</sub> etc. via mostly IR spectroscopy as summarized by Coperet et al.<sup>[1]</sup> Among many oxides, only a few such as ZnO, ZrO<sub>2</sub> and CeO<sub>2</sub> have been found able to active H<sub>2</sub> for hydrogenation reactions.<sup>[68]</sup> Since IR spectroscopy has been successfully utilized to study hydride species over ZnO and ZrO<sub>2</sub>, we will focus in this session on neutron investigation of H<sub>2</sub> interaction with CeO<sub>2</sub>-based oxides where traditional spectroscopy failed to detect the hydride species. There are recent neutron studies including neutron diffraction and neutron scattering of transition metal oxyhydrides<sup>[11, 69] [70] [71] [72] [73]</sup> which are emerging materials with intriguing chemical physical properties such as excellent anion and electronic conductivity. In this minireview, we will highlight findings about these materials as they relate to heterogeneous catalysis.

The first experimental evidence for the existence of metal hydride in ceria-based metal oxides was reported by C. Lamonier et al.<sup>[74]</sup> who characterized mixed oxides CeNi<sub>x</sub> (x=0.2, 0.5) using INS. As shown in **Figure 6**, a peak at 660 cm<sup>-1</sup> observed on CeO<sub>2</sub>

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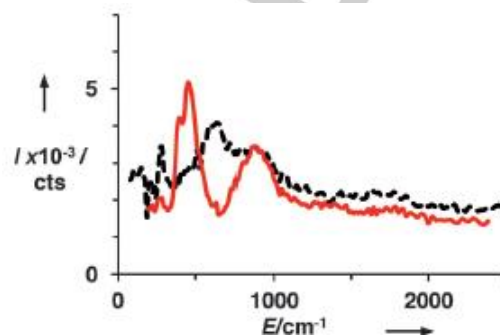
and  $\text{CeNi}_{0.2}$  was assigned to the deformation mode of hydroxyl groups. A new peak at  $490\text{ cm}^{-1}$  arises on the mixed oxides upon reduction by pure  $\text{H}_2$  at  $473\text{ K}$ . This peak disappears after the introduction of  $\text{O}_2$ , thus it was believed to originate from the hydride species, indicating a heterolytic dissociation of  $\text{H}_2$  over the mixed oxides. The hydride species was also shown to be reactive for hydrogenation of isoprene as the  $490\text{ cm}^{-1}$  feature disappears upon addition of isoprene at  $473\text{ K}$ .



**Figure 6** INS spectra of: a)  $\text{CeO}_2$ ; b)  $\text{CeNi}_{0.2}$ ; c)  $\text{CeNi}_{0.2}$  reduced; d)  $\text{CeNi}_{0.5}$  reduced; e)  $\text{CeNi}_{0.5}$  in situ calcined and reduced, f) (c) +  $\text{O}_2$  re-oxidation, g) (e) + isoprene. Reproduced with permission from Ref. [74]. Copyright 2000 Elsevier.

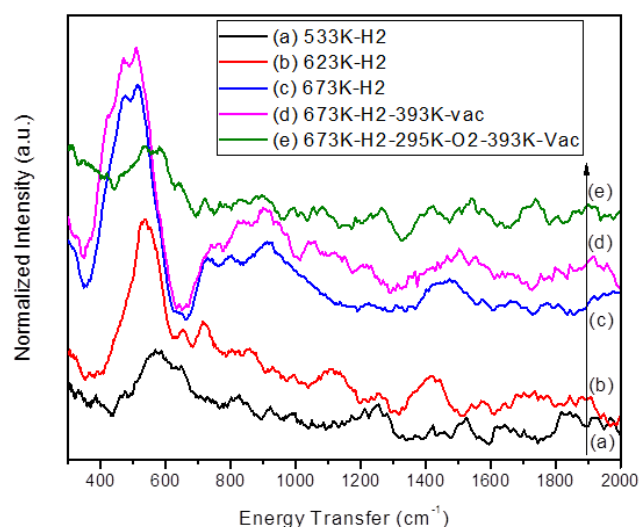
Later on, INS was employed to study hydrogen interaction with a series of  $\text{CeM}_2\text{Ni}_x\text{O}_y$  ( $\text{M}=\text{Zr}$  or  $\text{Al}$ ,  $\text{Z}=0$  or  $0.5$ ,  $0 \leq x \leq 3$ ) mixed oxides as promising hydrogen storage materials. Two intense peaks at  $480$  and  $870\text{ cm}^{-1}$  were observed with the treatment of  $\text{H}_2$ , which was assigned to hydride species and hydrogen species binding to metallic  $\text{Ni}^0$ , respectively. The hydride peak at  $480\text{ cm}^{-1}$  disappears when  $\text{O}_2$  is introduced and the peak at  $630\text{ cm}^{-1}$  related to the hydroxyl groups appears.[75] In another work,  $\text{CeNiH}_2\text{O}_y$  (Ni loading 20 wt%) was reported as an outstanding catalyst for  $\text{H}_2$  production from ethanol, in simultaneous presence of water and  $\text{O}_2$  (oxidative steam reforming of ethanol -OSRE). The reaction is highly benefited by the thermal energy released from the reaction between the hydride species of the catalyst and  $\text{O}_2$ , achieving high reaction temperatures (over  $250\text{ }^\circ\text{C}$  in some cases) while keeping the oven temperature at  $60\text{ }^\circ\text{C}$ . Further, the ability of the catalyst to accept hydrogen is crucial for the dehydrogenation of ethanol, claimed as the rate-determining step. As shown in Figure 7, INS experiments confirmed the presence

of hydride species  $\text{Ce--H--Ni}$  ( $460\text{ cm}^{-1}$ ), hydrogen species interacting with  $\text{Ni}^0$  ( $870\text{ cm}^{-1}$ ), and hydroxy groups ( $630\text{ cm}^{-1}$ ).[76] Further experimentation on OSRE, varying the amount of Ni in the catalyst  $\text{CeNi}_x\text{H}_2\text{O}_y$ , proved that the best catalyst is obtained when  $x=1$ . When the concentration of Ni in the catalyst reduced ( $\text{Ni}/\text{Ce}=0.5$ ), the interaction of hydrogen with  $\text{Ni}^0$  disappears (measured via INS), which is correlated with the high proportion of solid solution of Ce and Ni in this catalyst.[77]



**Figure 7** INS spectrum of  $\text{CeNiH}_2\text{O}_y$  (red solid line) treated in  $\text{H}_2$  at  $250\text{ }^\circ\text{C}$  after subtraction of the  $\text{CeNiO}_y$  spectrum, and INS spectrum of  $\text{CeNiH}_2\text{O}_y$  after oxidation and subtraction of the  $\text{CeNiO}_y$  spectrum (dashed line). Reprinted with permission from Ref. [76]. Copyright 2017 Wiley Company.

Noticeably, no direct observation of pure cerium hydrides was made by either traditional spectroscopy or neutron spectroscopy until recently Wu et al. reported INS observation of both surface and bulk Ce-H species on cerium oxide.[78] Initial  $\text{H}_2$ -reduction at low temperature resulted in surface hydroxylation as evidenced by the feature at  $\sim 600\text{ cm}^{-1}$  (Figure 8), also elaborated by both IR and Raman observations. Surface hydride species at  $400 \sim 600\text{ cm}^{-1}$  and bulk species around  $800 \sim 1000\text{ cm}^{-1}$  were observed in the INS spectra upon reduction by  $\text{H}_2$  at higher temperatures ( $> 623\text{ K}$ ). The assignment was supported by DFT calculation of INS spectra for surface and bulk Ce-H. The hydride species are stable at  $393\text{ K}$  in the absence of oxygen; however, after exposure to oxygen at room temperature, both hydride species readily react to form water and the surface hydroxyl feature was observable again. Combined with ambient pressure XPS results of  $\text{H}_2$  interaction with ceria at different temperatures, the authors were able to conclude that partially reduced ceria surfaces (with oxygen vacancies) promote the formation of hydride species via heterolytic dissociation of  $\text{H}_2$ ; however, a close-to-stoichiometric ceria surface favors only formation of OH groups, likely via a heterolytic pathway to form the thermodynamically more stable homolytic products as predicted by DFT calculations.[79-81] The finding from this work not only provide a molecular level understanding of  $\text{CeO}_2\text{-H}_2$  interaction but also has general implications for catalysis by ceria in selectively hydrogenation[68, 82-83] and redox reactions. The valuable insights will shed light on the design of more effective ceria-based catalysts in H-related reactions.



**Figure 8** INS spectra of CeO<sub>2</sub> collected at 10 K after H<sub>2</sub>-treated at (a) 533 K, (b) 623 K, (c) 673 K, (d) 393 K vacuum after (c), and (e) exposure to O<sub>2</sub> at RT and then 393 K vacuum after (d). Reproduced with permission from Ref. [78]. Copyright 2017 American Chemical Society.

As shown in some of the examples described in this review, computational modelling is an integral part of neutron studies. To summarize, computational tools have contributed to study hydride species in heterogeneous catalysts in: studying the stability of  $\beta$ -palladium hydride upon alloying with Pb via density functional theory (DFT) calculations,<sup>[33]</sup> the assignment of surface and bulk hydride species (Ce-H<sup>[78]</sup>, Pd-H<sup>[36]</sup>) via DFT calculations of INS spectra, prediction of H<sub>2</sub> dissociation pathway (DFT);<sup>[79-81]</sup> in addition, diffusion processes of alkanes and alcohols in porous materials, measured via quasielastic neutron scattering (QENS), have been simulated.<sup>[84]</sup> A recent publication reviews the computationally-aided interpretation of INS spectra of H<sub>2</sub> adsorption on clathrate hydrates, zeolites, and metal-organic frameworks (MOFs).<sup>[85]</sup> We refer the reader to this publication as these materials were not covered within the scope of the present minireview.

Since zeolites are considered as a separate group of catalysts apart from *metal oxide* catalysts, we will not devote much of the present paper to review work done on these materials. However, it is important to notice that in recent time, publications have reported the interaction of hydrogenous species (not necessarily hydride species) with zeolite materials using neutron scattering as reviewed by O'Malley et al.<sup>[84]</sup> Several authors have studied the diffusion of alkanes in zeolites using quasielastic neutron scattering (QENS).<sup>[86-89]</sup> Diffusion coefficients have been compared against various computational methods,<sup>[87, 90-91]</sup> with the closest agreement provided by hierarchical simulations.<sup>[91]</sup> Molecular dynamics (MD) simulations have also been used to model diffusion of alkanes in MFI zeolites, measured via QENS<sup>[90]</sup> and neutron spin-echo (NSE)<sup>[92]</sup>. Methanol diffusion (QENS), reaction and adsorption (INS) during the methanol-to-hydrocarbon process have also been studied.<sup>[93-94]</sup>

#### 4. Summary

Neutron scattering techniques are particularly suitable to study hydrogen species due to the extraordinary high scattering cross-section of hydrogen compared to other techniques including X-ray and optical spectroscopy. In this review, successful examples of characterizing the interaction of hydrogen

with supported-metal and oxide catalysts, via neutron scattering, have been surveyed. These studies provide unique information otherwise inaccessible with other techniques. Much has been learned about the adsorption, dissociation, spillover and reactivity of hydrogen, especially hydride species, over the two most common classes of heterogeneous catalysts in hydrogen-involved reactions. Neutron vibrational spectroscopy, i.e., INS, is among the most powerful tools in probing the chemical nature of hydrogen species along with neutron diffraction and quasi-elastic neutron scattering on the structure and dynamics of these species. Computational modeling plays a crucial role in interpreting the neutron scattering results and thus understanding the nature, molecular structure and dynamics of hydrogenous species on catalyst surfaces.

Challenges also exist for neutron scattering study of heterogeneous catalysis. Since neutron interaction with matters is intrinsically weak and the neutron flux is very low (compared to synchrotron X-ray), large quantity of samples is generally needed (in grams level). The time resolution of neutron scattering especially INS is low compared to the catalytic turnover rates in most reactions, making it difficult to follow catalytic process at real time. The mostly utilized INS is further limited by the required low temperature (< 100 K due to recoil and Debye-Waller factor) acquisition, and thus, it is not possible to follow most catalytic reactions at kinetically relevant temperatures. Due to the capital-intensive nature of neutron facilities, the use of this technique to study catalytic processes is still scarce compared to X-ray. Tailoring experiments, during the much valuable beamtime in a neutron facility, must be done considering learnings from less expensive and more readily available characterization techniques (*operando* IR, Raman, etc). However, with careful experimental design, the choice of proper catalytic systems, the brightest neutron flux at the spallation neutron source at Oak Ridge National Laboratory with *in situ/operando* sample environment, the novel design of neutron instrumentation with multimode approaches, and the coupling of supercomputing, neutron scattering will continue to play an important role in providing unique insights for catalysis on the nature of reaction intermediates and mechanisms, and the dynamics of catalyst structures under conditions close to reaction conditions.

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#### Conflict of interest

The authors declare no conflict of interest.

**Keywords:** neutron scattering • heterogeneous catalysis • hydride • supported metal catalysts • oxide catalysts

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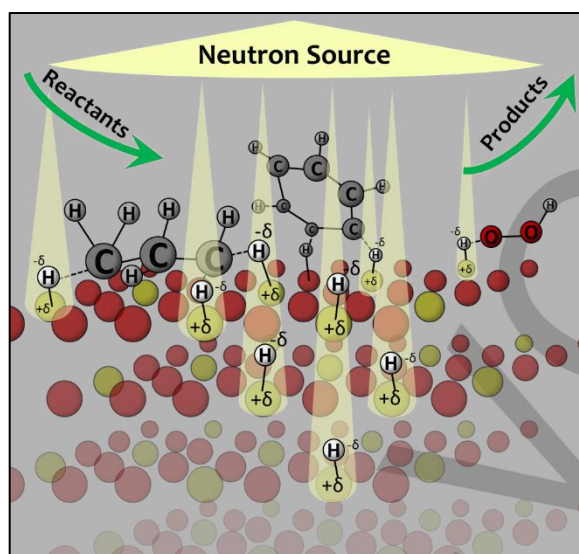
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## MINIREVIEW

In heterogeneous catalysis, hydrides play a critical role in many hydrogen-involved reactions. Neutron scattering has unique potential for characterizing hydrides. In this work, we review recent advances in neutron studies of hydride species over supported metal and oxide catalysts.



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Species in Heterogeneous  
Catalysis**