CO$_2$ Reduction

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The Origin of the Catalytic Activity of a Metal Hydride in CO$_2$ Reduction

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Abstract: *Atomic hydrogen on the surface of a metal with high hydrogen solubility is of particular interest for the hydrogenation of carbon dioxide. In a mixture of hydrogen and carbon dioxide, methane was markedly formed on the metal hydride ZrCoH$_x$ in the course of the hydrogen desorption and not on the pristine intermetallic. The surface analysis was performed by means of time-of-flight secondary ion mass spectroscopy and near-ambient pressure X-ray photoelectron spectroscopy, for the in situ analysis. The aim was to elucidate the origin of the catalytic activity of the metal hydride. Since at the initial stage the dissociation of impinging hydrogen molecules is hindered by a high activation barrier of the oxidised surface, the atomic hydrogen flux from the metal hydride is crucial for the reduction of carbon dioxide and surface oxides at interfacial sites.*

To secure future energy supplies and to limit anthropogenic carbon dioxide emissions, a sustainable energy society is to be based on a closed energy material cycle. Renewable energies need to be stored in energy carriers such as synthetic hydrocarbons with the energy density comparable to fossil fuels (e.g. petrol). The raw materials base by using carbon dioxide (instead of crude oil) needs to be expanded in the chemical industry.[1] In the short term, carbon dioxide (flue gas) is captured from the various point sources such as fossil fuel power stations and factories. In the long term, carbon dioxide is captured from the atmosphere to close the energy cycle (artificial photosynthesis). To store renewable energy in synthetic hydrocarbons, the reduction of carbon dioxide, as well as the capture of carbon dioxide, is a major challenge.[2–7]

Carbon dioxide can be reduced to hydrocarbons by binding hydrogen via the following heterogeneous catalytic reactions: $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O(g)$ (the Sabatier process, $\Delta H^{\circ}_{298\,K} = -165\ kJ\,mol^{-1}$), $CO_2 + H_2 \rightarrow CO + H_2O(g)$ (reverse water-gas-shift reaction (RWGS), $\Delta H^{\circ}_{298\,K} = 41\ kJ\,mol^{-1}$). The Fischer–Tropsch process delivers diverse hydrocarbon products in the range of 1 to 20 carbon atoms. The direct and indirect hydrogenation of carbon dioxide and carbon monoxide leads to several reactions, depending on the kinetics and thermodynamics, towards the production of hydrocarbons.[8]

For the hydrogenation, a surface of metal with high solubility of hydrogen is of particular interest, in view of control of the reaction. One of the simplest hydrogenation reactions is the formation of water from oxygen and hydrogen. In the atmosphere with an excess of hydrogen, the formation of water on palladium is dominated by the transport of atomic hydrogen between the surface and the bulk, which was shown by using a molecular-beam relaxation technique under ultra-high vacuum conditions.[9] In heterogeneous catalysis, palladium is one of the most important hydrogenation catalysts. However, it is generally not clear whether the formation of the metal hydride is important for industrially applied supported catalysts.[10,11] By using metal hydrides, the heterogeneous hydrogenation reactions were investigated. For example, the rate of the hydrogenation of ethene was increased on a hydrogen-absorbing intermetallic compound, LaNi$_5$H$_x$;[12] for the synthesis of ammonia and the conversion of synthesis gas, hydrogen-absorbing intermetallic compounds were reported as active catalyst precursors.[13,14]

Whether hydrogen absorbed in metals plays an important role in hydrogenation, for example, the reduction of carbon dioxide, remains open. In this study, we focused on the relationship between the catalytic activity of a metal hydride (Figure 1) and the hydrogen desorption. The aim was to elucidate the origin of the catalytic activity of a metal hydride.

In order to investigate the mechanism of the reduction of carbon dioxide, a zirconium cobalt alloy ZrCo and the intermetallic hydride $ZrCoH_{3-x}$ as catalyst were chosen for the following reasons: cobalt is a catalytically active metal, for example, for the Fischer–Tropsch process and the Sabatier process;[8,15] zirconium dioxide is an acid-base bifunctional catalyst in the diversified use for hydrogenation reactions, including the hydrogenation of carbon monoxide and carbon dioxide;[16–18] the hydrogen desorption temperature of $ZrCoH_{3-x}$ lies in the range of the reaction condition, which is important for investigating the role of the absorbed hydrogen. In the cobalt–hydrogen system, the formation of the hydride is an endothermic process. However, the formation of the intermetallic compounds (e.g. ZrCo) leads to an exothermic hydrogen absorption, forming the interstitial hydride $ZrCoH_{3-x}$, and to ready absorption (exothermic) at room temperature and 1 bar: $ZrCo + 3/2\,H_2 \rightarrow ZrCoH_3$.

The pressure composition isotherm of the ZrCo–H system for the hydrogen desorption shows three distinct regions

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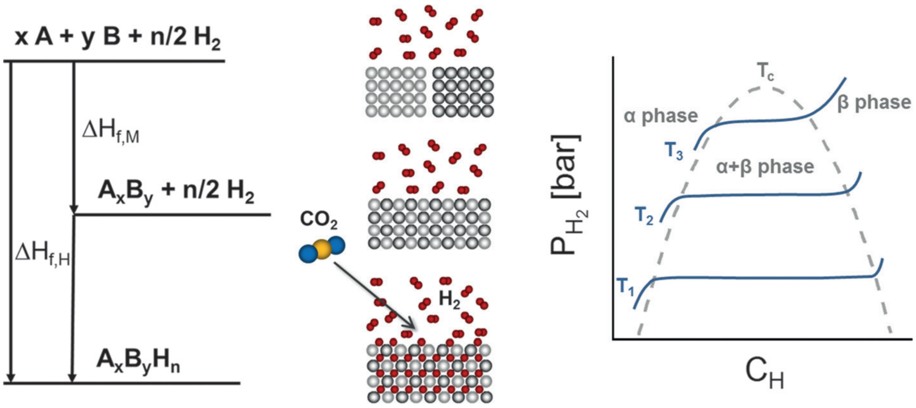

Figure 1. A metal hydride catalyst: formation of an intermetallic hydride (left). The metal A-hydrogen system is endothermic. The formation of an intermetallic compound, A_xB_y, leads to exothermic hydrogen absorption. The pressure–composition isotherms (pcT) of the A_xB_y–H system at three different temperatures ($T_1 < T_2 < T_3$) (right). During the hydrogen desorption, the metal hydride can deliver hydrogen to carbon dioxide at the surface, which is catalytically active in the reduction of carbon dioxide and formation of hydrocarbons.

(Figure 2 top): with an increase in the hydride composition, the solid solution phase (α phase), the coexistence of the solid solution phase and the hydride phase (α + β phase), and the hydride phase (β phase), as reported at 100–375 °C.[19–23] The equilibrium hydrogen pressure is a measure of the thermal stability of the hydride, depending on composition and temperature. At a plateau pressure (α + β phase), where hydrogen is reversibly absorbed/desorbed, $ZrCoH_x \leftrightarrow ZrCoH_{x-y} + y/2\,H_2$, the equilibrium hydrogen pressure depends strongly on temperature. This hydrogen absorbed in the metal lattice contributes to the catalytic reduction of carbon dioxide, as will be discussed later. Furthermore, the formation of methane (i.e. the Sabatier process), which is exothermic ($\Delta H^{\circ}_{298\,K} = -21$ kJ mol(H)$^{-1}$), might further lead to an increase of temperature and, therefore, to the endothermic hydrogen desorption ($\Delta H \approx 42$ kJ mol(H)$^{-1}$),[20] according to Le Chatelier principle, resulting in shifting the equilibrium toward the formation of methane.

The catalytic activity of the metal hydride $ZrCoH_x$ was analysed as a function of the hydride composition $ZrCoH_x$ ($x = 0$, 0.1, 1.2, 2.9) (Figure 2 bottom). The samples were loaded into a fixed-bed tubular flow reactor. Carbon dioxide, hydrogen and helium (carrier gas) were admitted into the reactor. For $ZrCoH_{2.9}$, a significant increase of hydrogen in the gas flow was observed above 190 °C. Simultaneously, with the hydrogen desorption from the metal hydride, the formation of methane commenced. Methane was markedly formed on the hydrides ($ZrCoH_{2.9}$ and $ZrCoH_{1.2}$), not on the pristine intermetallic, though hydrogen molecules from the gas phase impinge onto the surface. The formation of methane is increased with respect to the hydride composition x from 0 to 2.9. Thus, the hydrogen desorption leads to the formation of methane.

We performed surface analysis by means of time-of-flight secondary ion mass spectroscopy (ToF-SIMS) and near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS). For the ToF-SIMS images (Figure 3), $ZrCoD_{1.2}$ was analysed, in place of the hydride $ZrCoH_{1.2}$, by labelling the hydrogen isotope. The hydrogen dissociation pressure at 25 °C is by three orders of magnitude higher than the background pressure of 10^{-8} mbar.[24] Therefore, here, the hydrogen originates from the gas phase or hydroxy groups at the surface, while the deuterium originates only from the deuteride $ZrCoD_{1.2}$. As seen from the ToF-SIMS images, the local composition is inhomogeneous on a μm scale, and the distribution of deuterium correlates with that of zirconium oxides.

The XP spectra (Figure 4) show that the surface of the metal hydride $ZrCoH_x$ is initially covered with the surface oxides. In the Zr 3d spectra (Supporting Information S1), two sets of the spin–orbit doublets show formation of zirconium oxide (higher binding energies: e.g. ZrO_2) and hydroxyl groups or oxygen vacancies on zirconia (lower binding energies).[22] With an increase in temperature, the change of the Zr 3d spectra shows that formation of hydroxyl groups, as expected by a Fourier-transform infrared (FT-IR) spectroscopy study,[25] or oxygen vacancies further proceeds in hydrogen at 240 °C. The change of the Co 2p spectra (Figure 4) shows that cobalt is reduced by hydrogen. For $ZrCoH_{1.2}$, the hydrogen desorption leads to a complete reduction of cobalt. The catalytic activity of the metal hydride is explained by the reduction of cobalt oxide with hydrogen from the metal hydride.

A consideration of the relationship between the formation of methane and the hydride composition (Figure 5) gives a possible explanation for the high catalytic activity, compared to the pristine intermetallic ZrCo. Diffusion of hydrogen atoms in a metal and transition of hydrogen atoms at the metal/surface layer (e.g. surface oxide) interface are fast reaction steps; the subsequent surface processes, namely hydrogen permeation in surface layers and/or recombination of adsorbed hydrogen atoms, control the hydrogen desorption kinetics.[26–28] In both cases, the hydrogen flux is determined by the activity of hydrogen at the surface of a metal. Though a further detailed analysis is required to explain this relationship (Figure 5) in terms of the reaction kinetics, the activity of hydrogen at the surface is a key factor in the reduction of carbon dioxide, and increases the rate of the formation of methane.

The hydrogen diffusion from the metal hydride causes the reduction of carbon dioxide and the formation of methane. The atomic hydrogen plays an important role in the catalytic activity; the atomic hydrogen in the chemisorbed state is capable to react with the adsorbates of carbon dioxide and simultaneously reduce cobalt oxides. In the atmosphere of hydrogen (H_2), as shown by the surface analysis (Supporting Information S1), the reduction of cobalt oxides is much more pronounced on the metal hydride, with the higher hydride

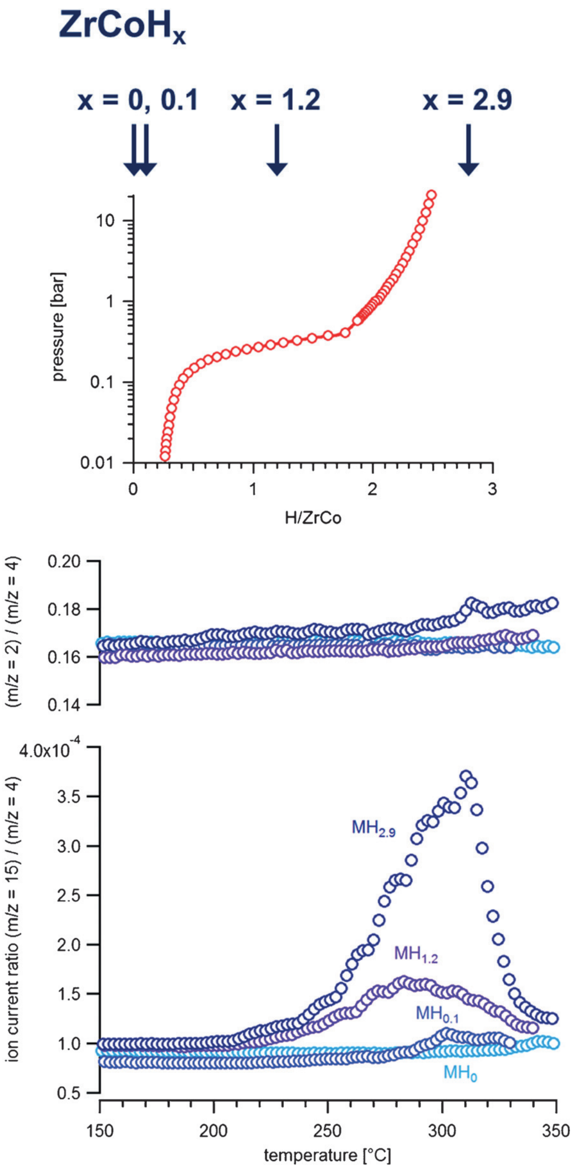

Figure 2. Top: the pressure–composition isotherm (pcT) of the ZrCo-H system for the hydrogen desorption at 375 °C. Bottom: the formation of CH_4 on $ZrCoH_x$ ($x = 0$, 0.1, 1.2, 2.9) in the flow of CO_2, H_2 ($H_2/CO_2 = 5$), and He (carrier gas). The ion current ratio $m/z = 2$ (H_2^+) to $m/z = 4$ (He^+) vs. temperature (5 °C min^{-1}). The ion current ratio $m/z = 15$ (CH_3^+) to $m/z = 4$ (He^+) vs. temperature (5 °C min^{-1}). For both, the intensities at 150 °C are the background levels. Except for CH_4, no other hydrocarbons ($C \geq 2$) were detected under our experimental conditions.

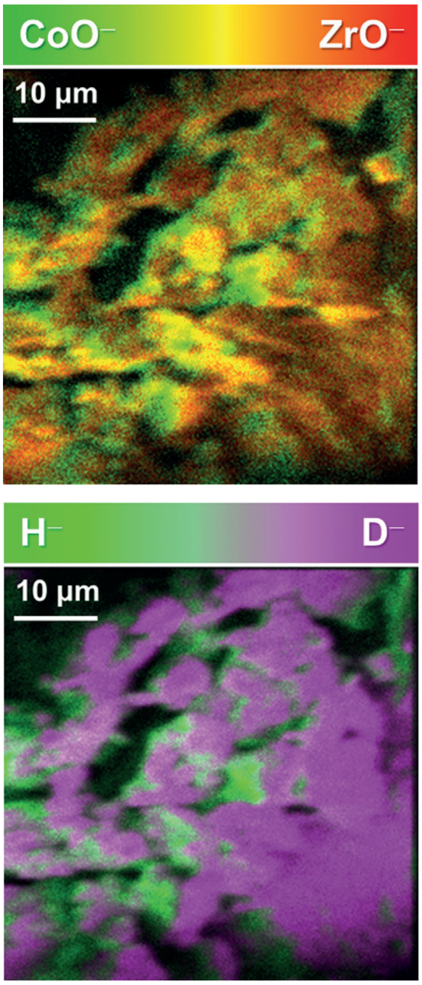

Figure 3. The ToF-SIMS chemical images of $ZrCoD_{1.2}$ powder, taken at 2×10^{-8} mbar and 25 °C. The distributions of ZrO^-/CoO^- (top) and D^-/H^- (bottom) on $ZrCoD_{1.2}$.

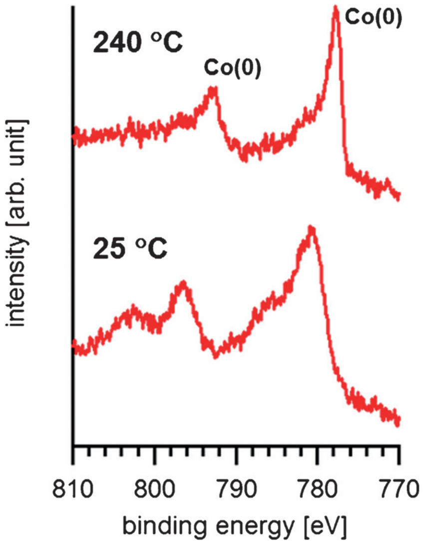

Figure 4. The Co 2p XP spectra of $ZrCoH_{1.2}$ measured in the atmosphere of hydrogen at 1.0 mbar and at the temperatures of 25 °C and 240 °C, respectively. At 240 °C, the equilibrium hydrogen pressure is 7 mbar.[20]

composition, namely with the higher concentration of hydrogen atoms at the surface in the course of hydrogen desorption.

The dissociation of impinging hydrogen molecules on the surface, namely the transfer of hydrogen from the physisorbed state to the chemisorbed state, is hindered by a high activation barrier of cobalt oxides.[26] The hydrogen atoms in the chemisorbed state, diffusing from the metal hydride, recombine at the interfacial sites on the metal hydride (and not in the metal lattice), resulting in desorption of hydrogen molecules, or react with adsorbates. Therefore, especially at the interfacial sites of cobalt and zirconium oxide, the

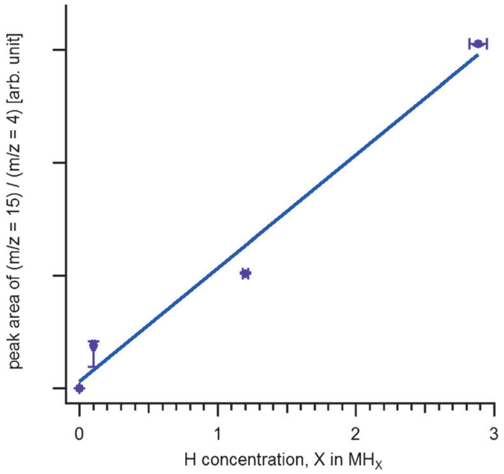

Figure 5. The peak area of the ion current ratio $m/z=15$ (CH_3^+) to $m/z=4$ (He^+) (in Figure 2) vs. the initial hydrogen concentration in $ZrCoH_x$ ($x=0$, 0.1, 1.2, 2.9).

catalytic reaction is greatly influenced by the atomic hydrogen out of the metal hydride.

The total amount of the formation of methane is linearly related to the hydride composition (Figure 5), although the thermal stability of hydrogen atoms in the metal hydride (i.e. hydrogen equilibrium pressure) varies according to the hydride composition (Figure 2, top). A higher concentration of hydrogen atoms in the metal hydride leads to a higher flux of atomic hydrogen from the bulk to the surface.[26,27] The higher availability of hydrogen atoms in the chemisorbed state at the interfacial sites of cobalt and zirconium oxide leads to a higher rate of the reduction of cobalt and consequently the dissociation of impinging hydrogen molecules, resulting in a higher rate of the formation of methane (Figure 2, bottom). The binding energies of hydrogen atoms in the chemisorbed state are determined by the interactions of hydrogen atoms with the substrate and adsorbates, and the metal hydride is a reservoir of atomic hydrogen to the chemisorbed state—this is crucial for the catalytic activity.

A possible reaction mechanism (Figure 6) is that the hydrogen desorption, namely, the atomic hydrogen flux from the metal hydride, leads to the reduction of carbon dioxide and cobalt oxide at the interfacial sites; consequently, the gas phase hydrogen participates in the formation of methane (Supporting Information S2). The hydrogen molecules impinging on the reduced cobalt dissociate into hydrogen atoms, and the hydrogen atoms, as well as hydrogen atoms diffusing from the metal hydride, spill over to zirconia;[29] the adsorption of carbon dioxide on surface hydroxyl groups on zirconia results in the formation of a formate precursor, as proposed by FT-IR studies,[18,30,31] and methane and water are formed. While hydrogen atoms diffuse from the metal hydride onto the surface, with an increase in temperature, the decrease in the formation of methane might be caused by the limited adsorption of carbon dioxide on zirconia.[32] To propose the further reaction scheme, a mechanistic study by in situ spectroscopies is required.

The interaction of gas molecules such as carbon dioxide, carbon monoxide and water with the surface is crucial for the

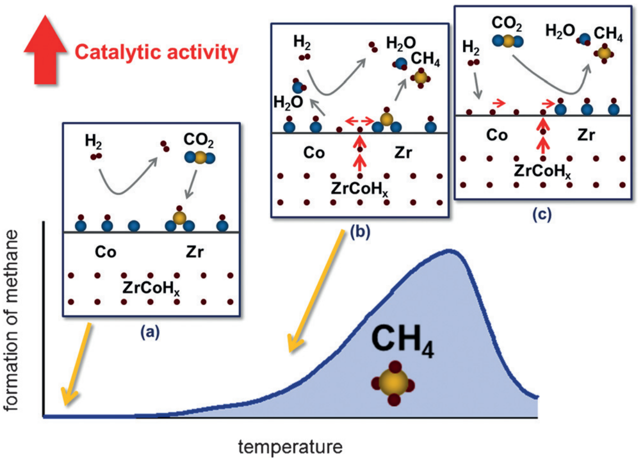

Figure 6. The schematic representation of the reduction of carbon dioxide on the metal hydride $ZrCoH_x$. a) Initially, the surface is covered with surface oxides. In the gas phase impinging hydrogen molecules do not dissociate on the surface, while carbon dioxide molecules adsorb on zirconia and form formate. b) The hydrogen atoms diffusing from the metal hydride react with the formate precursors, resulting in the formation of methane and water, and simultaneously reduce cobalt oxide and water is formed. c) Impinging hydrogen molecules on the reduced cobalt dissociate, and the hydrogen atoms as well as hydrogen atoms diffusing from the metal hydride spill over to formate, resulting in the formation of methane and water.

hydrogen sorption kinetics.[28,33,34] The proposed reaction mechanism might also explain the reason why hydrogen absorbing alloys exhibit superior cyclic properties under the operational conditions containing such impurity gasses in hydrogen. In the cyclic hydrogen sorption process, hydrogen desorption might cause a reduction of surface oxides at the grain boundaries, which enables, upon the exothermic hydrogen absorption, dissociation of hydrogen molecules, and the subsequent diffusion of hydrogen atoms into alloy.

In summary, methane was markedly formed on the metal hydride in the course of the hydrogen desorption, not on the pristine intermetallic, under our experimental conditions. This is because the atomic hydrogen flux from the metal hydride is crucial for the reduction of carbon dioxide. Moreover, it is expected that if metallic sites or oxygen vacancies at interfacial sites play an important role in catalysis, this effect of hydrogen desorption on catalytic activity might also be found for various supported and unsupported bulk catalysts, composed of hydrogen-absorbing materials.

Experimental Section

ZrCo chunks were purchased from SAES GETTERS S.p.A. Through five cycles of hydrogen absorption (in hydrogen at 25 bar and at 25 °C) and desorption (in vacuum and at 600 °C), the powder samples were prepared for all the experiments. The powder was analysed by X-ray diffraction and, after hydrogen desorption, all the peaks were assigned to ZrCo Pm-3m (221).

The pressure composition isotherms were measured by using a volumetric Sieverts type apparatus, after cyclic hydrogen desorption and absorption as described above.

For the catalytic activity measurement, the hydride powder with varied composition was prepared by a volumetric Sieverts type apparatus. The powder was pressed, sieved (fraction: 150–200 μm), and diluted with sea sand with the same size (weight ratio sample/sea sand = 1:2). This mixture was firmly packed between two plugs of quartz wool in a fixed-bed quartz reactor tube. Carbon dioxide (1 mol%), hydrogen (5 mol%) and helium (94 mol%) were admitted to the reactor; the total flow rate was 50 mL min^{-1} and the gas hourly space velocity (GHSV) was 4×10^4 hour^{-1}. The product analysis was performed with a mass spectrometer (Pfeiffer Vacuum, GSD 301 O2) and a gas chromatograph (Agilent Technologies 3000 A micro, equipped with Poraplot U and MolSieve 5 A columns). For the detection of methane, we used the mass-to-charge ratio $m/z = 15$ (CH_3^+) as an indicator for CH_4, instead of $m/z = 16$ (CH_4^+), since singly ionized oxygen O^+ is also $m/z = 16$ and, therefore, $m/z = 16$ overlaps with other fragments of residual gasses containing O (e.g. CO_2, H_2O, O_2, CO).

For the ToF-SIMS analysis, the powder sample of $ZrCoD_{1.2}$ was sieved (< 200 μm), pressed on an indium sheet and transferred into the spectrometer (ToF-SIMS.5, IONTOF GmbH, Germany). The ToF-SIMS surface analysis was performed at a base pressure of 2×10^{-8} mbar and a temperature of 25 °C. Bi_1^+ primary ions (25.0 keV, 2.0 pA, 50.0×50.0 μm^2) were used in high lateral resolution mode, in combination with a gentle Cs^+ sputtering to promote the D^- yield (2.0 keV, 85.4 nA, 200.0×200.0 μm^2). The detection was performed in the negative polarity, as hydrogen, deuterium and most oxides become preferentially negatively ionised during the bombardment process.

The NAP-XPS surface analysis was performed using the spectrometer SPECS PHOIBOS 150 NAP. The powder samples of $ZrCoH_{0.1}$ and $ZrCoH_{1.2}$ were sieved (< 200 μm) and pressed on a lead sheet and transferred into the in situ cell. The XP spectra were collected by using a monochromatic X-ray source ($Al_{K\alpha}$: 1486.6 eV), in hydrogen at 1.0 mbar and at the temperatures of 25 °C and 240 °C. For charge reference of Co 2p, the C 1s line of adventitious hydrocarbon was assumed to have a binding energy of 284.8 eV. The data processing was performed using CasaXPS software.

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