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Promotion of Hydrogen Desorption from Palladium Surfaces by Fluoropolymer Coating

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The catalytic activity of Pd surfaces towards hydrogen desorption was significantly improved by a nanometer-thin polytetrafluoroethylene (PTFE) layer, as shown by an enhancement in the permeability of a Pd membrane coated on the permeate side. The origin of this effect was found to be due to a lowering of the barrier for hydrogen desorption, as evidenced by a change in the rate-limiting mechanism of hydrogen permeation through the membrane from desorption (un-coated) to diffusion controlled. In situ X-ray photoelectron spectroscopy (XPS) revealed the electronic structure of the sputtered PTFE. Apart from C–F_n subunits ($n=1$, 2, 3), we found that nonsaturated carbon atoms became hydrogenated during hydrogen permeation, which was indicative of an interaction between Pd and PTFE. This interaction was weak; no Pd–F bonds were formed. We thus attributed the effect to an increase in the hydrophobicity of the surface by the porous PTFE layer and to a promoter effect of hydrogen desorption as a result of electrostatic interactions between chemisorbed hydrogen and physisorbed PTFE.

The chemistry of polymer coatings on metals is of importance in various disciplines ranging from tribology to catalysis and photovoltaics. In terms of the combination of inert materials such as polytetrafluoroethylene (PTFE) and copper, one expects only weak chemical interactions.[1] The case of Pd is special, though: Pd^0 sites are needed to deposit copper on PTFE and to increase the adhesion between the layers.[2] Still, the chemical interaction between metallic Pd and PTFE is negligible (Pd is catalytically active[1]). However, a profound chemical interaction of PTFE adlayers on thin Pd–Au alloy layers was recently found and was linked to the simultaneous observation of improved hydrogen absorption and desorption properties.[3]

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Metallic palladium, particularly its surface,[4,5] is stable under most conditions, in contrast to materials with superior bulk properties (i.e., other metal hydrides, complex hydrides), which easily oxidize. The oxide layer blocks hydrogen adsorption.[6] Despite the superiority of Pd-based surface modifications, Pd is still the object of fundamental research efforts, notably focusing on important issues such as catalytic activity, mechanical stability, and resistance to contamination. One application of dissociatively active Pd is hydrogen-selective membranes, which are used in energy applications and in the chemical industry for the separation and purification of hydrogen. For hydrogen, dense metallic membranes show better performance than porous membranes, both in terms of flux and selectivity.[7,8] Hydrogen dissociates at the surface of the metallic membrane, dissolves in the bulk, and diffuses through it before it recombines at the other side of the membrane.[9] The permeability of the membrane is determined by the surface properties of both sides (dissociation/recombination) and by the bulk permeability (diffusion and solubility). Although materials with a higher permeability than that of Pd are known (e.g., V, Nb, and Ta[10,11]), expensive Pd and Pd-based alloys remain the superior membrane materials owing to their favorable surface properties.[4,12,13] Although it is well known that embrittlement can be limited by alloying Pd with elements such as Ag,[14–20] Y,[21,22] and Cu,[23–27] the problem of contamination (e.g., competitive adsorption,[14,16,22,28,29] coking,[16,30] and sulfur poisoning[22,25–27]) remains unsolved. For porous membranes, Pd is also commonly used as a catalytic, dense coating layer. From such a system, one could expect the same permeability as that of the uncoated membrane (permeation limited by diffusion into the pores) and significantly better selectivity towards hydrogen. Surprisingly, it has been shown that Pd-coated PTFE membranes lose approximately 15% permeability,[31] an effect for which no definitive answer has been provided. Taking the structural point of view, one can also note that the growth of Pd on PTFE is known to be more problematic than that on other substrates,[31,32] which results in the generation of rough and defective coatings. These situations are the result of a poor understanding of the Pd–PTFE interface and its effects on the permeation mechanism.

In this letter, we show that PTFE adlayers on bulk Pd improve the catalytic properties of Pd surfaces for hydrogen desorption and thereby the permeability for hydrogen of the whole PTFE–Pd membrane system. We analyze the interface by X-ray photoelectron spectroscopy (XPS) and find—in contrast to Ref. [3]—no significant change in the binding energies of PTFE and Pd. Instead, we explain the improvement in the cata-

lytic properties by the hindrance of the adsorption of poisoning adsorbates such as water owing to hydrophobic properties of the PTFE and to the promotion of hydrogen desorption by electrostatic interactions between chemisorbed hydrogen and the anchored groups of PTFE. The idea of using an additional coating on the permeate side of a membrane is counterintuitive, because in the first instance it poses additional steric hindrance to hydrogen permeation. However, PTFE coatings are used for hydrophobic Pt catalysts for the liquid-phase catalytic exchange reaction between water and hydrogen gas. Here, porous PTFE prevents the formation of a liquid water film on Pt, which would be a kinetic barrier, but it allows access of gaseous species (e.g., hydrogen and gaseous water) to the catalytically active surface.[33,34] Electronegative atoms such as O and Cl are known to be poisons for the adsorption of hydrogen.[35,36] The electrostatic interaction between electronegative fluorine and hydrogen thus promotes hydrogen desorption. In this letter, we give experimental evidence of these effects, which may have additional applications in membrane development, catalysis, and chemical energy storage.

The experimental approach is as follows: the protective film is sputter deposited on the permeate side of a Pd membrane, and its performance is measured in detail by hydrogen permeation experiments, whereas its chemistry is probed in situ by XPS, in an experimental setup based on the use of membrane specimen holders.[37] In this novel setup, the membrane permeate side is actually the specimen holder surface, and it can be saturated with hydrogen coming from the feed side without critically affecting the vacuum level required for XPS measurements (see inset of Figure 1 a). The permeation of hydrogen through the membrane is measured by Sievert's method, that is, the pressure decrease dp/dt in the volume attached to the membrane feed side is indicative of the hydrogen flux through the membrane. The hydrogen flux through a 10 nm thick PTFE coated 100 μm thick Pd membrane is plotted as a function of the applied feed pressure (p_{feed}) in Figure 1 a. The PTFE coating on the permeate side is then removed by Ar sputtering, and the procedure is repeated. Although additional steric hindrance (the PTFE layer) is removed and the permeate side surface is cleaned by the sputtering process, the flux through the clean Pd membrane is decreased. A similar observation is made if the permeate side is exposed to air: the PTFE-coated membrane shows better performance than the pure Pd membrane by one order of magnitude. A first hint of the mechanism is given by analysis of the pressure dependence: A fit of the data to power functions reveals an exponent n of 0.35 and 0.73 for PTFE-coated and clean Pd membranes, respectively. According to classical kinetics theory, the pressure dependence of the flux is $j \approx p^n$, in which n defines the rate-limiting step, that is, n close to 1 is indicative of a surface-controlled mechanism and n close to 0.5 is indicative of a diffusion-controlled mechanism.[37,38] The derivation of n from Figure 1 a shows that whereas permeation through the membrane with the PTFE coating is limited by diffusion, the rate-limiting step tends towards a desorption-limited case after sputtering. In a previous study, we showed that n will further increase with the time spent by the Pd membrane in ultrahigh vacuum (UHV).[37] The

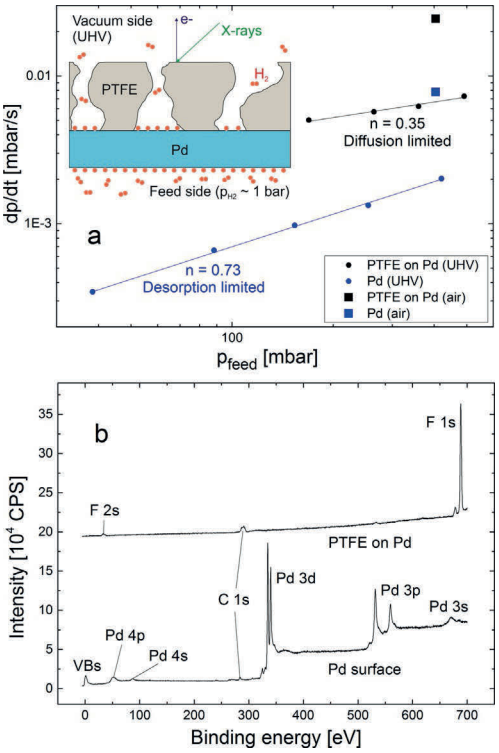

Figure 1. a) Hydrogen flux through a 10 nm thick PTFE coated 100 μm thick Pd membrane. Derivation of the power-law exponent n before and after sputtering out the protective PTFE coating. (Inset) Scheme of the membrane configuration, with in situ XPS on the permeate side. b) Overview spectra of the surface of the membrane permeate side before and after sputtering out the protective PTFE coating.

Pd surface will progressively collect impurities, which will slow down the desorption process, even in a vacuum environment. The surface properties of the vacuum side of the membrane are thus detrimental to the functioning of a membrane, and our setup allows one to access these properties by in situ XPS.

Figure 1 b shows the overview XPS spectra of the membrane surface on the permeate side, both before and after removal of the PTFE coating by sputtering. Direct current (DC) sputtering was performed with Ar plasma at a pressure of 3.10^{-6} mbar. Within the binding energy range shown in Figure 1 b and with an electron collection angle of 90°, as indicated by Figure 1 a, XPS typically probes a depth of a few nanometers, that is, a few tens of atomic layers.[39] This is the reason why the spectrum before sputtering only contains the F and C elements from the PTFE coating. Standard quantitative analysis[40] of high-resolution regions of the C 1s and F 1s peaks revealed a carbon concentration of 42 at% and a fluorine concentration of 58 at%. The carbon concentration was higher than that expected from a stoichiometric PTFE specimen (33.3%). Consequently, the PTFE sputtering process did not produce a perfectly stoichiometric composition, as previously shown by Ngene et al.[3] The fluorine peaks completely disappeared in the overview spectrum after sputtering. A small amount of carbon was still present. In fact, this irreducible carbon contamination was present in most XPS specimens and was even used as a standard calibration procedure,[40] for

which the C 1s peak was usually set to 284.5 eV. Apart from this small carbon signal, Pd was the only element left after sputtering.

Depth profiling was performed by repeatedly acquiring high-resolution XPS spectra over different regions during the sputtering process. Figure 2 shows these high-resolution regions (including regions acquired before performing the H_2 permeation study of Figure 1 a for C and F). As expected, the Pd 3d peaks shown in Figure 2 a became more and more intense as etching of the PTFE coating progressed. The Pd $3d_{3/2}$ peak appears at a binding energy of 340.6 eV, whereas the Pd $3d_{5/2}$ peak appears at a binding energy of 335.3 eV, in agreement with standard Pd foil data.[41] Moreover, the positions of these peaks were not affected by the deposition process. No Pd chemical shift was detected, in contrast with the results of Ngene et al.[3] This might be due to the fact that the Pd–Au surfaces studied by Ngene et al. are more prone to form chemical bonds with PTFE than the pure Pd surfaces studied here. Moreover, the PTFE in that case was sputtered directly onto Pd, without exposure to air. In contrast, we show here that the electronic configuration of Pd with PTFE is identical to that of a freshly sputtered Pd surface in UHV. Consequently, the interaction of hydrogen with Pd in this case is not strongly affected by the PTFE coating.

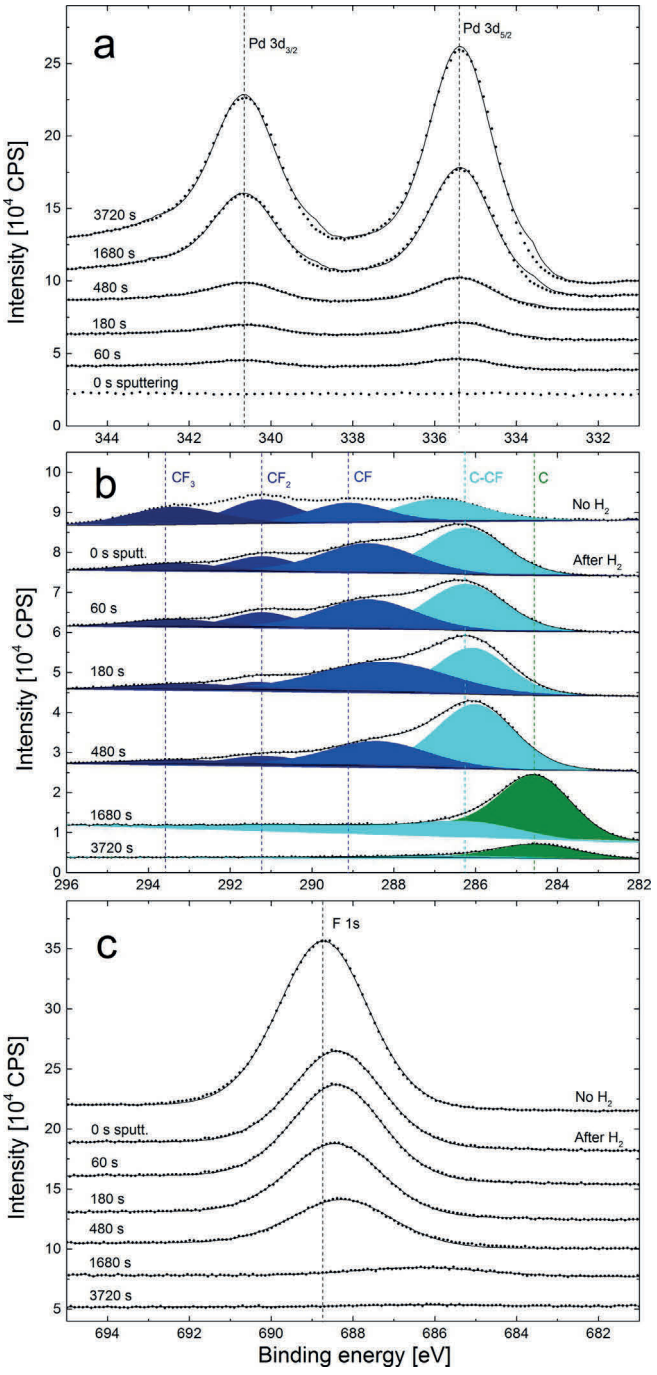

Figure 2. High-resolution XPS spectral regions acquired in situ during sputtering of the PTFE coating: a) Pd 3d, b) C 1s, and c) F 1s.

To obtain further insight into the surface chemistry, we focused on the electronic structure of the coating. The C 1s peaks shown in Figure 2 b were fitted according to models previously developed for vacuum-deposited PTFE. This particular type of synthesis is known to result in nonstoichiometric compositions.[3,42] It was then not surprising to find different CF_x bonds on the as-deposited material, indicative of nonsaturated carbon species. This initial composition changed upon the first hydrogenation, as also shown in Figure 2 b. The total carbon concentration increased further away from stoichiometry, reaching 49.5 %, and the relative proportions of the different CF_x species were altered. This indicated hydrogenation of the polymer coating—including C–F bonds and nonsaturated carbon atoms—catalyzed by Pd, a phenomenon that is well known in the field of catalysis.[43]

The sputtering process shown in Figure 2 b revealed the following behavior: the intensities of the peaks indicative of the most strongly fluorinated carbon atoms initially decreased, whereas the CF and C–CF components increased. Subsequently, once the CF_3 and CF_2 components had vanished—and did not convert into less-fluorinated components anymore—the CF and C–CF components decreased as well. In the end, only a small amount of graphitic carbon remained. The PTFE composition was not expected to exhibit such dramatic changes as a function of the coating thickness; the well-known phenomenon of preferential sputtering is more likely to occur in this case, as the fluorine atoms are much more easily removed from the surface by the argon plasma than the carbon atoms. The F 1s peak shown in Figure 2 c also reflects this behavior. It decreases gradually, whereas it exhibits a chemical shift consistent with a decrease in the fluorine concentration in the PTFE. Indeed, the peak starts at a binding energy of 688.8 eV—slightly below the value of 689.4 eV corresponding to stoichiometric PTFE[44]—and ends at approximately 686 eV, in agreement with previous data for compositions such as CHF–CH_2.[45]

A quantitative view of these observations is provided in Figure 3. Figure 3 a details the evolution of the concentrations of F, Pd, and C during sputtering. Given that the volume of Pd probed by photoelectrons linearly increases with decreasing PTFE thickness, it was not surprising to see the quasilinear evolution of the Pd concentration. The initial increase in the carbon concentration was only apparent because the fluorine atoms were preferentially sputtered; it only started to decrease

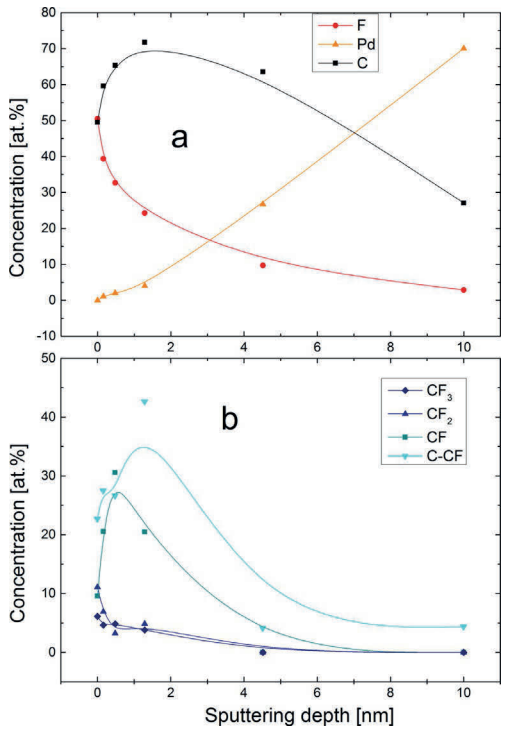

Figure 3. a) Evolution of the atomic concentrations of C, F, and Pd during sputtering of the PTFE coating. b) Evolution of the different carbon environments.

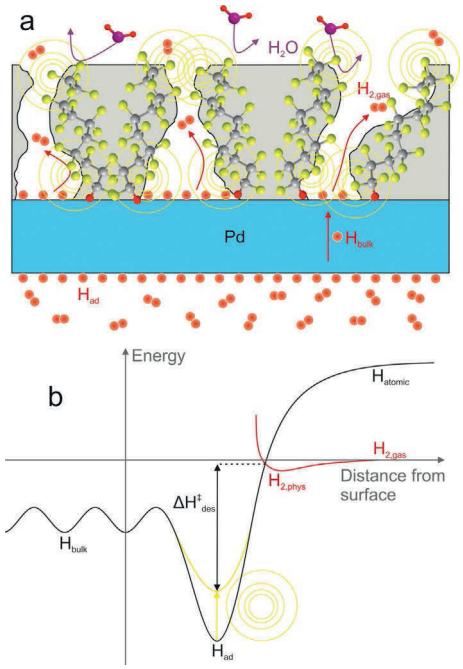

Figure 4. a) Schematic representation of the promoter effect. The hydrogenation of PTFE by replacement of one fluorine atom (yellow) by hydrogen (red). The hydrophobic properties are illustrated by circles depicting the electrostatic forces of the electronegative fluorine atoms. b) Influence of the promoter effect on energy potential surface of hydrogen on the Pd surface: the chemisorption of hydrogen on Pd is weakened, which improves hydrogen desorption but not hydrogen adsorption.

once the F concentration reached approximately 20 at%. Figure 3b confirms the trends observed above: whereas the CF_3 and CF_2 concentrations decreased right from the beginning of sputtering, the relative amounts of the less-fluorinated components initially increased, before decreasing as well. Here again, the preferential sputtering of fluorine is evident.

The clean Pd surface exhibits slower permeation kinetics than the same surface covered with PTFE, both in UHV and in air, as detailed above. From the fact that the interface between PTFE and Pd does not show any chemical bond—as shown here by in situ XPS—an alternative explanation for the promoter effect comes into play: The PTFE coating is porous,[3,46,47] that is, the surface is not fully covered by PTFE. Consequently, the Pd surface is accessible to gases, a property that is used in membrane and thin-film systems.[46,47] Still, the hydrophobic properties of PTFE prevent the formation of liquid water (see Figure 4a), which will be formed upon hydrogenation in an oxidizing environment. A liquid water film is more strongly bound to the surface than water monomers: the adsorption enthalpy of water on Pd increases from 28 kJ molecule^{-1} for low coverage to 48 kJ molecule^{-1} for full coverage, according to calculations.[48] The reason for this is illustrated by calculations of the related water/Pt system:[49] the dipole–dipole interactions between water molecules exist only for an ordered, dense water layer. Water formed by reaction with oxygen contaminations can thus leave the Pd surface through the PTFE layer and will not form a blocking layer. In contrast, the PTFE coating will not affect other potential contaminants such as CO and SO_2. Furthermore, the strong electrostatic potential generated by the fluorine atoms in the coating might have an effect on hydrogen desorption by reducing the adsorption energy of hydrogen on Pd, that is, it will facilitate desorption of hydrogen, as illustrated in Figure 4a. However, vice versa, it will not promote (or even inhibit) hydrogen adsorption if it is deposited on the feed side, in good agreement with thin-film results of Ngene et al.[3] Figure 4b shows how the electrostatic effect proposed here is expected to affect the activation enthalpy for hydrogen desorption $\Delta H^{\ddagger}_{des}$ and, therefore, also the desorption kinetics. The electrostatic field produced by the fluorine atoms in the physisorbed PTFE coating is indeed strong enough to affect the chemisorbed hydrogen, which in turn leads to a significant change in the rate constant for desorption, as the latter is affected by $\Delta H^{\ddagger}_{des}$ through Arrhenius' law.

To conclude, the present study showed that the permeation kinetics of hydrogen through a Pd membrane were significantly enhanced by the presence of a PTFE coating deposited on the permeate side. The hydrogen flux was indeed increased by one order of magnitude, both in UHV and in air. This effect was attributed to the combination of the hydrophobicity of PTFE and a promoter effect that enhanced the desorption kinetics by the electrostatic field generated by the halogen atoms present in the coating. This mechanism took place on the free surface sites left by the pores in the PTFE layer, at which hydrogen was allowed to be transported, whereas water was kept away from these active sites. The composition of the coating did not correspond to stoichiometric PTFE, as revealed by quantitative XPS elemental analysis performed in situ

during hydrogen permeation and sputtering. In our view, the (complex) control of this composition—namely, the fluorine/carbon ratio, which determines the concentration of active surface species—is an important chemical engineering aspect that, in the future, will determine the effective potential of the promoter effect described in the present study.

From an experimental point of view, such surface-driven kinetic tuning requires the design of specific approaches, involving an operating system representative of the target application (here an operating membrane system with continuous permeation monitoring) combined with an in situ surface analysis technique (here XPS). As a matter of fact, the present study was only possible subsequent to the development of a unique in situ XPS setup, the details of which can be found in Ref. [37]. The present study is one of the first steps towards unraveling the full potential of this setup. We believe that the latter can be adapted to other membrane systems, namely, those based on the permeation of gas species other than hydrogen. It will also be extended to other hydrogen-related systems, for example, catalysts, sensors, and electrodes. Finally, coming back to the topic of the present study, an emphasis was put on the performance of the peculiar interface properties of a porous polymer layer on Pd; however, the potential of interface design of polymer–metal junctions at the nanoscale may be explored in the future from a fundamental point of view, including its chemical, physical, and geometric aspects.

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[1] G. Pocock, P. Cadman, *Wear* **1976**, *37*, 129.
[2] R. R. Rye, A. J. Ricco, *J. Electrochem. Soc.* **1993**, *140*, 1763.
[3] P. Ngene, R. J. Westerwaal, S. Sachdeva, W. Haije, L. C. P. M. de Smet, B. Dam, *Angew. Chem. Int. Ed.* **2014**, *53*, 12081; *Angew. Chem.* **2014**, *126*, 12277.
[4] *Hydrogen in palladium and palladium alloys, E. Wicke, H. Brodowsky in Hydrogen in metals, Vol. 2* (Eds.: G. Alefeld, J. Voelkl), Springer Verlag, Berlin, **1978**.
[5] L. L. Jewell, B. H. Davis, *Appl. Catal. A* **2006**, *310*, 1.
[6] E. H. Van Deventer, T. A. Renner, R. H. Pelto, V. A. Maroni, *J. Nucl. Mater.* **1977**, *64*, 241.
[7] N. A. Al-Mufachi, N. V. Rees, R. Steinberger-Wilkens, *Renewable Sustainable Energy Rev.* **2015**, *47*, 540.
[8] A. C. Makrides, M. A. Wright, D. N. Jewett, *Separation of Hydrogen by Permeation*, U.S. Patent 3350846, **1967**.
[9] T. L. Ward, T. Dao, *J. Membr. Sci.* **1999**, *153*, 211.
[10] J. Völkl, H. Wipf, *Hyperfine Interact.* **1981**, *8*, 631.
[11] S. Hao, D. S. Sholl, *Energy Environ. Sci.* **2013**, *6*, 232.
[12] R. E. Buxbaum, A. B. Kinney, *Ind. Eng. Chem. Res.* **1996**, *35*, 530.
[13] D. J. Edlund, J. McCarthy, *J. Membr. Sci.* **1995**, *107*, 147.
[14] A. L. Mejdell, D. Chen, T. A. Peters, R. Bredesen, H. J. Venvik, *J. Membr. Sci.* **2010**, *350*, 371.
[15] L. S. McLeod, F. L. Degertekin, A. G. Fedorov, *J. Membr. Sci.* **2009**, *341*, 225.
[16] K. Hou, R. Hughes, *J. Membr. Sci.* **2002**, *206*, 119.
[17] K. Deshpande, J. H. Meldon, M. A. Schmidt, K. F. Jensen, *J. Microelectromech. Syst.* **2010**, *19*, 402.
[18] M. L. Bosko, D. Yepes, S. Irusta, P. Eloy, P. Ruiz, E. A. Lombardo, L. M. Cornaglia, *J. Membr. Sci.* **2007**, *306*, 56.
[19] J. Okazaki, D. A. Pacheco Tanaka, M. A. Llosa Tanco, Y. Wakui, F. Mizukami, T. M. Suzuki, *J. Membr. Sci.* **2006**, *282*, 370.
[20] Y. Zhang, J. Lu, R. Maeda, C. Nishimura, *Mater. Trans.* **2008**, *49*, 754.
[21] J. Okazaki, K. Ikeda, D. A. Pacheco Tanaka, M. A. Llosa Tanco, Y. Wakui, K. Sato, F. Mizukami, T. M. Suzuki, *Phys. Chem. Chem. Phys.* **2009**, *11*, 8632.
[22] S. I. Jeon, J. H. Park, *Int. J. Hydrogen Energy* **2013**, *38*, 6085.
[23] R. J. Westerwaal, E. A. Bouman, W. G. Haije, H. Schreuders, S. Dutta, M. Y. Wu, C. Boelsma, P. Ngene, S. Basak, B. Dam, *Int. J. Hydrogen Energy* **2015**, *40*, 3932.
[24] J. Y. Yang, M. Komaki, C. Nishimura, *Int. J. Hydrogen Energy* **2007**, *32*, 1820.
[25] A. Kulprathipanja, G. O. Alptekin, J. L. Falconer, J. D. Way, *J. Membr. Sci.* **2005**, *254*, 49.
[26] Y. She, S. C. Emerson, N. J. Magdefrau, S. M. Opalka, C. Thibaud-Erkey, T. H. Vanderspurt, *J. Membr. Sci.* **2014**, *452*, 203.
[27] P. Kamakoti, B. D. Morreale, M. V. Ciocco, B. H. Howard, R. P. Killmeyer, A. V. Cugini, D. S. Sholl, *Science* **2005**, *307*, 569.
[28] H. Abir, M. Sheintuch, *J. Membr. Sci.* **2014**, *466*, 58.
[29] K. Sato, M. Nishioka, H. Higashi, T. Inoue, Y. Hasegawa, Y. Wakui, T. M. Suzuki, S. Hamakawa, *J. Membr. Sci.* **2012**, *85*, 415.
[30] J. Galuszka, D. Liu, *Stud. Surf. Sci. Catal.* **2001**, *136*, 363.
[31] P. V. Mercea, D. Silipaş, V. Mecea, *Gas Sep. Purif.* **1990**, *4*, 137.
[32] G. Straczewski, J. Völler-Blumenroth, H. Beyer, P. Pfeifer, M. Steffen, I. Felden, A. Heinzel, M. Wessling, R. Dittmeyer, *Chem. Eng. Process.* **2014**, *81*, 13.
[33] M. K. Singh, R. Singh, A. Singh, D. K. Kohl, U. Deshpande, P. K. Gupta, *Bull. Mater. Sci.* **2014**, *37*, 1485.
[34] W. H. Stevens, *Process and catalyst for enriching a fluid with hydrogen isotopes*, Canadian Patent 907292, **1972**.
[35] B. Hammer, J. K. Nørskov, *Adv. Catal.* **2000**, *45*, 71.
[36] J. K. Nørskov, S. Holloway, N. D. Lang, *Surf. Sci.* **1984**, *137*, 65.
[37] R. Delmelle, B. Probst, R. Alberto, A. Züttel, D. Bleiner, A. Borgschulte, *Rev. Sci. Instrum.* **2015**, *86*, 053104.
[38] A. Borgschulte, R. Gremaud, R. Griessen, *Phys. Rev. B* **2008**, *78*, 094106.
[39] M. P. Seah, W. A. Dench, *Surf. Interface Anal.* **1979**, *1*, 2.
[40] N. Fairley, A. Carrick, *The Casa Cookbook—Part 1: Recipes for XPS Data Processing*, Acolyte Science, Knutsford, **2005**.
[41] M. C. Militello, S. J. Simko, *Surf. Sci. Spectra* **1994**, *3*, 387.
[42] T. Nobuta, T. Ogawa, *J. Mater. Sci.* **2009**, *44*, 1800.
[43] L. Li, H. Zhao, R. Wang, *ACS Catal.* **2015**, *5*, 948.
[44] C. Sleigh, A. P. Pijpers, A. Jaspers, B. Coussens, R. J. Meier, *J. Electron Spectrosc. Relat. Phenom.* **1996**, *77*, 41.
[45] G. Beamson, D. Briggs, *High resolution XPS of organic polymers: the scienta ESCA300 database*, Wiley, Chichester, **1992**.
[46] M. Mitsushio, A. Nagaura, T. Yoshidome, M. Higo, *Prog. Org. Coat.* **2015**, *79*, 62.
[47] C. Furuya, S. Motoo, Y. Shirakawa, *Water repellent microporous catalyst for gas-gas reaction and gas-gas reaction method*, Japanese Patent 6230554, **1987**.
[48] A. Roudgar, A. Groß, *Surf. Sci.* **2005**, *597*, 42.
[49] S. Meng, L. F. Xu, E. G. Wang, S. Gao, *Phys. Rev. Lett.* **2002**, *89*, 176104.

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