

Investigation of NO Reduction by H₂ on Pd Monolith with Transient and Isotopic Exchange Techniques

I. H₂/D₂ Exchange with H₂O and NH₃

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Isotope exchange of hydrogen atoms in water, ammonia, and hydrogen with deuterium, as well as adsorption of ammonia and water on an alumina-supported Pd monolith, were studied with transient step-response experiments. The investigation provided new insights into reaction mechanisms. Deuterium underwent an exchange reaction with hydrogen in ammonia and water. The step-response experiments yielded information about the surface reaction mechanisms, indicating adsorption-assisted desorption of hydrogen, decomposition of ammonia, and stepwise formation of deuterated water and ammonia. Detailed reaction pathways explaining isotope exchange of the hydrogen atoms in water, ammonia, and hydrogen with deuterium were proposed. The work forms the basis for the understanding of reaction mechanisms between nitrogen oxide and hydrogen, where ammonia is formed on Pd as a by-product.

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Key Words: nitrogen oxides; hydrogen; deuterium; ammonia; reduction; palladium; monolith; transient kinetics; isotopic exchange.

1. INTRODUCTION

Exhaust gases of automobiles contain several pollutants, such as hydrocarbons and carbon monoxide (CO), nitrogen oxides (NO, NO₂, and N₂O), sulphur oxides (SO₂ or SO₃), and greenhouse gases (CO₂ and CH₄). Because of the need to reduce these agents, it is indispensable to understand how they are formed and to know the reaction paths, along which the desired conversions occur. The catalytic conversion of nitric oxide (NO), one of the noxious components of exhaust gases, has provided one of the most important scientific challenges during the past decade. Hydrogen, which is present in the exhaust gas of automobiles, can be used as a reducing agent (1). Nitrogen, nitrous oxide, ammonia, and water have been detected as reaction products in the

reduction of nitrogen oxide by hydrogen on the modified alumina-based Pd monolith (2).

The use of transient techniques to obtain mechanistic and kinetic information about catalytic reactions has become increasingly popular in the last few decades, since experiments performed under transient conditions provide information which is impossible to obtain under steady-state conditions. Isotope-labelled components are frequently employed to follow reaction pathways and to determine reaction mechanisms. The basic ideas of the transient method applied to heterogeneous catalysis were set forth by Tamaru and Naito (3). The transient methods can be classified into two main groups. The first one is when, due to the perturbation, the system has been transformed into another thermodynamic state. For example the classical TPD and concentration jump methods belong to this group. The second group is when the system remains in the same thermodynamic state during the transient experiment. This means different kinds of labelling techniques. Steady-state isotopic transient kinetic analysis (SSITKA) involves a replacement of a reactant by its isotopically labelled counterpart, typically in the form of a step or pulse input function (4). Producing an input function with isotope-labelled reactants permits the monitoring of isotopic transient responses, while maintaining the total concentration of labelled plus nonlabelled reactants, adsorbates, and products at steady-state conditions. Tracing the hydrogen pathway by D₂ contributes to the fundamental understanding of the role of hydrogen in the reduction of NO over alumina-based palladium monolith (5). In the present study, the isotope exchange of hydrogen atoms in water, ammonia, and hydrogen with deuterium and adsorption of ammonia and water on a Pd monolith were studied with step-response experiments in order to obtain deeper understanding about the exchange reactions between deuterium and water as well as deuterium and ammonia.

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2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation and Characterisation

The catalyst supplied by Kemira Metalkat Oy was a promoted alumina-supported Pd monolith prepared by folding a corrugated metal foil together with a flat foil. Besides aluminium oxide, the washcoat of the support contained lanthanum oxide, zirconium oxide, as well as a very small amount of cerium oxide, i.e., promoters whose main function is to provide oxygen under fuel-rich conditions. The active metal, palladium, was attached by means of impregnation in an aqueous solution, using $\text{Pd}(\text{NO}_3)_2$ as a precursor. The support material content of the catalyst was 41 g/m^2 . The metal amount of Pd in the washcoat was 1.06 wt%. A macroscopic picture and a SEM (scanning electron microscopy) image of Pd on alumina are shown in Fig. 1.

BET (Brunauer–Emmett–Teller) analysis, carbon monoxide chemisorption, and X-ray photoelectron spectroscopy (XPS) were used as characterisation techniques. The specific surface area and pore volume were obtained from nitrogen adsorption–desorption isotherms. The total surface area (BET) was obtained by using the sorptometer

(Carlo Erba Sorptomatic 1900). For the determination of the precious metal dispersion, CO chemisorption measurements were carried out using the sorptometer (Carlo Erba Sorptomatic 1900).

A Perkin–Elmer PHI 5400 ESCA (XPS) spectrometer with a Mg K_α X-ray source was used with a 35-eV pass energy to analyse fresh, oxidised, and reduced 1 wt% Pd/Ce–Zr–La–alumina. The oxidation was carried out under flowing oxygen in a temperature-programmed experiment, where the temperature was increased from room temperature to 350°C at a rate of $10^\circ\text{C}/\text{min}$. The treatment was continued for 30 min at 350°C , after which the sample was cooled to room temperature under oxygen flow. The reduction was carried out in an analogous way, but under flowing hydrogen. The reduced sample was transferred under nitrogen atmosphere to the ultrahigh vacuum (UHV) system. The electric charging of the sample under X-ray bombardment resulted in a 4.5-eV shift in the spectra, which remained stable during the measurement. The pressure in the UHV chamber was 1×10^{-8} Torr during the measurement. A carbon impurity peak at 284.7 eV was used as the binding-energy (BE) reference. XP line background due to inelastically scattered electrons was removed using Shirley's method (6). The removal was carried out using a homemade Origin LabTalk script, and the peak-fitting procedure was carried out with Microcal Origin 6.1 Peak Fitting Module software. Both peaks of doublets, due to spin–orbit interaction, were included in the fitting. The intensity ratios were kept fixed at 1:2 and 2:3 for p and d shells, respectively. Zirconia satellite lines were observed at ca. a 13.8-eV higher BE than were the Zr $3p_{1/2}$ and $3p_{3/2}$ lines, with ca. 20% of the intensity of the corresponding main line. Zr $3p_{1/2}$ and $3p_{3/2}$ energy separation was kept fixed at 13.5 eV, as was observed in our reference ZrO_2 powder (Fluka zirconium(IV) oxide, CAS 1314-23-4); otherwise, values for Zr 3d, Pd 3d and La 3d energy separations were kept fixed at 2.4, 5.3, and 16.8 eV, respectively (7). The Voigt function, a mixture of the Gaussian and Lorentzian lines, was used in the peak-fitting procedure. The precision of the analysed binding energies was ca. ± 0.15 eV. Impurities other than carbon were not detected. Sensitivity factors used in the quantitative analysis for Al 2p, La 3d, Pd 3d, and Zr 3d were 0.234, 9.122, 5.356, and 2.576, respectively (7).

2.2. Equipment for Transient Studies

The apparatus for the step-response experiments consisted of four parts, namely, the reactor coupled to the heating, feeding, and analysing devices. Two different setups were used in the experimental section: a general setup used for gas-phase reactants such as H_2 , D_2 , NH_3 , and NO , and another one for the experiments involving H_2O . The difference was in the feeding procedure, due to the need to have water in the form of steam by using a liquid water pump.

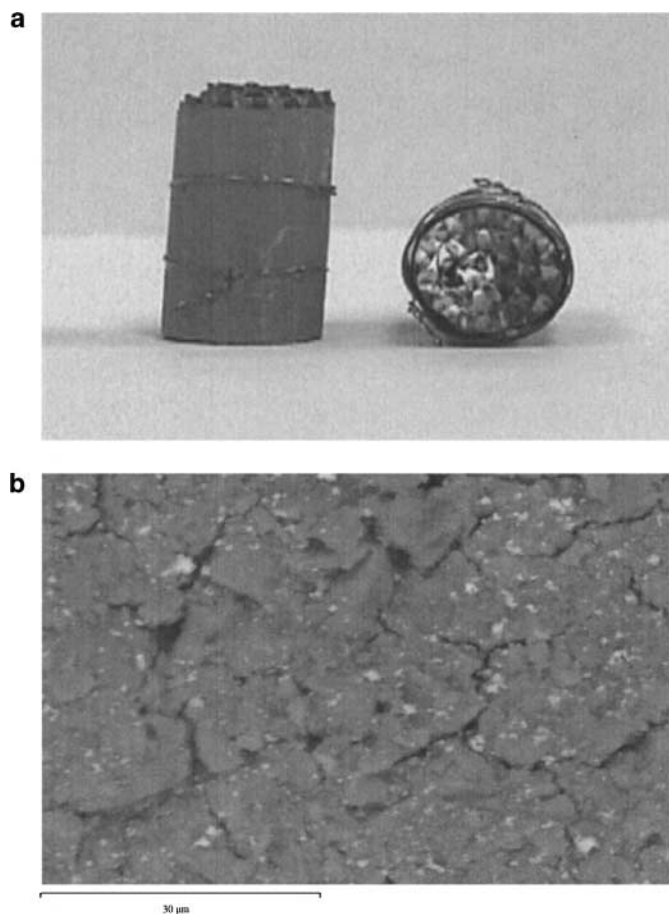


FIG. 1. A macroscopic picture and SEM image of Pd on alumina.

The reactor consisted of a cylindrical glass tube in which the monolith catalyst was tightly placed in such a way that the reactants stream went completely through the cavities of the support. The cylindrical-shaped monolith catalyst had a length of 1.5 cm and a diameter of approximately 0.9 cm. The weight of the Pd catalyst deposited on the monolith sample was 0.164 g and the weight of the support material in the absence of Pd was 0.166 g, respectively. The temperature of the system was controlled by a high-temperature heating oven (Carbolite) provided with a thermocouple (Pico TC-08). Above the catalyst, another thermoelement was placed in order to monitor the temperature of the catalyst. A personal computer, in which the Pico TC-08 software was installed, was used to control and record the temperatures of the oven and the catalyst during each experiment.

The flows of the gas reactants were regulated by mass-flow controllers (Brooks 5850S) with electronic panels to fix the percentage of the flow desired. Argon and nitrogen were used as carrier gases, which were kept on from the start-up until the end of the experiments. The reactants were premixed in the lines before entering the reactor. A four-way valve was used for deuterium and hydrogen in order to have more precise isotopic steps between these reactants. From the reactor outlet, a small amount of the gas mixture was withdrawn to a mass spectrometer (Balzers Omnistar) through a capillary tube. The mass numbers of interest were monitored as a function of time using a Balzers Quadstar 422 software connected to the mass spectrometer. The setup for experiments, including water, was virtually the same, but a feeding device for water was included. Water was introduced into the system by a Microdialysis pump CMA/02. Ar and N₂ were used as carrier gases of the water stream, connecting different channels and lines from the principal reactant line, where the gas mixture was fed into the reactor. The water and the outlet lines were covered by a heating cord to keep them hot to avoid condensation.

2.3. Experimental Procedure

The experiments were carried out under atmospheric pressure at $155 \pm 3^\circ\text{C}$. The fresh catalyst sample was always pretreated with a (1% NO + 1% H₂)/Ar mixture in a temperature-programmed experiment, where the temperature was increased from room temperature to 400°C at a rate of $10^\circ\text{C}/\text{min}$. The treatment was continued for 60 min at 400°C , after which the sample was cooled to room temperature under argon flow. The samples were reduced in a flow of 1% H₂/Ar at 350°C for 15 min, after which the sample was maintained under Ar flow for 30 min and cooled to the desired experimental temperature. After the hydrogen pretreatment, the reaction mixture was switched on. The total gas flow was $400 \text{ cm}^3 \text{ min}^{-1}$ at 25°C . The time $t = 100 \text{ s}$ corresponds the moment when the valve was switched from one feed to another. The sample was held at the reaction

temperature until steady-state reaction conditions were attained.

The dynamics of water and ammonia adsorption-desorption on the Pd/alumina catalyst were studied by introducing 1% H₂O in Ar and 1% NH₃ in Ar, respectively, into the reactor. The isotopic exchange between hydrogen and deuterium was studied using isotopic changes between 1% H₂ in Ar and 1% D₂ in Ar. Isotope exchange of hydrogen atoms in water and ammonia as well as hydrogen with deuterium were studied with different concentrations of reactants and pretreatment with each of the reactants. Blank experiments with an empty reactor were performed in order to verify the transient results of the behaviour of water and ammonia on the palladium catalyst. Calibration for all components except HDO, D₂O, and HD was carried out with gas mixtures containing known concentrations. Because the different isotopes of an element behave in almost the same way, the calibration factor of H₂O was used for HDO and D₂O, just as the average of H₂ and D₂ calibration factors was used for HD in Fig. 5.

A correction for the contribution of the mass fragments was carried out. In the case of isotopic tracer experiments, some of the isotopomers had the same mass number. Isotopomers also presented their own fragmentation patterns, which overlapped. In order to obtain the ion-intensity responses of pure molecules, corrections had to be made for the fragmentation values that contribute to the m/z signals. The reactants, NH₃ and H₂O, were passed separately over an empty reactor to determine their fragmentation patterns. With this pattern, along with the hypothesis that the degree of fragmentation of the isotopomers is identical, the disappearance of H₂O and NH₃ as well as the formation of their isotopomers can be identified.

3. RESULTS AND DISCUSSION

3.1. Characterisation of the Pd Monolith

The BET surface area of the Pd catalyst determined by nitrogen adsorption was $112 \text{ m}^2/\text{g}$. The pore volume of the catalyst was $0.33 \text{ cm}^3/\text{g}$ and the mean pore diameter was 12 nm. The palladium particle size determined by CO chemisorption was about 3.2 nm.

According to the XPS measurements, the surface atomic concentration Pd : Zr : La : Al was 0.095 : 0.11 : 0.18 : 1 prior to the treatment, 0.11 : 0.12 : 0.22 : 1 after oxidation, and 0.057 : 0.078 : 0.091 : 1 after reduction. The amount of cerium was too small to be reliably detected in the analysis. After the reduction at 350°C , the atomic surface concentrations of Pd, Zr, and La were smaller than the values prior to the treatment, which is probably due to an increase in the particle size. After oxidation, these concentrations were higher than initially, which could be due to redispersion.

The observed binding energies (BE) from the deconvolution of the XP lines are given in Table 1. The binding

TABLE 1
Observed XPS Binding Energies

Element	BE (eV)		
	Reduced	Not treated	Oxidised
O 1s	531.8	531.4	531.3
Al 2p	74.2	74.4	74.2
Pd 3d _{5/2}	334.9	336.3	336.7
Zr 3p _{3/2}	332.5	332.7	332.8
Zr 3d _{5/2}	181.8	181.9	182.0
La 3d _{5/2}	835.7, 839.4	835.8, 839.2	835.9, 839.4

energy observed for zirconium 3d_{5/2} (181.9 eV) shows that Zr is in the form of ZrO₂, and it changes very little during the treatments.

Before pretreatment, palladium was in the form of PdO (336.3 eV), but dispersed Pd⁰ (334.9 eV) was detected after reduction, which is in good agreement with the results reported in the literature (8). After oxidation, palladium remained in PdO with 336.7 eV binding energies as shown in Fig. 2. Otto *et al.* reported 336.7 eV for PdO and 338.3 eV for PdO₂ (8). In oxidation, Ce is known to promote the oxidation of palladium to PdO (9). It should also be noted that palladium particles tend to be bigger in the catalysts containing zirconia and lanthana modifiers compared to unmodified catalysts (10).

Schmal *et al.* (11) explained that the Pd particles are deposited over alumina, ceria, and ceria–alumina interface during the preparation. They reported that the strong interaction between Pd and Ce shifts the PdO reduction temperature under flowing hydrogen to temperatures below

200°C. In our catalyst, the ceria–alumina interface was replaced by a ceria–zirconia interface, due to the preparation method. In the present studies of untreated and oxidised catalysts, PdO did not reduce to Pd⁰ under the UHV conditions. This can be explained by the fairly small cerium concentration (ca. 1 wt%).

Lanthanum binding energies at 835.8 eV ± 0.1 eV remained almost unchanged during the treatments. They were significantly higher than the values reported for La₂O₃ in the literature (833.2 eV) (12), but close to La/Al₂O₃ values (835.0 eV) (12, 13) in the dispersed phase. Haack *et al.* (12) suggested that La is in a dispersed phase with deficiently coordinated La³⁺ ions at low concentrations (La/Al XPS ratio 0.05–0.15 fairly close to our catalyst); at higher concentrations La₂O₃ or LaAlO₃ is generally formed. However, they were able to see the presence of crystalline LaAlO₃ in XRD at these loadings, which was in agreement with the work of Bettman *et al.* (14). Ledford *et al.* (15), on the other hand, observed a slightly higher BE, 836.1 eV, with the Al 2p line at 74.5 eV, as a reference in their La-modified aluminas. This would correspond to ca. 835.9 eV in our BE calibration (Al 2p line at 74.3 eV), which is very close to our results (835.8 ± 0.1 eV). According to Ledford *et al.*, XRD patterns of the La-modified aluminas showed only lines characteristic of the alumina. Presumably, lanthanum in their and our catalysts was present in amorphous particles; hence the higher BE values were observed. In the present catalysts, we did not detect any shoulder at 73.2 eV (in the Al 2p line), which according to Haack *et al.* (12) would be due to LaAlO₃. This is due to the low concentration of surface lanthana, also in agreement with their studies. According to Miki *et al.* (16) and Taló *et al.* (13), lanthana is known to increase the oxygen storage capacity of ceria in the presence of noble metals by creating oxygen vacancies.

3.2. Adsorption–Desorption Dynamics on the Pd Monolith

The NH₃ adsorption capacity of the supported Pd catalyst and the support material in the absence of Pd was investigated with step-response experiments. The consumed amount of NH₃ was 0.845 mmol/g washcoat (79.76 mmol NH₃/g Pd) on the supported Pd catalyst. The adsorbed amount of ammonia compared to the Pd content of the catalyst (8.49 mmol NH₃/mmol Pd) is so high that the most of the inserted ammonia is adsorbed on the support material. This is confirmed also by the NH₃ adsorption experiment on the support material. Figure 3 presents a step-response experiment from Ar to 1% NH₃/1% He/Ar on the support. The consumed amount of NH₃ was 0.684 mmol/g washcoat. The amount of NH₃ remaining on the surface of the Pd catalyst was 0.0787 mmol and on the bare support material it was 0.0646 mmol.

According to Frankenburg (17, and references therein), ammonia decomposes to nitrogen and hydrogen on

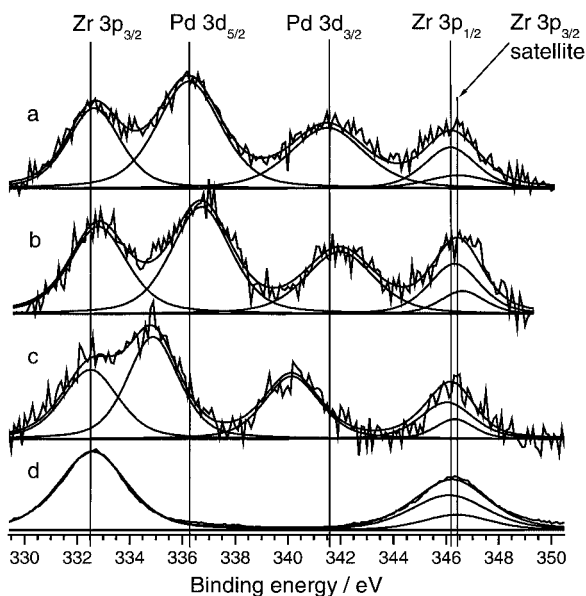


FIG. 2. XPS lines of Pd 3d and Zr 3p: (a) untreated; (b) oxidised; (c) reduced; (d) ZrO₂ reference.

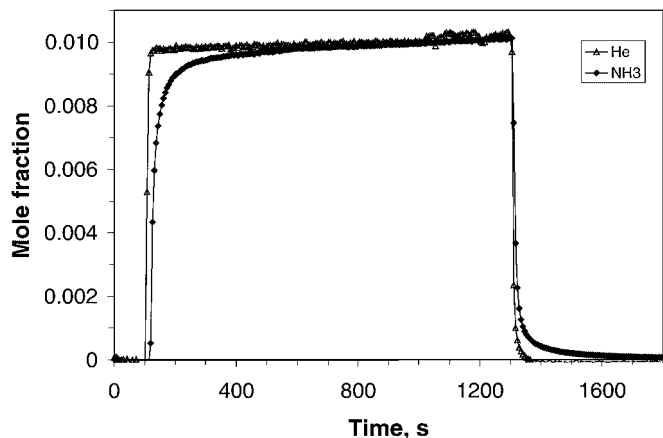


FIG. 3. Ar \rightarrow 1% NH₃/1% He/Ar \rightarrow Ar step responses on the support material at 155°C.

catalytically active metals at relatively low temperatures. Many kinds of experiments with ammonia were carried out at the beginning of the last century. In 1927 Dew and Taylor investigated the adsorption of ammonia on different metals and Frankenburg and Hodler made experimental observations in their work dealing with isotherms of ammonia on tungsten (17). On tungsten, the adsorbed ammonia started to decompose at 90°C with the evolution of hydrogen, while nitrogen remained in the adsorbed phase under these conditions. However, no formation of hydrogen was detected in the present study. Papapolymerou and Bontozoglou (18) reported that on Pd the NH₃ decomposition is very slow below 727°C.

The adsorption-desorption dynamics of water on the Pd/alumina catalyst is presented in Fig. 4. In the beginning of the experiment, water had a very slow response, which continuously increased until it attained the steady state. The consumed amount of H₂O was 1.25 mmol/g washcoat (117.58 mmol H₂O/g Pd) on the supported Pd catalyst.

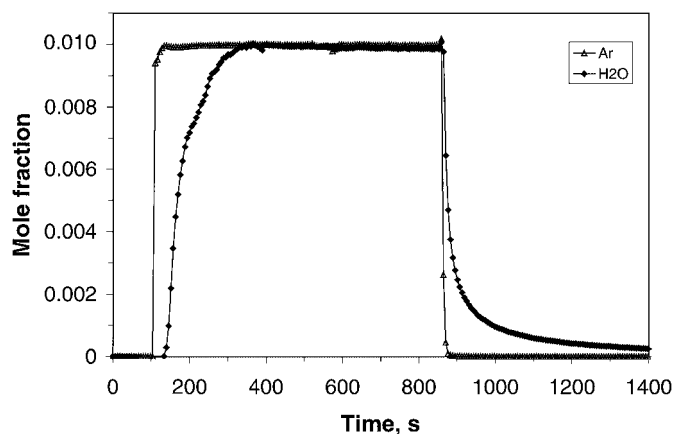


FIG. 4. N₂ \rightarrow 1% H₂O/1% Ar/N₂ \rightarrow N₂ step responses on the Pd monolith at 155°C.

The adsorbed amount of water compared to the Pd content of the catalyst (12.51 mmol H₂O/mmol Pd) is so high that the most of the inserted water is adsorbed on the support material. This is confirmed also by the H₂O adsorption experiment on the support material. The consumed amount of H₂O was 0.995 mmol/g washcoat. The amount of H₂O remaining on the surface of the Pd catalyst was 0.0582 mmol and on the support material it was 0.0371 mmol.

It can be assumed that water adsorbed on the catalyst surface and dissociated on the active sites. However, H* atoms and OH* groups blocked the active sites until the sites were occupied, without forming gas-phase hydrogen or any other species. It is possible to consider the idea of recombination of adsorbed hydrogen and adsorbed hydroxyl groups to form water, which then desorbs from the catalyst.

The experiments demonstrated that large amounts of NH₃ and H₂O were adsorbed on the support material. This is in good agreement with the literature data. For example, adsorption of ammonia has been used for long time to study the acidity of aluminas (19) and dry γ -Al₂O₃ is well-known to chemisorb water (20). According to Peri (20) water chemisorption on Al₂O₃ leads to the formation of surface hydroxyl groups.

3.3. H₂/D₂ Isotopic Exchange on the Pd Monolith

It is well-known that hydrogen eagerly adsorbs and dissociates on Pd (21). Therefore, H₂/D₂ experiments were carried out here. The dynamics of the isotopic exchange between hydrogen and deuterium is displayed in Fig. 5. A similar experiment was performed also on the support material in the absence of Pd. The steady-state values reached by these two compounds were slightly different on the Pd catalyst but were similar on the support. The mole fraction value of deuterium was lower at steady state than the value of hydrogen, which implies that consumption of D₂ was bigger than that of H₂. Even if there exists some uncertainty in converting the ion currents of HD, HDO, and D₂O to molar fractions, as described above, this can be considered to be negligible because the molar fraction values of HD, HDO, and D₂O are really small compared to values of H₂ and D₂.

The isotopic exchange from hydrogen to deuterium is displayed in Fig. 5a. Formation of HD was detected once deuterium was introduced into the reactor and hydrogen went to the bypass. At this point, the HD formation commenced to increase quickly, attaining a maximum, followed by a decrease in a short period of time. As indicated here, some of the chemisorbed H* atoms react with surface hydroxyls forming water and the rest recombine to H₂* or spill over the support. Once deuterium molecules reach the catalyst, they undergo an isotopic exchange with adsorbed hydrogen atoms. The opposite process, the D₂/H₂ exchange reaction, is illustrated in Fig. 5b, where the deuterium flow is switched off to allow hydrogen to enter the reactor. The HD responses were similar, having the same maximum value.

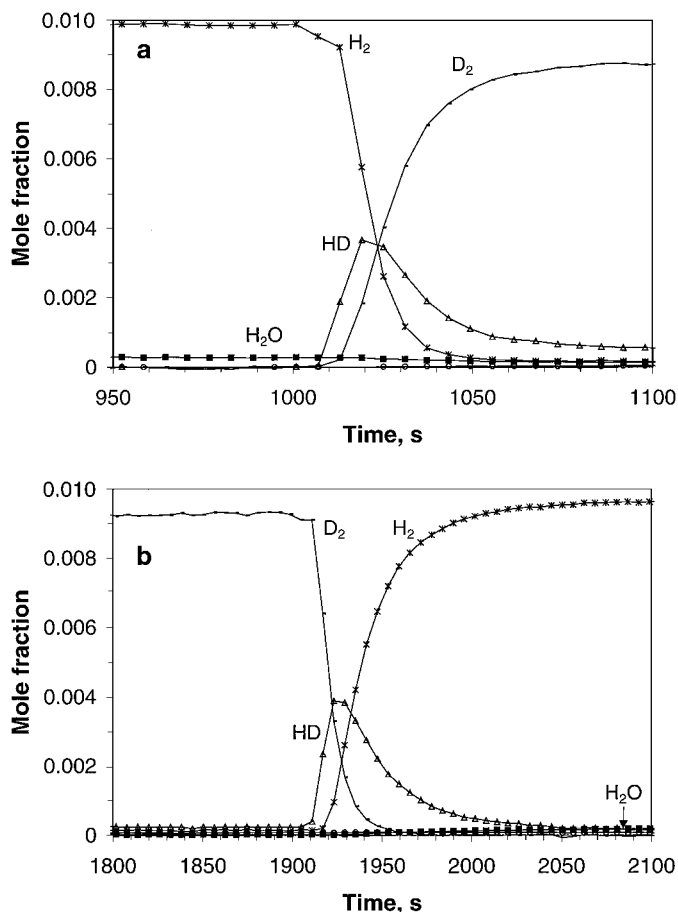


FIG. 5. (1% H₂)/Ar → (1% D₂)/Ar → (1% H₂)/Ar isotopic exchange experiment on the Pd monolith at 155°C: (a) (1% H₂)/Ar → (1% D₂)/Ar step; (b) (1% D₂)/Ar → (1% H₂)/Ar step.

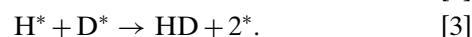
The production of water was noticed in the first and the third stage of the experiment both on the Pd catalyst and on the modified alumina support, as hydrogen entered the reactor. This formation can be attributed to the reaction of chemisorbed hydrogen atoms with OH groups present in the alumina support (22). Water formation indicates that Al₂O₃ is only partially dehydrated. Caldararu *et al.* (23) had similar findings on γ -Al₂O₃. The amount of formed HDO was less than half the amount of water. The amount of D₂O was on the detection limit during the second stage of the experiment (Fig. 5). Based on this observation it can be assumed that there was more adsorption and less dissociation with D₂ than with H₂, which implies that there was less D* to form deuterated water. This result is supported by the fact that deuterium kinetic effects are normally associated with a decrease in rate for D-labelled compounds (24). According to Okuyama *et al.* (25) absorption and diffusion of H and D in Pd exhibits an inverse kinetic effect and dissociation of H₂ and D₂ exhibits a normal isotope effect. These variations observed in the product and reactant responses under stable steady-state conditions might be due

to the isotopic perturbations indicating the isotope effect. It is known that the substitution of the isotope can affect the reaction rate as well as the reaction equilibrium, because of the mass differences between hydrogen and deuterium (4).

Due to the HD formation both on the Pd catalyst and on the support material without Pd it can be concluded that H₂ and D₂ dissociates and that the reactions $H^* + D^* \rightleftharpoons HD^* + *$ and/or $H^* + D_2 \rightleftharpoons HD^* + D^*$ happen also on the support material. Apparent zero-order rate constants for HD in the beginning of the changes are calculated. k_{HD} was $5.194 \times 10^{-5} 1/(s \cdot g)$ on the Pd catalyst and $4.888 \times 10^{-5} 1/(s \cdot g)$ on the support. The amount of Pd in the washcoat was 1.06 wt%. The small amount of Pd in the washcoat was probably the reason for quite similar k_{HD} values. It is known that transition aluminas can catalyze the H₂-D₂ equilibration (26, 27). This implied that H₂ and D₂ dissociates also on the support material. A small amount of H₂O was formed also on the modified alumina support. This indicated that the OH group on the support combines with hydrogen to form a water molecule.

Bonhoeffer and Farkas in 1931 (see 28, and references therein) stated that the mechanism of the exchange reaction involves dissociation (i.e., chemisorption) of hydrogen at the metal surface. According to this mechanism, chemisorbed atoms link up randomly in pairs and evaporate as molecules. An alternative mechanism was proposed by Rideal in 1939, who stated that interaction takes place between chemisorbed atoms and physisorbed molecules, according to an exchange reaction between H* and D₂ to form HD and D* (28).

Eley assumed a rapid exchange of deuterium with chemisorbed hydrogen and concluded that the Rideal mechanism was correct (28). Therefore it might be speculated that at the beginning of the experiment, when the surface of the catalyst was covered by H*, the exchange reaction was enhanced due to the lack of free active sites on which deuterium could dissociate. This assumption supports the Rideal mechanism with immediate reaction between H* and D₂ giving HD* and D*. In this case, the time delay in the D₂ response is due to fact that D* should diffuse to each other to form D₂* before it can desorb. Once more vacant sites were accessible, the formation of D* was started, enabling a reaction with H* according to the following reactions (29):



When more vacant sites are available for dissociation, both the Rideal and the Bonhoeffer and Farkas mechanisms can be valid.

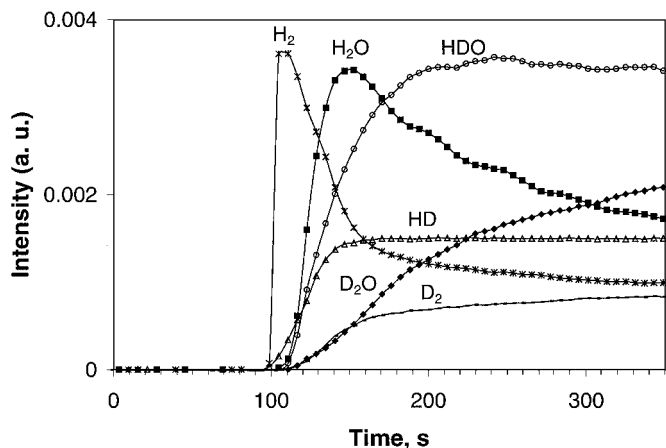


FIG. 6. $N_2 \rightarrow (1\% H_2O + 1\% D_2)/N_2$ step responses on the Pd monolith at 155°C.

3.4. H₂/D₂ Isotopic Exchange in H₂O on the Pd Monolith

The aim of the H₂/D₂ isotopic exchange in H₂O experiments was to determine the catalytic activity for the hydrogen isotope exchange in the reaction between water vapour and deuterium and to clarify the reaction mechanism. The rate of the hydrogen isotope exchange between H₂O and D₂ on a Pd catalyst at 155°C was determined by the analysis of D₂, H₂, HD, H₂O, HDO, and D₂O. Argon fragments to $m/z = 20$, which overlaps with the mass number of D₂O. Therefore, some of the experiments were performed with nitrogen as the carrier gas to confirm the interpretation of the data.

Responses of water and deuterium reactions with different concentrations are shown in Figs. 6–8. Figures 9 and 10 show the reaction of deuterium and hydrogen after pretreatments with water and deuterium. The products from the isotope exchange of hydrogen in water with D₂ were HDO, D₂O, and HD. The responses did not differ significantly,

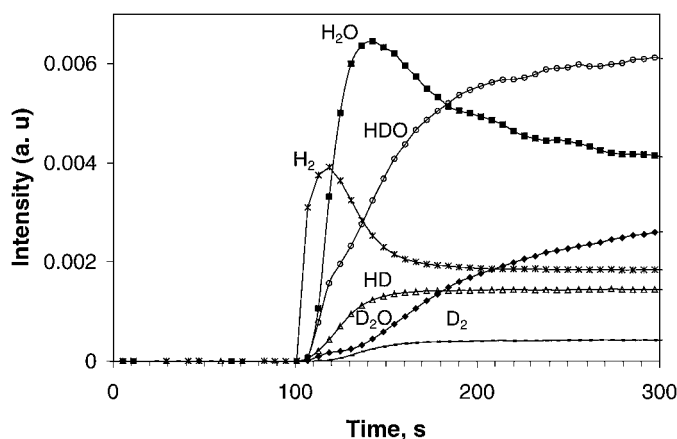


FIG. 7. $N_2 \rightarrow (2\% H_2O + 1\% D_2)/N_2$ step responses on the Pd monolith at 155°C.

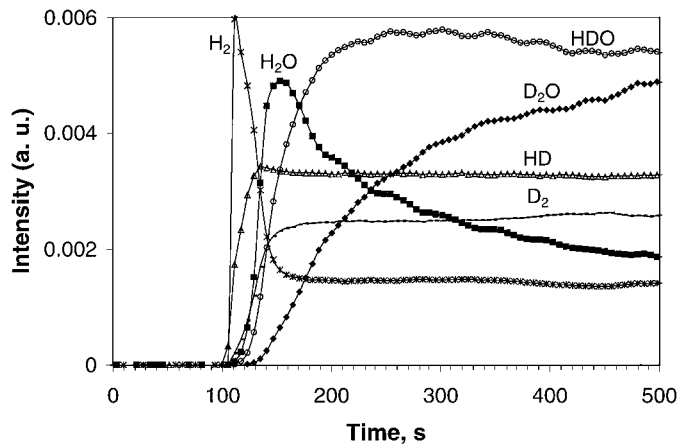


FIG. 8. $N_2 \rightarrow (1\% H_2O + 2\% D_2)/N_2$ step responses on the Pd monolith at 155°C.

cantly, but they showed similar characteristics at the steady state and during the transient period. In all of the experiments, a maximum of the hydrogen response was observed. An experiment with water and deuterium in an empty reactor was performed in order to confirm that the effects observed were caused by chemical reactions and not by any fragmentation in the filament or experimental mistakes. No hydrogen response was detected in this case, indicating a true chemical nature of the phenomenon described above. The step change switch from 1% H₂O/N₂ to 1% D₂/N₂ was performed to clarify the origin of the H₂ peak. After the switch, a sharp H₂ peak was observed. A smaller HD peak had a maximum, when the H₂ peak had already started to diminish.

In the case of an excess of water (Fig. 7), equal amounts of reactants (Fig. 6), as well as water (Fig. 9) and deuterium (Fig. 10) pretreatments, the most prominent product was HDO followed by D₂O at steady state. The isotopic exchange between water and deuterium did not occur

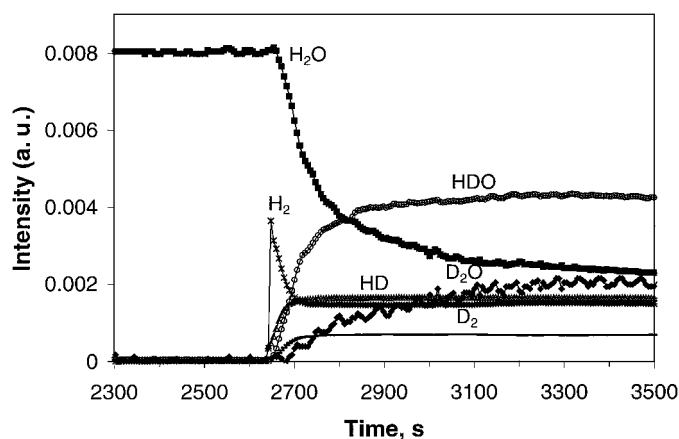


FIG. 9. $(1\% H_2O)/Ar \rightarrow (1\% H_2O + 1\% D_2)/Ar$ step responses on the Pd monolith at 155°C.

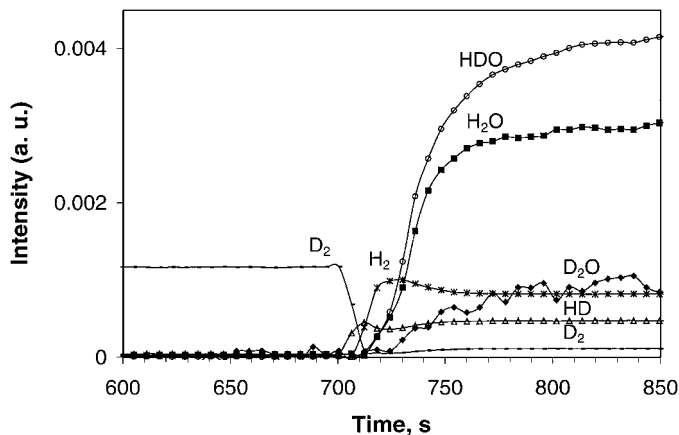


FIG. 10. (1% D₂)/Ar → (1% H₂O + 1% D₂)/Ar step responses on the Pd monolith at 155°C.

completely, but a part of water and deuterium remained unreacted. The high selectivity with respect to HDO reflects the availability of reactants and the fewer steps needed to form HDO in comparison with D₂O. The HDO response was in all cases faster than that of D₂O, demonstrating that D₂O is formed stepwise via HDO as an intermediate.

In the 2% H₂O + 1% D₂ experiment (Fig. 7) H₂ appeared as the main product compared to HD and D₂. However, in the 1% H₂O + 1% D₂ and 1% H₂O + 2% D₂ experiments more HD was formed than H₂, indicating that the excess isotopes enhanced the isotopic exchange due to the coverage of D* atoms on the surface near the H* atoms that were not able to associate with their homologues. With excess deuterium, the amount of unreacted deuterium was larger and the production of hydrogen was less.

A hydrogen peak immediately after the D₂ addition was always detected when the catalyst was pretreated with water (Fig. 9). The maximum in the response of H₂ was considerably smaller when the D₂ pretreatment was carried out (Fig. 10), but it was still noticeable once the HD signal started to appear, indicating that some hydrogen was present on the surface. The sites were evidently occupied by deuterium and there were no vacant sites on which water could dissociate before some deuterium was desorbed. In the beginning of the step change from argon to deuterium, minor signals of HD and H₂ were detected, indicating that some hydrogen was left on the catalyst after the reduction pretreatment. A blank experiment of the deuterium pretreatment experiment verified that the hydrogen peak was due to the catalytic effects.

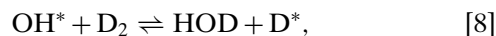
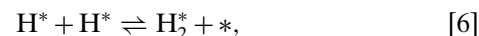
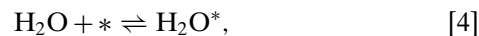
The fast evolution of H₂ in the reaction of H₂O and D₂ and during the switch from H₂O to D₂ indicates that there is a large concentration of H* present on the catalyst. This H* can only originate from H₂O. Once water entered the reactor, dissociation of it took place on the active sites, giving rise to H* and OH* species. The logical conclusion is that H₂O must dissociate much faster

than D₂. The H* atoms were assisted in desorbing from the surface by the D₂ molecules arriving at the catalyst at the same time. D₂ molecules interacted with adsorbed hydrogen atoms and enhanced their association and, finally, their desorption. The formation of hydrogen evidently follows the adsorption-assisted desorption concept first proposed by Tamaru and Naito (4). They demonstrated that the ¹³C¹⁸O desorption process in the presence of ¹²C¹⁶O gas is remarkably enhanced due to the repulsive interaction between preadsorbed ¹³C¹⁸O and incident ¹²C¹⁶O molecules from the gas phase arriving at nearby sites of adsorbed ¹³C¹⁸O. This effect was called adsorption-assisted desorption and it has been reviewed largely by many authors (30). The step-change switch from 1% H₂O/N₂ to 1% D₂/N₂ provided clear evidence that the deuterium-assisted desorption of H₂ is a correct mechanistic hypothesis for the sharp H₂ peak observed, since a clear H₂ peak was visible directly after the switch.

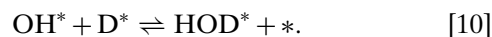
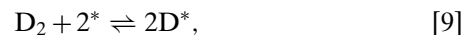
When deuterium was present in excess (Fig. 8), the hydrogen peak was higher and sharper, which indicates a more revealing case of adsorption-assisted desorption, due to the increase in the interaction between the H* and the excess deuterium. It might be that D₂ pretreatment case represents as well the adsorption-assisted desorption of chemisorbed hydrogen originating from the dissociation of water. No deuterium response was detected at the beginning of the step (Figs. 6–9), indicating the consecutive adsorption and dissociation of its molecules.

An experiment (1% H₂O + 1% D₂)/N₂ was done also on the support to clarify the role of the support material. The D₂ response reached the steady state much faster than H₂O, indicating that the adsorbed amount of D₂ was small compared to the adsorbed amount of H₂O. A H₂ peak, which was formed on the Pd catalyst, was not observed on the support material. The result indicated that the adsorption-assisted desorption concept is connected to the presence of Pd. Small amounts of HD and HDO were formed on the modified alumina support.

A time delay in the response of water indicates a rapid and profound adsorption of H₂O on the support followed by decomposition into H* and OH* as long as empty sites are available. A mechanism for the formation of hydrogen can thus be written as

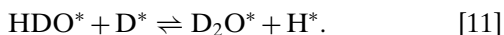


or



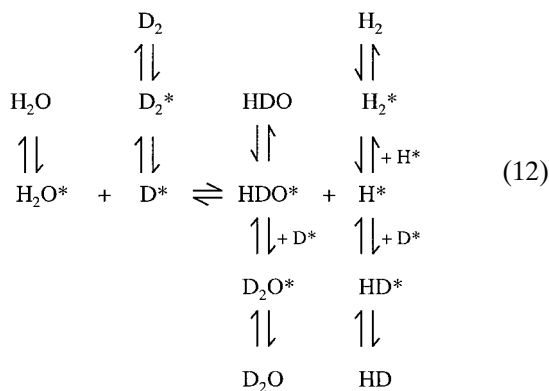
Once the active sites were occupied and no place for the adsorption of H₂O was left, the response of water increased. The water peak started to decline as its isotopic homologues HDO and D₂O started to form.

In the case of excess deuterium (Fig. 8), D₂O was the major product formed at steady state. Because the reaction is a consecutive one (Eq. [11]), it goes via HDO, which is the prominent product in the transient period. The excess chemisorbed D* enhanced the exchange reaction between HDO* and D*:



HD was continuously produced during the reaction. Its response appeared to be rapid in the presence of deuterium in excess, indicating a fast dissociation of deuterium as well as a quick association with H* or a fast exchange reaction between H* and deuterium. On the other hand, when water was the excess reactant, the response of HD was slower, even compared to HDO. In the case of excess water in the feed, the higher surface coverage of OH species can affect the adsorption and dissociation of D₂. Because both OH* and H* originate from the dissociation of H₂O*, D* has an equal possibility of reacting with either OH* or H*. Therefore, the slow response of HD demonstrates the higher affinity (rate constant) of D* to OH* than to H*.

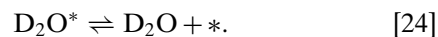
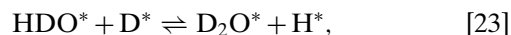
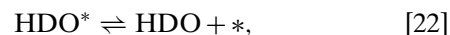
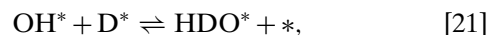
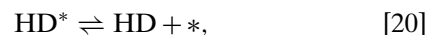
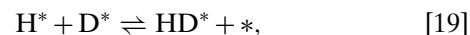
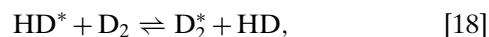
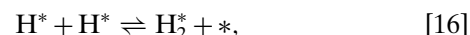
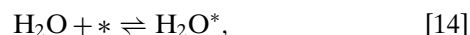
Let us consider the possible mechanisms, which explain the observed experimental data. The following two reaction mechanisms for the D₂/H₂O exchange reaction could be imagined:



The proposed scheme finds its origin in the Rolston and Goodale mechanism (31). According to the mechanism, HDO* is produced through an exchange reaction of H₂O* and D*, avoiding the premise of dissociation of water. For this mechanism to be consistent with current experimental data, the formation of H₂ and HD should be faster compared to the formation of HDO and D₂O. According to this mechanism H₂ and HD should have similar responses; however, as revealed by Figs. 6–10 the responses of H₂ and HD are quite different. The difference in H₂ and HD responses can possibly be due to the kinetic isotope effect. However,

even if this effect is present, it is rather minor. As can be seen in Figs. 6–10, the H₂ response becomes visible before the HDO response. Under the non-steady-state conditions the H₂ response can become visible before the HDO response if the desorption of HDO is a slow step. This assumption can be rationalised by the adsorption experiments of water (Fig. 4), which indicate that the desorption of water from the support is a slow process.

According to Schmal *et al.* (32) water adsorbs dissociatively on palladium sites with the possible formation of Pd–OH bonds at the surface, and according to Koper and van Santen (33) the dissociation products of water are adsorbed H, O, and OH. In the actual case, a hydrogen peak is detected, which might indicate that water dissociates to adsorbed H, O, and OH and that these OH* groups could associate with D* to form HDO*. Studies by Beutl *et al.* (34) on hydrogen adsorption on Pd(111) supports the existence of molecularly adsorbed H₂ species. These observations give rise to an alternative mechanism:



The experiments with the support implied that the reactions $\text{H}^* + \text{D}^* \rightleftharpoons \text{HD}^* + ^*$ and $\text{OH}^* + \text{D}^* \rightleftharpoons \text{HDO}^* + ^*$ happened also on the support material to some extent. The extent of the reactions in question is much larger on the Pd catalyst, which indicated that the active site was more likely Pd. There are two possible explanations for this. One is that water does not dissociate on alumina, although there are reports in the literature according to which water dissociates on alumina (35, 36). The second possibility is that the amount of chemisorbed deuterium on alumina is very small. According to Lukinskas and Fărcașiu (37) the equilibrium concentration of hydrogen chemisorbed on alumina is extremely small. Their conclusion can be consistent with our observation that the amount of dissociated deuterium on modified alumina is fairly small.

Alumina has an important effect in the adsorption of water. Beside these reactions, the support plays an important role in the exchange reaction between the adsorbed species. Previous H₂/D₂ experiments showed that OH

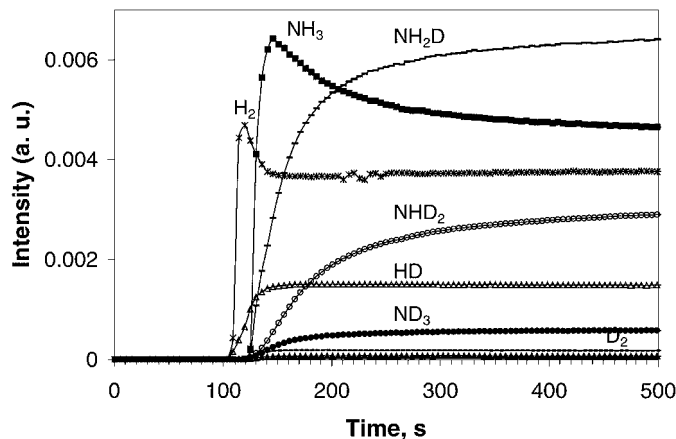


FIG. 11. $\text{Ar} \rightarrow (1\% \text{NH}_3 + 1\% \text{D}_2)/\text{Ar}$ step responses on the Pd monolith at 155°C .

groups from alumina can take part to some extent in the water formation (Eqs. [21]–[24]), giving additional mechanistic support to the latter mechanism. Also, the experimental data from the 1% $\text{H}_2\text{O}/\text{N}_2$ to 1% D_2/N_2 experiment supports the latter mechanism, which includes the dissociation step of water (Eq. [15]). However, further studies are needed to discriminate between these two proposed mechanisms.

3.5. H_2/D_2 Isotopic Exchange in NH_3 on the Pd Monolith

The transient and steady-state states of the $\text{NH}_3 + \text{D}_2$ reaction are displayed in Figs. 11–14. Some of the experiments were performed with nitrogen as the carrier gas, due to the fragmentation of Ar to $m/z = 20$, which overlaps with the mass number of ND_3 , one of the main products. However, the results found do not differ significantly, which enables a comparison between them.

The products from the isotope exchange of hydrogen in ammonia with D_2 were NH_2D , NHD_2 , ND_3 , and HD .

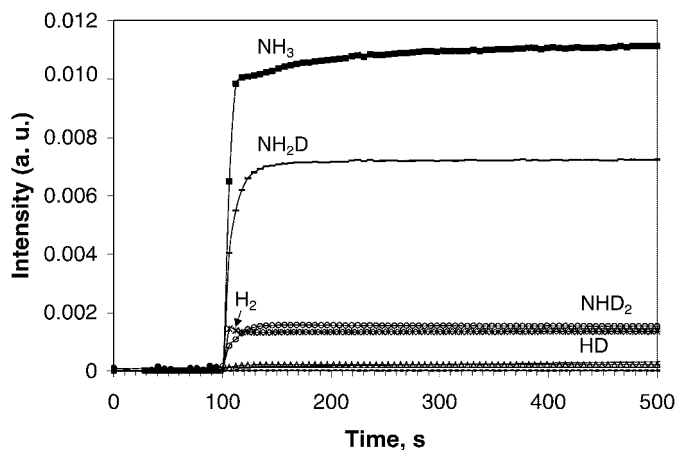


FIG. 12. $\text{Ar} \rightarrow (2\% \text{NH}_3 + 1\% \text{D}_2)/\text{Ar}$ step responses on the Pd monolith at 155°C .

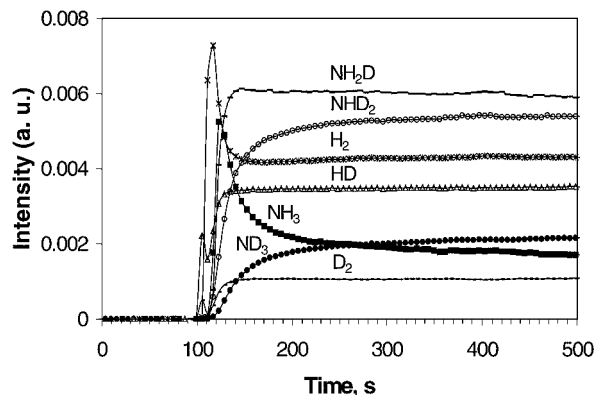


FIG. 13. $\text{N}_2 \rightarrow (1\% \text{NH}_3 + 2\% \text{D}_2)/\text{N}_2$ step responses on the Pd monolith at 155°C .

It was observed that the response pattern of the products and reactants behaved quite similarly in all the experiments even though the NH_3 and D_2 concentrations were varied, demonstrating that pretreatment with ammonia and different concentrations of reactants has a minor influence on the responses. The amount of NH_2D formed was higher when an excess of ammonia was used (Fig. 12). In contrast NHD_2 and ND_3 signals reached higher levels when deuterium was used in excess (Fig. 13). This effect can be understood from the availability of reactants. In the first case, there were more molecules of nitrogen and less of deuterium, and the first step product (NH_2D) was formed in abundance. Under these conditions the ND_3 response was almost unnoticeable. The degree of isotopic exchange is definitely less in the excess of NH_3 . The explanation for the decrease in NH_3 conversion with increasing NH_3 concentration is probably the limited availability of the second reactant, D^* , on the surface highly covered with NH_3 .

In all the experiments, a maximum in the response of hydrogen was observed when deuterium and ammonia were fed together into the reactor. The maximum was more prominent when deuterium was in excess at the inlet (Fig. 13), reaching at the beginning of the switch a level that was even higher than values of products during the steady state. In contrast, H_2 response was much smaller when the excess reactant was ammonia (Fig. 12). No hydrogen peak was detected when no catalyst was present inside the reactor. Thus, we can conclude that the effect was catalytic.

An ammonia pretreatment experiment is presented in Fig. 14. The pretreatment with ammonia was carried out twice, to clarify the origin of the H_2 maximum. Deuterium was added to the 1% NH_3/N_2 flow during the second NH_3 adsorption step. A maximum in the response of hydrogen was observed immediately. The result indicated that the desorbed hydrogen cannot originate from the reduction done by 1% H_2/Ar gas mixture before the experiment. This implied that the already adsorbed ammonia molecules dissociated on the catalyst surface. The deuterium molecules

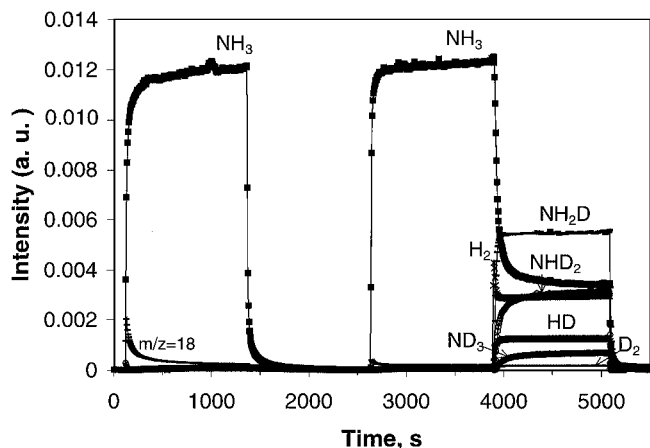


FIG. 14. $N_2 \rightarrow (1\% NH_3)/N_2 \rightarrow N_2 \rightarrow (1\% NH_3)/N_2 \rightarrow (1\% NH_3 + 1\% D_2)/N_2 \rightarrow N_2$ step responses on the Pd monolith at 155°C.

entering the reactor promoted the desorption of H₂. Also, the step-change switch from 1% NH₃/N₂ to 1% D₂/N₂ was performed to clarify the source of the H₂ peak. After the switch a sharp H₂ peak was observed. A smaller HD peak had a maximum, when the H₂ peak has already started to diminish.

Almasan *et al.* (38) have discussed in their work dealing with the H/D isotopic exchange on nickel catalysts that the processes associated with D₂ adsorption at the beginning are more rapid than the spillover, which causes the desorption of H₂. It can be speculated that the hydrogen atoms present on the active sites of the catalyst due to decomposition of ammonia or in the OH groups of the support desorb instantaneously, as the deuterium molecule reaches the catalyst surface, liberating vacant sites for the D₂ molecule to adsorb and dissociate. A similar adsorption-assisted desorption phenomenon was described by Tamaru and Naito (4) for ¹³C¹⁸O and ¹²C¹⁶O, as discussed above.

The step-change switch from 1% NH₃/N₂ to 1% D₂/N₂ and the ammonia pretreatment experiment (Fig. 14) provided clear evidence that the deuterium-assisted desorption of H₂ is a correct mechanistic hypothesis for the sharp H₂ peak observed, since a clear H₂ peak was visible directly after the switch. The hydrogen peak observed in the NH₃ + D₂ experiments can therefore be explained by adsorption-assisted desorption, where the hydrogen atoms originating from the NH₃^{*} are enhanced to associate and desorb due to the interactions with deuterium. Since the most prominent response of H₂ was detected in the experiment performed with an excess of D₂, it indicates that the surface coverage of deuterium was even higher and therefore more molecular hydrogen was desorbed from the catalyst surface. In the case of ammonia as the excess reactant, the hydrogen peak was the smallest one. In this case, evidently NH₃^{*} and its dissociatively adsorbed species covered the surface almost entirely, preventing deuterium for

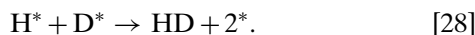
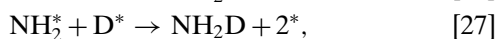
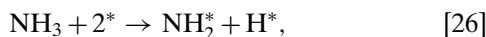
adsorbing and dissociating. In the case of the 1% NH₃ + 1% D₂ and 1% NH₃ + 2% D₂ experiments (Figs. 11 and 13), the NH₃ responses appeared after the hydrogen peak was clearly noticeable. This indicates that ammonia adsorbed and dissociated quickly in order to provide hydrogen atoms that associated and desorbed as H₂.

An experiment (1% NH₃ + 1% D₂)/N₂ was done also on the support to clarify the role of the support material. Results and conclusions are congruent with the experiment (1% H₂O + 1% D₂)/N₂ on the support. The D₂ response again reached the steady state much faster than NH₃, indicating that the adsorbed amount of D₂ was small compared to the adsorbed amount of NH₃. A H₂ peak, which was formed on the Pd catalyst, was also not observed in this case on the support material. The result indicated that the adsorption-assisted desorption concept is connected to the presence of Pd. Small amounts of HD, NH₂D, and H₂ were formed on the modified alumina support.

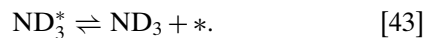
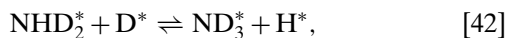
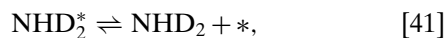
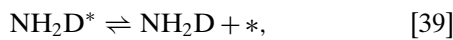
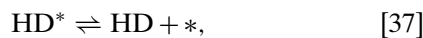
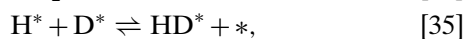
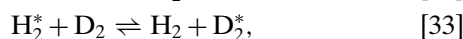
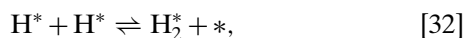
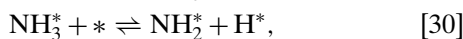
According to Papapolymerou and Bontozoglou (18), decomposition of NH₃ on Pd should most likely proceed through successive dehydrogenation reactions of adsorbed NH_x species. The main products of the isotopic exchange experiments were NH₂D, NHD₂, and ND₃ and their amount at steady state was found to decrease in the following order: NH₂D > NHD₂ > ND₃ (Figs. 11–14). The transient production amounts of these compounds were related to the number of steps involved in their formation. Probably the mono-, bis-, and terdeuterated ammonia were formed in a consecutive way: NH₃ → NH₂D → NHD₂ → ND₃. The monodeuterated product was formed first. The H/D exchange of ammonia was stepwise via the exchange of one H/D atom at time. Since the formation of NH₂D requires adsorption and dissociation of NH₃ and D₂ and the following association of NH₂^{*} + D^{*}, or an exchange reaction between NH₃^{*} and D₂^{*}, it was the compound with major selectivity of nitrogen. The production rates of NHD₂ and ND₃ seem to be smaller than the production rate of NH₂D. In this case, the rate constant for the reaction NH₂^{*} + D^{*} → NH₂D + 2^{*} is bigger and the surface coverage of NH₂ is larger.

In the present study, in all cases the HD response reached the steady state rapidly. The results allow us to conclude that the adsorbed hydrogen atoms, which react with deuterium, originate from the dissociation of NH₃^{*}. Also, the results obtained by Farkas (28) support our conclusion. Farkas has proposed, based on his studies on the exchange between ammonia and deuterium on the surface of an evaporated iron film, a mechanism which includes the formation of HD involving hydrogen atoms from the dissociation of ammonia. He also has stated that the catalyst surface is mainly covered by NH₂^{*} rather than H^{*} or D^{*}. The results were explained in terms of the following steps (30):





Based on the transient responses recorded in this study it can be concluded that chemisorbed atoms of H^* recombine to H_2 , preferring a reaction with their homologues over one with their isotopic counterpart. The following mechanism for the isotope exchange of hydrogen in NH_3 with D_2 is proposed:



The experiments with the support implied that the reactions $\text{H}^* + \text{D}^* \rightleftharpoons \text{HD}^* + *$, $\text{H}^* + \text{H}^* \rightleftharpoons \text{H}_2^* + *$, and $\text{NH}_2^* + \text{D}^* \rightleftharpoons \text{NH}_2\text{D}^* + \text{D}^*$, happen also on the support material to some extent. The extent of the reactions in question was much larger on the Pd catalyst, which indicated that the active site is now more likely Pd. There are again two possible explanations for this, as described in the case of $\text{H}_2\text{O} + \text{D}_2$ experiments: either ammonia does not dissociate on alumina, although, there are in the literature reports according to which ammonia dissociates on alumina, or the amount of chemisorbed deuterium on alumina is very small. For example, according to Monterra and Magnacca, ammonia can dissociate on acid–base pair sites of alumina, yielding surface amino groups ($-\text{NH}_2$) and surface OH groups (19).

The steps of crucial importance are the ammonia decomposition step, Eq. [30], and the reaction between adsorbed hydrogen and deuterium from the gas phase, Eq. [33]. The coexistence of these steps explains the maximum detected in the H_2 response. In addition to these reactions the support plays an important role in the exchange reaction between the adsorbed species.

4. CONCLUSIONS

Transient experiments were used to study the isotopic exchange of hydrogen atoms in water, ammonia, and hydrogen with deuterium, as well as the adsorption of ammonia and water on the Pd monolith. The study provided new insights into reaction mechanisms.

Deuterium was able to exchange with hydrogen atoms in water and ammonia. In both cases, a maximum in the hydrogen response was observed at the beginning of the experiment. The formation of hydrogen can be rationalised by invoking the adsorption-assisted desorption concept. The hydrogen atoms present on the active sites of the catalyst due to the decomposition of ammonia and water desorb instantaneously, as D_2 appears on the surface of the catalyst. The present study indicates that the plausible surface intermediate NH_2^* reacted with D^* to form NH_2D^* , which was further converted to NHD_2^* and ND_3^* . Adsorbed hydroxyl groups (OH^*) react with D^* to form HDO^* , which was the surface intermediate of deuterated water. The results presented in this contribution form the basis for the understanding of the water and ammonia formation mechanisms in the reaction between NO and H_2 over Pd, which is the topic of part II of this work.

ACKNOWLEDGMENTS

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