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Steady-state isotopic transient kinetic analysis of the H_2/D_2 exchange reaction as a tool for characterising the metal phase in supported platinum catalysts

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Abstract

The steady-state isotopic transient kinetic analysis (SSITKA) technique has been applied to the characterisation of the metal phase in Pt/CeO_2 and Pt/SiO_2 catalysts by studying the H_2/D_2 exchange process. The time scale of the exchange process is close to the delay in the transport of the gases through the reactor. The behaviour of the reactor has been studied by analysing the curves corresponding to blank experiments and it can be satisfactorily modelled with the mathematical equation corresponding to two continuous stirred-tank reactors (CSTRs) in series. The curves in the presence of catalyst can be modelled with a simple mathematical equation that yields the values of the total number of sites active in the isotopic exchange and the apparent first order rate constant for the H_2/D_2 exchange process. The results so derived are in good agreement with those obtained from the analysis of the TPD experiments following the ITK runs. Although the results suggest a normal equilibrium isotope effect and an inverse kinetic isotope effect, the measured isotope effects are moderate in both cases and include possible contributions from the uncertainties in the calibration of the HD signal. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: SSITKA; H_2/D_2 exchange; Pt/CeO_2; Pt/SiO_2

1. Introduction

Precious metals (Rh, Pt, and Pd) supported on ceria or ceria-containing materials are being extensively investigated, mainly because of their relevance as models for TWC catalysts. Surely, the major efforts are being dedicated to the understanding of the origins of the deactivation effects that limit the performance of TWC converters [1,2]. A better characterisation of these catalysts is highly desired, but the determination of the number of metal active sites and the intrinsic activity of these sites is very difficult even under “well-controlled” environments [3]. For example, the presence of ceria causes chemical side-processes when conventional chemisorption techniques based in the adsorption of molecular probes as H_2 or CO are used [4]. The occurrence of hydrogen spillover processes does not permit a straightforward interpretation of the data obtained by H_2 chemisorption or desorption experiences. The extension and rate of the hydrogen spillover processes are controlled by factors as the ceria-support surface area, the treatment of the samples prior to H_2 adsorption, and the presence or not of chlorinated species in the catalyst according to the metal precursor used.

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We decided to use the steady-state isotopic transient kinetic analysis (SSITKA) technique as a tool to obtain information specifically related to the metal phase in catalysts based in ceria, thus minimising the contribution of the support. These techniques are now being widely used for determining the mechanism of catalytic processes [5]. In the present work, the technique has been applied to the study of the H_2/D_2 exchange reaction on a Pt/CeO_2 catalyst. Although the H_2/D_2 exchange occurs rapidly and the curves are obscured by the response of the experimental system to the isotopic change, a simple numerical analysis is proposed that leads to values of the number of active sites as well as the rate constant for the desorption process. The paper focuses on the analysis of the experimental curves to obtain the chemically relevant parameters, whereas the application to the study of the deactivation of Pt/CeO_2 catalysts caused by ageing under an H_2 atmosphere will be the subject of a future contribution. As not all the hydrogen atoms on the catalyst surface participate in the exchange process, the results are complemented with those obtained from temperature programmed desorption (TPD) experiments carried out at the end of the ITK experiences. In this way, information is obtained about the total number of sites on the surface of the catalyst (TPD) and the fraction that participates in the H/D exchange. In addition, as the rate constants derived from the analysis of the ITK curves are a measure of the activity of these sites, the changes in activity caused by treatment of the catalyst are expected to lead to changes in the values of the rate constant. In order to check the validity of the method, a parallel study has been carried out on a standard Pt/SiO_2 catalyst (EUROPT-1) for which comprehensive characterisation data are available in the literature [6,7].

2. Experimental

A Pt (7.5%)/CeO_2 catalyst was prepared from an aqueous solution of $[Pt(NH_3)_4](OH)_2$ using the incipient wetness impregnation technique. The support was previously prepared from a ceria sample provided by Rhône–Poulenc and submitted to a sintering treatment to stabilise its texture. No evidence of microporosity and a BET surface area of $79\,m^2\,g^{-1}$ were found for this cerium oxide used as support. The metal dispersion of the Pt/CeO_2 catalyst was estimated to be 62% and the mean particle size was 1.9 nm when the methodology previously reported [8] is applied to analyse metal particle size distribution data obtained from high-resolution electron microscopy (HREM) images.

The Pt (6.3%)/SiO_2, EUROPT-1, catalyst was prepared by Johnson Matthey Chemicals using an ion exchange method from $Pt(NH_3)_4Cl_2$ as metallic precursor. Preparation details as well as characterisation data obtained by different techniques can be found elsewhere for this standard platinum catalyst [6,7]. An estimated metal dispersion about 65% corresponding to a mean particle size of 1.7 nm was obtained by means of transmission electron microscopy (TEM) [9].

SSITKA studies for H_2/D_2 exchange reactions and TPD experiments were carried out with samples pre-reduced and evacuated in situ. Weighed amounts of the sample (150–200 mg) were placed into the reactor with the help of a quartz wool bed. Blank experiments were carried out in the absence of catalyst but with the quartz wool in the reactor. A VG Sensorlab 200-D mass spectrometer connected to the exhaust of the reactor by a continuously evacuated heated capillary was used as analytical device. The experimental flow system was designed in order to minimise the effects due to the transport of the gases. A tubular quartz reactor with a bulb (total volume of $7.9\,cm^3$) and conducting gas lines of minimum internal volume were used. Four-way valves with electronic coupling to the mass spectrometer and flow mass controllers (Brooks, model 5850-TR) permitted us to avoid pressure and flow perturbations occurring in the switch between different feeds.

The applied methodology can be summarised as follows. Samples were reduced during 1 h in a flow of H_2 ($60\,cm^3\,min^{-1}$) at 200 °C (Pt/CeO_2) or 350 °C (Pt/SiO_2). After an evacuation step at 500 °C (1 h) under Ar flow ($60\,cm^3\,min^{-1}$), the samples were treated with H_2 (5%)/Ar during 1 h at 35 °C, and the ITK experiments were then started by switching the feed to D_2 (5%)/N_2. The evolution of the H_2, HD, and D_2 species was monitored versus time and a high rate of data acquisition (a complete set of values every 0.2 s) was used in order to improve the quality of the recorded profiles. After 15 min of treatment at 35 °C under D_2 (5%)/N_2, the sample was cooled at −80 °C still under D_2 (5%)/N_2 flow. Then the feed was switched to Ar ($60\,cm^3\,min^{-1}$) and a TPD-MS experiment was run in two steps, from −80 °C up to room temperature (RT) in a free-regime heating and then, from RT up to 500 °C at 10 °C min^{-1}. Samples were then maintained during 1 h at 500 °C in an isothermal step that leads to the total desorption of the species adsorbed during the ITK experiment.

The amounts of hydrogen and deuterium evolved from the catalysts in the TPD-MS experiments were calculated from the integration of the recorded profiles. The calibration factors were obtained by means of hydrogen (or deuterium) volumetric adsorption data and TPD-MS parallel studies on CeO_2 samples reported elsewhere [10].

3. Results and discussion

The ITK experiments consist of monitoring the time dependence of the composition of the gas in contact with a catalyst sample following a rapid change in the isotopic composition of the gas. The experiments involve a minimal perturbation of the experimental conditions and the analysis of the transient response allows the characterisation of the catalyst under operating conditions. Although the actual experimental set-up may include a variety of reactors and gas compositions, the transient response always contains two contributions that come from the delay in the transport of gases through the reactor and from the kinetics of the chemical processes involved. If the reaction is much slower than the response of the experimental device to the gas switch, the whole process becomes chemically controlled and the analysis of the transient curves results simplified. On the contrary, for extremely fast reactions, the dynamics of gases in the reactor dominates the transient response and, hence, information about the kinetics of the chemical process cannot be obtained. In the intermediate case, i.e. when the time scales of both the reactor response and the chemical process are similar, though some mathematical treatment of the experimental signals has to be developed, meaningful chemical information may still be obtained from them.

3.1. The behaviour of the reactor

As preliminary experiments [11] had shown that the time scale for H_2/D_2 exchange on Pt/CeO_2 catalysts is close to that recorded for blank experiments, a detailed analysis of the reactor response in the absence of catalyst was carried out before facing the chemical problem. After switching the gas composition from 5% H_2/Ar to 5% D_2/N_2, in the absence of the catalyst, the time dependence of the signals for $m/z = 2$ (H_2) and $m/z = 4$ (D_2) is shown in Fig. 1. The curves were normalised to facilitate comparison and an ordinate value of 1 indicates 5% of the corresponding species in the gas mixture. The signal corresponding to $m/z = 3$ remains always below the noise level. The results obtained from the analysis of normalised curves can be easily converted to real values by considering the total gas flow and the composition of the gas, and the experimental conditions of pressure and temperature [12].

The curves in Fig. 1 deviate from the ideal behaviour (a step function) and show an induction period of ca. 5–10 s before starting another period of ca. 10 s during which the H_2 and D_2 signals vary before reaching their final steady-state values. Thus, the delay in the transport of gases through the reactor causes changes in the MS signals during a time of ca. 15–20 s, and consequently, the response from any chemical process occurring in shorter or comparable reaction times will be severely affected by the reactor response.

The reactor response was found to be very reproducible for a given set of experimental conditions, although it is significantly affected by the changes in the gas flow. In any case, the shape of the curves was always similar to those shown in Fig. 1 and could be well fitted by Eqs. (1) and (2); Eq. (1) being valid for upward curves such as that of D_2 in Fig. 1, and Eq. (2) being valid for the downward curves. The subscript b in these equations indicates that they deal with the blank experiments.

$$[H_2]_b \quad \text{or} \quad [D_2]_b = 1 - e^{(t-\delta)/\tau} \sum_{i=1}^{n} \frac{(t-\delta)^{i-1}}{\tau^{i-1}(i-1)!} \tag{1}$$

$$[H_2]_b \quad \text{or} \quad [D_2]_b = e^{(t-\delta)/\tau} \sum_{i=1}^{n} \frac{(t-\delta)^{i-1}}{\tau^{i-1}(i-1)!} \tag{2}$$

The fit of experimental curves by these equations only requires the inclusion of terms up to $n = 2$, which indicates that the reactor system can be satisfactorily modelled by two equivalent continuous stirred-tank

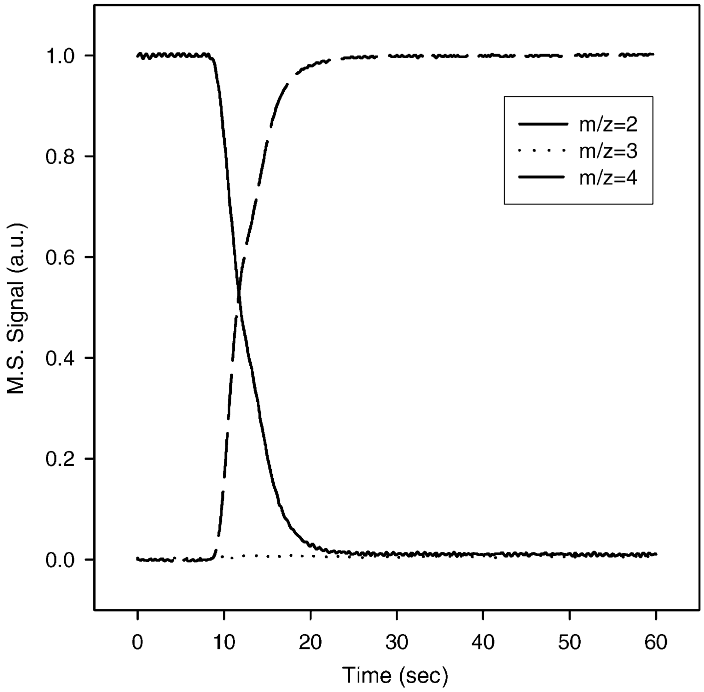

Fig. 1. Profiles registered for $m/z = 2$, 3 and 4 during an ITK-H_2/D_2 in blank experiment. Conditions were 60 $cm^3\,min^{-1}$ and 35 °C as gas flow and temperature, respectively.

reactors (CSTRs) in series [13]. The δ parameter refers to the dead time of the reactor and the τ parameter represents the mean residence time of the gas molecules in the reactor. As expected, the values of both parameters decrease with increasing the gas flow (Table 1) and they also show small differences for the different *m*/*z* ratios. This effect may probably be due to the characteristics of the sample introduction system to our mass spectrometer. In any case, a detailed explanation is out of the scope of this work, where blank experiments were carried out to separate the contributions from the reactor and the sample to the ITK curves in the presence of catalyst. Although the differences in Table 1 are small, they can be significant when the time scale of the ITK experiment is close to that of the blank experiments, which is always the case in this work. The differences between the values of τ and δ for the different *m*/*z* ratios led us to use the values derived from the blank curves in the analysis of ITK experiments, instead of the more common practice of using the trace for an inert gas as He, N_2 or Ar [12,14,15]. It can be argued that this practice ignores the changes in the τ and δ values caused by the different effective reactor volume in the presence of catalyst and in the blank experiments. However, the volume occupied by the sample is very small as compared with the total volume of the reactor

Table 1
The values of the δ and τ parameters derived from blank experiments at 35 °C

Flow ($cm^3\,min^{-1}$)	*m*/*z*	δ (s)[a]	τ (s)[a]
40	2	9.90 ± 0.10	3.49 ± 0.04
	4	10.47 ± 0.07	2.81 ± 0.05
60	2	8.40 ± 0.10	2.22 ± 0.03
	4	8.50 ± 0.08	1.97 ± 0.03
80	2	5.67 ± 0.06	1.90 ± 0.01
	4	6.02 ± 0.07	1.40 ± 0.01
100	2	4.06 ± 0.07	1.51 ± 0.02
	4	4.46 ± 0.09	1.06 ± 0.02

[a] The values in the table were obtained by using Eqs. (1) and (2) in the text and they correspond to the mean value and standard deviation of five independent experiments.

(it represents less than ca. 0.5%), thus suggesting a rather minor effect. In good agreement with this assumption, it will be shown below that ITK curves in the presence of catalyst can be satisfactorily modelled using the values of τ derived from blank experiments.

The quality of the fit of experimental curves by Eqs. (1) and (2) decreases as the gas flow increases and for flow rates higher than ca. 80 $cm^3\,min^{-1}$, the curves show an additional curvature that cannot be well modelled by including additional terms in Eqs. (1) and (2). In accordance with this limitation, the experiments in the presence of catalyst were run at 35 °C using flow rates of 60–80 $cm^3\,min^{-1}$; these values minimise the transient period caused by the reactor without significant deviation of the curves from Eqs. (1) and (2).

3.2. The effect of the catalyst

A typical H_2/D_2 ITK experiment on the Pt/CeO_2 catalyst reduced at 200 °C is shown in Fig. 2. A major difference with the curves in Fig. 1 is the appearance of significant amounts of HD ($m/z = 3$), which is formed by H_2/D_2 exchange on the surface of the catalyst. The shape of the curves for $m/z = 2$ and 4 is quite similar to the one in the blank experiments, but they show a delay with respect to the blank. The delay in the H_2 curve indicates that some H_2 is desorbed from the surface during the transient period, whereas the delay in the curve for $m/z = 4$ indicates D_2 consumption. The time dependence of the desorption or consumption of H_2, HD, and D_2 is more clearly illustrated by the difference curves in Fig. 3, which were obtained by subtracting the blank curves from the curves in the presence of catalyst. According to the difference curves in Fig. 4, the response of the Pt/SiO_2 catalyst is slightly different; although the qualitative features are similar to those of Pt/CeO_2, the transient period lasts now for a time significantly longer.

Also worth of noting is that the maximum concentration of HD in these ITK experiments coincides with almost equimolar concentrations of H_2 and D_2; actually, the HD curve parallels that of the product $[H_2] \times [D_2]$ and indicates that the output of the reactor consists of an equilibrium mixture of H_2, HD, and

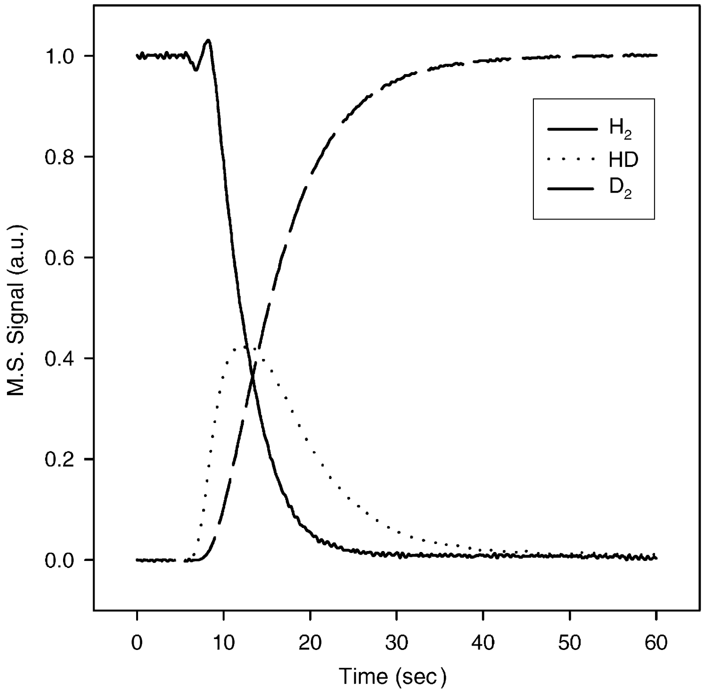

Fig. 2. Evolution of H_2, HD, and D_2 species during an ITK-H_2/D_2 experiment on the Pt/CeO_2 catalyst.

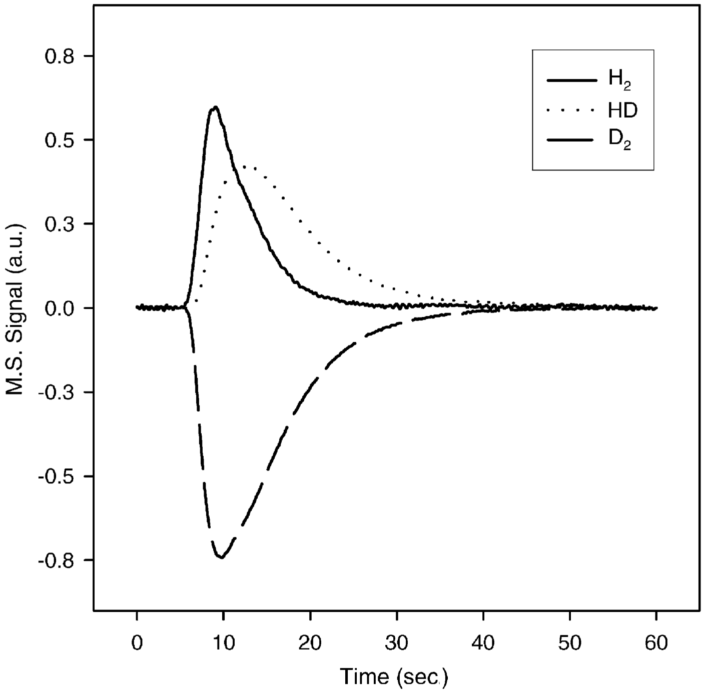

Fig. 3. Difference curves corresponding to experiment in Fig. 2 for Pt/CeO$_2$ sample.

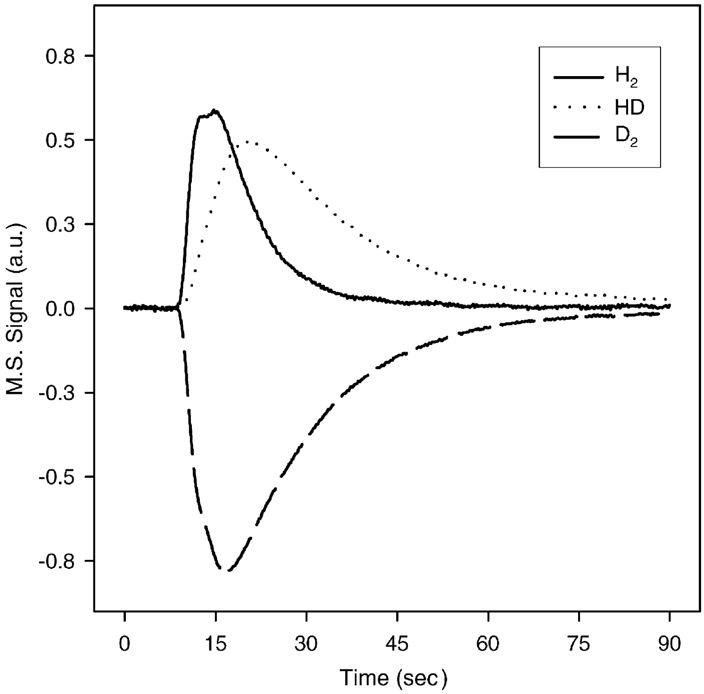

Fig. 4. Difference curves obtained from an ITK-H$_2$/D$_2$ experiment on Pt/SiO$_2$ sample.

D_2 (Eq. (3)).

$$H_2 + D_2 = 2HD \tag{3}$$

It is important to note that previous studies [11] had shown that ceria and silica non-metalled samples were inactive under the experimental conditions here used, which suggests that platinum is responsible for the observed isotopic exchange. The high activity of metal surfaces for this reaction is well-documented [16–19]. In fact, H_2/D_2 exchange has been observed in earlier ITK experiments using other supported metal catalysts [14,15].

3.3. *The results of the thermal desorption experiments*

At the end of the ITK experiments, the sample was cooled at −80 °C under flowing D_2/N_2, then the gas flow was switched to Ar, and finally, always under flowing Ar, from sub-ambient temperature up to 500 °C. The desorption profiles from −80 °C up to RT for both Pt/CeO_2 (Fig. 5a) and Pt/SiO_2 (Fig. 5b) catalysts show that D_2 is the only desorption product, no signals due to HD or H_2 being detected. Desorption occurring within this low-temperature range has been interpreted as an evidence of hydrogen (deuterium)

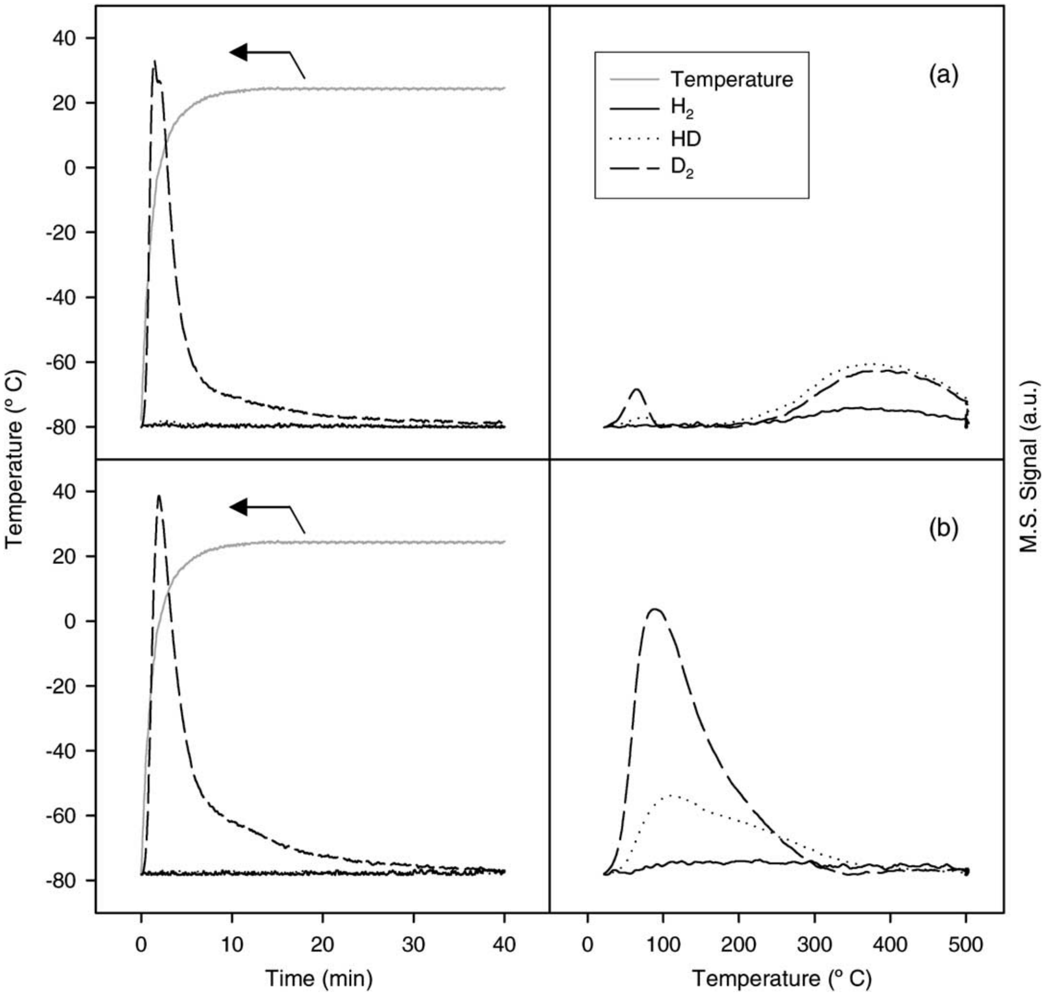

Fig. 5. Thermal desorption studies on Pt/CeO_2 (a) and Pt/SiO_2 (b) catalysts after ITK-H_2/D_2 experiments.

species weekly bound to the surface of some supported platinum catalysts [20,21].

Above 25 °C, the trace for hydrogen desorption typically shows a number peaks [4,22–24]. As previously reported in [4], TPD-H_2 diagrams recorded for a Pt/CeO_2 catalyst pre-treated in the same way consist of two features peaking at about 80 and 400 °C. A similar trace is observed in the present case for the D_2 signal recorded in the TPD diagram following the H_2/D_2 exchange experiment (Fig. 5a). In [4], the peak at 80 °C was interpreted as due to H_2 directly desorbed from the metal; whereas the high temperature peak was attributed to the desorption from the support of hydrogen species which had been previously transferred from the metal to ceria via a spillover mechanism. This latter process might well occur during the heating of the sample inherent to the TPD experiment [4]. Hydrogen spillover phenomena are well known to occur on ceria-supported noble metal catalysts [25].

Our TPD study of the Pt/CeO_2 catalyst also shows that, besides D_2, significant amounts of HD and even H_2 are desorbed (Fig. 5a). This observation clearly shows that H exchange by D is partial, thus suggesting that, under our experimental conditions, a significant fraction of the hydrogen initially chemisorbed on the catalyst is not exchanged. In accordance with the quantitative data reported in Table 2, about 20% of the hydrogen chemisorbed on the Pt/CeO_2 catalyst does not participate in the exchange process.

Under the experimental conditions used in this work, the occurrence of some spillover during the initial treatment with H_2 (5%)/Ar, at 35 °C, cannot be excluded [25]. The likely existence of hydrogen chemisorbed on the support might well explain its inactivity against the exchange process. However, other alternative interpretations are possible. Thus, Tsuchiya et al. [26,27] have reported the occurrence of four types of hydrogen adsorbed on Pt, those referred to as β and δ not being active against the exchange with D_2 in the gas phase. In the present case, additional studies would be required in order to make a well sounded proposal about the nature of the inactive-to-the-exchange hydrogen species.

The TPD diagrams for the Pt/SiO_2 catalysts (Fig. 5b) show the release of larger amounts of deuterium, which indicates a higher number of active sites (see Table 2 for quantitative data). These results are in fairly good agreement with those reported previously [28], where desorption of H_2 in the range of temperatures above RT seems to involve both the metal and support phases. The percentage of H-containing sites active for H_2/D_2 exchange is also higher than for Pt/CeO_2. A different behaviour in the hydrogen spillover processes and/or differences in the nature of the hydrogen–metal interactions might well explain differences observed in the degree of the H/D exchange in Pt/CeO_2 and Pt/SiO_2 catalysts. However, the influence of some residual chlorinated species on the hydrogen adsorption and the spillover processes in the case of the Pt/SiO_2 catalyst [29], and the occurrence of metal-support interaction effects in the case of the Pt/CeO_2 catalyst [4] cannot be discarded.

Table 2
Quantitative data (μmol per g of catalyst) corresponding to the thermal desorption studies on Pt/CeO_2 and Pt/SiO_2 catalysts

Catalyst	−80 °C → RT[a]			RT → 500 °C[a]			H/Pt[b]	D/Pt[b]
	H_2	HD	D_2	H_2	HD	D_2		
Pt/CeO_2	–	–	39.7	7.0	35.0	34.9	0.13	0.48
Pt/SiO_2	–	–	68.5	–	52.1	110.2	0.16	1.27

[a] The figures correspond to the amount of molecular species evolved in the range of temperatures indicated. No HD or H_2 was detected in the sub-ambient temperature range.

[b] Apparent H(D)/Pt ratios obtained from the amount of gas evolved during the thermal desorption experiment.

3.4. *The determination of the number of active sites and the time course of the H/D exchange process from ITK-H_2/D_2 experiments*

As previously described the output of the reactor during an ITK experiment consists of an equilibrium mixture of H_2, HD, and D_2. However, the net amount of H and D atoms in the gas phase depends at any time on the composition feeding the reactor and, more importantly, on the rate at which H atoms are desorbed from the surface. This observation is similar to that found by Tsuchiya et al. [27] for the case of Pt pellets: the isotopic equilibration of gaseous mixtures on Pt occurs much faster than the surface exchange reaction. In our case, invoking the schematic model of Fig. 6, where three types of chemisorbed hydrogen are considered to be present in the catalyst, can easily

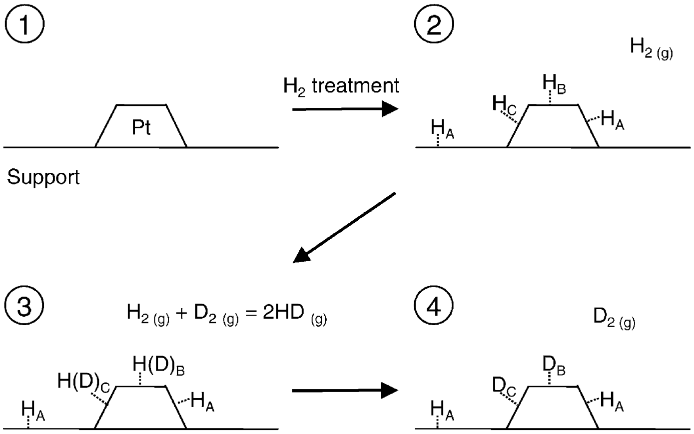

Fig. 6. Scheme of the process involved in a ITK-H_2/D_2 experiment on Pt supported catalyst. After the reduction/evacuation step (1) the sample is treated with H_2 and different species appear on the surface of metal particles and support (2). Although all species are represented as atomic hydrogen, the possibility of molecular adsorption must be also considered, but it is not included in the scheme for simplicity. During the ITK experiment, only H_B and H_C species are exchanged (3). During the transient period, deuterium replaces hydrogen on sites B and C and the gas is an equilibrium mixture of H_2, HD, and D_2. At the end of the experiment (4), sites B and C are occupied by D, but site A contain unexchanged H that is only desorbed at high temperature in the TPD experiment following the ITK process.

accommodate the observations. The disposition of the sites is only qualitative and no structural consequences should be inferred from the figure, it simply illustrates the existence of different types of hydrogen on the sample. Type A consists of hydrogen atoms chemisorbed either on the metal or the support not participating in the exchange reaction. Hydrogen adsorbed on B sites would be very reactive towards equilibration and because of its high activity a low number of such sites would be enough to rapidly equilibrate the gas mixture. Finally, type C chemisorbed hydrogen would be exchanged during the ITK experiment, though the process would be much slower than the isotopic equilibration occurring on B sites. The proposal of two types of sites active for H_2/D_2 exchange (B and C) is based on the ITK results and no information about them were previously available from other experimental techniques. The rapid equilibration of H_2, HD, and D_2 in the gas phase requires sites on the surface very active for exchange (type B), but the isotopic substitution at the surface of the catalyst is much slower and establishes the existence of more inert active sites (type C). As an equilibrium mixture of gases is observed from the beginning of the ITK experiments, when the amount of H exchanged is very small, the number of B sites must be much smaller than that of C sites. In any case, the ITK curves provide information about the number of active sites and the time course of the H_2/D_2 exchange process.

At any time, the net rate at which H atoms evolve from the catalyst surface in an H_2/D_2 experiment can be calculated by simply adding the rate of HD formation to twice the rate of H_2 appearance. Similarly, the rate at which D atoms are adsorbed on the solid surface can be calculated from the corresponding rates of HD formation and D_2 consumption. As the difference curves in Fig. 3 represent the desorption and consumption of H_2, HD, and D_2 at any time, the rates of H and D transfer between the gas and solid phases can be easily calculated for every experimental point and the resulting curves are plotted in Fig. 7. In this figure, the normalised values of the MS signal are maintained to make it comparable to other figures in the work. However, in order to facilitate the mathematical analysis, the times have been corrected by a value of δ to make the initial time to coincide with the point at which the curves begin to deviate from zero.

Fig. 7a illustrates the time dependence of the rate at which H atoms are desorbed from the catalyst. Accordingly, the integration of the curve allows estimating the total amount of atoms transferred and the resulting value may be considered as a direct measurement

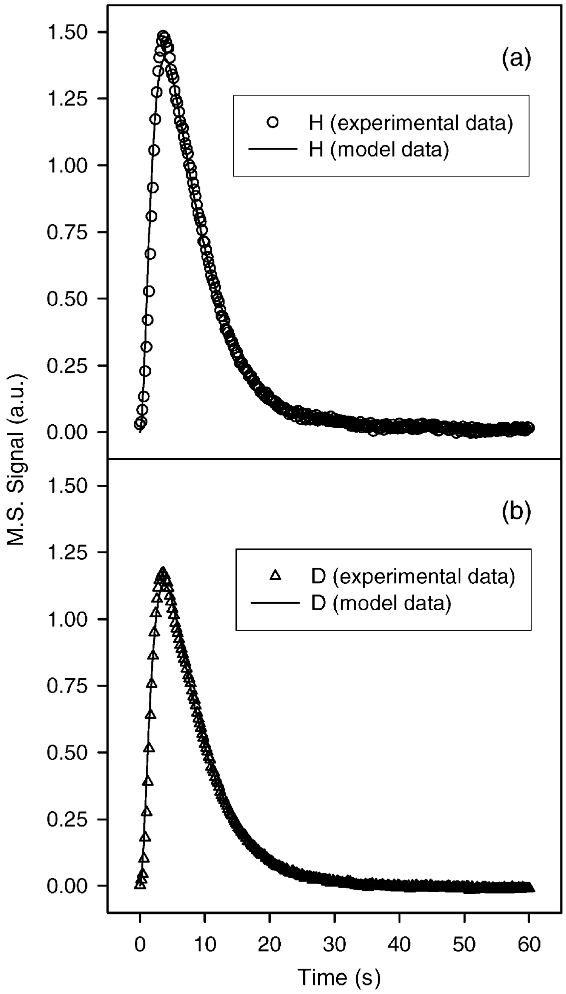

Fig. 7. H evolved (a) and D consumption (b) experimental curves in an ITK-H_2/D_2 experiment on Pt/CeO_2 catalyst. Curves obtained from the SSITKA are also shown.

of the active sites during the exchange process. As the number of sites of type B is very small, the values are a measure of the hydrogen chemisorbed on C sites. In addition to the number of active sites, the curves provide information about the kinetics of the exchange process. Actually, the shape of the curve in Fig. 7a can be well simulated by assuming that the exchange process is first order with respect to the H-containing sites in the solid (Eq. (4)).

$$-\frac{d[H]_s}{dt} = k_H[H]_s \tag{4}$$

In this equation, k_H is the apparent first order rate constant for the exchange process on C sites and $[H]_s$ is the fraction of H-containing active sites in the solid; because of the first order kinetics, $[H]_s$ is expected to show an exponential decay from the initial value (N_H). However, the expected single exponential decay of the curve is modified by the transport of the evolved gases through the reactor and so, the experimental curve will also include the step-function derived from the blank experiments. In that case, Eq. (4) must be written in the form of Eq. (5), where $[H_2]_b$ can be calculated with Eq. (1) and a value of $\delta = 0$.

$$-\frac{d[H]_s}{dt} = f_n k_H N_H [H_2]_b \, e^{-k_H t} \tag{5}$$

The term f_n is a normalisation factor that is required to make the integral of the curve to coincide with N_H and its value is easily calculated to be $(1+\tau k_H)^2$ by imposing the condition in Eq. (6).

$$\int_0^\infty f_n k_H N_H [H_2]_b \, e^{-k_H t} = N_H \tag{6}$$

Substitution in Eq. (5) of the values for f_n and $[H_2]_b$ leads to Eq. (7), and the fit of the curve in Fig. 7a to this equation leads to the values of both the total number of active sites (N_H) and the rate constant of the exchange process (k_H). As the τ parameter for simulating the reactor behaviour was independently determined from the blank experiments, it can be fixed during the refinements at the corresponding values in Table 1. Thus, only N_H and k_H were refined and the final results are included in Table 3, where the values of N_H derived from the normalised curves have been corrected to indicate the total number of sites in the sample.

$$-\frac{d[H]_s}{dt} = (1+\tau k_H)^2 k_H N_H \, e^{-k_H t} \times \left(1 - e^{t/\tau}\left(1 + \frac{t}{\tau}\right)\right) \tag{7}$$

The curve in Fig. 7b represents the rate at which D atoms disappear from the gas and are adsorbed on the catalyst. This curve can be also simulated with Eq. (7) and the values of N_D and k_D so derived are also included in Table 3. As the values of N and k derived from the H and D curves do not coincide, it can be considered an evidence of the operation of isotope effects. Thus, the differences in the number of active sites and

Table 3
Number of active sites and rate constants obtained from the analysis of the curves of H desorption and D consumption during the ITK experiments

Catalyst	H curve		D curve		Mean value	
	N_H (μmol g^{-1})	k_H (s^{-1})	N_D (μmol g^{-1})	k_D (s^{-1})	N (μmol g^{-1})[a]	k (s^{-1})
Pt/CeO$_2$	199	0.153	154	0.163	173 (0.45)	0.158
Pt/SiO$_2$	392	0.078	296	0.080	344 (1.07)	0.079

[a] Apparent H(D)/Pt ratios obtained from N mean values data provided by the mathematical analysis of the H and D curves of SSITKA studies.

k values would indicate an equilibrium isotope effect (EIE) and a kinetic isotope effect (KIE), respectively. The EIE calculated was 1.30 for Pt/CeO$_2$ and 1.32 for Pt/SiO$_2$, whereas the KIE can be estimated in 0.94 for Pt/CeO$_2$ and 0.97 for Pt/SiO$_2$.

Isotope effects are usually neglected in the analysis of ITK experiments [12], but this approximation is not necessarily valid for H$_2$/D$_2$ adsorption because of the large relative difference between the zero point energies for X–H and X–D bonds [30]. Actually, the operation of significant isotope effects is well illustrated in the literature both in homogeneous [31–33] and heterogeneous processes [34], and the values in the present work would simply indicate a moderate normal EIE and a very small inverse KIE. However, there is also the possibility that the differences between the values of N_H and N_D are not caused by isotope effects and that they actually result from errors in the calibration of the MS signals. The errors are expected to be small for the H$_2$ and D$_2$ signals, because the stable readings for $m/z = 2$ or 4 at the beginning or the end of the ITK experiment correspond to 5% H$_2$ or D$_2$ and provide an internal calibration in every experiment. Unfortunately, the same is not true for HD. The absence of signal at $m/z = 3$ during the blank experiments indicates that the only contribution to this signal is that coming from HD, but there is no way in this case to make an internal calibration to obtain the HD concentration. All the curves in this work have been obtained assuming that the response of the mass spectrometer changes linearly within the narrow m/z used (2–4), but any deviation from this behaviour may result in significant errors in the determination of HD concentrations. Consequently, the different values of N and k determined from the H and D curves in Fig. 7 cannot be used to obtain a precise measure of the EIE and KIE and they must be considered to result from the combined effect of calibration errors and isotope effects. In any case, the effect of both factors is not very large and the number of active sites for H$_2$/D$_2$ exchange and the rate constant for the exchange process can be estimated with reasonable precision from the mean values of N and k (see Table 3).

4. Conclusions

The results presented in this work show that the data from H$_2$/D$_2$ ITK experiments carried out on platinum supported catalysts can be easily analysed with a relatively simple mathematical model that provides direct information about the number and activity of the sites involved in the H$_2$/D$_2$ exchange process. On the other hand, the results are well complemented with those derived from thermal desorption studies carried out after the ITK experiments, thus providing a very complete information about the relative amount of the different types of H atoms on the catalyst. The study of the exchange process by combining both techniques is particularly interesting in metal supported catalytic systems, for which conventional characterisation techniques cannot be applied in a straightforward manner [4].

A direct comparison of the mean values of N derived from the SSITKA investigation show that Pt/SiO$_2$ catalyst is able to adsorb hydrogen and then exchange it with deuterium in a significantly larger extension than the Pt/CeO$_2$ sample. As both catalysts have a rather similar metal dispersion, 62 and 65% from electron microscopy results [8,9], our results point out to a different interaction between H$_2$ or D$_2$ and the metal phase in these catalysts. The different rate constants obtained for both catalysts are also consistent with this conclusion. Thus, this kind of results suggests differences in the chemical activity of the platinum microcrystals derived from the different nature of the interaction occurring with the SiO_2 and CeO_2 supports.

The *N* values, expressed as apparent D/Pt ratios in Table 3, are close to those obtained by area integration of the thermal desorption diagrams (Table 2), which constitute an indicator of the reliability of the SSITKA results. However, a precise correlation between the values obtained from both techniques is not possible because of the different approximations involved in each case. The methodology used in this work also allows the estimation of the percentage of hydrogen previously adsorbed that is involved in the isotopic exchange reaction. We are currently carrying out a comprehensive SSITKA-thermal desorption investigation of the Pt/CeO_2, Pt/SiO_2 and related catalysts. The essential features of the experimental curves are similar to those shown in this work and the same mathematical treatment can be applied. Moreover, the analyses of the way in which both parameters change as a consequence of the different treatments provide a very useful information about the catalyst performance, specially in studies aimed to deactivation processes. It can be anticipated at this time that the conclusions so derived about the number and activity of the sites are in good agreement with those obtained from other experimental techniques as HREM and FTIR-CO.

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