

## Mobility of Surface Species on Oxides. 2. Isotopic Exchange of D<sub>2</sub> with H of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, MgO, and CeO<sub>2</sub>: Activation by Rhodium and Effect of Chlorine

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Exchange of D<sub>2</sub> with the OH groups of several oxides was carried out on the samples on which we investigated the <sup>18</sup>O<sub>2</sub>/<sup>16</sup>OH exchange (part I, *J. Phys. Chem.* **1996**, *100*, 9429). Temperature-programmed isotopic exchange was first carried out on the bare oxides. In every case, the reaction follows a simple heteroexchange mechanism, with HD as a primary product. The maximal rates of exchange are obtained at the following temperature: CeO<sub>2</sub> (prereduced), 100 °C > MgO, 120 °C > ZrO<sub>2</sub>, 145 °C > CeO<sub>2</sub> (preoxidized), 160 °C > γ-Al<sub>2</sub>O<sub>3</sub>, 190 °C > Cl-Al<sub>2</sub>O<sub>3</sub>, 200 °C ≫ SiO<sub>2</sub>, 540 °C. The first two samples exchange their hydrogen at a significant rate at room temperature. Secondary peaks and shoulders show the multiplicity of the OH groups on most oxides. Compared to oxygen, hydrogen exchange occurs at much lower temperatures, the shift of the temperature ranges of O and H exchange being between 250 and 430 °C. Isothermal isotopic exchange was carried out between 25 and 100 °C over rhodium catalysts supported on these oxides. The presence of rhodium accelerates the hydrogen exchange, at least by 2 orders of magnitude. As with oxygen exchange, three main steps must be considered: (i) adsorption–desorption on the metal, (ii) transfer of D atoms onto the support (spillover), and (iii) hydrogen diffusion. Contrary to what was observed with O<sub>2</sub> exchange, step i is never a rate-determining step (rds) for H<sub>2</sub> exchange, the rate of H<sub>2</sub> + D<sub>2</sub> equilibration being much higher than the rate of exchange. The results are in accordance with a model where at  $T < 75$  °C the rds of exchange would be the hydrogen transfer from the metal to the support (spillover step), while at  $T \geq 75$  °C, the rds would be the surface diffusion. This model is valid for all the supports except silica, for which most of the hydroxyl groups exchange at high temperatures. The rate of exchange depends linearly on the density of the hydroxyl groups and tends toward zero for a fully dehydroxylated support. Coefficients of surface diffusion give the following order for the hydrogen mobility at 75 °C (base 100 for γ-Al<sub>2</sub>O<sub>3</sub>): CeO<sub>2</sub>, 770 > MgO, 230 > γ-Al<sub>2</sub>O<sub>3</sub>, 100 > ZrO<sub>2</sub>, 23 ≫ SiO<sub>2</sub>, nd. There is no correlation between the hydrogen mobility and the surface acidity of the oxides, the highest hydrogen mobility being found on basic oxides with a very high oxygen mobility. A model of isotropic heterogeneous diffusion is proposed to explain certain discrepancies observed between the present isotopic exchange method and direct IR spectroscopic methods previously published.

### 1. Introduction

In the first part of this study,<sup>1</sup> temperature-programmed isotopic exchange (TPIE) of <sup>18</sup>O<sub>2</sub> with <sup>16</sup>O of several oxides has been used to characterize the ability of the oxides to exchange their surface oxygen. In these experiments the oxide was contacted with pure <sup>18</sup>O<sub>2</sub>, and the temperature was increased from 25 to 800 °C. Monitoring the exchange reaction by mass spectrometry allowed us to determine both the temperature at which the oxide exchanged oxygen and the temperature at which the rate of exchange was maximum. The maximal rates of exchange were obtained at the following temperatures: CeO<sub>2</sub>, 410 °C ≫ CeO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>, 480 °C ≈ MgO, 490 °C > ZrO<sub>2</sub>, 530 °C ≫ γ-Al<sub>2</sub>O<sub>3</sub>, 620 °C ≫ SiO<sub>2</sub>, 850 °C. Moreover, the presence of rhodium accelerated dramatically the oxygen exchange with the support: the maximal rates of exchange could be observed at much lower temperatures, around 200–300 °C, than with the bare oxides. This was attributed to a spillover of oxygen from the rhodium particles to the support. Isothermal isotopic exchange (ISIE) experiments performed on supported Rh catalysts at temperatures at which the direct exchange is negligible (300–400 °C) allowed us to calculate the coefficient of surface diffusion of oxygen on the oxides. At 400 °C, the relative oxygen surface mobility (base 100 for γ-Al<sub>2</sub>O<sub>3</sub>) was CeO<sub>2</sub>, 28 100 ≫ MgO, 500 > ZrO<sub>2</sub>, 280 > CeO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>, 180

> γ-Al<sub>2</sub>O<sub>3</sub>, 100 ≫ SiO<sub>2</sub>, 1.7. We tried to link this surface oxygen mobility to the concentration of the surface basic sites and, except for CeO<sub>2</sub>, there was a good correlation between this surface mobility and the metal–oxygen bond strength in the oxide crystal.

In the second part of this work, we are concerned with the determination of hydrogen surface mobility at the surface of the same oxides. By contrast to oxygen, a great number of works dealing with hydrogen exchange on oxides or supported metal catalysts are available in the literature, and three reviews are concerned mainly with hydrogen spillover.<sup>2–4</sup> Two techniques have been used to study the hydrogen exchange: analysis of the partial pressure of the hydrogen isotopomers [two isotopomers of one molecule are two isomers in which isomerism is due only to the presence of different isotopes of the same element (for example HD and D<sub>2</sub> are two isotopomers of the H<sub>2</sub> molecule)] in the gas phase generally by mass spectrometry (MS) and analysis of the surface hydroxyl groups (OH and OD) by infrared (IR) spectroscopy. The first technique allows one to carry out quantitative, kinetic studies on the exchangeable hydrogen species,<sup>5–7</sup> while the second is well adapted for the determination of the nature of the different hydroxyl groups that could be present and exchanged on the oxides.<sup>8–12</sup> In certain works both methods are used.<sup>13,14</sup> In our work the temperature range of hydrogen exchange and the number of exchangeable hydrogens will be determined by MS analysis. As for the study of hydrogen spillover on supported metal

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**TABLE 1: Nomenclature and Characteristics of the Oxides and the Catalysts**

oxide	principal impurities (ppm)	BET area ( $\text{m}^2 \text{g}^{-1}$ )	catalyst name	metal loading (wt %)	$N_{\text{metal}}$ ( $\mu\text{mol g}^{-1}$ )	metal dispersion (%)
$\text{SiO}_2$	Al: 500 Ti: 300 Cl: 250	200	RhSi	Rh: 0.6	58.3	38
$\gamma\text{-Al}_2\text{O}_3$	Na: 460 Ca: 560 Si: 310 Cl: 80	100	RhAl	Rh: 0.5	48.5	87
$\text{ZrO}_2$	Al: 2000 Si: 100 Ti: 100 Cl: 1000	40	RhZr	Rh: 0.6	58.3	66
MgO	Si: 20 Ca: 20	150	RhMg	Rh: 0.5	48.5	46
$\text{CeO}_2$	La: 1500	60	RhCe	Rh: 0.6	58.3	32

catalysts, two types of strategy can be employed. The first method consists in exchanging the hydrogen through small metal particles dispersed on the surface of the oxide, which implies a multitude of hydrogen species sources (each metal particle).<sup>5,8,15–20</sup> In the second method, the hydrogen diffusing on the support issues from a single source: a grain of a supported metal catalyst deposited on, or in contact with, the oxide studied.<sup>21–30</sup> The above two methods lead to very different coefficients of hydrogen surface diffusion on the oxide surfaces. In this work, we used supported metal catalysts to determine the coefficients of hydrogen surface diffusion on the surface of oxides.

A previous work done in our laboratory<sup>31</sup> showed that oxygen exchange was strongly inhibited by chlorine ions. As for hydrogen exchange, similar results were obtained by Carter et al.<sup>8</sup> on chlorinated  $\text{Pt}/\text{Al}_2\text{O}_3$ , while Hall et al.,<sup>5</sup> who studied the exchange of hydrogen on a fluorinated alumina, showed that the amounts of exchangeable hydrogen were twice less than those observed on an unmodified alumina. So in this work we will also pay particular attention to the effect of a chlorine additive on the hydrogen exchange.

The very nature of the exchangeable hydrogen atoms has been the object of debates in the literature. Some authors<sup>13,32</sup> have suggested that the exchangeable hydrogen species on the surface of alumina were responsible for the oxide acidity. On the contrary, Hall et al.<sup>5</sup> claimed that the acidity of alumina was not due to the exchangeable hydrogen species. In the last part of this paper we will compare the hydrogen mobility determined on the oxides with their Brønsted acidity determined by their catalytic behavior in model reactions.<sup>33</sup>

## 2. Experimental Section

**2.1. Materials.** The characteristics of the five oxides used in this study and the preparation of the supported metal catalysts have been described elsewhere.<sup>1</sup> Their main characteristics are listed in Table 1. To study the effect of chlorine on the exchange and equilibration of hydrogen, oxides and supported metal catalysts were also prepared (Table 2). Chlorine was introduced in two ways: either by HCl adsorption on a chlorine-free precursor or together with the rhodium by using rhodium trichloride.

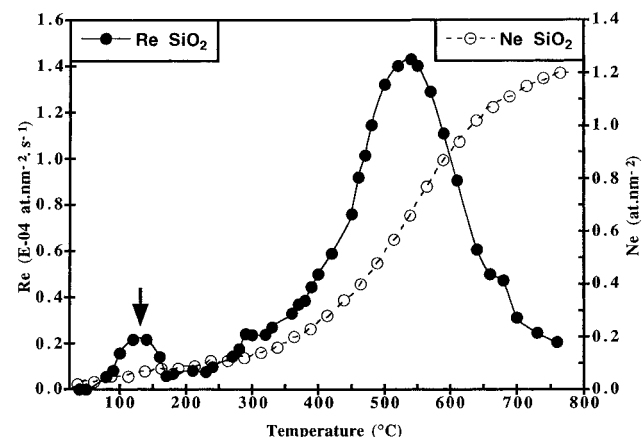
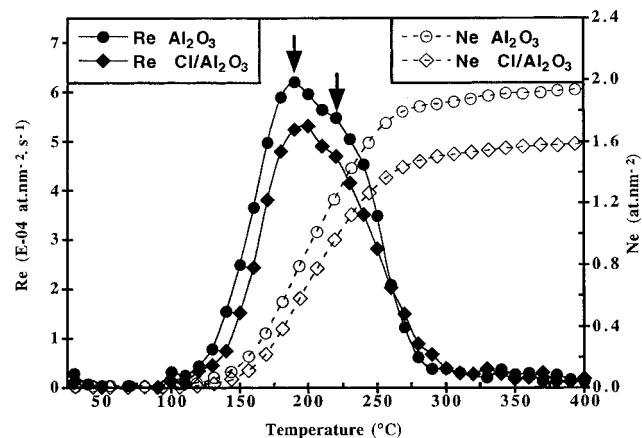
**2.2. Isotopic Exchange Experiments.** All the details concerning temperature-programmed isotopic exchange (TPIE) and isothermal isotopic exchange (ISIE) were given in part 1.<sup>1</sup> The exchange was performed with deuterium supplied by Air Liquide ( $\text{D}_2$  content 99.8%).

Traces of water are well-known to promote hydrogen exchange on the surface of oxides<sup>34</sup> and hydrogen spillover on

**TABLE 2: Chlorinated Alumina and Rh/Alumina Catalysts**

sample	metal precursor	Rh loading (wt %)	chlorine precursor	Cl loading (wt %)
$\text{Cl}/\text{Al}_2\text{O}_3$		0	HCl	0.25
$\text{Rh}/0.1\text{Cl}/\text{Al}$	$\text{Rh}(\text{NO}_3)_3$	0.5	HCl	0.1
$\text{Rh}/0.5\text{Cl}/\text{Al}$	$\text{Rh}(\text{NO}_3)_3$	0.5	HCl	0.5
$\text{Rh}/\text{ACl}/\text{Al}$	$\text{Rh}(\text{Cl})_3$	0.5	$\text{Rh}(\text{Cl})_3$	0.5
$\text{Rh}/\text{DCl}/\text{Al}$	$\text{Rh}(\text{Cl})_3$	0.5	$\text{Rh}(\text{Cl})_3$	0.1 <sup>a</sup>

<sup>a</sup> Obtained from  $\text{Rh}/\text{ACl}/\text{Al}$  sample dechlorinated following the method previously described in ref 31.

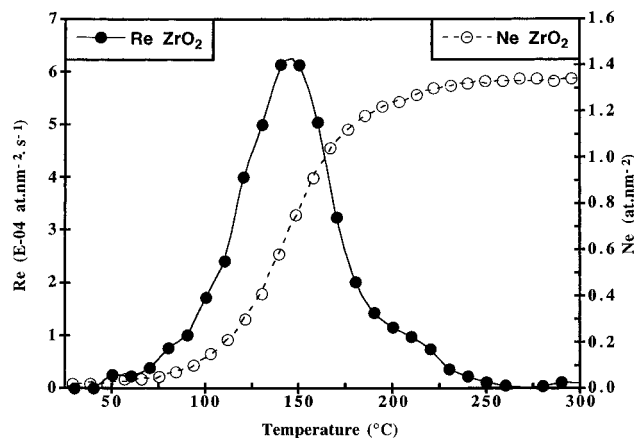
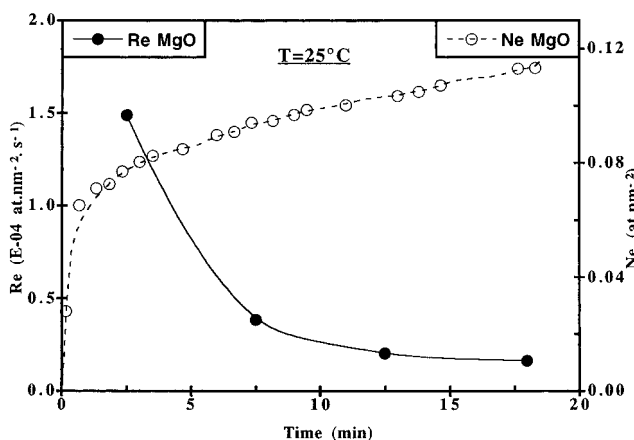
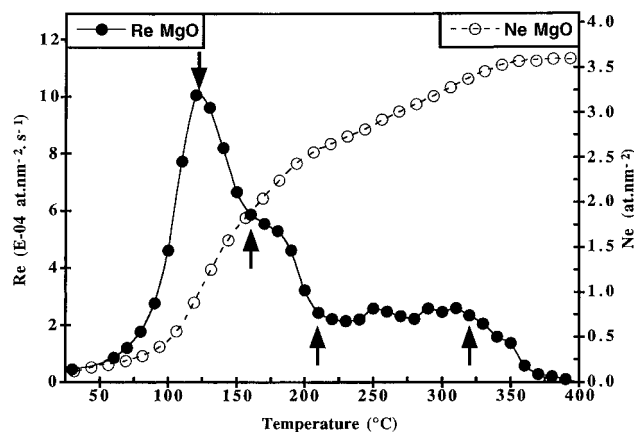
**Figure 1.** Hydrogen TPIE on  $\text{SiO}_2$ .**Figure 2.** Hydrogen TPIE on  $\text{Al}_2\text{O}_3$  and  $\text{Cl}/\text{Al}_2\text{O}_3$ .

metal-supported catalysts.<sup>17,28</sup> For that reason, all the hydrogen exchange experiments were carried out by inserting a liquid nitrogen trap in the closed loop reactor.

## 3. Results

**3.1. Isotopic Exchange on Oxides.** **3.1.1. Exchange Mechanism.** Contrary to what was observed with oxygen exchange, for which there could be two mechanisms (simple and multiple heteroexchange),<sup>1</sup> hydrogen exchange follows, on all the oxides, the simple mechanism that involves the exchange of mononuclear hydrogen species, in agreement with Carter et al.<sup>8</sup> and Shido et al.<sup>14</sup>

**3.1.2. Temperature Range and Number of Hydrogen Species Exchanged during TPIE.** The variations, with the temperature, of the rate of exchange ( $R_e$ ) and of the number of exchanged hydrogen species ( $N_e$ ) for each oxide are shown in Figures 1–7. TPIE experiments were carried out on all the oxides. For those samples for which hydrogen exchange was extremely fast, ISIE experiments were also carried out at 25 °C (MgO, Figure 4;  $\text{CeO}_2$ , Figure 6). Table 3 gives the main results.

Figure 3. Hydrogen TPIE on  $\text{ZrO}_2$ .Figure 4. Hydrogen ISIE at 25 °C on  $\text{MgO}$ .Figure 5. Hydrogen TPIE on  $\text{MgO}$ .

(1) Except for silica (Figure 1), all the oxides exchange hydrogen at low temperature (100–400 °C).

(2) This hydrogen exchange needs a lower activation energy ( $26 \text{ kJ mol}^{-1} < E_a < 72 \text{ kJ mol}^{-1}$ ) than oxygen exchange ( $100 \text{ kJ mol}^{-1} < E_a < 170 \text{ kJ mol}^{-1}$ ).<sup>1</sup>

(3) The maximum rate of exchange ( $R_{e,\text{max}}$ ) is at least 6 times slower than the rate of oxygen exchange. However  $R_{e,\text{max}}$  is obtained at a much lower temperature for  $\text{H}_2$  exchange than for  $\text{O}_2$  exchange.

(4) The amount of hydrogen exchanged varied between 1.2 and 3.0 at  $\text{nm}^{-2}$ , which corresponds to the number of hydroxyl groups present on the oxides after a vacuum treatment at 450 °C.

On silica (Figure 1), the rate of hydrogen exchange is very slow compared to the other oxides (Table 3). The exchange

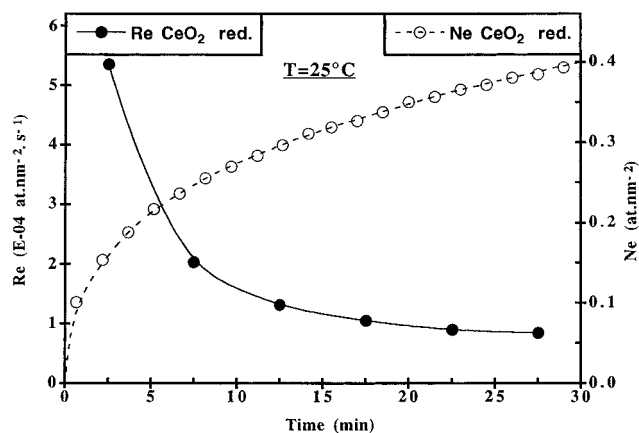
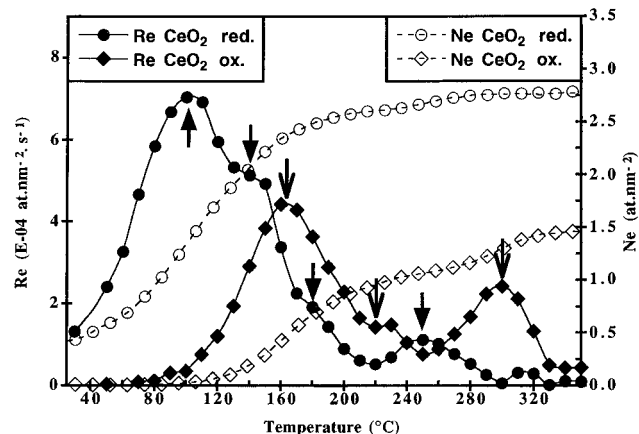
Figure 6. Hydrogen ISIE at 25 °C on reduced  $\text{CeO}_2$ .Figure 7. Hydrogen TPIE on oxidized and reduced  $\text{CeO}_2$ .

TABLE 3: Results of TPIE Experiments on Oxides

oxide	exchange temperature range (°C)	temperature of maximum rate (°C)	$R_{e,\text{max}}$ ( $10^{-4}$ at $\text{nm}^{-2} \text{ s}^{-1}$ )	$E_a$ ( $\text{kJ mol}^{-1}$ )	$N_e$ final (at $\text{nm}^{-2}$ )
$\text{SiO}_2$	80–800+	540	1.4	30	1.2
$\gamma\text{-Al}_2\text{O}_3$	100–400	190	6.2	72	2.0
$\text{Cl/Al}_2\text{O}_3$	100–400	200	5.3	62	1.6
$\text{ZrO}_2$	50–300	145	6.3	48	1.4
$\text{MgO}$	25–400	120	10.1	47	3.6
$\text{CeO}_2$ red.	25–350	100	7.1	26	2.8
$\text{CeO}_2$ ox.	80–350	160	4.5	59	1.4

process occurs mainly between 400 and 800 °C, which proves that hydrogen is very difficult to exchange on silica. The amount of exchanged hydrogen (1.2 at  $\text{nm}^{-2}$ ) and the temperature of exchange are in agreement with the results of Hall et al.,<sup>6</sup> who found a maximum rate of exchange between 610 and 625 °C and a number of exchanged species between 1.6 and 2.6 at  $\text{nm}^{-2}$ . It can be seen in Figure 1 that a very small amount of reactive hydrogen ( $\sim 0.1$  at  $\text{nm}^{-2}$ ) is able to exchange between 100 and 180 °C.

On alumina (Figure 2), hydrogen exchange occurs between 100 and 400 °C. The TPIE experiment allows us to distinguish between two types of hydrogen, the temperature of their maximum rates of exchange being respectively 190 and 220 °C. When fully hydroxylated,  $\gamma$ -alumina possesses five<sup>35,36</sup> or six<sup>37</sup> types of hydroxyl groups. Peri et al.<sup>13,35</sup> showed that after a treatment at 400 °C there was no longer any physisorbed water on alumina. At 450 °C the amount of hydrogen on alumina is around 3 at  $\text{nm}^{-2}$ , and at 650 °C, only three types of hydroxyl groups (1.5 at  $\text{nm}^{-2}$ ) remain detectable on alumina. Our results obtained after a vacuum treatment at 450 °C are in good agreement with these data.

Concerning the *chlorinated alumina* sample, the temperature range and the shape of the curve of the hydrogen exchange are the same as those of the unmodified sample (Figure 2). Chlorine decreases the number of exchangeable hydrogen species. The impregnation of 0.25 wt % of chlorine (0.42 atoms of Cl per nm<sup>2</sup>) leads to the disappearance of 0.4 exchangeable atoms of H per nm<sup>2</sup> (Table 3). This is in agreement with the hydrogen substitution mechanism during chlorine impregnation proposed by Ahmed.<sup>38</sup> The decrease of the maximum rate of exchange is due to the decrease of the amount of exchangeable hydrogen, but the shoulder at 220 °C is always present on the curve of the chlorinated sample.

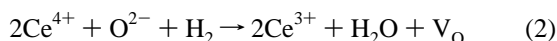
On *zirconia* (Figure 3), only one type of hydroxyl group could be distinguished. The exchange occurs between 50 and 300 °C and 1.4 at nm<sup>-2</sup> of hydrogen is exchanged. This quantity is small and suggests that zirconia is highly dehydroxylated after a vacuum thermal treatment at 450 °C. Although zirconia is known to dissociate molecular hydrogen at room temperature,<sup>11,12,39</sup> the exchange of hydrogen occurs only above 50 °C.

On *magnesia*, hydrogen exchange can be observed at 25 °C (Figure 4). At this temperature, the rate of exchange is initially high ( $1.5 \times 10^{-4}$  at nm<sup>-2</sup> s<sup>-1</sup>) but decreases rapidly. However the amount of hydrogen exchangeable at 25 °C (0.11 at nm<sup>-2</sup>) is relatively small. When the temperature is ramped (Figure 5), a first peak of exchange is observed at 120 °C, with a shoulder at 160 °C and a plateau between 210 and 320 °C. Lastly the exchange is total around 400 °C. The multiplicity of the peaks, shoulders, and secondary peaks on the plateau suggests the presence of numerous types of hydroxyl groups on MgO. This is in accordance with the work of Shido et al.,<sup>14</sup> who distinguished six types of hydroxyl groups with different reactivity on magnesia. On the other hand, Dunski et al.<sup>40</sup> found by hydrogen thermodesorption eight types of hydrogen on magnesia.

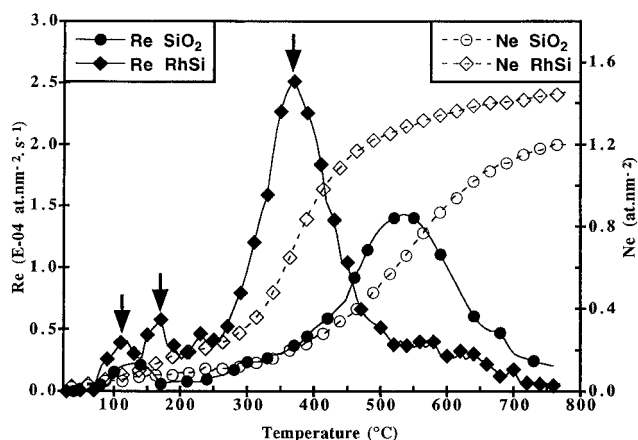
On *ceria*, two cases must be considered depending on the state of its surface. (i) When ceria is reduced at 450 °C before exchange, hydrogen exchange starts at room temperature (Figure 6). This exchange could be due to the presence of reduced sites of cerium, which can be formed at low temperature (200 °C and above) under hydrogen atmosphere.<sup>41–43</sup> At 25 °C, the initial rate of exchange is about  $5.5 \times 10^{-4}$  at nm<sup>-2</sup> s<sup>-1</sup> and decreases rapidly when the total amount of exchangeable hydrogen (0.4 at nm<sup>-2</sup>) is exchanged. When the temperature is ramped (Figure 7), a first peak of exchange is observed at 100 °C, with two shoulders at 140 and 180 °C. Lastly a second peak is observed at 250 °C. The total amount of hydrogen exchanged on this sample is 2.8 at nm<sup>-2</sup>. (ii) When ceria is submitted only to an oxidative treatment before exchange, the exchange begins only at 100 °C. A first peak centered at 160 °C can be observed with a shoulder at 220 °C. A second peak appears at 300 °C. On this sample the amount of hydrogen exchanged is twice less (1.4 at nm<sup>-2</sup>) than on the prereduced sample. Above 350 °C the exchange reaction is significantly altered by the reaction of D<sub>2</sub> with CeO<sub>2</sub>, leading to a reduction of the ceria surface. The relatively large amount of H exchanged on the prereduced ceria is in agreement with the formation of hydroxyl groups and hydrides during the H<sub>2</sub> treatment:



where V<sub>O</sub> is an oxygen vacancy that could pre-exist on ceria or be formed during the reducing treatment at 450 °C,

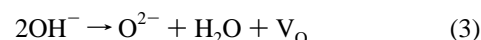


while H<sub>O</sub><sup>-</sup> designates an oxygen vacancy filled with a hydride anion.



**Figure 8.** Effect of the presence of Rh on the hydrogen exchange on silica.

Depending on the duration of the outgassing, new vacancies can be created by condensation of two adjacent hydroxyl groups:



The formation of hydride species by reaction 1 has been recently verified by Lamonier et al., who used specific catalytic probe reaction of these hydride species.<sup>44,45</sup>

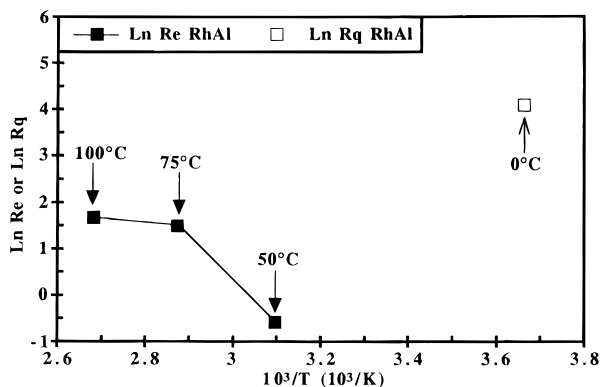
To summarize, we wish to underline that, except on silica, hydrogen exchanges on the surface of the oxides at low temperature (100–200 °C). Temperature-programmed isotopic exchanges (TPIE) of hydrogen allows us to rank the oxides according to their maximal rates of exchange obtained at the following temperatures: CeO<sub>2</sub> red., 100 °C > MgO, 120 °C > ZrO<sub>2</sub>, 145 °C > CeO<sub>2</sub> ox., 160 °C > γ-Al<sub>2</sub>O<sub>3</sub>, 190 °C > Cl/Al<sub>2</sub>O<sub>3</sub>, 200 °C ≫ SiO<sub>2</sub>, 540 °C. For the first two samples, hydrogen exchange starts at room temperature.

### 3.2. Isotopic Exchange on Supported Rh Catalysts. 3.2.1.

*Presence of Rhodium.* The specific effect of rhodium on hydrogen exchange was studied on silica. This support was used because, compared to other oxides, it exchanged hydrogen at higher temperature. TPIE of hydrogen on Rh/SiO<sub>2</sub> (denoted RhSi) and SiO<sub>2</sub> is shown in Figure 8. On the rhodium catalyst like on silica, a small amount of hydrogen is exchanged below 200 °C (14% of the total in the case of RhSi). On RhSi, two little peaks at 110 and 170 °C can be observed within the 20–200 °C temperature range. However, most hydrogen is exchanged between 250 and 450 °C ( $T_{\text{max}}$  370 °C) on RhSi and between 400 and 700 °C ( $T_{\text{max}}$  540 °C) on silica. The amount of exchanged hydrogen is slightly higher (+20%) on RhSi than on silica, but the maximal rate of exchange is definitely higher (+79%) on the catalysts than on the bare support. The presence of rhodium decreases by about 200 °C the temperature at which the hydrogen exchange occurs on silica. Nevertheless, this temperature remains relatively elevated, which shows the difficulty of exchanging hydrogen on silica.

### 3.2.2. Choice of the Temperature for ISIE on Supported

*Metal Catalysts.* As for oxygen,<sup>1</sup> the surface mobility of hydrogen can be evaluated from exchange experiments provided that two conditions are fulfilled: (i) the exchange must occur through the metal particles, the rate of direct exchange with the oxide being negligible, and (ii) the hydrogen mobility on the oxide must be the rate-determining step of the exchange process. Preliminary experiments were carried out on RhAl in order to determine the most convenient temperature for isothermal exchange. In practice, these experiments have to be performed within a temperature range where (i) the rate of exchange on the bare support is significantly lower than on the

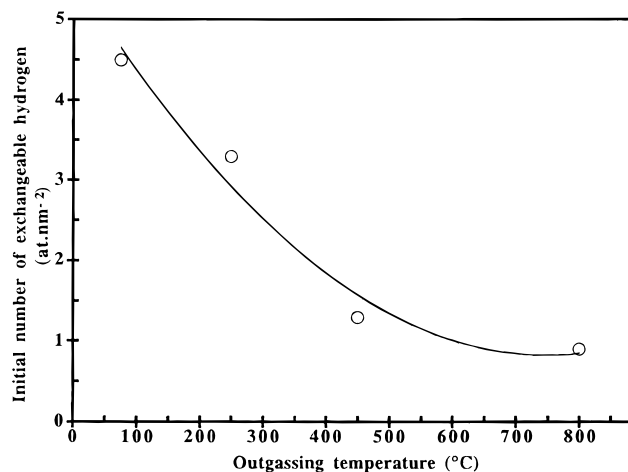


**Figure 9.** Arrhenius plot of the initial rate of exchange and rate of equilibration at 0 °C on RhAl.

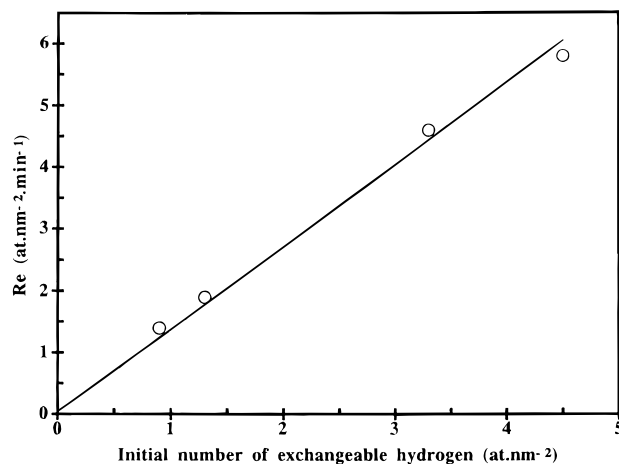
supported rhodium catalyst and (ii) the rate of equilibration (representing the rate of adsorption–desorption of H<sub>2</sub> on the metal surface) is definitely higher than the rate of exchange on the same catalyst. Considering the reduced temperature range (100–200 °C) where the hydrogen exchange on the oxides could be observed, we carried out ISIE experiments at 25, 50, 75, and 100 °C and H<sub>2</sub> + D<sub>2</sub> isotopic equilibration at 0 °C on the RhAl catalyst (Figure 9). At 25 °C the rate of hydrogen exchange is too slow to be accurately measured. On the Arrhenius plot of the initial rate of exchange, a break point is observed at  $T_0 = 75$  °C. This change in the energy of activation indicates a change in the rate-determining step of the exchange process. A similar behavior was observed for oxygen exchange on RhAl at  $T_0 = 285$  °C and also interpreted as a change in the rate-determining step.<sup>1</sup> At  $T < T_0$ , the oxygen exchange was shown to be limited by the adsorption–desorption step on the metal: below 285 °C, O<sub>2</sub> equilibration and O<sub>2</sub> exchange occurred at the same rate on RhAl.<sup>1</sup> This is not the case for H<sub>2</sub> exchange: owing to the high value of the rate of equilibration measured on RhAl at 0 °C (Figure 9), we can conclude that the rate of the adsorption–desorption step on metal particles is never the rate-determining step of exchange within the 25–100 °C temperature range. We can propose that below 75 °C, the step of hydrogen transfer from metal particles to the surface of the oxide (spillover step) is likely to be the rate-determining step of exchange so that ISIE experiments must be carried out at  $T \geq 75$  °C. As the first condition implied that hydrogen exchange could be carried out below 100 °C, we decided to perform all the ISIE experiments on supported rhodium catalysts at 75 °C.

**3.2.3. Effect of the Degree of Dehydroxylation (Case of Zirconia).** The hydroxyl coverage of RhZr was changed by outgassing the catalyst at different temperatures between 75 and 800 °C. ISIE experiments carried out on these samples allowed us to determine the number of exchangeable hydrogen species ( $N_s$ ) as well as the initial rate of exchange  $R_e^\circ$ . When the outgassing temperature is increased between 75 and 450 °C,  $N_s$  decreases rapidly (Figure 10). In contrast, between 450 and 800 °C the number of hydrogens seems to be stable around 1–1.5 at nm<sup>-2</sup>. The initial rate of hydrogen exchange  $R_e^\circ$  increases linearly with the number of hydrogen species at the surface of the oxide (Figure 11). As expected,  $R_e^\circ$  tends toward zero for a fully dehydroxylated surface. Similar results were obtained with Rh/Al<sub>2</sub>O<sub>3</sub> catalysts.<sup>19</sup> The standard temperature for the vacuum thermal treatment before the ISIE experiments on supported Rh catalysts was fixed at 450 °C. At this temperature we expected to have roughly the same density of hydroxyl groups on each oxide investigated in this study (1–2 OH nm<sup>-2</sup>).

**3.2.4. Exchange on Supported Rh Catalysts.** The ISIE experiments on supported Rh catalysts were carried out at 75



**Figure 10.** Initial number of exchangeable hydrogens at 25 °C on RhZr versus the temperature of the vacuum thermal treatment.



**Figure 11.** Change of the initial rate of exchange with the initial number of exchangeable hydrogens.

**TABLE 4: Results of ISIE Experiments on Supported Rh Catalysts at 75 °C**

catalyst	initial rate $R_e$ (at nm <sup>-2</sup> min <sup>-1</sup> )	$N_e$ after 3 min (at nm <sup>-2</sup> )	$N_e$ after 30 min (at nm <sup>-2</sup> )	$R_e$ Rh/oxide/ $R_e$ oxide
RhSi	0.8	0.2	1.6	1300
RhAl	4.5	2.3	3.7	7500
RhZr	4.8	1.4	2.5	1300
RhMg	1.3	0.8	2.0	140
RhCe (red.)	4.2	1.4	4.0	130

°C, after a vacuum thermal pretreatment at 450 °C. The results are given in Table 4. On all the catalysts, the exchange occurs mainly through rhodium particles. For each sample, the rate of exchange at 75 °C is at least 130 times higher than on the bare oxide at the same temperature (see column 5, Table 4). Except on magnesia, the amounts of hydrogen exchanged after 30 min (Table 4) are larger than those observed after TPIE experiments carried out on the bare oxides. This is due to the presence of Rh particles, which act as a donor of hydrogen atomic species onto the support during the catalyst reduction. A part of this spilled-over hydrogen could not be removed during the sample evacuation. In the case of magnesia, for which the amount of hydrogen exchanged on RhMg is lower than on the bare support, two explanations can be proposed: (i) the presence of the rhodium would allow an advanced dehydroxylation of the oxide surface during the vacuum thermal treatment and the amount of exchangeable hydrogen on the support would then be smaller; (ii) the temperature of 75 °C is

**TABLE 5: Initial Rate for Hydrogen Equilibration at 0 °C on Chlorinated Rh/Alumina Catalysts**

sample	initial rate $R_q$ ( $10^{21}$ at $\text{m}^{-2}$ Rh $\text{min}^{-1}$ )	Cl loading (wt %)
RhAl	3.0	0.0
Rh/0.1Cl/Al	4.7	0.1
Rh/0.5Cl/Al	6.6	0.5
Rh/ACl/Al	6.9	0.5
Rh/DCI/Al	4.8	0.1

**TABLE 6: Initial Exchange Rate and Number of Hydrogens Exchanged for ISIE at 75 °C on Chlorinated Rh/Alumina Catalysts**

sample	initial rate $R_e$ (at $\text{m}^{-2}$ $\text{min}^{-1}$ )	$N_e$ after 3 min (at $\text{nm}^{-2}$ )	$N_e$ after 30 min (at $\text{nm}^{-2}$ )
RhAl	4.5	2.3	3.7
Rh/0.1Cl/Al	3.9	1.8	3.5
Rh/0.5Cl/Al	1.5	1.4	3.4
Rh/ACl/Al	1.2	0.7	2.5
Rh/DCI/Al	6.1	2.4	3.9

too low to exchange the whole of the hydrogen present on magnesia. From these ISIE measurements, we can propose the following order for the catalysts according to their initial rate of exchange at 75 °C:

$$\text{RhZr}, 4.8 > \text{RhAl}, 4.5 > \text{RhCe (red.)}, 4.2 \gg \text{RhMg}, 1.3 \gg \text{RhSi}, 0.8$$

**3.3. Effect of Chlorine on Hydrogen Exchange on Supported Rh/Alumina.** *3.3.1. Hydrogen Equilibration.*  $\text{H}_2/\text{D}_2$  equilibration was carried out at 0 °C on the different chlorinated Rh/alumina catalysts (Table 2) to determine the effect of chlorine on the rate of the adsorption–desorption on rhodium particles. The results, in terms of initial equilibration rates by unit of rhodium surface area, are listed in Table 5. By contrast to what was previously observed for oxygen equilibration,<sup>31</sup> chlorine is a promoter for hydrogen equilibration on rhodium particles. Moreover whatever the chlorine precursor (HCl or  $\text{RhCl}_3$ ) the same equilibration rate was observed for those catalysts having the same chlorine content. A content of 0.5 wt % of chlorine doubles the rate of exchange of the unmodified sample. The results should be compared with those of Goodman,<sup>47</sup> who showed that chlorine inhibited the hydrogen chemisorption on metal particles. In our case we can propose that, at 0 °C, the rate of equilibration is controlled essentially by the rate of hydrogen desorption from rhodium particles. Owing to its electron-acceptor property, chlorine decreases the strength of the metal–hydrogen bond, which leads to an increase of the equilibration rate.

*3.3.2. Hydrogen Exchange.* As observed by Carter et al.,<sup>8</sup> chlorine is a poison for hydrogen exchange. The initial rate of exchange and the amount of exchanged hydrogen (Table 6) decrease when the chlorine content increases. There are two explanations for this inhibiting effect.

(i) The first concerns the amount of hydrogen species. We have already seen that chlorine impregnation occurred according to a hydrogen substitution mechanism (section 3.1.2) and that the rate of exchange depended on the amount of hydrogen on the oxide (section 3.1.2). Thus we can expect that, when the amount of chlorine increases, the amount of hydrogen will decrease and the rate of exchange decreases.

(ii) The second explanation is linked to the presence of chlorine atoms directly bonded to terminal Al at the surface of alumina. These  $-\text{Al}-\text{Cl}$  groups create electronic interactions which could increase the strength of the O–H bond for the hydroxyl group localized close by when the exchange of these hydrogen species is more difficult. For a chlorine content of

**TABLE 7: Coefficients of Hydrogen Surface Diffusion on Oxides at 75 °C**

catalyst	$D_s$ ( $10^{-19}$ $\text{m}^{-2}$ $\text{s}^{-1}$ )
RhAl	4.3 (5.3 at 100 °C)
RhZr	1.0
RhMg	9.5
RhCe (red.)	33.2
Rh/0.1Cl/Al	3.5
Rh/0.5Cl/Al	0.5
Rh/ACl/Al	0.3
Rh/DCI/Al	8.9

0.5 wt %, the amount of exchanged hydrogen and the rate of exchange are lower on the catalysts prepared from metal chloride salt (Rh/ACl/Al) than on the catalysts chlorinated with HCl (Rh/0.5Cl/Al) (see Table 6). In the case of Rh/ACl/Al, this is probably due to a localization of chlorine near and around the metal particles. Thus, the additive acts as a barrier against hydrogen surface diffusion on the oxide surface. When this catalyst is dechlorinated (Rh/DCI/Al) with a  $\text{H}_2/\text{H}_2\text{O}$  mixture at 500 °C,<sup>31</sup> the residual chlorine content is about 0.1 wt %. Nevertheless, on this catalyst the amount of exchanged hydrogen and the initial rate of exchange are higher than on the unmodified sample. An explanation for these results could be found if we consider the technique used for the dechlorination process. As suggested, chloride ions are located around the metal particles when chlorine is impregnated on the support at the same time as rhodium from  $\text{RhCl}_3$ . During the dechlorination, these chloride species are substituted by hydroxyl groups, which confers to these catalysts a high hydroxyl group density in the vicinity of the metal particles. In this case the slight negative effect of the residual chlorine (about 0.1 wt %) is compensated by the positive effect due to the proximity between the hydroxyl groups and the metal particles. The hydrogen migration on the oxide surface occurs over a shorter distance than in the unmodified sample, and for a same amount of exchanged hydrogen atoms, the rate is higher on the dechlorinated sample.

## 4. Discussion

**4.1. Determination of the Coefficients of Hydrogen Surface Diffusion.** In the first part of this series of papers, we have reported that ISIE experiments carried out on supported metal catalysts allow the determination of the coefficients of surface diffusion.<sup>1</sup> However, certain conditions must be fulfilled. This has been verified for oxygen exchange<sup>1</sup> and here for hydrogen exchange. We showed that, at 75 °C, the rate of direct exchange between the gas phase and the oxide surface was extremely slow when compared to the rate of exchange via the rhodium particles (Table 4). Furthermore, we observed that the rate of hydrogen equilibration on Rh particles at 0 °C was 13 times higher than the rate of exchange at 75 °C (Figure 9). We concluded that the adsorption–desorption of  $\text{H}_2$  on rhodium particles was not the rate-determining step of the exchange process at 75 °C. However, a change in the activation energy was observed around 75 °C and interpreted as a change of the rate-determining step for the exchange process. At  $T < 75$  °C, the transfer of hydrogen between metal particles and oxide surface (spillover step) is likely to be the rate-determining step, while at  $T \geq 75$  °C, the migration of hydrogen on the support would be the rate-controlling step of exchange.

Thus the model of surface diffusion of oxygen on Rh catalysts<sup>1</sup> can apparently be used for hydrogen at 75 °C. The coefficients of hydrogen surface diffusion are listed in Table 7. On  $\text{SiO}_2$  and RhSi (Figure 8), only a few of the hydrogen species

of silica are exchanged at 75 °C. Therefore, in Table 7, we do not report the coefficient of hydrogen diffusion on silica because it is not representative of the most abundant species present on the surface of silica. As for the other oxides, reduced ceria presents the highest hydrogen mobility, followed by magnesia, alumina, and zirconia. For a given oxide, the coefficient of hydrogen diffusion depends on the degree of dehydroxylation (see Figure 12 for RhZr).

The literature reports on a wide range of values for the coefficient  $D_s$  of hydrogen diffusion on oxides and on carbon.<sup>47</sup> The values of  $D_s$  depended mainly on the experimental method used for diffusion measurements, which led to conflicting conclusions about the limiting step of exchange.

Cevallos Candau and Conner<sup>29,30</sup> have developed a spatially and temporally resolved IR method allowing them to determine the OD concentration profiles on a silica wafer versus the distance to a point source constituted of a small amount of Pt/Al<sub>2</sub>O<sub>3</sub> catalyst.<sup>27,29,30</sup> Their results are in agreement with a model in which the transfer of H species from the metal to the support (spillover step) should be the rate-determining step of exchange. Assuming a kinetics of diffusion based on Fick's law, the values of hydrogen diffusion measured between 200 and 250 °C on silica are found between 10<sup>-7</sup> and 10<sup>-8</sup> m<sup>2</sup> s<sup>-1</sup>.<sup>27,30</sup> These values are 10 orders of magnitude higher than those measured in the present work.

Cavanagh and Yates,<sup>16</sup> Bianchi et al.,<sup>28</sup> and Kramer and Andre<sup>48</sup> consider that the diffusion of hydrogen across the surface of oxide is the rate-determining step during the exchange process<sup>16,28</sup> or during the thermodesorption of hydrogen species that have migrated on the oxide surface.<sup>48</sup> Assuming a surface diffusion of hydrogen species coming from the metal particles considered as circular sources of hydrogen, Kramer and Andre<sup>48</sup> have found a value of 0.9 × 10<sup>-19</sup> m<sup>2</sup> s<sup>-1</sup> for the diffusion of hydrogen on alumina at 400 °C. This value is on the same order of magnitude as those measured on several oxides in this article (Table 7). However, the activation energy of diffusion calculated from the values of  $D_s$  obtained at 75 and 100 °C on RhAl (Table 7) is 9.5 kJ mol<sup>-1</sup>. This value corresponds to a weakly activated diffusion process as opposed to a highly activated process like in the case of Kramer and Andre.<sup>48</sup>

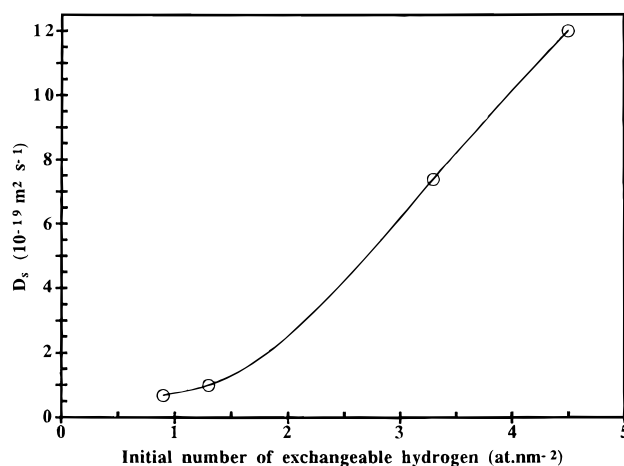
In summary, direct measurements based on the determination of concentration profiles from a point source give very high values of  $D_s$  (~10<sup>-8</sup> m<sup>2</sup> s<sup>-1</sup>). On the contrary, indirect measurements based on the determination of fluxes of diffusion from a very high number of point sources give values of  $D_s$  in the 10<sup>-17</sup> to 10<sup>-19</sup> m<sup>2</sup> s<sup>-1</sup> range. As shown in the first part,  $D_s$  is calculated by

$$D_s = \left( \frac{\pi}{4} \right) \left( \frac{S_1}{C_{*X} I_0} \right)^2 \quad (4)$$

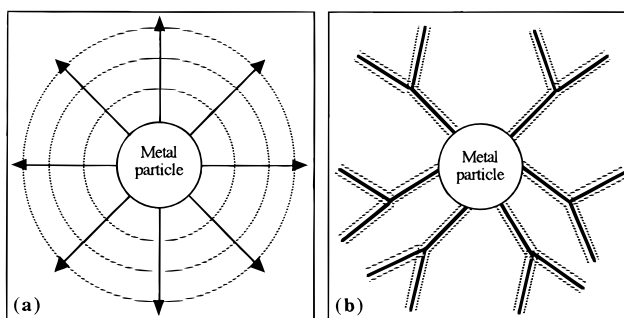
where  $S_1$  is the initial slope of the curve representing the variation of the number of exchanged atoms  $N_e^t$  as a function of  $\sqrt{t}$ ,  $C_{*X}$  is the concentration of D atoms on the metal particles at  $t = 0$  (assumed to be close to the monolayer, i.e. 1.33 × 10<sup>19</sup> atoms m<sup>-2</sup> for Rh), and  $I_0$  is the total circumference of the metal particles.  $I_0$  can be related to the rhodium content  $x_m$  (wt %) and the percentage of dispersion  $D$ :<sup>49</sup>

$$I_0 = \alpha x_m D^2 \quad (5)$$

where  $\alpha$  is a parameter depending on the nature of the metal and on the particle shape. For hemispherical particles of rhodium  $\alpha = 8.8 \times 10^5$  m g<sup>-1</sup> cat, while for cubic particles of the same metal,  $\alpha = 4.2 \times 10^5$  m g<sup>-1</sup> cat. For the calculation of  $D_s$  (Table 7), the value of 8.8 × 10<sup>5</sup> corresponding to



**Figure 12.** Effect of the degree of dehydroxylation on the coefficient of hydrogen surface diffusion.



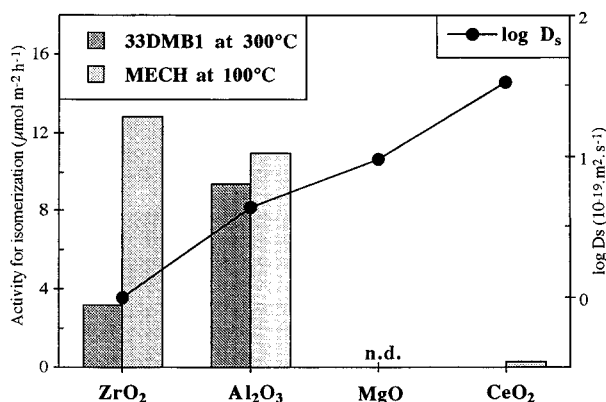
**Figure 13.** (a) Model of homogeneous diffusions. (b) Model of heterogeneous diffusion along preferential pathways. In a and b, dotted lines present isoconcentration lines.

hemispherical particles was used. The following points concerning the calculation of  $D_s$  must be stressed.

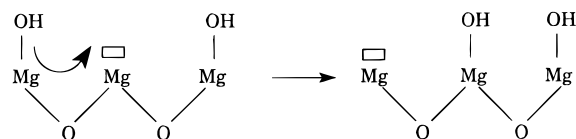
(i) Very great values of  $I_0$  are currently obtained with supported catalysts (10<sup>8</sup> or 10<sup>9</sup> m g<sup>-1</sup>), which means that there is no need for great values of  $D_s$  to have significant fluxes of diffusion across the metal/support interface.

(ii) The calculated values of  $D_s$  depend closely on the values of the metal dispersion ( $D_s \approx D^4$ ). However the precision on the dispersion measurements is sufficient to obtain coherent values of  $D_s$ . At the worse, this dispersion effect can only account for a variation of 1 order of magnitude on the values of  $D_s$ .

(iii) The determination of  $D_s$  is based on a homogeneous diffusion model: the diffusion occurs in all the directions around the metal particles, and all the atoms located at the metal/support interface serve as a porthole for the diffusion on the support (Figure 13a). In the case of silica, Cevallos Candau and Conner<sup>30</sup> have proposed a mechanism of hydrogen diffusion along chains of OH species, named "associated hydroxyls", exchanging hydrogen as a "bucket brigade". In this case, the model of heterogeneous diffusion represented in Figure 13b would be valid and the value of  $I_0$  in eq 4 should be restricted to the size of the "gates" at the metal/support interface, allowing the hydrogen to diffuse on the support. The size of these gates would be very small (less than 1% of the total perimeter), which induces extremely large variations in the calculated values of  $D_s$ . In the model of heterogeneous diffusion, only a small fraction of the OH groups could normally be exchanged. However, the presence of a very great number of particles (10<sup>13</sup>–10<sup>14</sup> per m<sup>2</sup>) can create an interconnected network of these chains of diffusion like those represented in Figure 13b.

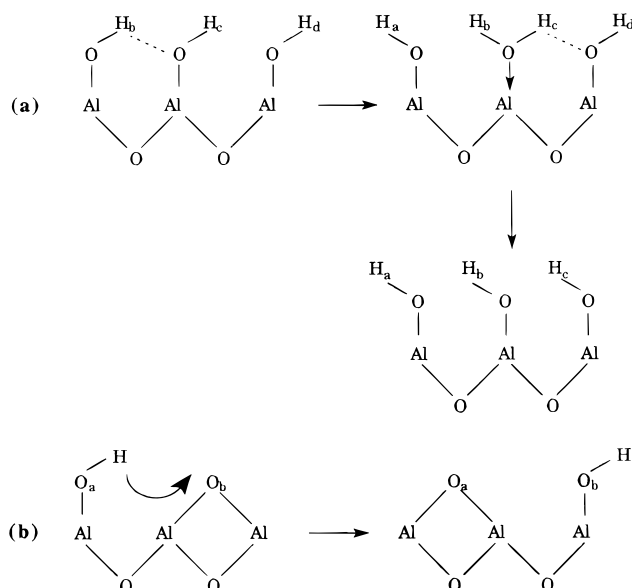


**Figure 14.** Change of the coefficient of hydrogen diffusion with the Brønsted acidity of the oxides determined by 3,3-dimethylbut-1-ene isomerization (33DMB1) and methylenecyclohexane isomerization (MECH).



**Figure 15.** Mechanism of the hydrogen migration across the surface of basic oxides like MgO and CeO<sub>2</sub>.

**4.2. Acidity of the Oxides and Mechanisms of Hydrogen Migration.** In the first part, we showed that there existed a good correlation between the oxygen surface diffusion and the basicity of the oxides.<sup>1</sup> Having determined here the coefficients of hydrogen diffusion on these oxides, we attempt to search for a possible correlation with the acidity of the oxides. The acid properties of the oxides have been determined by means of three model reactions described elsewhere.<sup>33</sup> Here we wish only to evaluate the change of the coefficients of hydrogen diffusion with the Brønsted acidity of the oxides. The working hypothesis is that the Brønsted acidity is linked to the strength of the O–H bond and, in this way, to the hydrogen mobility. For this purpose, we have represented in Figure 14 the change of the coefficient of hydrogen diffusion at 75 °C with the acidity of the oxides determined by 3,3-dimethylbut-1-ene isomerization (33DMB1) at 300 °C and methylenecyclohexane isomerization (MECH) at 100 °C.<sup>33</sup> As we can observe in Figure 14, there is no apparent correlation between the hydrogen mobility and the Brønsted acidity of the oxides. Moreover, basic oxides like ceria and magnesia present the highest hydrogen mobility. By contrast, an amphoteric oxide like zirconia presents the lower hydrogen mobility. The activation energy for hydrogen exchange (26–72 kJ mol<sup>-1</sup>) and for hydrogen diffusion (9.5 kJ mol<sup>-1</sup>) are much lower than the corresponding values for oxygen exchange (100–170 kJ mol<sup>-1</sup>) and oxygen diffusion (20–90 kJ mol<sup>-1</sup>).<sup>1</sup> At low temperature, hydrogen diffusion is more rapid than oxygen diffusion, but the rates of these two processes tend to similar values at high temperatures. This is the case for hydrogen and oxygen diffusion at 400 °C on alumina<sup>19</sup> and at 450 °C on zirconia.<sup>20</sup> On basic oxides (CeO<sub>2</sub>, MgO) oxygen is very mobile,<sup>1</sup> and it could act as a mobility vector of hydrogen at relatively low temperatures (300–400 °C). In this case, the migration of hydrogen could occur without a prerequisite O–H bond dissociation on the oxide surface (Figure 15). For oxides like ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, which present a mild acidity, we can propose two types of hydrogen migration mechanisms following the degree of hydroxylation of the oxide surface (Figure 16). In the case of a high degree of hydroxylation (Figure 16a) hydrogen can migrate with formation of OH<sub>2</sub> species as intermediates. If the dehydroxylation is high (Figure 16b), the



**Figure 16.** Mechanism of the hydrogen migration across the surface of oxides with a mild Brønsted acidity like Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>: (a) in the case of a high degree of hydroxylation; (b) in the case of a low degree of hydroxylation.

hydrogen migration could then occur by hydrogen jumps. These two mechanisms involve a different activation and correspond to the two regions observed during the study of the change of the coefficient of surface diffusion with the degree of dehydroxylation (Figure 12). At a low degree of dehydroxylation, the migration with OH<sub>2</sub> species as intermediates is less energetic and the coefficient of surface diffusion increases more rapidly with the hydroxyl group coverage than with a higher degree of dehydroxylation (migration by hydrogen jumps). Lastly, with silica, the low amount of hydrogen exchanged (1.2 at nm<sup>-2</sup>) between 25 and 800 °C during the TPIE experiment on RhSi (Figure 8) indicated that after the vacuum thermal treatment at 450 °C the oxide is highly dehydroxylated. Under these conditions, the hydroxyl groups associated in “bucket brigade”, as suggested by Cevallos Candau and Conner,<sup>30</sup> responsible for the hydrogen mobility on this oxide are no longer present on silica. This is in agreement with the results of Lenz et al.,<sup>51</sup> who showed that after an activation treatment at temperatures above 480 °C there is no activity for H<sub>2</sub>–D<sub>2</sub> exchange on silica. These results explain why there is difficulty in exchanging the hydrogen of silica at 75 °C on RhSi and an impossibility of determining the coefficient of hydrogen surface diffusion on this oxide at this temperature.

## 5. Conclusion

The following conclusions can be drawn from this study.

(a) TPIE of D<sub>2</sub> with OH groups of oxides shows that hydrogen exchanges at a much lower temperature than oxygen. The following order of temperature was obtained (first number, temperature of the beginning of exchange; second number, temperature of the maximal rate of exchange): CeO<sub>2</sub>, prerduced (25 °C, 100 °C) > MgO (25 °C, 120 °C) > ZrO<sub>2</sub> (50 °C, 145 °C) > CeO<sub>2</sub>, preoxidized (80 °C, 160 °C) > γ-Al<sub>2</sub>O<sub>3</sub> (100 °C, 190 °C) ≫ SiO<sub>2</sub>, (80 °C, 540 °C). On SiO<sub>2</sub>, a very small amount of hydroxyls (0.08 OH nm<sup>-2</sup>) can be exchanged between 80 and 180 °C. Most of the silanol groups are exchanged between 200 and 800 °C. For all the oxides, a simple exchange mechanism can be observed.

(b) The presence of rhodium increases the rate of exchange by several orders of magnitude. Adsorption–desorption of H<sub>2</sub>



on the metal, very fast even at 0 °C, is never the rate-determining step (rds) of exchange. H spillover (metal → support transfer) is likely to be the rds below 75 °C, while at  $T \geq 75$  °C, the exchange would be controlled by H surface diffusion. The activation energy for exchange is then very low ( $\sim 8$  kJ mol<sup>-1</sup>), which contrasts with the values found for oxygen exchange (20–90 kJ mol<sup>-1</sup>) within the 280–400 °C temperature range. Extrapolating the Arrhenius plots for H<sub>2</sub> exchange shows that hydrogen and oxygen should have the same mobility on alumina above 350–400 °C. These results were obtained with Rh catalysts. It is likely that changing the metal (Pd, Pt instead of Rh) could change the rate-determining steps.

(c) There is a linear relationship between the rate of exchange and the density of the OH group. As expected, the rate extrapolated to zero-coverage is also zero. Chlorine is a promoter for H<sub>2</sub> equilibration on the metal, while it is an inhibitor for H<sub>2</sub> exchange on the support. Dechlorination leaves a significant density of OH groups in the vicinity of metal particles, which explains why the dechlorinated samples have a higher H mobility than the chlorine-free catalysts.

(d) The relative order for the hydrogen mobility at the surface of supported rhodium catalysts is at 75 °C (base 100 for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>), CeO<sub>2</sub>, 770 > MgO, 230 >  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 100 > ZrO<sub>2</sub>, 23 >> SiO<sub>2</sub>, very low. Apparently, hydrogen mobility is not linked to surface acidity. Basic oxides, like CeO<sub>2</sub> and MgO, have both the highest oxygen and the highest hydrogen mobility. Coefficients of surface diffusion calculated on the basis of a homogeneous isotropic diffusion lead to very low values compared to coefficients determined by spectral methods. A model of heterogeneous diffusion is proposed to explain these discrepancies.

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