

Titration by H₂ and O₂ of Bare or Covered Pt Surfaces followed by ¹²⁹Xe NMR

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Diffusion of H₂ and O₂ into the pores of pellets made from Pt/γ-Al₂O₃ powders, chemisorption of H₂ or O₂ with O or H, respectively, prechemisorbed on Pt have been studied by ¹²⁹Xe NMR. Information on the distribution of chemisorbed species along the pores has been obtained by observing one to two NMR peaks and recording their chemical shifts. In this manner, competition between diffusion and reaction can be followed by ¹²⁹Xe NMR under reaction conditions. © 1991 Academic Press, Inc.

INTRODUCTION

When a gas is introduced into a packed bed consisting of porous grains of a solid material capable of chemisorbing the gas or reacting with it, two distinct phenomena are known to occur. First, the gas may penetrate along the bed, layer by layer: this is the so-called bed effect (1). Second, the gas may penetrate into each grain progressively from shell to shell: this is the so called pore-mouth diffusion effect, particularly prominent in catalyst poisoning (2).

In both cases, two distinct regions may appear in the packed bed or in the solid grains, respectively: a zone that has chemisorbed or reacted with the gas, and a zone that has not. The sharpness of distinction between the two depends on the competition between rates of diffusion and reaction along the bed or into the pores.

If two zones exist, what happens if the progress of chemisorption or reaction is followed by ¹²⁹Xe NMR according to the method of the Fraissard group that has been reviewed in Ref. (3)? As Xe probes the two zones in the bed or in the grains, one or two NMR peaks will be observed when the time it takes for Xe atoms to diffuse from one region to the next is smaller

or larger than the characteristic time of the NMR experiment.

Thus, after introduction of successive doses of H₂ at room temperature (RT) into a cell containing grains of Y zeolite with Pt clusters in them, a second NMR peak starts to develop next to that observed prior to the introduction of H₂. These two peaks may be interpreted either by a pore-mouth diffusion effect (4) or by a bed effect (5). In any event, when the temperature is raised to 450 K in the closed cell between successive doses of H₂ at RT, before the NMR spectra are taken, only one peak is observed, with chemical shift δ, shifting with successive doses (6, 7). Chemisorption at RT creates two zones with bare Pt and H covered Pt, while adsorbed H is evenly redistributed among all Pt clusters during the retreatment at 450 K.

In recent work, the chemisorption of H₂ and O₂ on a bed of γ-Al₂O₃ with bare Pt supported on it was studied as well as the reaction between O₂ and prechemisorbed H on the metal (8). In this work, two peaks were sometimes observed that were attributed to shellwise penetration into the grains of the sample. However, it was subsequently observed that shaking the packed bed prior to taking the NMR spectra before admitting the next dose of gas changed the intensity and the linewidth of the NMR

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peaks (9). These observations can be explained by a bed effect. Similarly, a moving reaction front was observed during dehydration of isopropanol in a packed bed of H-ZSM-5 between 370 and 450 K either by *in situ* ^{13}C or by ^{129}Xe NMR (10). To discriminate between bed and pore-mouth effects, we decided to fill the NMR cell with a few large pellets of compressed powder of Pt/ γ - Al_2O_3 , to avoid entirely the bed effect and focus on the competition between diffusion and reaction within the pellets. The results are reported and discussed in the paper.

METHODS

All samples used in this work came from a batch of powdered 5.15 wt% Pt/ γ - Al_2O_3 . The powder contained approximately equal amounts by weight of 38 to 75 μm grains. Preparation and treatment of the sample as well as the NMR procedure have been described elsewhere (8). Before the sample was transferred to the NMR cell (7), the powder was pressed at ca. 85 MPa for 0.5 h into a disk in a cylindrical die 15 mm in diameter and subsequently shaped with a razor blade into one pellet 10 mm wide, 10 mm long, and 5 mm thick. Typically, one or two such pellets were introduced in the NMR cell.

The percentage of metal exposed in the Pt/ γ - Al_2O_3 sample was measured by irreversible chemisorption at RT of H_2 (Matheson Co. Hydrogen Generator, Model 8325) and by titration of chemisorbed O by H_2 at RT (11) in a standard volumetric system equipped with a differential pressure gauge (Texas Instruments, model 145-01). Prior to the H_2 chemisorption the sample was reduced for 1 h at 570 K in $\sim 500\text{ cm}^3$ of static H_2 at $\sim 100\text{ kPa}$, and degassed at 670 K for 2 h to 1.3 mPa. The temperature of the sample was then dropped to RT *in vacuo* for 0.25 h. The H_2 chemisorption was carried out between 5 and 50 kPa over a period of 2 h, followed by evacuation to 1.3 mPa at RT for 0.1 h, and H_2 back-sorption at RT in the same pressure range. After H_2 chemisorp-

tion, the sample was evacuated for 2 h at 670 K after which the temperature of the sample was dropped to RT *in vacuo*. The O_2 chemisorption (Matheson Co., 99.99%) was carried out at RT over a period of 2 h, the pressure after the first dose reaching equilibrium within 1 h, and within 0.1 h for the subsequent doses. The cell was then evacuated at RT and the titration of the chemisorbed O by H_2 carried out in the pressure range between 5 and 50 kPa H_2 . The sample showed 62% metal exposed, with assumed stoichiometric ratios $\text{H}:\text{Pts} = 1.1$ and $\text{O}:\text{Pts} = 0.65$, according to the values proposed by Boudart *et al.* (12). The average particle size for the Pt clusters, obtained from the percent metal exposed, is 1.6 nm.

All NMR spectra were taken at RT and a Xe pressure between 90 and 110 kPa in the cell (Matheson Co., 99.995%). The reaction of H_2 with adsorbed O was carried out at either RT or 450 K. In all experiments, Xe was first transferred at RT to a storage bulb containing $\text{MnO}_2/\text{SiO}_2$ used as O_2 indicated, and doses of H_2 or O_2 were introduced suddenly into the cell, except during the reaction of H_2 with prechemisorbed O at 141 K, as described below. Before the NMR spectrum was taken, Xe was transferred back to the cell to atmospheric pressure. The reaction of H_2 with chemisorbed O at 450 K was performed in two manners: H_2 was added at RT with subsequent heating at 450 K, or H_2 was added at 450 K. In both cases the cell remained at 450 K for 0.25 h after the H_2 addition. Subsequently, the cell temperature was dropped to RT and Xe introduced into the cell to atmospheric pressure. For the Pt surface completely covered with O, the equilibrium pressure after the first dose of H_2 was always negligible, whether the experiment was done at RT or at 450 K. Further additions of H_2 always resulted in a small but measurable residual pressure from 10 to 100 Pa.

In the reaction between H_2 and prechemisorbed O, O_2 was first introduced at RT into the cell containing bare Pt clusters. Then,

TABLE 1

P_i^a /kPa	P_f^b /kPa	H ₂ add./ μmol^c	H ₂ cons./ μmol^d	O/Pt _s calc. ^e
4.630	0.892	33.1	18.2	0.3†
9.237	2.926	66.2	17.1	0.31

^a Initial pressure of H₂ added to Pt/ γ -Al₂O₃ at 77 K in the titration of chemisorbed O.

^b Equilibrium pressure of H₂ in the titration of chemisorbed O at 141 K after 1.5 h.

^c H₂ added, calculated from P_i .

^d H₂ consumed, calculated from P_f .

^e O coverage at the end of the reaction.

following evacuation, H₂ was slowly introduced at 77 K in two separate experiments until no change of pressure was observed (~1.5 h). Then, the cell temperature was rapidly raised to 141 K (bath of solid-liquid *n*-pentane). Irrespective of the amount of H₂, the amount of chemisorbed O removed from the Pt surface was the same (Table 1). Following evacuation at 141 K, the cell temperature was raised to RT *in vacuo* and a spectrum was taken after Xe was introduced to atmospheric pressure.

Two NMR instruments were used: a Nicolet NMC-300 pulsed at 83.0 MHz and 7.0 T with an internal deuterium locking system, and a Varian VXR-400S pulsed at 110.7 MHz and 9.4 T. The locking material was D₂O, placed in the annular space between the sample cell (diameter = 10 mm) and the commercial NMR tube (diameter = 12 mm) (7). For the zero value of δ , the primary ¹²⁹Xe reference signal was that of xenon gas extrapolated to zero pressure by the equation of Jameson *et al.* (13). For the scale of δ , a secondary reference was used in this work, for xenon atoms adsorbed at 53.4 kPa in a K/Y zeolite, obtained from the Fraissard group (7), with δ equal to 95.1 ppm at RT. All the δ values of ¹²⁹Xe on the metal clusters or on the support had higher values than that of the reference gas. They are considered positive in this paper. All the spectra taken throughout this work

showed a peak between 0 and 1 ppm. From the change in δ with pressure for the assignment of the reference, from the work of Jameson *et al.* (13), δ for Xe in the gas phase at RT and 100 kPa is 0.453 ppm, or very close to the value obtained in this work. Thus, the peak with δ close to 0.5 ppm was assigned to Xe in the gas phase (8).

RESULTS

The ¹²⁹Xe NMR spectra were taken at RT for Pt/ γ -Al₂O₃ pelletized samples at various values of nominal surface coverage, H/Pt_s or O/Pt_s, corresponding to repeated doses of H₂ or O₂ gas chemisorbed on bare Pt or on Pt with prechemisorbed O or H, respectively, at RT, 450 K or 141 K. All spectra are shown in Figs. 1 to 7. Values of δ for the single peak or both peaks, as the case may be, vs nominal coverage are shown in Figs. 8 to 11. The nominal surface coverage is defined as the number of H or O atoms dosed in, per surface Pt atom, Pt_s, as obtained from the percent metal exposed. All experiments were done on the same Pt/ γ -Al₂O₃ sample, with constant adsorption characteristics for Xe. Thus, the observed changes in the NMR chemical shift result from changes that occur in the interaction between Xe and the metallic surface due to chemisorption of H or O. Besides, the support remains practically unaffected by small amounts of physisorbed gases, although it adsorbs water produced by the titration on the metal.

DISCUSSION

One-Peak Spectra

When only one ¹²⁹Xe NMR peak is recorded, the situation is simple: chemisorbed species are uniformly distributed on the surface of the Pt clusters throughout the pellet or along the bed of small particles of zeolite. This is the case in this work when H₂ was chemisorbed on pellets at 450 K (Figs. 1, 1a) or in the case of Pt/Y zeolite

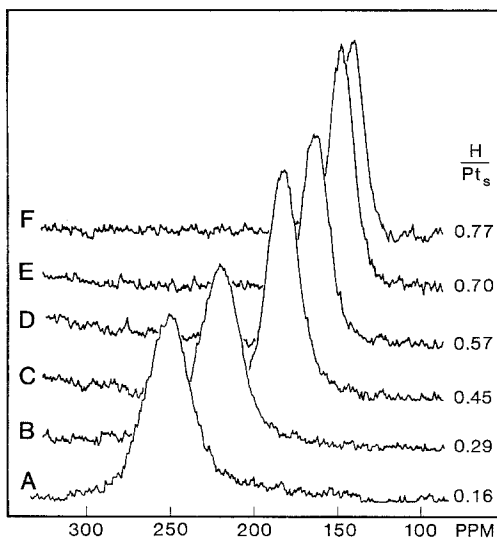


FIG. 1. Chemisorption of H_2 at 450 K on the initially bare Pt surface. Spectra A through F correspond to increasing nominal coverage, H/Pt_s .

when H chemisorbed on Pt at RT was redistributed throughout the adsorbent bed by heating at 450 K in the closed adsorption cell before spectra were taken (4, 6). Similarly, when O_2 is chemisorbed at RT, O atoms are distributed uniformly throughout the pellet at the end of the adsorption process. When H_2 is introduced to the evacuated cell at 77 K, it fills the pores of the pellet evenly without reacting with surface oxygen (14). Then, as the temperature is raised to 141 K, H_2 reacts uniformly with surface oxygen. After evacuation at 141 K and heating to RT, residual surface O (Table 1) is uniformly distributed throughout the pellet and only one peak is recorded (Figs. 7, 7a).

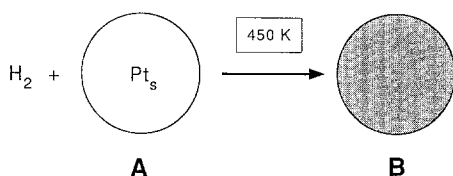


FIG. 1a. Chemisorption and diffusion of H_2 at 450 K into the pellet with uniform redistribution of chemisorbed H between successive doses. See Fig. 1.

Two-Peak Spectra: Generalities

By contrast, when chemisorption or surface reaction proceed progressively along the adsorbent bed or into the pellets, two ^{129}Xe NMR peaks are observed and the chemical shift of the peaks due to the adsorbed species will shift or not depending on whether the chemisorption or reaction front is fuzzy or sharp, respectively. In the case of a pellet, the competition between diffusion and reaction or chemisorption can be understood in simple terms as follows.

Consider first the case of a steady-state catalytic reaction in a cylindrical pore of diameter d and length L with a gas reacting in first-order manner with a reaction probability γ per collision with the pore wall. If diffusion is slow, the concentration of reactant gas drops exponentially along the length of the pore and becomes zero before the gas reaches the end of the pore. This case can be called that of a severe diffusion limitation. It will occur when

$$\gamma^{1/2} \geq \frac{d}{L}$$

if the diffusion of the gas is in the Knudsen regime, i.e., when d is smaller than the mean free path, γ , in the gas at the pressure of the experiment (15). In all above experiments in samples with $d \sim 10^{-6}$ cm, Knudsen diffusion prevails since they were all carried out below atmospheric pressure for which $\lambda \sim 10^{-5}$ cm. In the case of diffusion and reaction in a cylindrical pore, the above relation still applies, but for our sample only a fraction α of the pore surface is covered with reactive material, so that the relation becomes

$$(\alpha\gamma)^{1/2} \geq \frac{d}{L}$$

with $\alpha \sim 10^{-1}$ and $L \sim 10^{-1}$ cm. To decide whether we deal with a case of severe diffusion limitation, we need to know the sticking probability for chemisorption or reaction. This is not an easy number to come by as it may depend strongly on surface cover-

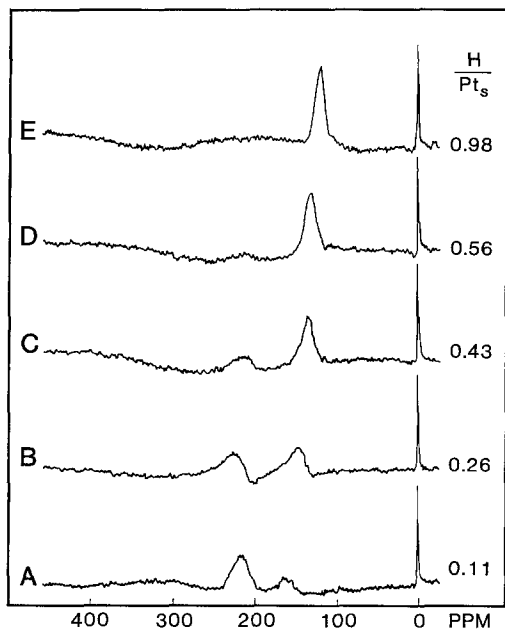


FIG. 2. Chemisorption of H_2 at room temperature on the initially bare Pt surface. Spectra A through E correspond to increasing nominal coverage, H/Pt_s .

age and on surface temperature. At low coverage, $\gamma \sim 1$ and clearly we deal with a diffusion limited chemisorption since $d/L \sim 10^{-5}$.

Surface temperature will depend on the size of the grain or pellet or bed, and on the speed at which the gas is dosed into the pellet or bed. The temperature rise due to chemisorption on supported metals can be high (16). It can be high enough that gas previously adsorbed can be desorbed and be redistributed in part inside the grain, pellet, or bed. As a result, the adsorption or reaction front into the adsorbent may lose

its sharpness and become fuzzy over a length of the penetration coordinate, that may become of the order of magnitude of the diffusion path of Xe in the porous medium during the characteristic time of the NMR experiment. Thus, Xe will probe a range of surface compositions within a fuzzy chemisorption or reaction front. A difference between H and O chemisorbed on Pt is expected as desorption of a monolayer of H occurs in part even at room temperature upon evacuation and completely at 450 K (17). By contrast, no chemisorbed O is desorbed from Pt below 600 K (18). Thus as a dose of H_2 introduced to the sample is chemisorbed or reacts with evolution of heat, the transient rise in the surface temperature will bring about desorption of already chemisorbed H with its redistribution in the grains, pellets or bed with creation of a fuzzy front of surface concentration. This phenomenon apparently does not take place in the case of strongly chemisorbed O. Let us consider now the cases of two-peak spectra observed in this and other work.

Two-Peak Spectra: Examples

Chemisorption of O_2 on Pt at RT. The simplest example is that of chemisorption of O_2 at RT on a bare Pt surface in the porous pellet. Because of the large heat of chemisorption, transient heating of the surface during chemisorption may be high but not high enough to bring about desorption and redistribution of already chemisorbed O. As a result, the adsorption front inside the pellet is sharp as defined above and Xe atoms visit two distinct environments lead-

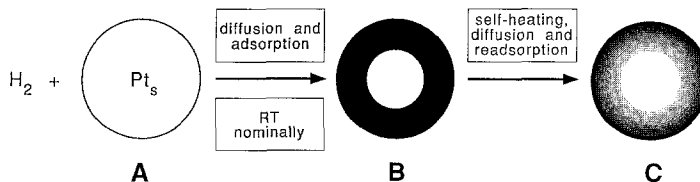


FIG. 2a. Chemisorption and diffusion of H_2 at RT into the pellet with partial redistribution of chemisorbed H due to local heating: fuzzy adsorption front. See Fig. 2.

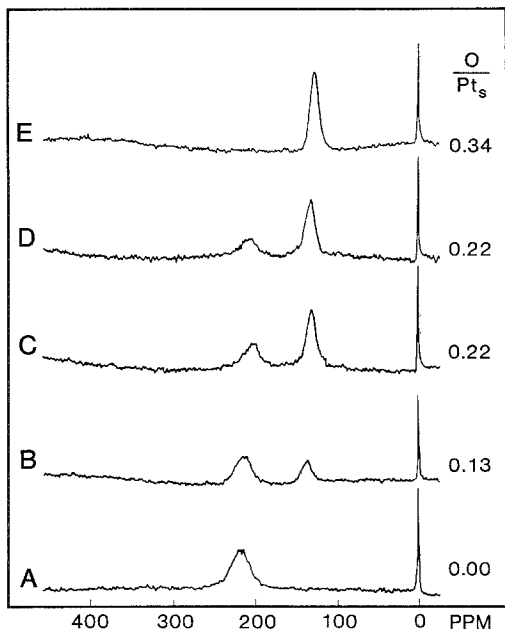


FIG. 3. Chemisorption of O_2 at room temperature on the initially bare Pt surface. Spectra A through E correspond to increasing nominal coverage, O/Pt_s .

ing to two peaks: one due to Pt_s and the other to Pt_sO . With repeated doses, the bare surface shrinks and the covered fraction of the surface grows so that the original peak decreases as the new peak rises but both peaks keep their distinct constant chemical shift (Figs. 3, 3a, and 8).

A similar observation was first reported by the Fraissard group in the case of the RT chemisorption of H_2 on Pt clusters in Y zeolite grains forming a packed bed within the NMR cell (4). This is best interpreted as a bed effect rather than a grain

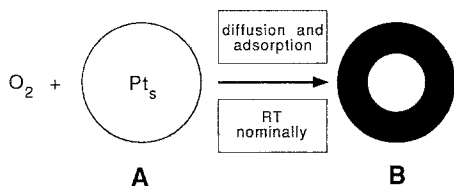


FIG. 3a. Chemisorption and diffusion of O_2 at RT into the pellet. Penetration with sharp adsorption front. See Fig. 2.

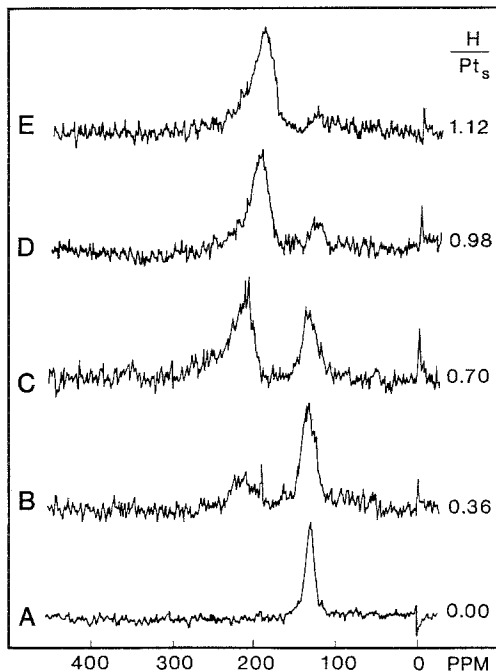


FIG. 4. Titration with H_2 at 450 K of the Pt surface initially covered with chemisorbed O. Spectra A through D correspond to increasing dosage by H_2 , expressed by a nominal coverage, H/Pt_s .

effect for reasons that will be apparent in the next case study.

Chemisorption of H_2 on Pt at RT. The difference between the one-peak spectra of Fig. 1 (chemisorption of H_2 on Pt at 450 K) and the two-peak spectra of Fig. 2 (same as RT) immediately suggests that H_2 is chemisorbed uniformly in the pellet at 450 K but shell-wise at RT. But in the latter case, the second peak due to the probing by Xe of a Pt_sH environment of variable surface com-

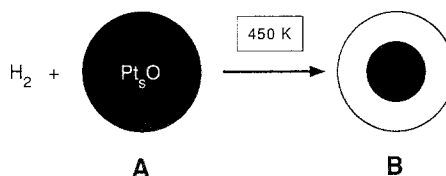


FIG. 4a. Chemisorption and diffusion of H_2 at 450 K into the pellet with prechemisorbed O. Sharp titration front. See Fig. 4.

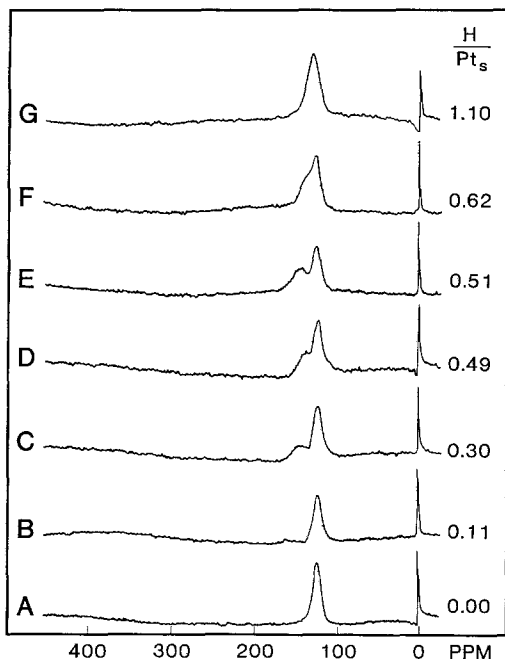


FIG. 5. Titration with H_2 at RT of the Pt surface initially covered with chemisorbed O. Spectra A through G correspond to increasing dosage by H_2 , expressed by a nominal coverage, H/Pt_s .

position shifts steadily with increasing dosage of H_2 (Fig. 8). This indicates a fuzzy front between bare and occupied clusters within the pellet (Fig. 2a). While a quantitative explanation of the observations is beyond reach, it is clear that ^{129}Xe NMR is an incisive probe of the details of chemisorption within a porous pellet. When H_2 was chemisorbed on Pt clusters in the cages of Y zeolite, in slightly different experimental setups, a similar result was found. Thus, when H_2 was dosed to a packed bed of 10

wt% Pt/Y zeolite in a glass cell inside the NMR probe, two peaks were observed at first, one due to the interaction between Xe and Pt_s and the other assigned to the interaction between Xe and Pt_sH . As the peak due to Xe in the supported Pt_s region disappeared, a third peak at lower δ 's appeared, close to the peak assigned to supported Pt_sH . This process was observed subsequently for a fourth peak (19). Instead, when H_2 was dosed in a standard volumetric apparatus and the cell was subsequently transferred to the NMR probe, a constant shift of the peak due to Xe- Pt_sH was observed, and the peak after complete coverage of H had a downfield tail (higher δ 's) (7). In both cases, the discrete and continuous shift of δ with increasing dosage of H_2 is due to a moving chemisorption front affected by bed effects.

Reaction of H_2 with O prechemisorbed on Pt at 450 K. At 450 K no H_2O or H_2 is adsorbed on the Pt surface while no O is desorbed from the Pt surface (17, 18). Thus, each dose of H_2 added to O prechemisorbed on the Pt surface in the pores of the $\gamma\text{-Al}_2\text{O}_3$ pellet is progressively consumed in the titration of the chemisorbed O until no O is left on the Pt surface at $H/Pt_s = 1.0$. As a result, Xe probes two distinct environments separated by a sharp boundary, with two peaks at a fixed position in the ^{129}Xe NMR spectrum for $H/Pt_s < 1.0$ (Figs. 4, 4a and 9). The first of these regions has bare Pt clusters and grows as H_2 is dosed in, while the second has Pt clusters covered with chemisorbed O and shrinks with increasing H_2 dosage. These two different environments remain in the pellet un-

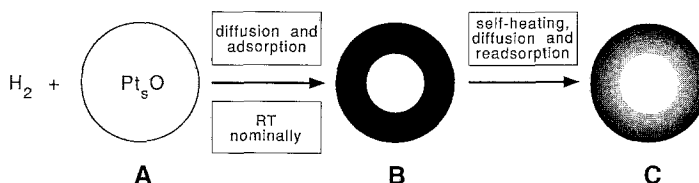


FIG. 5a. Chemisorption and diffusion of H_2 at RT into the pellet with prechemisorbed O with partial redistribution of H due to local heating: fuzzy titration front. See Fig. 5.

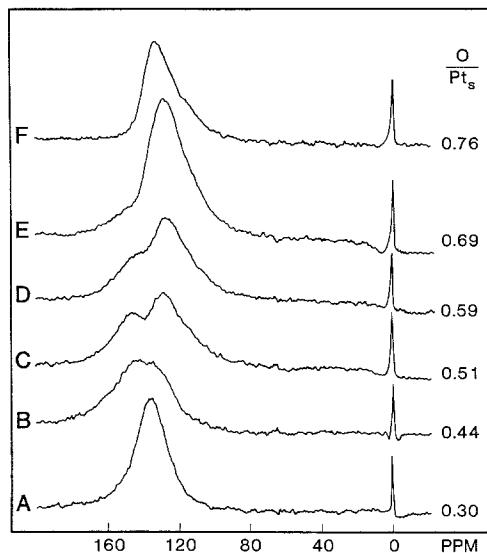


FIG. 6. Titration with O_2 at RT of the Pt surface initially covered with chemisorbed H. Spectra A through F correspond to increasing dosage by O_2 , expressed by a nominal coverage, O/Pt_s .

til all chemisorbed O has been reacted away from the Pt surface, at $H/Pt_s = 1.0$. Further addition of H_2 at 450 K results in the uniform chemisorption of H on the bare Pt surface as the temperature decreases to RT, and the ^{129}Xe NMR spectrum has a single peak that decreases in δ as H_2 is added to the sample, as discussed before. It should be noted that the scales of the abscissae in Figs. 8 and 9 are different and that the difference between the decreases in δ as H_2 is added to the sample in both figures is not very large. In addition, the data obtained for Fig. 4 have the worst signal-to-noise ratio in this work, with a great difficulty of assigning the peak positions. Still, the dif-

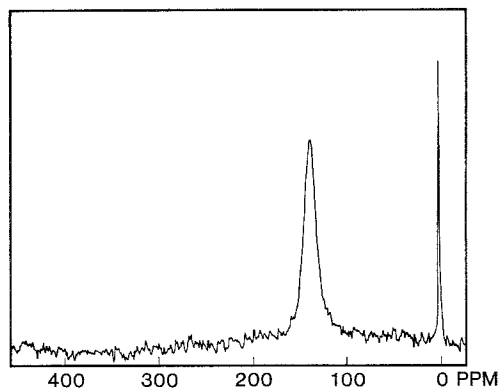


FIG. 7. Spectrum at RT following partial reaction at 141 K between H_2 and O prechemisorbed at RT.

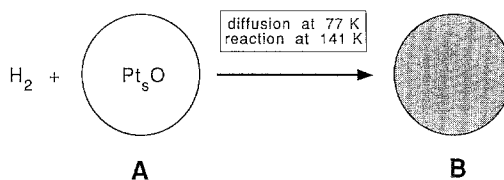


FIG. 7a. Diffusion of H_2 at 77 K into the pellet and uniform reaction at 141 K with prechemisorbed O. See figure 7.

ference between Figs. 8 and 9 is less than 10%.

Reaction of H_2 with O prechemisorbed on Pt at RT. Similarly to the reaction of H_2 with prechemisorbed O at 450 K, the ^{129}Xe NMR spectrum after the reaction of H_2 with prechemisorbed O at RT has two peaks, suggesting a shellwise reaction of H_2 in the pores of the pellet. As in the case of the reaction at 450 K, one region contains Pt clusters saturated with chemisorbed O, and shrinks as H_2 is dosed in (Fig. 5a), the

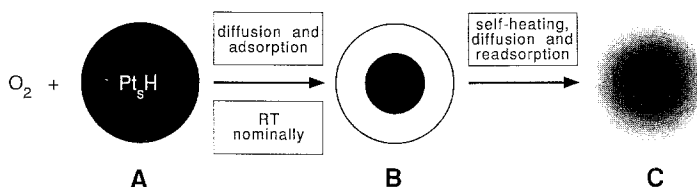


FIG. 6a. Chemisorption and diffusion of O_2 at RT into the pellet with prechemisorbed H with partial redistribution of H due to local heating: fuzzy titration front. See Fig. 6.

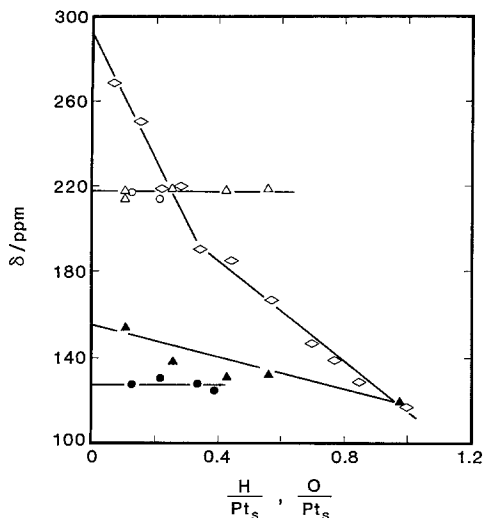


FIG. 8. Chemical shift, δ , vs nominal coverage following chemisorption on Pt. (\diamond): data of Fig. 1; (\blacktriangle) and (\triangle): data of Fig. 2; (\bullet) and (\circ) data of Fig. 3.

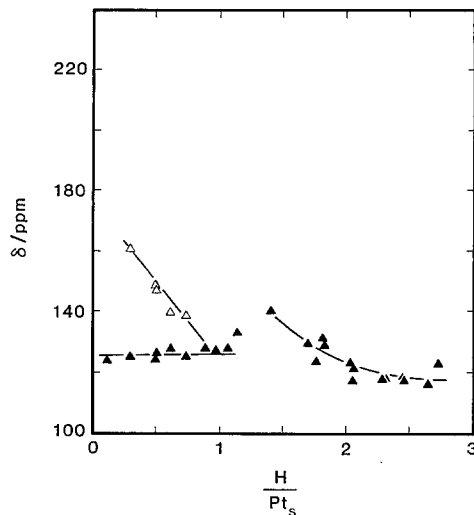


FIG. 10. Chemical shift, δ , vs nominal coverage, H/Pt_s , after repeated doses of H_2 at RT to Pt with prechemisorbed O. (\blacktriangle) and (\triangle) are data from Fig. 7.

^{129}Xe NMR spectrum having a peak at a fixed position (Fig. 5). However, the second region in the pellet does not contain bare Pt clusters but H-covered Pt clusters, the peak due to the Xe in this region having a decreasing δ with increasing H_2 dosage (Fig. 10). Thus, as in the case of the H_2

chemisorption on Pt at RT, the reaction front is fuzzy due to the transient increase of the local temperature in the Pt cluster due to the high heat of reaction and adsorption, that forces some of the previously adsorbed H to desorb and readsorb or react elsewhere (Fig. 5a).

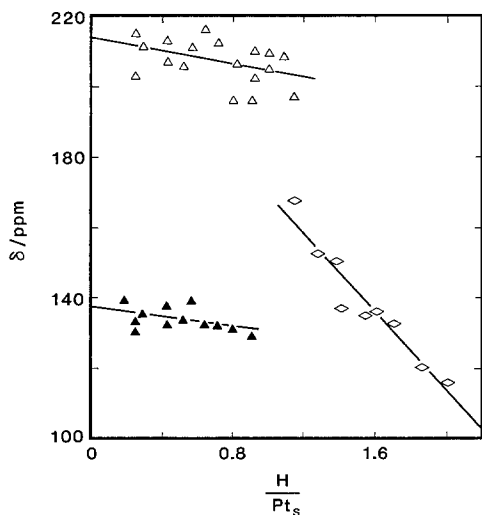


FIG. 9. Chemical shift, δ , vs nominal coverage, H/Pt_s , after repeated doses of H_2 at 450 K to Pt with prechemisorbed O. (\blacktriangle) and (\triangle) are data from Fig. 4.

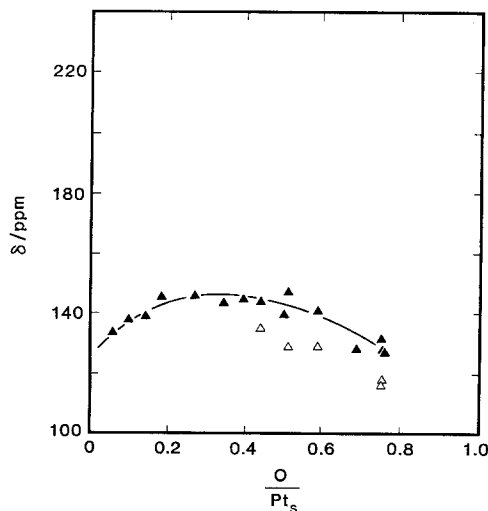


FIG. 11. Chemical shift, δ , vs nominal coverage, O/Pt_s , after repeated doses of O_2 at RT to Pt with prechemisorbed H. (\blacktriangle) and (\triangle) are data from Fig. 9.

Reaction of O₂ with H prechemisorbed on Pt at RT. As in all cases seen so far for chemisorption and reaction at RT, the reaction of O₂ with prechemisorbed H at RT is diffusion limited and occurs shellwise in the pores of the pellet. However, the ¹²⁹Xe NMR spectrum shows only one peak for small doses of O₂ (O/Pt_s < 0.3) (Fig. 6). The position and linewidth of this single peak change with O₂ dosage (Fig. 11) in the vicinity of the peak positions for Xe in the Pt_sO region and in the Pt_sH region ($\delta = 125$ and 115 ppm, respectively). For O₂ dosages larger than O/Pt_s \sim 0.3 the NMR peak splits into two. This suggests that the original peak was a coalescence of two peaks, one with a fixed peak position due to Xe probing Pt_sO and the other, with variable peak position due to Xe probing Pt_sH. Thus, as O₂ is dosed in, the heat evolved in the reaction of O₂ with H creates a fuzzy front and the pellet is made of two regions: one containing Pt_sO and fixed δ and the other containing a variable concentration of H near the front and variable δ (Fig. 6a). As the region with Pt_sO swells at the expense of the shrinking of the one with Pt_sH the peak due to Xe and Pt_sO prevails and the single peak splits into one large peak centered at $\delta = 125$ ppm, and a shoulder of variable position.

CONCLUSION

The different examples of chemisorption or reaction of H₂ and O₂ on the bare and covered Pt surface present in the pores of large γ -Al₂O₃ pellets seen in this work illustrate how ¹²⁹Xe NMR can be used as a valuable tool to probe the penetration of reactive gases into porous materials. Thus, detailed information about the distribution of adsorbed species after chemisorption or reaction could be obtained by ¹²⁹Xe NMR under reaction conditions. Although ¹²⁹Xe NMR cannot provide precise quantitative information about the distribution of adsorbed species in the pores of solids, it is able to distinguish between three different

penetration processes: uniform, or shellwise with a sharp or fuzzy penetration front. Finally, the interpretation of the results was made easier by the use of large pellets that avoided bed effects.

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