

Alumina Dissolution during Impregnation with PdCl_4^{2-} in the Acid pH Range

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Long lasting impregnation ($t > 50$ h) of γ -alumina with PdCl_4^{2-} at 50 °C was investigated in an acid pH range (3.5–5) by using a dialysis membrane reactor. Three types of simultaneous processes were analyzed: (I) alumina dissolution, (II) proton consumption, and (III) adsorption density of PdCl_4^{2-} on the surface of alumina. It was observed that some amount of support was mobilized in the liquid phase during impregnation. The amount of dissolved alumina depends on the pH of the solution as well as on the nature of the impregnating ion (PdCl_4^{2-}). The rates of alumina dissolution were $0.0603 \mu\text{mol m}^{-2} \text{h}^{-1}$ at pH 3.5 and $0.0177 \mu\text{mol m}^{-2} \text{h}^{-1}$ at pH 4. At pH 5, the presence of Al^{3+} in solution could not be detected. It is demonstrated that the protons are consumed in two distinct processes: (I) reversible adsorption of H^+ (Langmuir-type adsorption) and (II) irreversible adsorption of H^+ (leading to dissolution of alumina). A clear distinction between the reversible and irreversible adsorbed protons has not been made by now. Both reversible as well irreversible adsorbed protons were determined quantitatively. The amounts of reversible adsorbed protons at equilibrium were $4.05 \mu\text{mol m}^{-2}$ at pH 3.5, $3.3 \mu\text{mol m}^{-2}$ at pH 4, and $1.0 \mu\text{mol m}^{-2}$ at pH 5. It was observed that the rate of alumina dissolution at pH 3.5 is depressed by PdCl_4^{2-} (the rate decreased from 0.0603 to $0.0353 \mu\text{mol m}^{-2} \text{h}^{-1}$) whereas at pH 4 such phenomena could not be evidenced. However, PdCl_4^{2-} is not involved in the mechanism of alumina dissolution. It is proved that the adsorption of PdCl_4^{2-} is blocking the neighboring sites for proton adsorption. The same amount of PdCl_4^{2-} (around $0.68 \mu\text{mol m}^{-2}$) was found to be adsorbed on alumina at pH 3.5 and 4. It is likely that the high rate of alumina dissolution at pH 3.5 is an important factor for retarding the adsorption of PdCl_4^{2-} on alumina. The experimental results suggest that always aluminum ions, originating from support, will be present in the catalytic active phase (i.e., palladium) and this may affect to some extent further catalytic behavior of impregnated material.

1. Introduction

Support impregnation with metal(s) precursor(s) solution is a widespread method for catalysts preparation. Usually, the impregnation studies investigate the relationship between the surface density of a metal precursor and experimental parameters such as pH, concentration, temperature, and time. In most cases, the support is viewed as an inert material participating in the impregnation process only with its surface hydroxyl groups. In most of the experimental arrangements utilized by now, it would be difficult to monitor at the same time the evolution of the metal precursor (in the liquid phase) and support during impregnation. In certain conditions, alumina, that is, one of the most utilized supports, is not inert, even at a pH close to its point of zero charge (PZC).^{1–3} All the more so, in the

acid pH range it is likely that some amount of alumina is dissolved during impregnation with metal precursors. The extent of alumina dissolution should be dependent on the pH as well as on the nature of the impregnating metal precursor. The behavior of alumina (support) during impregnation with a metal precursor (i.e., PdCl_4^{2-}) in the acid pH range has not been investigated as of yet. The partial dissolution of the support during impregnation may have significant consequences on the catalyst final activity. We already reported that alumina should not be regarded as inert material, even when impregnation is carried out in mild conditions.³ For example, $\text{Cu}(\text{OH})_2$ (mainly) but copper basic sulfate too, formed at pH near the zero point charge (pH 7 or 9), showed relatively high activity for alumina dissolution.³ Therefore, it is likely that some amount of aluminum, originating from support, is always present in the catalytic active phase. The amount of aluminum contained in the active phase depends on the impregnation

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(1) Pauliac, J. L.; Clause, O. *J. Am. Chem. Soc.* **1993**, *115*, 11602.

(2) Caillerie, J. B. E.; Kermarec, M.; Clause, O. *J. Am. Chem. Soc.* **1995**, *117*, 11471.

(3) Balint, I.; Miyazaki, A.; Aika, K. *Chem. Mater.* **1999**, *11*, 378.

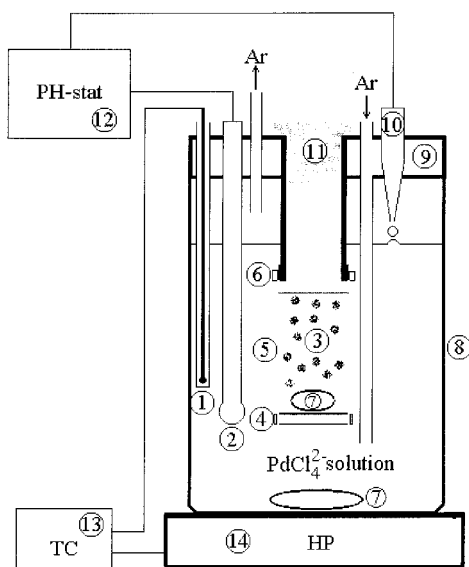


Figure 1. Experimental system used for the study of alumina impregnation with PdCl_4^{2-} in the pH range from 3.5 to 5: (1) glass-shielded thermocouple; (2) pH electrode; (3) γ -alumina; (4, 6) Teflon rings; (5) dialysis bag; (7) Teflon-coated magnetic stirring rods; (8) glass beaker; (9) Teflon cap; (10) buret; (11) Teflon cap with screw; (12) pH-stat; (13) temperature controller; (14) hot plate and stirrer.

conditions (nature of metal precursor used, temperature, pH, and impregnation time).

From a practical point of view, PdCl_4^{2-} is a convenient metal precursor for alumina impregnation because of its good stability and solubility in the acid pH range. For example, if properly activated, the catalysts prepared using PdCl_4^{2-} as the precursor show high catalytic activity for methane oxidation.⁴

The aim of this paper is to investigate simultaneously the evolution of the support (alumina) and metal precursor (PdCl_4^{2-}) during impregnation in an acid domain, at constant pH. We want to prove that the support is not inert during impregnation. In our view, impregnation should be considered as a dynamic process in which both the support and impregnating metal precursor participate in the creation of the new (catalytically active) phase.

2. Methods

To find out the influence of PdCl_4^{2-} on alumina dissolution in the acid pH range, the following procedure was applied. First, the proton-promoted dissolution of alumina was investigated, in the absence of any additional ligand, at pH 3.5, 4, and 5. Then, the dissolution of alumina in the presence of PdCl_4^{2-} was studied in similar conditions. In this manner the differences observed would be due to the presence of PdCl_4^{2-} . Once these differences would be reported, then a model attempting the processes occurring could be proposed.

All impregnating experiments were performed with the system shown in Figure 1. The experimental system was composed of two parts (liquid phase and alumina support), separated by a dialysis membrane (5) (Wako/Wiscase Sales Corp., MWCO 12000–14 000; pore diameter 25 Å). The tubular membrane was closed tightly with a Teflon cap (9) and two Teflon rings (4, 6). Inside the dialysis membrane bag was placed the support (3). Outside the dialysis membrane was the impregnating solution containing PdCl_4^{2-} ions. Using this system, it was possible to separate the impregnating liquid

from the support. In this experimental arrangement, the alumina particles cannot pass through the membrane, while the ions (i.e., Al^{3+} or PdCl_4^{2-}) can do so. The sealing of the bag was checked by blank experiments performed at 50 °C using only distilled water. Even after 80 h of experiment, we could not detect the presence of aluminum in the solution outside the bag.

During the experiment, the pH value of the solution outside the bag was monitored with a pH electrode (2) (TOA) and maintained constant (± 0.2 pH units) at an adequate pH value with a pH-stat (12) (TOA, model AUT-211). The temperature of the system was kept constant at 50 °C. Accurate temperature control of the solution (± 0.5 °C) was performed by inserting a temperature controller (13) (Shimadzu SR 22) in the heating circuit of a hot plate (14) provided with a magnetic stirrer (Iwaki Glass, PC-351). The temperature was measured with a K-type thermocouple (1) (shielded with a glass tube) placed into solution. The Teflon-coated magnetic stirring rods, located inside and outside of the bag (7), minimizes the temperature gradients along the vertical axes and maximized the contact time with the liquid phase. The system was purged slowly (3.6 L/h) with argon gas to maintain an inert atmosphere.

General Experimental Procedure. The standard experimental procedure will be described in the following. Any departure from it will be noted in the Results section.

One gram of γ -alumina was loaded inside the membrane bag together with 12 mL of 0.1 M KCl (Wako Pure Chemicals) solution and then sealed tightly from the bulk solution with two Teflon rings. The γ -alumina (supplied by Aerosil) was produced by flame hydrolysis and has a surface area of 100 m²/g. The grains of the fine powder produced were approximately spherical in shape with an average diameter of 13 nm. The pH_{ZPC} of the alumina used in the experiments was determined to be 8.0 by a mass titration method. Impregnation experiments were carried out below pH_{ZPC} (pH 3.5, 4, and 5) because of the good stability of PdCl_4^{2-} in the acid range.⁵

A 250-mL aliquot of 0.1 M KCl was poured into a glass beaker, and the membrane bag was hung in the beaker. The alumina was equilibrated with the solution overnight at 50 °C, and then the pH was adjusted to the desired values by adding 0.1 M HCl (Wako Pure Chemicals) with pH-stat.

The stock solution of K_2PdCl_4 for alumina impregnation was prepared by adding a stoichiometric amount of KCl solution to PdCl_2 (Aldrich, 99.9%). The palladium concentration in stock solution, determined by ICP, was 10 945 ppm (0.1026 M). At the beginning of the impregnation experiment, after the pH was adjusted to the desired value, then 1 mL from K_2PdCl_4 stock solution was dropped slowly into the glass beaker. The concentration of the palladium at the beginning of impregnation was around 39.2 ppm (0.367 mmol of Pd/L), depending on the initial amount of HCl acid added for the correction of pH.

During the impregnation experiment aliquots of 2 mL were sampled periodically from the solution outside the bag. The impregnation experiments lasted from 46 to 96 h. At the end of the experiment the alumina inside the bag was collected by filtration, washed several times with distilled water, and then dried overnight at 100 °C.

The composition of the solution collected at several time intervals was determined by ICP (inductively coupled plasma spectroscopy, Seiko SPS 4000). The standard solutions (1000 ppm) for ICP calibration (Al and Pd) were supplied by Wako. The alumina support was analyzed after impregnation at different pHs by ICP, XRF (X-ray fluorescence). Prior to the ICP analysis, the impregnated alumina was dissolved in an autoclave at 150 °C, 12 h, using a mixture of $\text{HF-HClO}_4\text{-HNO}_3$ acids.

The XRF (X-ray fluorescence) spectra were recorded at room temperature in a vacuum using SII-Seiko Instruments SEA 2001 L-type apparatus.

(4) Baldwin, T. R.; Burch, R. *Appl. Catal.* **1990**, *66*, 337.

(5) Middlesworth, J. M.; Wood, S. A. *Geochim. Cosmochim. Acta* **1999**, *63*, 1751.

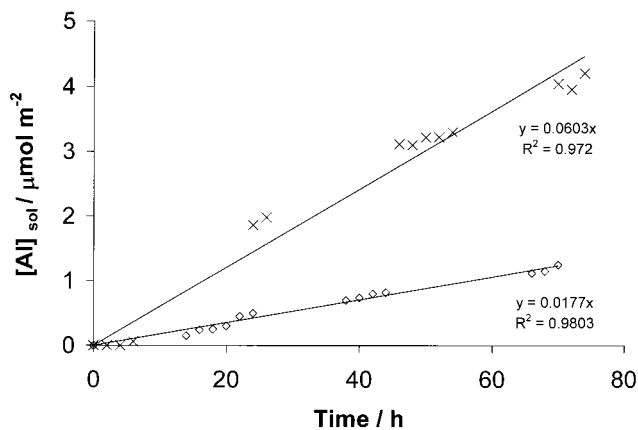


Figure 2. Proton-promoted dissolution of γ -alumina at pH 3.5 (\times) and pH 4 (\diamond).

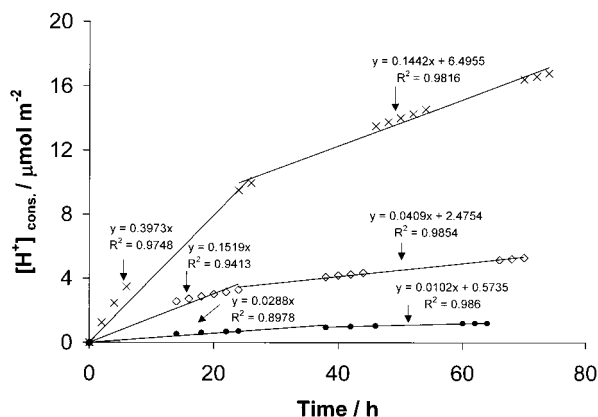


Figure 3. Proton consumption during alumina dissolution at pH 3.5 (\times), pH 4 (\diamond), and pH 5 (\bullet).

3. Results

3.1. Proton-Promoted Dissolution of Alumina over the pH Range from 3.5 to 5. Two long lasting processes were investigated in the acid pH range: (I) alumina dissolution and (II) proton consumption.

The proton-promoted dissolution of alumina is presented in Figure 2. The total amount of dissolved alumina during 74 h of experiment, calculated from the concentration of Al^{3+} in solution (5.67 mg), was 10.71 mg (1.07% of alumina was dissolved). The rate of Al^{3+} formation was $0.0603 \mu\text{mol m}^{-2} \text{h}^{-1}$.

The proton consumption in time at pH 3.5 is presented in Figure 3. The linear regression model was applied to the experimental data to approximate the rate of proton consumption at different time intervals. As can be seen in Figure 3, the rate of proton consumption had a decreasing trend in time. In the first 26 h of experiment, the rate of proton consumption was $0.397 \mu\text{mol m}^{-2} \text{h}^{-1}$. In the same period of time, the apparent amount of protons consumed for the formation of one Al^{3+} (calculated from the rates of Al^{3+} formation and H^+ consumption) was higher ($[\text{H}^+]_{\text{cons.}}/[\text{Al}^{3+}]_{\text{sol.}} \approx 6.6$) than the theoretical one (three) predicted. At longer experimental times ($t > 26$ h), the rate of proton consumption decreased to $\approx 0.144 \mu\text{mol m}^{-2} \text{h}^{-1}$ (Figure 3). Correspondingly, only 2.4 protons were apparently consumed for the formation of one Al^{3+} . This value is slightly lower than the stoichiometric one. At pH 3.5, the ratio between consumed protons and the amount of Al^{3+} formed in 74 h of experiment was 4.

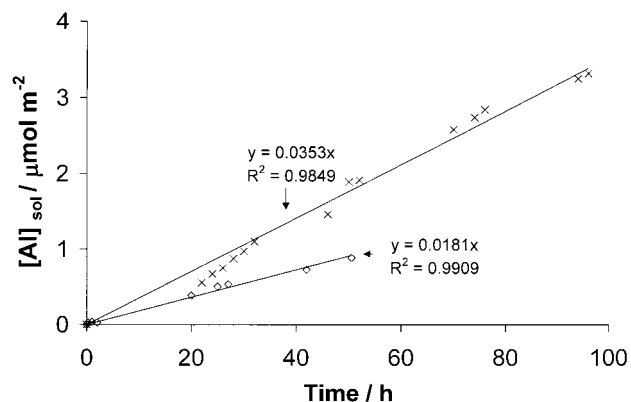


Figure 4. Dissolution of γ -alumina during impregnation with PdCl_4^{2-} at pH 3.5 (\times) and pH 4 (\diamond).

Alumina dissolution at pH 4 was investigated in the same manner as previously described. The rate of Al^{3+} formation at pH 4 was $0.0177 \mu\text{mol m}^{-2} \text{h}^{-1}$ [6.375 mg (0.64%) of alumina was dissolved in 70 h].

At pH 4, the rate of proton consumption decreased progressively in time (Figure 3), as at pH 3.5. In the first 24 h of experiment, the rate of proton consumption was $\approx 0.152 \mu\text{mol m}^{-2} \text{h}^{-1}$. In this time interval, $\approx 8.6 \text{H}^+$ were apparently consumed for the formation of one Al^{3+} . For a long lasting time ($t > 24$ h), the rate of proton consumption decreased to $\approx 0.0409 \mu\text{mol m}^{-2} \text{h}^{-1}$ (Figure 3). This time only $\approx 2.3 \text{H}^+$ were apparently consumed for each Al^{3+} formed.

At pH 5, the formation of Al^{3+} could not be evidenced after 64 h of experiment. However, alumina dissolution cannot be completely ruled out. It is possible that the small amount of Al^{3+} formed at pH 5 was quickly reabsorbed by alumina. This hypothesis is reasonable because the amount of proton adsorbed on the alumina surface at pH 5 is significantly lower than that at pH 3.5 or 4 and therefore the electrostatic repulsion between Al^{3+} and the surface of protonated alumina should be small enough to allow Al^{3+} reabsorption.

At pH 5, the rate of proton consumption, measured at different time intervals, decreased progressively from $\approx 0.0288 \mu\text{mol m}^{-2} \text{h}^{-1}$ (0–38 h) to $\approx 0.0102 \mu\text{mol m}^{-2} \text{h}^{-1}$ (38–64 h) (Figure 3).

3.2. Alumina Dissolution during Impregnation with PdCl_4^{2-} over the pH Range from 3.5 to 5. Three types of simultaneous processes have been investigated: (I) alumina dissolution during impregnation with PdCl_4^{2-} , (II) proton consumption in time, and (III) adsorption density of PdCl_4^{2-} on the alumina surface in time.

Figure 4 evidences a lower dissolution rate for alumina when PdCl_4^{2-} is present in the system [the rate of Al^{3+} formation decreases from $0.0603 \mu\text{mol m}^{-2} \text{h}^{-1}$ (Figure 2) to $0.0353 \mu\text{mol m}^{-2} \text{h}^{-1}$ (Figure 4)]. The amount of dissolved alumina after 96 h of experiment was 14.71 mg (around 1.47% of alumina was dissolved during impregnation with PdCl_4^{2-} at pH 3.5).

The proton consumption in time during the impregnation of alumina with PdCl_4^{2-} at pH 3.5 decreased progressively, as in the case of proton-promoted dissolution of alumina (Figure 5). In the first 32 h of impregnation, the rate of proton consumption of $\approx 0.206 \mu\text{mol m}^{-2} \text{h}^{-1}$ was roughly corresponding to ≈ 5.8 protons for each Al^{3+} released into solution. For a longer

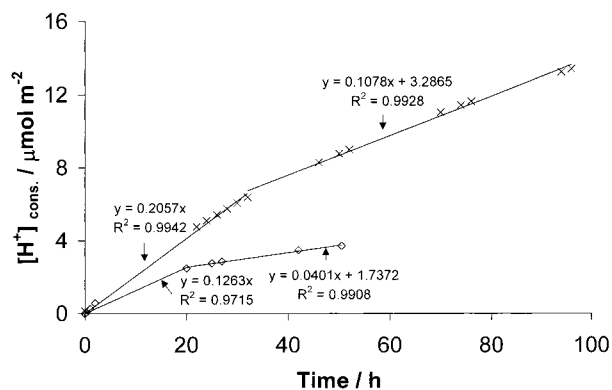


Figure 5. Proton consumption during impregnation of γ -alumina with PdCl_4^{2-} at pH 3.5 (x) and pH 4 (\diamond).

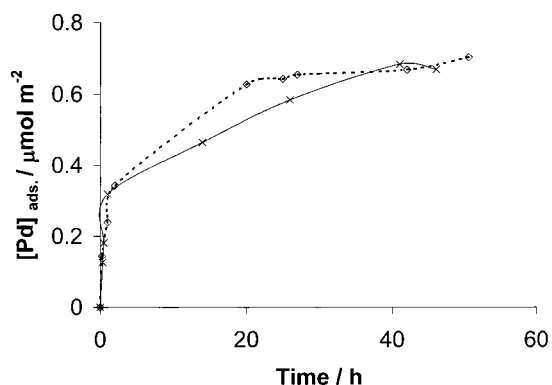


Figure 6. Adsorption density of PdCl_4^{2-} on alumina versus time: pH 3.5 (x) and pH 4 (\diamond).

Table 1. Elementary Composition of Alumina inside the Bag after Impregnation with PdCl_4^{2-} at pH 3.5–5 as Measured by ICP and as Estimated by XRF

sample	analysis method	composition/wt %		
		Pd	Al	Cl
alumina impregnated with PdCl_4^{2-} at pH 3.5	ICP	0.597	50.96	
	XRF	0.197	49.12	7.03
alumina impregnated with PdCl_4^{2-} at pH 4	ICP	0.55	41.28	
	XRF	0.32	48.47	8.13
alumina impregnated with PdCl_4^{2-} at pH 5	ICP	0.226	52.22	
	XRF	0.167	48.91	7.14

impregnating time ($t > 32$ h), the rate of proton consumption decreased to $\approx 0.108 \mu\text{mol m}^{-2} \text{h}^{-1}$ (Figure 5). A simple calculation shows that 3.05 protons were consumed for the formation of one Al^{3+} .

The amount of PdCl_4^{2-} adsorbed on the alumina surface ($\mu\text{mol m}^{-2}$), calculated from the decrease in palladium concentration in the impregnating solution, increased rapidly to $0.32 \mu\text{mol m}^{-2}$ in the first 2 h of impregnation (Figure 6). Then, the rate of adsorption of PdCl_4^{2-} decreased to reach finally (after 46 h of impregnation) an equilibrium value at $\approx 0.68 \mu\text{mol m}^{-2}$.

After impregnation, alumina was dissolved in a mixture of $\text{HF}:\text{HClO}_4:\text{HNO}_3$ and then the composition was determined by ICP. The composition of the alumina was estimated by XRF, too (Table 1).

There is a fair agreement between the palladium coverage estimated from the impregnation experiment ($0.68 \mu\text{mol m}^{-2}$) and from ICP analysis ($0.56 \mu\text{mol m}^{-2}$ or $\approx 0.6\%$ Pd) (Table 1). The estimation of the palladium concentration by XRF is rather poor (see Table 1) because of the relatively low sensitivity of the XRF method compared to the ICP one. But, on the other

hand, XRF data evidence the high affinity of alumina for chlorine (7.03% Cl). The sources of chlorine are (I) adsorbed PdCl_4^{2-} , (II) KCl (used to keep constant ionic strength), and (III) alumina itself (prepared by flame hydrolysis of AlCl_3).

The rate of alumina dissolution was constant ($0.0181 \mu\text{mol m}^{-2} \text{h}^{-1}$) during impregnation with PdCl_4^{2-} at pH 4 (Figure 4). But this time, the effect of PdCl_4^{2-} on the rate of alumina dissolution was insignificant (see for comparison Figures 2 and 4).

The proton consumption in time, during alumina impregnation with PdCl_4^{2-} at pH 4, is represented in Figure 5. The initial high rate of proton consumption, of $\approx 0.126 \mu\text{mol m}^{-2} \text{h}^{-1}$, decreased after 20 h of impregnation to $\approx 0.0401 \mu\text{mol m}^{-2} \text{h}^{-1}$. In the above-mentioned time intervals, the ratio between consumed protons and Al^{3+} was ≈ 7 and 2.2, respectively.

The amount of PdCl_4^{2-} adsorbed on alumina at pH 4 increased rapidly, up to $0.343 \mu\text{mol m}^{-2}$, in the first 2 h of impregnation (Figure 6). The adsorbed amount of PdCl_4^{2-} at equilibrium (after 20 h of impregnation) was $0.66 \mu\text{mol m}^{-2}$.

The elementary composition of the alumina inside the dialysis bag after impregnation with PdCl_4^{2-} at pH 4 is presented in Table 1. There is fair agreement between the palladium loadings calculated from the adsorption isotherm ($0.66 \mu\text{mol m}^{-2}$) or from ICP analysis (0.55% corresponding to $0.51 \mu\text{mol m}^{-2}$). A high amount of chlorine (8.13%) was found on the alumina surface.

At pH 5, the PdCl_4^{2-} ion underwent progressive hydrolysis. The initial brownish color of PdCl_4^{2-} solution slowly turned, during impregnation, to a dark green one. But the formation of palladium precipitate could not be observed. The nanometer size hydrolyzed palladium chloride particles partly adhered either to the walls of the glass beaker or to the dialysis membrane. In the hydrolyzed state, only a small amount of palladium chloride could diffuse through the dialysis membrane to reach the alumina surface. Consequently, low coverage of palladium on alumina was observed at the end of impregnation.

The elementary analysis of impregnated alumina with PdCl_4^{2-} at pH 5 is presented in Table 1. From Table 1 it can be observed that the amount of chlorine taken up by alumina, ranging between 7 and 8%, is relatively independent of the pH of impregnation.

4. Discussion

4.1. Proton-Promoted Dissolution of Alumina.

Alumina dissolution in the acid pH range was already, to some extent, investigated.^{6–8} The rate of dissolution depends on, besides the pH of the solution and the temperature, the particular structure of alumina. Therefore, we referred the behavior of γ -alumina during impregnation with PdCl_4^{2-} to that of γ -alumina in the absence of palladium complex, keeping the same experimental conditions.

(6) Stumm W. *Aquatic Surface Chemistry, Chemical Processes at the Particle–Water Interface*, John Wiley & Sons: New York, 1987; p 205.

(7) Maatman, R. W.; Mahaffy, P.; Hoekstra, P.; Addink C. *J. Catal.* **1971**, *23*, 105.

(8) Furrer, G.; Stumm, W. *Geochim. Cosmochim. Acta* **1986**, *50*, 1847.

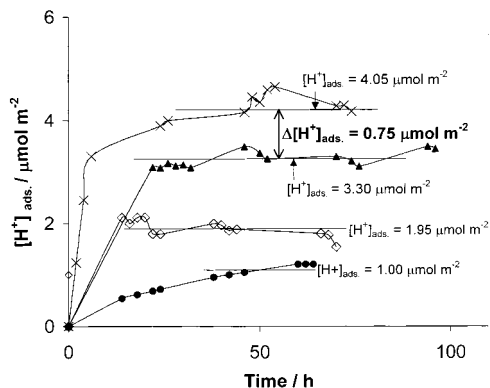


Figure 7. Evolution of reversibly adsorbed protons on the surface of alumina in time at pH 3.5 (x), pH 4 (◇), and pH 5 (●) and the evolution of reversibly adsorbed protons during alumina impregnation with PdCl_4^{2-} at pH 3.5 (▲).

A clear identification of the aluminum species that resulted in the first stage of alumina dissolution has not been made as of yet. It is possible that hydrolyzed Al species are formed in the early stages of the dissolution process. However, there are two points we would like to draw attention to here. One is that the size of the Al species that can diffuse through the membrane in the liquid phase should be smaller than 25 Å (the pores size of the dialysis membrane). The other point is that there is a general consensus in the literature that the final product of alumina dissolution in the acid pH range is Al^{3+} .^{6–8} Therefore, we assume that, regardless of the intermediate species, three H^+ are consumed for the formation of one Al^{3+} .

Kinetics of alumina dissolution consists of three fast protonation steps followed by the slow removal of one Al^{3+} ion from the alumina surface.⁶ The protons become bound to the surface hydroxyl groups or to the oxide ions closest to the surface. When the three closest sites to Al^{3+} ions (OH or O) are protonated, the bonds between oxide and metal ions are polarized critically and Al^{3+} is detached from the surface by H_2O molecules.

In practice, we observed higher proton consumption than the stoichiometric one in the first 24 h (Figure 3). From here it is obvious that the surface protonation step is faster than the formation of Al^{3+} . As the surface of alumina became saturated with protons, the consumption of protons for one Al^{3+} dropped below the stoichiometric value ($[\text{H}^+]/[\text{Al}^{3+}] < 3$) (Figure 3). It is worth noticing that the rate of Al^{3+} formation kept constant regardless of the rate of proton consumption.

Proton consumption in time, as represented in Figure 3, represents the combination of two distinct simultaneous processes: (I) reversible adsorption of H^+ (Langmuir type) and (II) irreversible adsorption of H^+ (consumed for dissolution of alumina). A clear distinction between these two types of proton reactions has not been made as of yet. In this work, both reversibly and irreversibly adsorbed protons are determined quantitatively.

The reversibly adsorbed protons were determined, at each experimental point, by extracting the protons consumed for alumina dissolution (irreversibly adsorbed) from the total amount of protons consumed ($[\text{H}^+]_{\text{ads}} = [\text{H}^+]_{\text{cons}} - 3[\text{Al}^{3+}]$). The reversibly adsorbed protons on the surface of alumina in time, over the pH range from 3.5 to 5, is presented in Figure 7. The

adsorption equilibrium of protons on $\gamma\text{-Al}_2\text{O}_3$ was reached, at constant pH, after $t > 20$ h (Figure 7). The experimentally determined concentration of reversibly adsorbed protons on alumina at equilibrium was $\approx 4.05 \mu\text{mol m}^{-2}$ at pH 3.5 (curve x), $\approx 1.95 \mu\text{mol m}^{-2}$ at pH 4 (curve ◇), and $\approx 1.0 \mu\text{mol m}^{-2}$ (curve ●) (Figure 7).

In the following we would like to focus on the significance of so-called reversibly adsorbed protons, represented in Figure 7. The protons we can “see” on the alumina surface, by using the above-presented procedure ($H_{\text{ads}} = H_{\text{cons}} - 3[\text{Al}^{3+}]$), are the not consumed protons in the dissolution reaction (in other words, protons that remain in the adsorbed state). The question is, which is the maximum number of nonreactive protons (H^+_{ads}) coordinating one Al^{3+} (protons that are not consumed in the dissolution reaction)? From the above discussion it is obvious that only one or two protons can be adjacent to one Al^{3+} ion without promoting alumina dissolution. The third protonation step in the vicinity of Al^{3+} would lead to critical polarization of Al–O bonds and further to removal of three adsorbed protons as the reaction product (water).

Consequently, our discussion can be summarized as follows. The maximum amount of nonreactive protons adsorbed on the surface at equilibrium can be expressed as $[\text{Al}_{\text{surf}}]_{\text{Total}} \times n$ (where $0 \leq n \leq 2$ and $[\text{Al}_{\text{surf}}]_{\text{Total}}$ represents the surface aluminum sites). The value of n (in other words the extent of surface protonation at equilibrium) depends on the proton concentration in solution (pH) (see Figure 7).

4.2. Alumina Dissolution during Impregnation with $[\text{PdCl}_4]^{2-}$. The adsorption densities of PdCl_4^{2-} on alumina, obtained by using the dialysis membrane ($0.68 \mu\text{mol m}^{-2}$ at pH 3.5 and $0.70 \mu\text{mol m}^{-2}$ at pH 4), are close to those obtained by classic impregnation methods. The densities of PdCl_4^{2-} on alumina range, depending upon the condition of impregnation, between 0.8 and $1.2 \mu\text{mol m}^{-2}$.^{9,10}

One hydration sheath model predicts a maximum coverage of $1.53 \mu\text{mol m}^{-2}$ for PdCl_4^{2-} on alumina.⁹ To this point, the retardation of palladium adsorption was explained either by the effect of high ionic strength of an indifferent electrolyte or by the influence of the metal precursor itself.⁹ In most cases, regardless of the pH of impregnation, alumina dissolution was considered only a coincidental process. This is rather surprising because, in most cases, alumina is impregnated at a very acidic pH (i.e., PdCl_4^{2-}).

We take under investigation, for the first time, the dissolution of alumina during impregnation with PdCl_4^{2-} in the acid pH range. In the first 2 h of impregnation, the quick adsorption of PdCl_4^{2-} [$0.16 \mu\text{mol m}^{-2}\text{h}^{-1}$ (Figure 6)] takes place parallel to alumina dissolution [$0.035 \mu\text{mol m}^{-2} \text{h}^{-1}$ at pH 3.5 (Figure 4) and $0.0181 \mu\text{mol m}^{-2} \text{h}^{-1}$ at pH 4 (Figure 4)]. As the surface of alumina became saturated in PdCl_4^{2-} , the rate of palladium adsorption decreased below that of alumina dissolution [$0.009 \mu\text{mol m}^{-2} \text{h}^{-1}$ at pH 3.5 and $0.008 \mu\text{mol m}^{-2} \text{h}^{-1}$ at pH 4 (Figure 6)]. The amount of PdCl_4^{2-} on alumina is limited by the (I) strong electrostatic forces of adsorbed species and by (II) dissolution of

(9) Santhanam, N.; Conforti, T. A.; Spieker, W.; Regalbuto, J. R. *Catal. Today* **1994**, *21*, 141.

(10) Contescu, C.; Vass, M. I. *Appl. Catal.* **1987**, *33*, 259.

Table 2. Influence of PdCl₄²⁻ on [H⁺]_{cons./[Al³⁺]_{sol. Ratio at pH 3.5 and 4}}

[H ⁺] _{cons./[Al³⁺]_{sol.}}	experiment time	pH	system
3.99	72	3.5	Al ₂ O ₃ + H ⁺
4.24	74	3.5	Al ₂ O ₃ + H ⁺ + PdCl ₄ ²⁻
4.23	70	4	Al ₂ O ₃ + H ⁺
4.19	50.5	4	Al ₂ O ₃ + H ⁺ + PdCl ₄ ²⁻

alumina. However, it is clear that some amount of the adsorbed PdCl₄²⁻ is detached together with Al³⁺ during the dissolution process. Therefore, we assume that one important consequence of alumina dissolution, in addition to the effect of ionic strength, is the retardation of PdCl₄²⁻ adsorption.

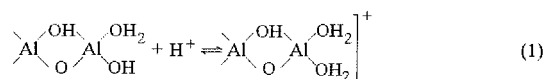
To find out whether the proton consumption is affected by PdCl₄²⁻ adsorption, the ratio between [H⁺]_{cons.} and [Al³⁺]_{sol.} is analyzed in Table 2.

From Table 2 it is clear that PdCl₄²⁻ does not promote alumina dissolution because the ratio between [H⁺]_{cons.} and [Al³⁺]_{sol.} remained practically constant (≈4.2), regardless of whether PdCl₄²⁻ was present or not in solution. If PdCl₄²⁻ would promote alumina dissolution, the proton consumption should decrease significantly in comparison to the amount of Al³⁺ formed. In practice, only the rate of alumina dissolution was affected by PdCl₄²⁻ [the rate of alumina dissolution decreased from 0.060 μmol m⁻² h⁻¹ (Figure 2) to 0.035 μmol m⁻² h⁻¹ (Figure 4) whereas at pH 4 such an effect could not be observed]. This aspect will be discussed in what follows.

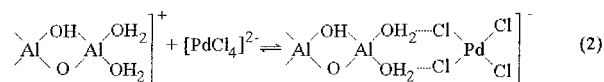
The inhibiting effect of PdCl₄²⁻ on the rate of alumina dissolution was already indirectly observed by Contescu et al.¹⁰ The decrease in alumina buffering power in the presence of adsorbable palladium complexes¹⁰ can be easily explained by the decrease in the rate of alumina dissolution (or decrease in the rate of proton consumption).

To find out the reason for the decrease in the rate of alumina dissolution in the presence of PdCl₄²⁻, the amount of protons adsorbed reversibly (in the presence of PdCl₄²⁻) was determined at equilibrium. At pH 3.5, the concentration of proton on the surface of alumina at equilibrium was ≈3.3 μmol m⁻² (Figure 7, curve ▲). The decrease in proton concentration, of 0.75 μmol m⁻², roughly corresponds to the amount of PdCl₄²⁻ adsorbed on alumina at pH 3.5 (0.68 μmol m⁻²). To this point, there is little information about the detailed adsorption mechanism of PdCl₄²⁻ on the alumina surface in the acid domain. It is assumed that PdCl₄²⁻ should adsorb via an electrostatic mechanism⁷ (the negatively charged PdCl₄²⁻ is adsorbed onto the protonated surface of alumina).

Assuming that and that PdCl₄²⁻ is adsorbed onto the protonated sites of alumina, it comes out that only two protonation steps are allowed in the vicinity of one adsorbed PdCl₄²⁻ molecule (alumina dissolution cannot take place because three protons are necessary for the formation of one Al³⁺). At the beginning of impregnation, a fast protonation of the surface of alumina takes place (eq 1):⁶

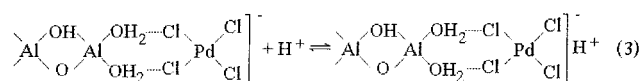


Then, PdCl₄²⁻ is adsorbed onto protonated (positively charged) surface sites (Al–OH₂⁺):



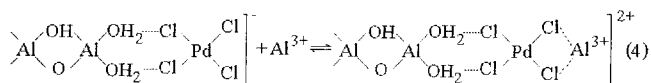
The structure of PdCl₄²⁻ is preserved after adsorption.⁷ It is not likely that exchange takes place between surface hydroxyl groups (Al–OH) and the chlorine(s) of PdCl₄²⁻ to give, for example, surface Al···PdCl₃(OH)⁻ and Cl⁻. After impregnation, most of the adsorbed PdCl₄²⁻ can be removed (recovered) completely by washing, at neutral pH, with excess high ionic strength solution. PdCl₄²⁻ precursor desorbs almost completely, even after it has been dried at room temperature.⁹

In the absence of PdCl₄²⁻, the next proton attach would take place at the OH or O bridging two surface aluminum ions (see model presented in eq 2) followed by the detachment of Al³⁺ ion from the surface of alumina.⁶ The adsorption of PdCl₄²⁻ on the alumina surface gives rise to a high local negative charge. Therefore, the next protonation step takes place at the adsorbed palladium complex to neutralize the local negative charge:



In other words, the negative charge of adsorbed PdCl₄²⁻ prevents the protonation of the adjacent Al–O–Al bonds. The third protonation step at the vicinity of adsorbed PdCl₄²⁻ (at Al–OH–Al or Al–O–Al sites) cannot occur probably because of steric reasons, the PdCl₄²⁻ ion being a relatively large molecule (1.09 nm² with one hydration sheath⁹).

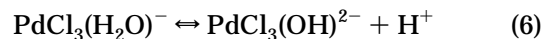
Not only protons but also other positive ions, such as Al³⁺ (formed by support dissolution), are likely to be retained by the negatively charged palladium complex adsorbed on the surface of alumina:



From eq 4 is clear that the catalytic behavior of impregnated material would be affected as a result of aluminum presence in the palladium active phase.

The rate of alumina dissolution at pH 4 is significantly lower (around 3.4 times) than that at pH 3.5 and therefore the effect of PdCl₄²⁻ on the rate of alumina dissolution is more difficult to be evidenced.

At pH 5, PdCl₄²⁻ undergoes partial hydrolysis and/or ligand substitution reactions. The resultant polynuclear species are PdCl₃(H₂O)⁻¹¹ and/or PdCl₃(OH)²⁻⁵.



The large polynuclear hydrolyzed palladium species cannot diffuse through the dialysis membrane to reach

(11) Contescu, C.; Macovei, D.; Craiu, C.; Teodorescu, C.; Schwarz, J. A. *Langmuir* **1995**, *11*, 2031.

the surface of alumina and consequently the palladium loading on alumina at the end of impregnation was low.

Conclusions

1. Alumina dissolution during impregnation with PdCl_4^{2-} in the acid pH range was evidenced and measured quantitatively.

2. The extent of alumina dissolution is significant at low pH (3.5 and 4).

3. Protons are consumed in two distinct processes, taking place simultaneously: (I) reversible adsorption of H^+ (Langmuir-type adsorption) and (II) irreversible adsorption of H^+ (leading to dissolution of alumina).

4. At pH 3.5, PdCl_4^{2-} adsorption blocks the sites for proton adsorption and therefore the rate of alumina dissolution decreases.

5. It is likely that one of the reasons for the retardation of PdCl_4^{2-} adsorption is alumina dissolution.

6. Alumina dissolution during impregnation may have significant consequences on the formation of the catalytic active phase. It is expected that aluminum ions, originating from the support, will always be present in the catalytic active phase (i.e., palladium phase), inducing the formation of lattice defects.¹² Therefore, the aluminum presence in the palladium active phase should be taken into consideration in explaining the catalytic behavior in a chemical reaction.

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CM000693I

(12) Balint, I.; Aika, K. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 1797.