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UV-Vis Diffuse Reflectance Spectroscopic Study of Pt, Pd, and Ru Catalysts Supported on Silica

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In this work, metal (Pt,Pd,Ru)/SiO₂ catalysts obtained by the sol-gel method have been studied. When the catalysts are prepared by this method, the metal is on the support surface and part of it is inserted into the silica network. By UV-vis (diffuse reflectance) spectroscopy it is shown that the ≡Si-O-M- interaction given in the sol-gel catalyst is different from the one in the catalysts obtained by a traditional impregnation method. The metal inserted into the support structure and the metal complex attached to the silica surface behave independently.

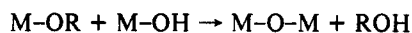
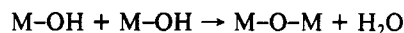
Introduction

For the past few years, the sol-gel method has been widely used in the preparation of new materials, ceramics and glasses, for example.¹⁻⁴ The process consists of the reaction of metal alkoxides with water in the presence of an alcohol.⁵ The two main reactions involved in the process are

hydrolysis



condensation



During condensation a polymer can be formed by increasing the number of cross linked M-O-M bonds. The result is a gel which can be dried to obtain the solid. Both reactions take place at the same time, and the structural and surface characteristics of the new materials can be controlled by the reaction conditions.⁶ This method can be used in the synthesis of new solids which can be used as catalytic supports.^{7,8} In this work the solid which has been prepared by the sol-gel method is silica. It has been observed in this type of silica that the surface area and the degree of hydroxylation of the surface depend upon the reaction conditions. The surface hydroxylation is an important characteristic of the supports, because the OH groups are involved when the support is impregnated with a metal complex.

A metal salt can be initially added to the reactants in the sol-gel procedure. The final result is a solid in which the metal has been inserted into the silica network. The solids mentioned above have been made and they show catalytic activity.⁹ In these types of catalysts, it is very important to study the main characteristics of the metal which is on the surface in comparison to catalysts obtained by conventional impregnation. Also it is very important to analyze the effect of the metal inserted into the solid network. For this study, the UV-vis technique was selected.

Experimental Section

Pt-0.1 Catalyst. Tetraethoxysilane (TEOS) (24.1 mL) and 10 mL of ethanol are refluxed with a solution containing 0.017 g of hexachloroplatinic acid, 10 mL of water, and 1.5 mL of NH₄OH. The reflux under constant stirring is maintained for 30 h until the gel is formed. The gel is dried at 70 °C until a solid is obtained. The final solid has 0.1% of metal.

TABLE I: Gelation Times of the Catalysts

catalyst	adding time TEOS, h	gelling time after TEOS addition, h
Pt-0.1	instantly	30
Pt-0.3	instantly	27
Pt-0.5	instantly	22
Pt(D)0.5	24	1
Pt0.3(I)0.5	instantly	27
Pd-0.1	instantly	35
Pd-0.3	instantly	32
Pd-0.5	instantly	26
Pd(D)0.5	24	2
Ru-1	instantly	1
Ru(D)0.5	24	1/6

Pt-0.3 and Pt-0.5 Catalysts. They are prepared in a similar way as the previous one, but increasing the metal content.

Pt(D)-0.5. Hexachloroplatinic acid (0.86 g), 10 mL of water, 20 mL of ethanol, and 1.5 mL of NH₄OH are refluxed with constant stirring. TEOS (24.1 mL) is added dropwise for 24 h. The reflux continues for 1 h until the gel is obtained.

Pt0.3(I)0.2 Catalyst. A 3-g portion of Pt-0.3 catalyst and a H₂PtCl₆·6H₂O solution (0.15 g of H₂PtCl₆·6H₂O/20 mL of H₂O) are uniformly mixed and heated at 60 °C for 2 h with stirring until the water has been evaporated. The metal is now impregnated on the solid.

Pt(I)0.5 Catalyst. Three grams of sol-gel silica (obtained by using TEOS at pH 9) is impregnated for 2 h with 0.04 g of hexachloroplatinic acid and 20 mL of water.

Pd-0.1, Pd-0.3, and Pd-0.5 Catalysts. TEOS (24.1 mL), 0.016 g of PdCl₂, 1.5 mL of NH₄OH, and 10 mL of water are refluxed under constant stirring until the gel is obtained. The same method has been used for Pd-0.3 and Pd-0.5 catalysts, using the required PdCl₂ amount.

Pd(D)0.5 Catalyst. A 0.082-g of portion of PdCl₂, 10 mL of water, 20 mL of ethanol, and 1.5 mL of NH₄OH are refluxed under constant stirring. TEOS, 24.1 mL, is added dropwise for 24 h. The reflux is maintained until the gel is formed.

Pd(I)0.5 Catalyst. Five grams of sol-gel silica is impregnated for 2 h at 60 °C, with 0.0414 g of PdCl₂ and 20 mL of water.

Ru-1.0 Catalyst. TEOS (24.1 mL), 10 mL of EtOH, 1.5 mL of NH₄OH, 0.148 g of RuCl₃·3H₂O, and 10 mL of water are refluxed with constant stirring until the gel is formed.

Ru(D)0.5 Catalyst. Ethanol (10 mL), 1.5 mL of NH₄OH, 10 mL of water, and 0.074 g of RuCl₃·3H₂O are refluxed. A 24.1-mL volume of TEOS is added dropwise into the former solution for 24 h. The reflux is maintained until the gel is formed.

Ru(I)1.0 Catalyst. Six grams of silica sol-gel is impregnated in conventional process with 0.154 g of RuCl₃·3H₂O and 20 mL of water.

All the gels (fresh catalysts) are dried at 70 °C for 12 h and characterized by UV-vis (diffuse reflectance) spectroscopy using Varian equipment, Cary 17, with integrating sphere. To obtain

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- (6) Mackenzie, J. D. *J. Non-Cryst. Solids* **1982**, *48*, 1.
- (7) Lopez, T.; Lopez-Gaona, A.; Gomez, R. *Langmuir*, in press.
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- (9) Lopez, T.; Romero, A.; Gomez, R. *J. Non-Cryst. Solids*, in press.

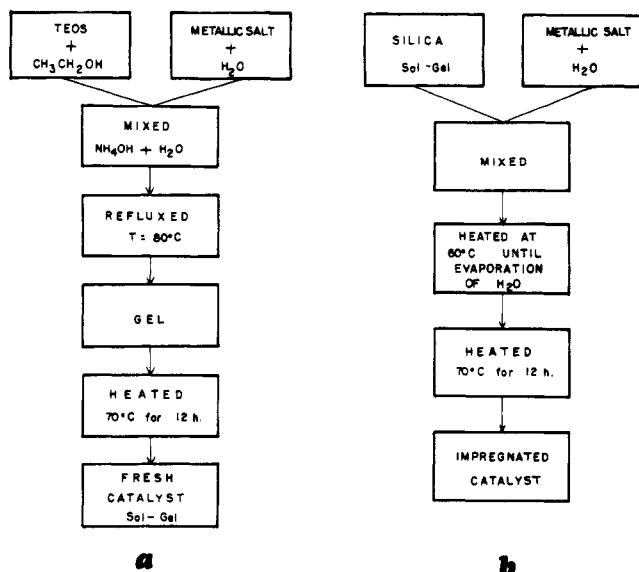


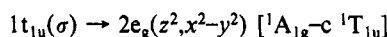
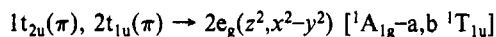
Figure 1. Synthesis diagram: (a) sol-gel method, and (b) conventional impregnation.

the spectra, self-supporting pellets were prepared. The reference was a 100% reflectance sample. The reactants used and their suppliers were TEOS (Alfa Products, 99%), ethanol (Baker, 99.8%), NH_4OH (Baker, 99%), $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (ICN K&K Inc., 99.9%), PdCl_2 (ICN K&K Inc., 99.9%), and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (ICN K&K Inc., 99.9%). A summary of the preparation methods (sol-gel and impregnation) is given in Figure 1.

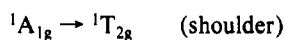
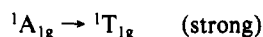
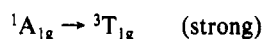
Results and Discussion

The catalyst is a yellow powder when the silica contains Pt, white in the case of Pd, and gray for the Ru. The gelling time for the sol-gel catalysts (Table I) varies depending upon the metal used.

Platinum Catalysts. Table II shows the bands corresponding to the UV-vis (diffuse reflectance) spectra for the Pt catalysts. The Pt in the catalyst surface forms a d^6 complex in a strong field, and a $[t_{2g}(xy,xz,yz)]^6$ ground-state configuration. The spectra show two intense charge-transfer (CT) bands (204 and 262 nm) due to the charge transfer between the ligand and the metal e_g empty level.¹⁰ The high 10Dq value makes the CT bands appear in the high-energy region. The two bands (Table II) can be assigned to the permitted transitions.^{11,12}



Five bands are observed in the d-d region, of less intensity than the CT ones, and corresponding to the following transitions (Table II):



These bands vary in position and intensity, and disappear in some cases, depending upon the catalyst preparation. The first is a spin-forbidden strong transition, always accompanied by a

TABLE II: UV-Vis (Diffuse Reflectance) of Pt Catalysts

catalyst	CT bands, nm	d-d bands, nm
Pt-0.1		485, 521, 536, 555, 590
Pt-0.3	238, 264	
Pt-0.5	212, 261	526, 538, 555, 580, 591
Pt(D)0.5	214, 240	521, 552, 557
Pt0.3(I)0.5	264	374, 460, 480, 565
Pt(I)0.5	204, 262	460, 485, 565
$\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$	202, 266	353, 358, 379, 465, 483

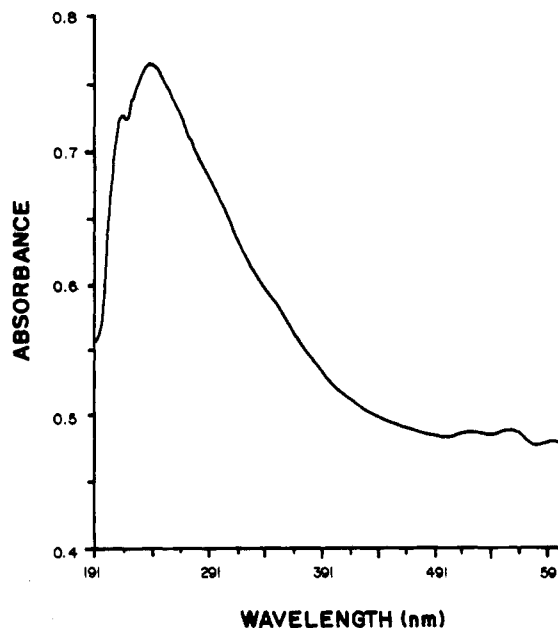
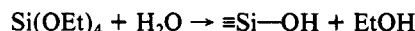


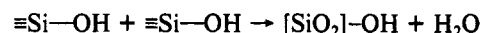
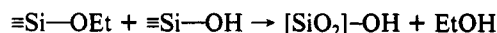
Figure 2. UV-vis (diffuse reflectance) spectrum of Pt(D)0.5.

small shoulder. The second one is similar in intensity and spin-allowed.^{13,14}

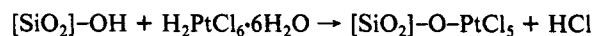
In the Pt(I)0.5 and Pt0.3(I)0.5 solids, impregnated by the conventional method, a similar behavior is observed, although in the second case some part of the metal is inserted inside the silica. In both cases the two strong d-d bands are shifted toward low-energy compared with the ones in the complex. The Pt on the surface of the Pt0.3(I)0.5 catalyst comes mainly from the impregnation process, and it can be assumed in general that the bands are shifted due to the metal-support interaction. Furthermore, the Pt present inside the silica does not have a strong influence on the former interaction. The support (SiO_2) is prepared from a silicon alkoxide and the result is a partially hydroxylated solid: hydrolysis



condensation



The OH groups on the surface are species that can be interchanged with the complex chlorides.



When the catalyst are prepared by the sol-gel method (Pt-0.1, Pt-0.3 and Pt-0.5) the metal-support interaction becomes somewhat stronger, and this is shown in the electronic spectra (Figure 2). The bands are shifted toward lower energy compared with the impregnated catalyst. The shift is due to the electronic rearrangement in the complex, caused by the Si-O-Pt bond, resulting in the decreased separation of the energy levels involved in the transitions. During the gelling process, the metal complex

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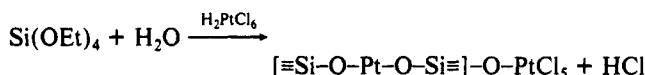
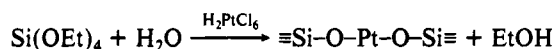
(13) Jorgensen, C. K. *Acta Chem. Scand.* **1956**, *10*, 518.

(14) Schlesinger, H.; Tapley, M. J. *Am. Chem. Soc.* **1924**, *46*, 276.

TABLE III: UV-Vis (Diffuse Reflectance) of Pd Catalysts

catalyst	CT band, nm	d-d bands, nm
Pd-0.1	330	500, 650
Pd-0.3	330	480, 680
Pd-0.5	330	485, 680
Pd(D)0.5		470, 675
Pd(I)0.5	365	510, 680
Pd/SiO ₂ (ref 16)	370	500

is present from the beginning; the Pt which will be inside the silica and in the silica surface are generated at the same time:



The surface complex interacts with the silanol groups ($\equiv\text{Si}-\text{OH}$) before the complete support formation, whose final step is the condensation. The result is a completely different $\equiv\text{Si}-\text{O}-\text{Pt}$ interaction from the one obtained in the impregnation case. The band shift cannot be due to the Pt present in the silica network, because it is not observed for the Pt0.3(I)0.2 catalyst. In the sol-gel solids the surface hydroxylation becomes very important. The low metal concentration in the Pt-0.1 catalyst is present mainly inside the silica, and there is no absorption in the UV-vis region.

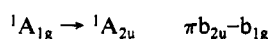
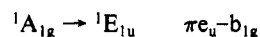
In the Pt-0.3, Pt-0.5, and Pt(D)0.5, part of the metal is found in the silica network and the rest is on the surface as a pseudo-octahedral complex. The large differences observed among the Pt-0.3, Pt-0.5, and the Pt(D)0.5 spectra are due to different degrees of hydroxylation. When the TEOS is slowly added dropwise to the refluxed metal solution (Pt(D)0.5), the nucleation process is very uniform. Most of the ethoxy ($\equiv\text{Si}-\text{OEt}$) and silanol ($\equiv\text{Si}-\text{OH}$) intermediates are condensed for the silica formation, and the solid surface has very few OH groups. This allows less metal-support interaction to take place through the surface hydroxyls, resulting in observation of only two bands (521 and 555 nm) in the d-d region. The CT band which for PtCl₆ appears at 202 nm is shifted to 214 nm (Figure 2). Gonzalez et al.¹⁵ proposed a similar model for conventional catalysts impregnated on commercial silica Ketjen F2.

In the Pt-0.3 and Pt-0.5 catalysts the surface is totally hydroxylated, which has been verified by IR spectroscopy,⁹ and five d-d bands are observed in the electronic spectra. Two of the d-d bands are intense and the other three are shoulders. Concerning the CT bands, in the Pt-0.3 spectrum the first band is shifted up to 238 nm due to the high number of OH groups in the support surface which strongly interact with the metal complex. This interaction weakens the Pt-Cl bonds and lessens the energy levels separation.

Palladium Catalysts. Table III shows the results for the Pd catalysts. Although the solids were prepared with PdCl₂, which is a linear complex, the catalyst spectra correspond to a square planar (*D*_{4h}) complex.

Bozon-Verduraz et al.¹⁶ impregnated commercial silica with PdCl₂, and they found two bands (370 and 500 nm). According to Rasmussen,¹⁷ the second one can be attributed to complexes which do not have chlorine in the coordination sphere. The other one indicates that in the surface of the support there exists platinum chloride.

In our catalysts, besides these two bands, a third one appears around 680 nm (Table III). The d-d bands can be assigned to the transitions



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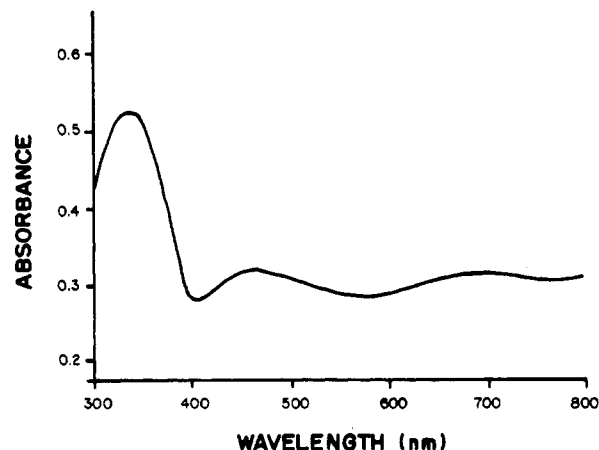


Figure 3. UV-vis (diffuse reflectance) spectrum of Pd-0.5.

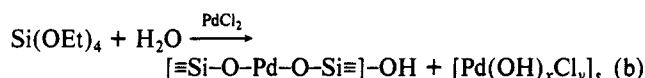
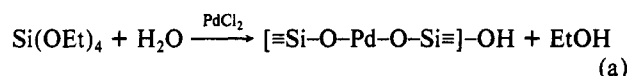
TABLE IV: UV-Vis Bands (Diffuse Reflectance) of Ru Catalysts

catalyst	CT band, nm	d-d bands, nm
Ru-1	325	500, 600, 680, 750
Ru(D)0.5	325	480, 680
Ru(I)1.0	325	500, 680, 750
RuCl ₃ /LiCl (ref 26)	424, 460	520, 559, 625, 831
Ru(H ₂ O) (ref 27)	333, 392	600

The CT band observed at 330 nm is assigned to the $L_{\text{TB}}-\text{d}\sigma^*$ transition.^{18,19}

The OH groups present in the sol-gel silica surface cause a slight shift (500–510 nm) compared with the Pd(I)0.5 and the Pd/SiO₂²⁰ catalysts. The hydroxylated support gives a metal-support interaction.

For the sol-gel catalysts (Pd-0.1, Pd-0.3, and Pd-0.5) the d-d and CT bands are shifted toward higher energy (Figure 3). There is a stronger metal-support interaction than in the impregnated catalysts, and the metal energy levels are separated. The square planar complex is formed at the same time as the silica. As in the Pt case, $\equiv\text{Si}-\text{O}-\text{Pd}-$ species are formed in the reaction medium, giving a different interaction than the one observed in the traditional catalysts. It can be proposed that the following reactions take place:



In this catalyst, the silica network is saturated more rapidly with Pd than in the case of Pt; even the Pd-0.1 catalysts have Pd in the surface. The Pd catalysts have more metal on the surface than the corresponding Pt ones. On increasing the metal concentration, the 500-nm d-d band is shifted toward higher energy values. In the $[\text{Pd}(\text{OH})_x\text{Cl}_y]$, the value of *x* increases and the metal-support interactions become stronger. The energy levels involved in the transition become separated.

For the Pd(D)0.5 catalyst the band is shifted up to 470 nm because the Pd(OH)₄ complex is formed before the TEOS is added dropwise during the gelation process. The CT band is not observed because the Pd-Cl charge transfer does not exist.

Ruthenium Catalyst. The Ru behavior is quite different from Pt and Pd because is very unstable. A most unusual discussion was once made with respect to the Ru oxidation state. Howe^{21,22}

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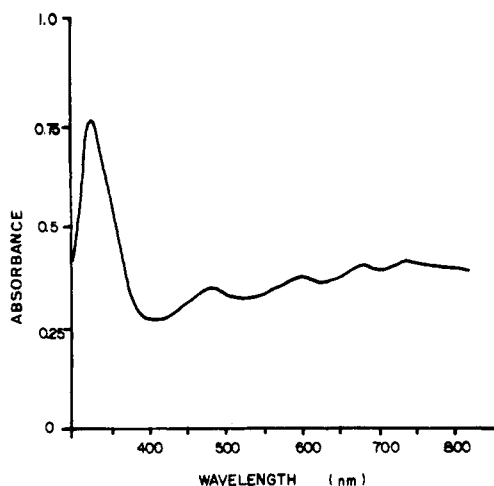
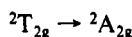
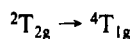


Figure 4. UV-vis (diffuse reflectance) spectrum of Ru-1.

prepared a rose-red isomer of the dark-brown $K_2RuCl_5 \cdot H_2O$ and maintained that these two salts and the yellow anhydrous K_2RuCl_5 all contain trivalent ruthenium. Charonnat²³ demonstrated that the dark-brown salt was really K_2RuCl_5 . The red complexes $RuCl_6$ and $RuCl_5(H_2O)$ are well known, the first one is stable only in very strong HCl medium. It was resolved that the Ru(III) complexes are always hexacoordinated (octahedral field).

The Ru in our catalysts form d^5 complexes with a $[2t_{2g}(xy, xz, yz)]^5$ ground-state configuration. This type of complex has an intense Ct band in the high-energy region and three d-d bands having intensities that are low and sometimes cannot be observed. Low-symmetry Ru(III) complexes are quite common but their spectra have rarely been studied in detail. Figure 4 shows the UV-vis for the Ru-1 catalyst. An intense band appears at 330 nm which can be assigned to electronic transfer between the π orbitals of the chlorides and the $[\pi 1t_{2u}-2t_{2g}]$ metal orbitals. The d-d bands from Table IV are assigned to the following transitions:^{24,25}



The two lowest (λ) absorptions, which are spin-forbidden, can be frequently observed as shoulder.^{26,27}

Table IV shows the results for the bands obtained in the Ru catalysts spectra. In the table the data reported for the $RuCl_3$

and $Ru(H_2O)_6$ complexes have been included in order to facilitate the spectra interpretation.

The Ru-1 and Ru(1)1 catalysts spectra are quite similar and can be compared with $RuCl_3$. It is observed that for the catalysts the bands are shifted toward lower energy. The silanols ($\equiv Si-OH$) interact with the metal and the Ru-Cl bond becomes weaker giving the band shift mentioned above. On the other hand, according to the former discussion, the Ru coordinates very easily with the water molecules present in the reaction medium forming $[RuCl_x(H_2O)_y]$ complexes.

For the Ru(D)0.5 catalyst, the Ru forms $[RuCl_x(H_2O)_y]$ complexes before the silanol formation. When the silicon alkoxide initially is added dropwise, it interacts immediately with the Ru complex, which is different than in the Ru-1 case. The d-d band shift up to 480 nm is the result of the basic medium (pH 9) in which the reaction takes place. Furthermore, no $Ru(H_2O)_6$ is evident in the medium.

Conclusions

1. UV-vis spectroscopy is sensitive to the metal-support interactions present on the catalyst surface.

2. By the sol-gel method, part of the metal is inserted into the silica network giving rise to $\equiv Si-O-M-$ species. The rest of the metal is on the surface. In a conventional impregnation method all the metal is on the surface. Previous results prove that a large number of OH groups are present on the surface.^{7,28,29}

3. In the sol-gel catalysts the metal interacts with the silanol and ethoxy groups before the silica formation, resulting in different metal-support interactions than for the impregnated catalysts. The difference is reflected in their UV-vis spectra.

4. Pt-0.1 and Ru-0.1 catalysts do not show absorption spectra. In these catalysts all the metal is inserted into the silica network. For the Pd-0.1 catalyst an absorption spectra can be obtained. In this case part of the metal is on the catalyst surface. It can be assumed that the silica network has been saturated with lower metal contents than in the Pt and Ru catalysts.

5. By the method where silicon alkoxide is added dropwise into the solution which contains the metal salt, the interaction between the reactants is greater. The silanols react easily to form silica, and the degree of hydroxylation of the surface of the final solid is low.⁹

6. The oxidation state of the metal on the catalysts surface does not change with the preparation method. Pt and Ru form octahedral complexes, and the Pd a square planar complex.

7. In the Ru and Pd catalysts, the water molecules are easily incorporated into the coordination sphere, giving $[M(H_2O)_xCl_y]$ type complexes.

Acknowledgment. We acknowledge support from SEP-PROIDES for this research.

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