Pt Effect on the Particle Morphology and Crystalline Structure of Pt/MgO Catalysts

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We have made Pt/MgO catalysts by cogelling magnesium ethoxide and hexachloroplatinic acid. The reduction capability of the hydrolysis reaction brings about the formation of metallic platinum in air, even at 70 °C. In the course of the magnesium alkoxide gelation, platinum catalyzes the synthesis of brucite crystallite elongated along the (110) direction. Platinum also promotes the formation of small MgO crystallites, which are highly magnesium deficient. Platinum atoms, however, do not incorporate into the periclase lattice.

Introduction

Subjected to special heating and pressurizing conditions, magnesium oxide has very interesting properties when it is used as a support in catalysis.[1-3] It stabilizes the supported metals in unusual oxidation states and affects the activity of the catalysts,[4-8] for instance, in the hydrogenation of carbon monoxide, platinum supported on magnesium oxide has higher selectivity than when it is supported on silica.

Using magnesium oxide as a support, Logan *et al.*[9] showed that the stabilization of the metallic phase depends on the morphology, the crystalline structure, and the crystallite size of the support. The use of silica and alumina supports, instead of magnesium oxide, reduces these effects.

Magnesium oxide by itself has a catalytic activity that can be modified either by defects in the lattice or by adding impurities,[10-12] for example, Holt *et al.*[1] studied the morphology of MgO—Cl solids. They found that the crystallinity of the periclase—brucite system is determined by the presence of chlorine. From the differential thermal analysis of magnesium oxide, Leofanti *et al.*[13] observed that the desorption of water in brucite, as a function of temperature, has an important temperature shift when chlorine is present. The above results show that the preparation method of the catalyst modifies the support.

In the preparation of metal-supported catalysts, the addition of the aqueous solutions containing the active metal can strongly modify the support. The hydrolysis produced during the impregnation of magnesium oxide transforms periclase (MgO), the crystalline phase of magnesium oxide, into brucite (Mg-(OH)₂), which is the precursor of MgO. This could cause the metallic particles to adsorb hydroxyls,[9] bringing about strong modifications of the metal activity. The metal precursor also affects the support.

In the present work, we studied the effect of the metal precursor on the morphology, the crystallinity, and the crystallite size of metal magnesium oxide-supported catalysts. To magnify this effect, we prepared platinum magnesium oxide-supported catalysts, starting from magnesium alkoxides and using the sol—gel method.[14-17] Applying X-ray diffraction and refining the crystalline structure by the Rietveld technique, we also analyzed
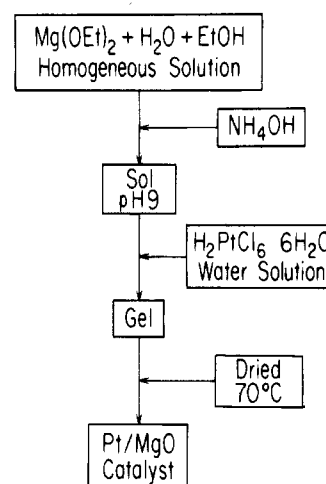

Figure 1. Diagram describing the synthesis of Pt/MgO catalysts.

the effect of hexachloroplatinic acid on the morphology of the magnesium oxide crystals.

Experimental Section

Synthesis of Mg(OC₂H₅)₂. We mixed 0.21 mol of metallic magnesium with 1.7 mol of anhydrous ethanol and 3.9×10^{-4} mol of iodine, stirring continuously. After 24 h of reaction, 6.82 mol of ethanol was added to the sol so that all magnesium reacts. After that, the excess ethanol was vaporized. The residue was washed and dried, and a white powder was obtained.

Synthesis of Sol—Gel Pt/MgO. With constant stirring, 0.13 mol of magnesium diethoxide with 1.39 mol of water, 0.17 mol of anhydrous ethanol, and 0.02 mol of NH₄OH were refluxed. After 10 min of reaction, to the samples with 1 wt % Pt were added drops of a pH 9 solution containing 1.39 mol of water and 2.56×10^{-4} mol of H₂PtCl₆·6H₂O. The amount of H₂-PtCl₆·6H₂O added to the samples with 2 wt % Pt was 5.12×10^{-4} mol. The gels have a dark blue color, which changes to a gray color after drying them in air at 70 °C (fresh samples). Preparation of the catalyst is summarized in Figure 1.

Characterization. *X-ray Diffraction.* X-ray powder diffraction (XRD) measurements were done at room temperature with an X-ray diffractometer in the reflection geometry, with Cu Kα radiation and a secondary beam monochromator. XRD specimens were prepared by packing the sample powder in a glass sample holder. Intensity data were measured in the 2Θ

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range between 35° and 110°, with a 2Θ step size of 0.02° and a measuring time of 4 s/point. With these measuring times, the intensity of the principal peak is larger than 10^4 counts.

The crystalline structure of the observed phases was refined by the Rietveld technique using the DBWS-9006PC[18] and the WYRIET[19] (version 3) programs. The crystalline structures of periclase and metallic platinum were refined using in each case a cubic unit cell with space group *Fm3m*. Since we were also interested in obtaining the average crystallite size of each phase, as profiles for the diffraction peaks, we used a pseudo-Voigt function modified by Thompson et al.,[20] which has average crystallite size and microstrain as two of the profile-breadth fitting parameters.[21] The breadth at half maximum (fwhm) has a Gaussian contribution H_G and a Lorentzian contribution H_L given by[20,21]

$$H_G = U \tan^2 \Theta + V \tan \Theta + W \qquad (1)$$

and

$$H_L = X \tan \Theta + Y/\cos \Theta \qquad (2)$$

Since all the samples were annealed at the temperature of interest for at least 12 h, we assumed that they were free of microstrains ($X = 0.0$). According to this assumption, only the crystallite size contributes to the broadening of the Lorentzian part ($Y \neq 0.0$). The crystallite size values that we report in the present paper are obtained from this parameter. The instrumental broadening is contained in the parameters U, V, and W of the Gaussian contribution. Their values were determined in a Rietveld refinement with data of a polycrystalline corundum sample. These values were fixed in the Rietveld refinements described in the present work.

In the refinement, the U term in the Gaussian contribution was always positive. This result contrasts with that found by Young et al.[21] in their Rietveld analysis of the crystallite size of anatase, where the U values were negative. Their U values were negative because the crystallite morphology in their anatase sample was anisotropic. Therefore, Young et al.[21] omitted the reflections 200, 220, and 400 of anatase from the Rietveld refinement.

The specimen displacement is the first refined parameter; its value is nearly the same as those observed in the Rietveld refinement of the crystalline structure of all the samples measured in the same diffractometer. Background was refined using a polynomial function. All the programs for the Rietveld refinement used the atomic scattering factors for neutral atoms from the *International Tables for X-ray Crystallography*.[22]

After refining all the parameters used in our analysis, we additionally refined the parameters associated with the transparency and absorption of the sample. These parameters, however, did not take values significantly different from zero, and their refinement did not change the values of all the other parameters. Therefore, the parameters associated with the transparency and with the absorption of the sample were finally fixed at zero.

The estimated standard deviations, indicating the variation of the last figures of the corresponding number, are given in a parentheses. They are obtained from the Rietveld refinement. It is important to note that these deviations are not estimates of the probable error in the analysis as a whole but only of the minimum possible probable errors based on normally distributed random errors alone.[23]

Transmission Electron Microscopy (TEM). The samples were ground and dispersed in distilled water in an ultrasonic bath. Some drops of this mixture were deposited on a 200-mesh copper grid covered with a carbon film. Bright field
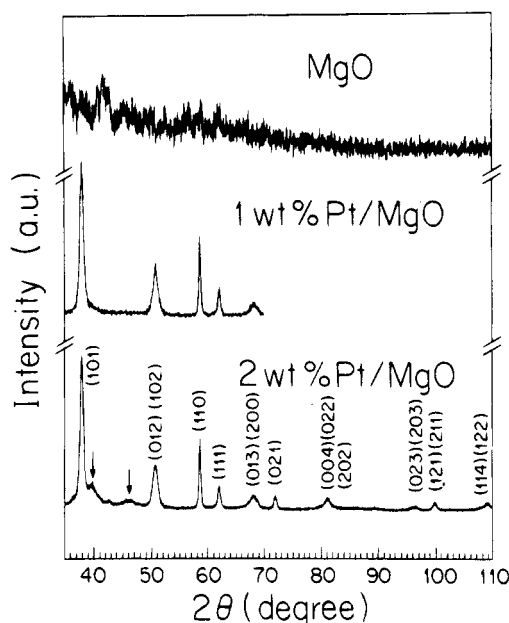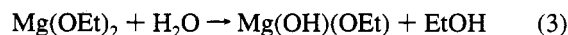

Figure 2. X-ray diffraction patterns of fresh MgO and Pt/MgO catalysts. The indexing corresponds to brucite, while the arrows show peaks corresponding to metallic platinum.

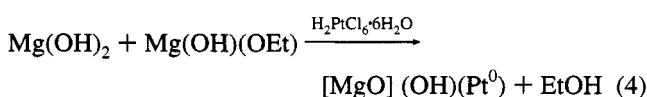images and selected area electron diffraction patterns of the deposited crystallites were obtained.

Results and Discussion

All the phases present in the fresh samples of the sol—gel MgO catalyst are different from those in the fresh samples of the sol—gel Pt/MgO catalysts (Figure 2). The fresh sol—gel MgO catalyst prepared at pH 9 has an amorphous structure, which partially converts into periclase when the sample is heated at higher temperatures.[10] Brucite is the phase generated in the fresh sol—gel Pt/MgO catalysts, instead of the amorphous phase. The width of the (110) diffraction peak of this brucite is smaller than the width of the other diffraction peaks. This shows that brucite crystallites are larger along this direction. They have an anisotropic morphology. This result is confirmed by the transmission electron microscopy analysis (Figure 3). The TEM micrograph shows the presence of needle-like crystallites, which, according to their selected area electron diffraction patterns, correspond to brucite.

In the X-ray diffraction pattern of the fresh 2 wt % sol—gel Pt/MgO catalyst (Figure 2), the (101) diffraction peak of brucite has a broad shoulder, which is shown in Figure 2 by an arrow. This shoulder corresponds to the (111) diffraction peak of metallic platinum. A second diffraction peak of metallic platinum is found at 2Θ = 46.3°, which is also shown by an arrow in Figure 2. This broad peak corresponds to the (002) diffraction peak of metallic platinum and confirms the existence of this phase in the fresh samples. We want to remark that this metallic platinum is obtained in air at only 70 °C. Metallic platinum and its support are obtained in only one step, because of the reduction capability of the hydrolysis reaction inherent to the sol-gel technique. The reactions in the sol—gel process consist of the hydrolysis reaction:

$$Mg(OEt)_2 + H_2O \rightarrow Mg(OH)(OEt) + EtOH \qquad (3)$$

followed by the condensation reaction:

$$Mg(OH)_2 + Mg(OH)(OEt) \xrightarrow{H_2PtCl_6 \cdot 6H_2O}$$

$$[MgO](OH)(Pt^0) + EtOH \qquad (4)$$

This result contrasts with results obtained in the traditional

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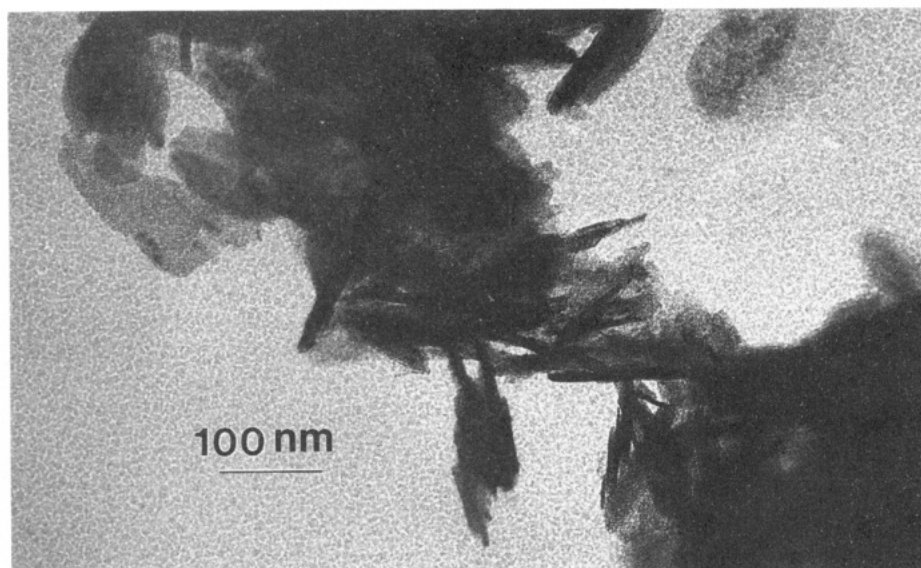

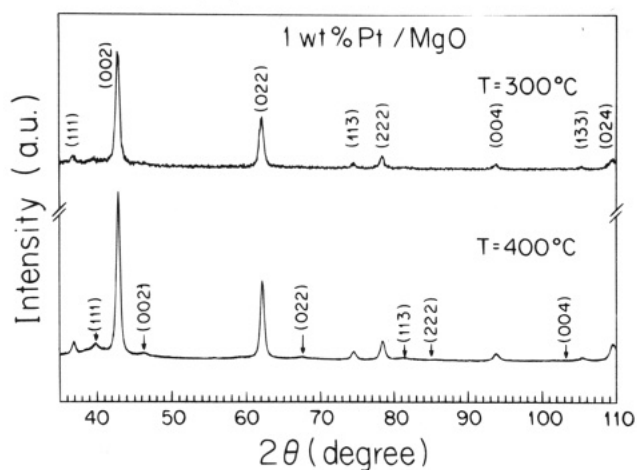**Figure 3.** TEM micrograph of a fresh 1 wt % Pt/MgO catalyst.

Figure 4. X-ray diffraction patterns of the 1 wt % Pt/MgO catalyst after heating in air at 300 °C and after reducing in H_2 at 400 °C. The indexing of the diffraction pattern at 300 °C corresponds to periclase, and the indexing of the diffraction pattern at 400 °C corresponds to Pt^0. Both structures are cubic with space group *Fm3m*. Therefore, the indices in both curves are the same, but they correspond to different structures.

Figure 5. X-ray diffraction patterns of the 2 wt % Pt catalyst, after heating in air at 300 °C and after reducing in H_2 at 400 °C. The indexing shown in the figure corresponds to Pt^0.

methods used for preparing Pt/MgO catalysts. There, to obtain supported metals, the samples will be prepared in two steps. In the first one, the support will be prepared, and in the second one, the metal will be supported.

The broad peaks of platinum correspond to a small crystallite size. The average size of these crystallites could not be extracted from the Rietveld refinement, because the X-ray diffraction patterns of brucite and metallic platinum are superimposed and the crystalline structure of brucite could not be refined. This, because the crystallites of brucite have an anisotropic morphology, and the program we used for the Rietveld refinement demand that the crystallites of the phases to be refined have an isotropic morphology. The important finding, however, is that by the sol−gel preparation of Pt/MgO catalysts, metallic platinum is formed even after drying the sample in air at 70 °C.

When the samples of the Pt/MgO catalyst with 1 wt % Pt were heated in air at 300 °C, the brucite completely converts into periclase (Figure 4). The reduction of these samples at 400 °C in H_2 does not produce any changes, either in their phase composition or in the crystalline structure of their phases. When the samples of the Pt/MgO catalyst with 2 wt % Pt are heated
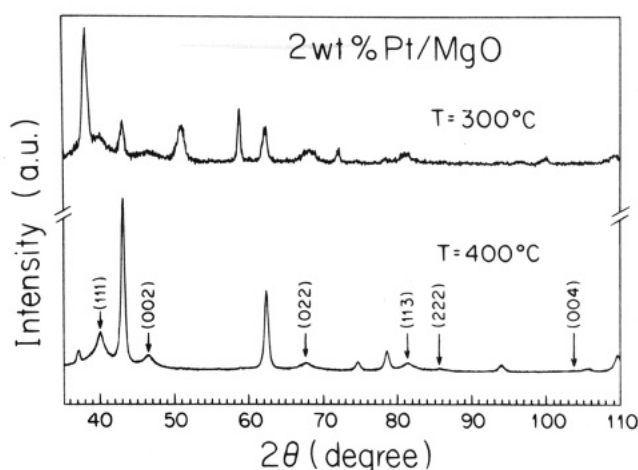
in air at 300 °C, brucite, the majority phase, partially changes into periclase (Figure 5). The conversion of brucite into periclase is only complete after heating the samples at 400 °C (Figure 5). Table 1 resumes the refined parameters that characterize the reduced samples for the platinum concentrations studied in the present work.

After reducing the samples at 400 °C in hydrogen, they have two crystalline phases. The two phases are periclase, having an average crystallite size of 21.5 (5) nm, and metallic platinum, having an average crystallite size of 4.5 (1) nm. These values were obtained from the Rietveld refinement. Figure 6 shows the Rietveld refinement plot for a sample of the Pt/MgO catalyst with 1 wt % Pt. From this figure, we observe that the difference curve, obtained by finding the difference between the experimental data of the X-ray diffraction pattern and the respective theoretical values, has a small peak at the position of the (111) diffraction peak of platinum. This small peak is marked in the figure by an arrow. Its presence indicates that a fraction of the metallic platinum phase has a higher average crystallite size. Therefore, the Rietveld refinement was done with two metallic platinum phases with different average crystallite sizes. After the refinement, we found that the sample has a small fraction of metallic platinum with an average crystallite size of 44 (10) nm. Its contribution is only 3 wt % of all the platinum in the Pt/MgO catalyst with 1 wt % Pt and 5 wt % of all platinum in

TABLE 1: Parameters^a Obtained from the Rietveld Refinement of the Crystalline Structure of MgO and Pt^0 in Pt/MgO Catalysts Reduced in H$_2$ at 400 °C and in MgO Catalyst Heated in Air at 600 °C[10]

catalyst	periclase lattice parameter (nm)	periclase average crystallite size (nm)	Mg occupancy	Pt^0 lattice parameter (nm)	Pt^0 average crystallite size (nm)
1 wt % Pt/MgO	0.42184 (1)	21.6 (4)	3.50 (1)	0.39187 (6)	4.5 (1)
2 wt % Pt/MgO	0.42166 (1)	21.5 (5)	3.52 (2)	0.39208 (4)	4.5 (1)
MgO	0.421179 (9)	64.4 (1.5)	3.82 (2)		

^{a} Estimated standard deviations are also obtained from the refinement. The Mg occupancy for a stoichiometric composition is 4.00.
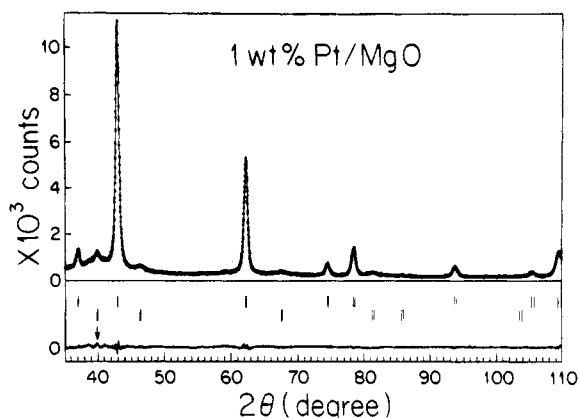

Figure 6. Rietveld refinement plot for the reduced 1 wt % Pt/MgO catalyst, $R_{wp} = 0.059$. The crystalline structure of periclase, corresponding to the upper tick marks and $R_F = 0.008$, and the crystalline of Pt^0, corresponding to the lower tick marks and $R_F = 0.016$, were refined with space group $Fm3m$.

the catalyst with 2 wt % Pt. Since more than 94 wt % of all the metallic platinum crystallites have an average size 5 times smaller than the crystallite size of the support, they could be supported on the anatase crystallites. The rest of the platinum (less than 6 wt %) has a larger average crystallite size than the support and, therefore, is probably segregated and not supported.

From Table 1, we conclude that platinum promotes the formation of smaller crystallites of magnesium oxide than those obtained when it is absent. It also promotes a larger magnesium deficiency in the crystalline structure of periclase. The Mg:O molar ratios are 3.50 (1):4.00 for the Pt/MgO catalyst with 1 wt % Pt and 3.52 (2):4.0 for the catalyst with 2 wt % Pt. These values correspond to a magnesium deficiency, because the Mg:O molar ratio for a stoichiometric composition in periclase is 4.0: 4.0. The magnesium deficiency in the presence of platinum was larger than that obtained when it was absent.[10] As in the systems without platinum,[10,24] the introduction of hydrogen into the crystalline lattice of anatase in the Pt/MgO catalysts probably produces the magnesium deficiency.

From our analysis, within the range of the resolution of the techniques used to perform it, we do not have any indication that platinum atoms incorporate into the crystalline structure of periclase. The unit cell of periclase neither was distorted nor showed any appreciable expansion. Because platinum has a larger atomic number than magnesium, the substitution of some magnesium by platinum atoms would produce a magnesium occupancy larger than 4.0 in the refinement. The magnesium occupancy obtained after the refinement, however, was always lower than 4.0. This value of 4.0 corresponds to the occupancy for a stoichiometric composition.

Conclusions

Should platinum be added to MgO catalysts when they are produced by the sol–gel technique, the crystalline phases formed during the process are different from those made up without platinum. The fresh samples of the Pt/MgO catalyst, dried in air at 70 °C, are composed of metallic platinum with a small crystallite size and brucite crystallite elongated in the (110) direction. The platinum precursor is hexachloroplatinic acid, which during the gelling process converts into metallic platinum. This result is very important for the synthesis of supported catalysts, because support and supported metal are prepared simultaneously, in only one step. Hexachloroplatinic acid, the platinum precursor, brings about a morphological effect in MgO. Platinum promotes the formation of small periclase crystallites and a high magnesium deficiency in the crystalline structure of periclase, but it does not incorporate into this structure.

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