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Synthesis and Characterization of Sol–Gel Pt/TiO_2 Catalyst

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Pt/TiO_2 catalysts with 1.0 wt% Pt were prepared by using the sol–gel technique with $Ti(OBut)_4$ and platinum acetylacetonate. The catalysts were prepared in only one step, without the need to reduce the sample in hydrogen. All fresh samples have three nanophases: rutile (the majority phase), anatase, and platinum. Their crystalline structure was obtained by X-ray powder diffraction and refined with the Rietveld technique. Samples were also characterized by FTIR spectroscopy. Platinum promoted the formation of rutile. This could stem from either the presence of PtO_2, which has the rutile structure, as an intermediate phase, or the platinum-catalyzed dehydroxylation of anatase. Although PtO_2 and rutile have the same crystalline structure, platinum atoms did not go into the crystalline structure of rutile. © 1996 Academic Press, Inc.

1. INTRODUCTION

For the past decade, the sol–gel technique has received a lot of attention in science and technology. In comparison to traditional techniques, it offers many advantages (1–5). For example, in the sol–gel process, precursor materials are metallic alkoxides that favor the building of a solid network in a gel which eventually transforms into a stable solid. Since the final characteristics of sol–gel samples depend on the precursors used in the initial solutions, materials with very special requirements can be made (6–10).

When the sol–gel technique is used for developing catalytic materials, it provides very interesting results. For instance, in metal supported catalysis, the active metal and the support can be prepared in one step (11). This allows an economy in the catalyst preparation, and also allows one to develop catalysts with new properties. The sol–gel technique can also be used for preparing the support alone. This support determines the dispersion and stabilization of the active metal (12, 13) and has a specific surface area that can be regulated by controlling its particle size and porosity. Since the sol–gel process is associated with a hydrolysis reaction, OH groups are deposited on the surface or in the bulk of the support. The active metal can also be supported by an impregnation method; the results, however, can differ from those obtained by co-gelling active metal and support (11).

Changing hydrolysis catalyst and pH changes the initial properties of the catalyst support. These properties are also affected by doping the sol with oxides (14) or oxide precursors (15).

In summary, the three synthesis parameters, the hydrolysis catalyst, the pH, and the type of doping oxide, determine many of the properties of the fresh catalyst.

In the present paper, we report the characterization of the platinum titania-supported catalyst prepared by the sol–gel technique. Because of the high degree of hydroxylation of the generated titania, the sol–gel technique caused the titania crystalline lattice to have a large density of defects. The sol–gel catalysts had crystallite sizes in the range of nanocrystals, and were obtained in only one step, without the need to reduce them in hydrogen, since the reactions produced during the sol–gel process provided the reduction (16-18).

2. EXPERIMENTAL

Synthesis of Sol–Gel TiO_2

We mixed 3.2 mol of deionized distilled water with 1.2 mol of butanol and an adequate amount of HCl to obtain pH 3, refluxing at 70°C and stirring constantly. Then, we added drop by drop while refluxing 0.2 mol of $Ti(OBut)_4$ to the mixture during 4 h until the gel was formed. This gave a water/alkoxide molar ratio of 16.

Synthesis of Sol–Gel Pt/TiO_2

While refluxing and continuously stirring, we mixed 1.2 mol of butanol, 3.2 mol of distilled water, 1.2 mol of HCl (to obtain pH 3), and 0.2 mol of $Ti(OBut)_4$, which gave a water/alkoxide molar ratio of 16. In order to have 1.0 wt% of Pt, we added the corresponding amount of platinum

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acetylacetonate solution to this mixture. Refluxing and stirring were maintained until the gel was formed.

In both systems, samples were dried at 70°C for 24 h. For the analysis 2 g of each system were annealed in air for 12 h at 200, 400, 600, and 800°C, with a heating rate of 20°C/min.

Sample Characterization

X-ray diffraction and Rietveld refinement. The crystalline structure of the phases in the samples was obtained by X-ray powder diffraction, using a reflection diffractometer with CuKα radiation and a graphite secondary-beam monochromator. Each specimen for the X-ray diffraction analysis was prepared by packing the sample powder in a glass holder. Intensity data were measured by step scanning in the 2θ range between 18° and 130°, with a 2θ step size of 0.02° and a measuring time of 2 s per point. In the analysis, the atomic scattering factors for neutral atoms from the "International Tables for X-ray Crystallography" (19) were used. The crystalline structure of the observed phases was refined by the Rietveld technique using DBWS-9006PC (20) and WYRIET (21), version 3, programs. Since we were also interested in obtaining the average crystallite size of each phase, as peak profile we used a pseudo-Voigt function modified by Thompson *et al.* (22), having average crystallite size and microstrain as two of the profile-breadth fitting parameters. We assumed that the crystallites have isotropic morphology.

Standard deviations, showing the variation of the last figures of the corresponding number, were given in parentheses. When the number corresponded to a parameter obtained from the Rietveld refinement, the estimated standard deviation was not an estimate of the probable error in the analysis as a whole, but only of the minimum possible probable error on its normal distribution (23).

FTIR Spectroscopy

FTIR of the solids was performed with a 170-SX Fourier Nicolet spectrometer. In order to avoid using KBr, the transparent pellets were prepared by pressing the sample powders.

3. RESULTS AND DISCUSSION

X-ray Diffraction Analysis

The parameters characterizing each crystalline structure, its average crystalline size, and its weight concentration were obtained from the Rietveld refinement. In the present study, the only crystalline phases observed were anatase, rutile, and platinum (Fig. 1). For the refinement of each phase we used the same unit cell that characterizes the phase for large crystallite sizes. These were as follows: for anatase a tetragonal four-TiO_2-molecule unit cell with space group $I4_1/amd$ and the atom positions given in Table 1; for rutile a tetragonal two-TiO_2-molecule unit cell with space group $P4_2/mnm$ and the atom positions given in

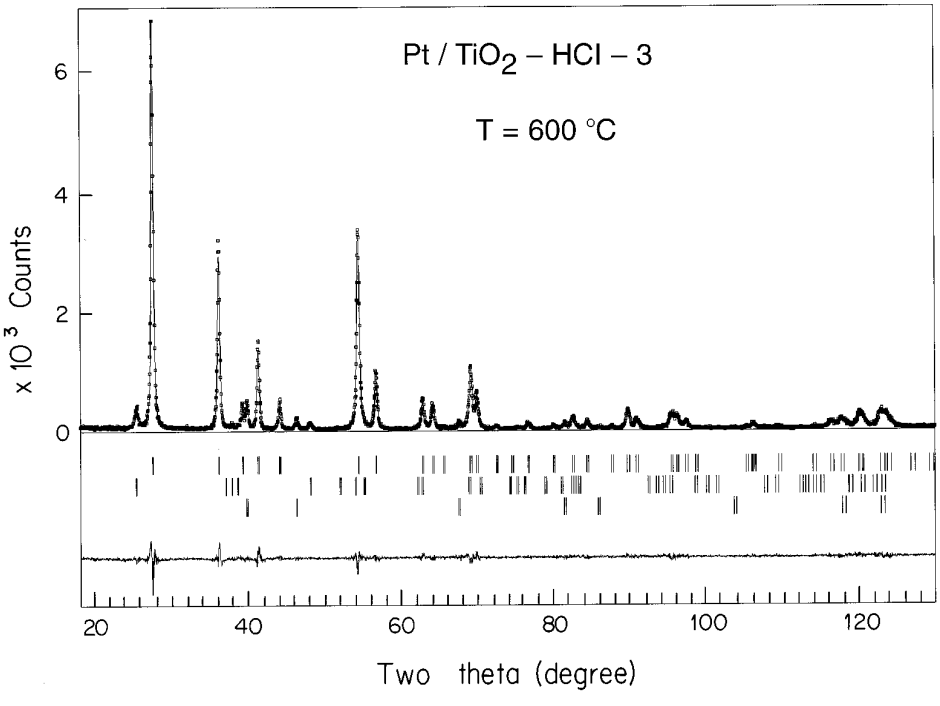

FIG. 1. Rietveld refinement plot for the sol–gel Pt/TiO_2 catalyst with 1.0 wt% Pt. It has three phases: rutile (upper tick marks) with $R = 0.042$, anatase (middle tick marks) with $R = 0.12$, and metallic platinum (lower tick marks) with $R = 0.075$.

TABLE 1
Anatase (Space Group $I4_1/amd$): Atomic Fractional Coordinates

Atom	Site	*x*	*y*	*z*
Ti	4*a*	0.0	0.75	0.125
O	8*e*	0.0	0.25	0.0782

Table 2; for metallic platinum the four-Pt-atom unit cell with space group *Fm3m* and the platinum atom positioned at the center of the cell.

Brookite, anatase, and rutile are the most common allotropic forms of titania (24). When titania catalysts are produced by the sol–gel technique the initial phases in the sample depend on its preparation (10). When the sol–gel titania catalyst was prepared at pH 3 with HCl as the hydrolysis catalyst, the fresh sample (Fig. 2) had anatase as the principal phase (84.7 wt%), brookite as the minority phase (13.6 wt%) and rutile as an impurity phase (1.7 wt%). The weight percentages were obtained from the Rietveld refinement of the crystalline structure of the three nanocrystalline phases.

When samples were calcined, the average crystallite sizes increased, and anatase, the majority phase, and brookite were transformed into rutile. Therefore, after heating the samples at high temperatures, the samples only contained rutile. In accordance with the FTIR studies, the transformation of anatase into rutile was correlated with the dehydroxylation of the sample.

In the sol–gel Pt/TiO_2 catalysts prepared at pH 3 with HCl as the hydrolysis catalyst, the initial concentrations of the crystalline phases were different from those observed in the platinum-free sol–gel titania (Fig. 3, Table 3). Here, rutile was the majority phase (80.4 wt%) and anatase the minority phase (18.6 wt%). Metallic platinum, having a weight concentration that corresponded to the nominal composition of 1.0 wt%, was the third phase. We also found that rutile nanocrystallites were deficient in titanium (Table 3). Calcining the samples at higher temperatures not only increased the average crystallite size of all three phases but also caused the transformation of anatase into rutile (Fig. 3).

Trying to explain why the presence of platinum promoted the formation of rutile, we point out that PtO_2 has a rutile structure with lattice parameters $a = 0.49915$ and $c = 0.28794$ nm. These values are similar to those obtained for rutile in the fresh sol–gel titania samples, which were $a = 0.4604(2)$ and $c = 0.2951(3)$ nm. The difference in the values of the parameters corresponded to a mismatch of 7.7% for lattice parameter *a* and 2.5% for lattice parameter *c*. If PtO_2 exists in the sol–gel Pt/TiO_2 catalyst as an intermediate product during sample preparation, it will work as a seed for the formation of rutile. This proposition is reinforced by the reported finding that doping the solution with cassiterite (SnO_2) promotes the formation of rutile too, (14)—Cassiterite has a rutile structure with lattice parameters $a = 0.47382(4)$ and $c = 0.31871(1)$ nm (25). In this case, the mismatch between these lattice parameters and those of the fresh sol–gel titania was 2.8% for the lattice parameter *a* and 3.2% for the lattice parameter *c*.

The formation of rutile as the majority phase in the fresh sol–gel Pt/TiO_2 samples happened even at a platinum concentration of 0.1 wt%.

Although PtO_2 has the rutile structure, in the X-ray diffraction analysis we did not find any indication that platinum atoms go into the crystallite structure of either anatase or rutile.

TABLE 2
Rutile (Space Group $P4_2/mnm$): Atomic Fractional Coordinates

Atom	Site	*x*	*y*	*z*
Ti	4*a*	0.0	0.0	0.0
O	8*e*	*u*	*u*	0.0

Note. According to Table 3, *u* takes values between 0.3029(4) and 0.3049(4).

FTIR Analysis

The spectrum of the fresh sol–gel titania samples had a wide band at 3172 cm^{-1} (Fig. 4) produced by the stretching vibration of the Ti–OH bonding. Near to this band, at 2360 cm^{-1}, a shoulder was generated by an asymmetric vibration of the residual butoxyl groups of the nonreacted alkoxide. The intensity of the 3172 cm^{-1} band was high, suggesting that the Ti–OH bonding dominated the gelling reaction. This result supports the fact that an acid environment favors hydrolysis and slows condensation (6). Since titania crystallites were very small, the local environment of the Ti–OH bonding was not homogeneous, widening the 3172 cm^{-1} band.

The bending vibration of the Ti–OH bonding generated a band at 1600 cm^{-1} that moved to 1630 cm^{-1} when the samples were heated at 400°C; it eventually disappeared with temperature (Fig. 4). In the low energy region (800–400 cm^{-1}), the structure of the spectrum was not well defined, which is a characteristic of sol–gel titania.

When the samples were heated, they dehydroxylated, causing the intensity of the band at 3172 cm^{-1} to decrease; this intensity was zero when the samples dehydroxylated totally. According to the present X-ray diffraction analysis and those previously reported for sol–gel titania (10), this dehydroxylation was correlated with the transformation of

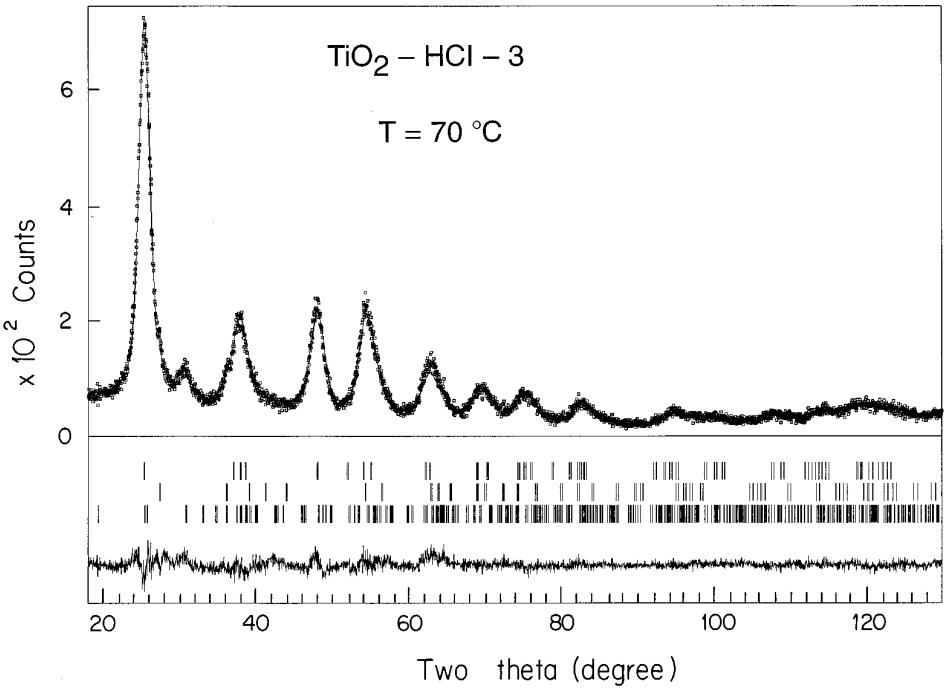

FIG. 2. Rietveld refinement plot for fresh sol–gel titania prepared by using HCl hydrolysis catalyst. It has three phases: anatase (upper tick marks) with $R = 0.023$, rutile (middle tick marks) with $R = 0.032$, and brookite (lower tick marks) with $R = 0.031$.

anatase into rutile. Therefore, after heating the sample at 800°C, it totally dehydroxylated and had rutile as the only crystalline phase (10); its FTIR spectrum showed a well-defined band at 556 cm^{-1}.

Platinum acetylacetonate FTIR spectrum showed the typical bands of the carboxyl group (Fig. 5). At 1530 cm^{-1}, the asymmetric bending vibration of this carboxyl group produced a high intensity band. Stretching vibrations of the ligand –C–O^- produced one band at 1390 cm^{-1}, while the stretching vibrations of the C–(CO)–C group produced two bands: one at 1280 cm^{-1} and another at 1200 cm^{-1}. This group also produced a band at 1022 cm^{-1} generated by a bending vibration. At 784, 687, and 476 cm^{-1} three bands appeared produced by the stretching and bending vibrations of the C–H groups of the platinum acetylacetonate molecule (26).

Addition of platinum acetylacetonate to the titanium alkoxide, during gelling of the sol–gel Pt/TiO_2 system, significantly changed the infrared spectra (Fig. 6). In the high energy region, the fresh sample (heated at 70°C) produced two very weak bands that disappeared with temperature. The small intensity of the band at 3563 cm^{-1} pointed to the absence of the Ti–OH bonding, because anatase, which contains this kind of bonding, was the minority phase in these samples.

The two low-intensity bands at 1530 and 1553 cm^{-1} could correspond to the stretching vibration of Pt–O bonding (16, 18). By X-ray diffraction, however, within the limits

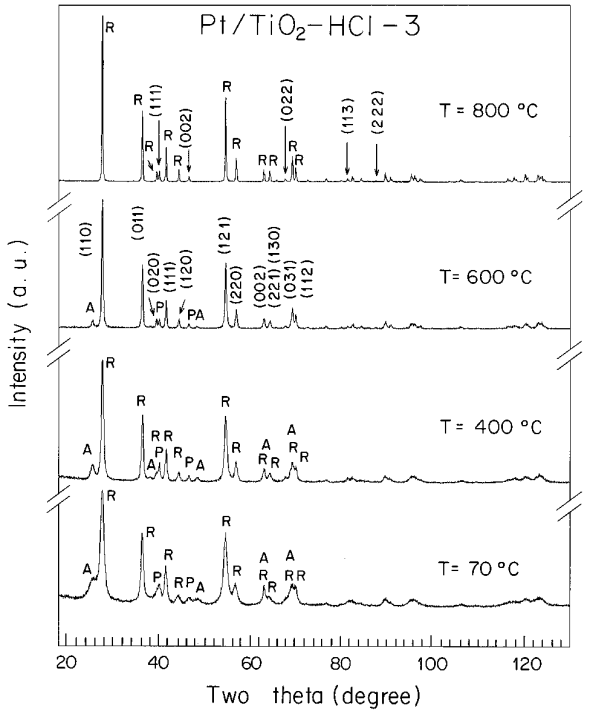

FIG. 3. X-ray diffraction patterns of the sol–gel Pt/TiO_2 catalyst with 1.0 wt% Pt. The catalyst was prepared at pH 3 by using HCl as hydrolysis catalyst. The patterns were obtained after annealing the sample at temperature T. A, P, and R indicate anatase, platinum and rutile, respectively. The indexing of the pattern at 600°C corresponds to rutile and that of the pattern at 800°C corresponds to platinum.

TABLE 3
Parameters Obtained from the Rietveld Refinement after Heating the Sample at Temperature *T*

Phase	*T*(°C)	Phase concentration (wt%)	Crystallite size (nm)	Titanium occupancy	*a* (nm)	*c* (nm)	*u*
Rutile	70	80.4(3.3)	12.7(4)	0.116(1)	0.4601(4)	0.2956(3)	0.3029(4)
	400	88.5(2.5)	22.4(6)	0.114(1)	0.45925(2)	0.29560(2)	0.3036(4)
	600	91.2(2.8)	41(1)	0.117(1)	0.4590(2)	0.2957(1)	0.3049(4)
	800	99.0(1.9)	106(2)	0.1155(8)	0.459053(5)	0.295800(4)	0.3044(3)
Anatase	70	18.6(6)	8(1)	0.098(1)	0.3807(2)	0.909(2)	
	400	10.6(3)	21(1)	0.098(1)	0.3780(2)	0.9510(1)	
	600	7.8(1.7)	30(9)	0.09(1)	0.3783(1)	0.9497(6)	
Platinum	70	0.96(3)	4(5)		0.39188(1)		
	400	0.95(5)	37(5)		0.39188(1)		
	600	0.94(5)	40(9)		0.39202(4)		
	800	1.00(3)	75(9)		0.39214(1)		

Note: The titanium occupancy for a stoichiometric composition is 0.125.

of the technique, we could not identify platinum oxide in the sample. If it was present, it must be in small quantities observable by FTIR spectroscopy but not by X-ray diffraction.

At low energy, the FTIR spectra were like those of titania without platinum.

Platinum favored the formation of rutile instead of anatase. We want to point out that when sol–gel TiO_2 is prepared without platinum, the process of dehydroxylation of the sol–gel titania is associated with the transformation of anatase into rutile. According to this, a possible second explanation for rutile abundance in the fresh samples with platinum was that platinum catalyzed the process of dehydroxylation, producing rutile instead of anatase. With the results of the present paper, it was difficult to decide which of the two models that we have proposed was the right one.

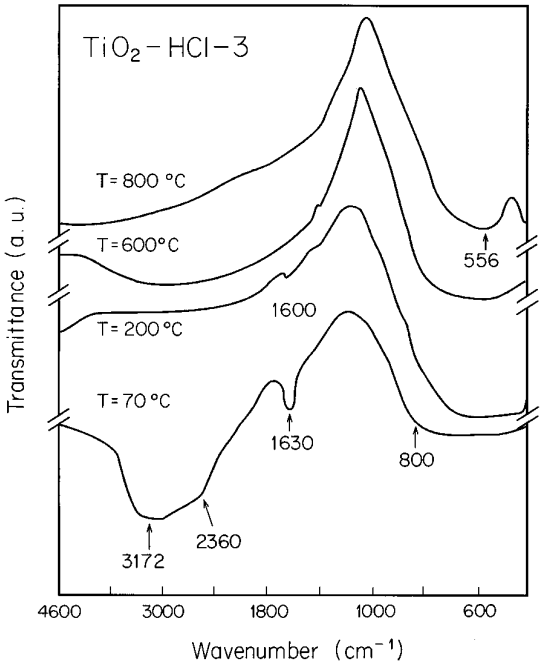

FIG. 4. FTIR spectra of the sol–gel TiO_2 catalyst prepared at pH 3 by using HCl as the hydrolysis catalyst. The spectra were obtained after annealing the sample at temperature *T*.

4. CONCLUSIONS

When Pt/TiO_2 catalysts with 1 wt% Pt were prepared by the sol–gel technique, the samples had three crystalline phases, rutile, anatase, and metallic platinum, with rutile as the majority phase. All phases were nanophases. From the Rietveld refinement of the crystalline structure of these phases we found a platinum weight concentration equal

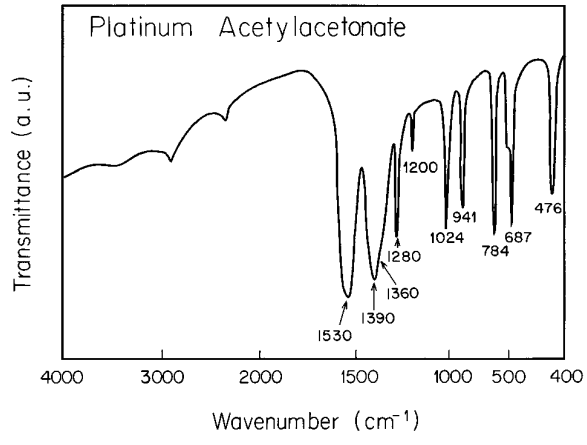

FIG. 5. FTIR spectrum of platinum acetylacetonate.

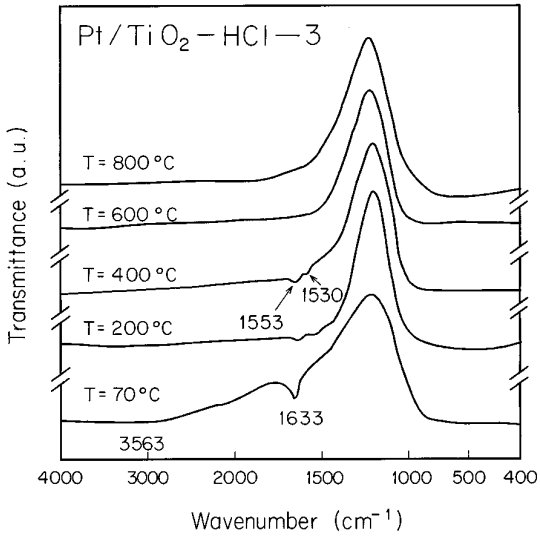

FIG. 6. FTIR spectra of sol–gel Pt/TiO_2 catalyst with 1.0 wt% Pt. The catalyst was prepared at pH 3 by using HCl as hydrolysis catalyst. The spectra were obtained after annealing the sample at temperature *T*.

to its nominal value; therefore, we conclude that most platinum was segregated forming metallic platinum. From the refinement we also obtained the average crystallite size for each phase and their evolution with temperature.

Platinum promoted the formation of rutile, even at a platinum concentration of 0.1 wt%. We proposed two models: in the first model, we assumed that PtO_2, which has a rutile structure, was formed as an intermediate phase. PtO_2 crystallites must function as seeds on which rutile crystallites grow. In the second model, we assumed that the presence of platinum favored the dehydroxylation of the sample, transforming anatase into rutile.

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