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Thermal decomposition and FTIR study of pyridine adsorption on Pt/SiO$_2$ sonogel catalysts

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Abstract

Platinum/SiO$_2$ sonogel has been compared with the corresponding xerogel and an impregnated catalyst. The thermal behavior, the FTIR spectra and the pyridine adsorption show that Lewis acidity is present in the impregnated sample. In the sonogel, Lewis acidity turns to be very low and insensitive to desorption temperature. In the xerogel, both Lewis and Brönsted acidity was observed. In each sample, reduction in situ (without hydrogen flow) of the metal phase is determined by the OH content. Platinum is highly reduced in the sonogel, partially reduced in the xerogel and very slightly reduced in the impregnated sample.

Keywords: Catalyst; Coupled technique; Decomposition; FTIR; Pyridine; Sonogel

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1. Introduction

In the study of platinum supported on metal oxides [1–5], the correlation between structure and catalytic or chemisorptive properties has shown, among other things, the effect of the support on metal dispersion, interaction between the metal and the support, and also deactivation by thermal treatments [6–10].

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Nowadays, as a result of physico-chemical studies, it has been concluded that morphology, surface composition and support acidity may vary depending on the catalyst synthesis method. In previous work we found that, if the support and the active metal are simultaneously synthesized by the sol–gel method, the active phase turns out to be nanodispersed [11]. The sol–gel support is fully hydroxylated, and thus the platinum is reduced in situ. There is no need to treat the catalyst with a high temperature flow of hydrogen [12,13].

In the present work, catalysts were synthesized by the sol–gel method using ultrasound as the energy source. The samples were characterized by FTIR spectroscopy, differential thermal analysis, thermogravimetric analysis and pyridine adsorption to estimate their acid sites.

2. Experimental

2.1. Sample preparation

Tetraethoxysilane (TEOS) was used as SiO_2 precursor in all the preparations. The water used for hydrolysis of the alkoxide was previously acidified with HCl to pH 1.5. The platinum precursor was hexachloroplatinic acid. The metal loading of all the Pt/SiO_2 catalysts was 0.5 wt%.

Ultrasound was generated by means of a Vibracell Sonics Materials sonifier operating at 20 kHz, with a titanium transducer of 1.3 mm diameter. The tip of the sonifier was introduced for 10 min into the reaction mixture contained in a 50 ml glass beaker. The power used to irradiate the liquid was 1.5 W cm^{-3}.

2.1.1. Pt–SG catalyst

The Pt–SG catalyst (sonogel) was prepared by sonicating a mixture of 25 ml of tetraethoxysilane and 8.1 ml of $H_2PtCl_6 \cdot 6H_2O$ solution. The gel thus obtained at 298 K was dried in air at 343 K.

2.1.2. Pt–SG–Imp catalyst

The Pt–SG–Imp catalyst (conventionally impregnated) was prepared as follows. The silica sonogel support used for preparation of the Pt–SG–Imp sample was synthesized by sonicating a mixture of 25 ml of TEOS and 8.1 ml of acidified water. After gelling, the sample was dried in air for 170 h at 343 K. A H_2PtCl_6 solution was further used to impregnate the silica support. The impregnated catalyst was dried overnight in an oven at 343 K.

2.1.3. Pt–XG catalyst

The Pt–XG catalyst (xerogel) was prepared by dropwise addition, under constant stirring, of 8.1 ml of H_2PtCl_6 solution to a mixture of 25 ml of TEOS and 10 ml of ethanol. In the absence of ultrasound, addition of ethanol is needed in order to obtain a homogeneous mixture of reactants. After gelling at 298 K, this sample was dried under the same conditions as the SG catalyst.

2.2. *Characterization*

2.2.1. *DTA–TGA technique*

The DTA–TGA curves were recorded on a Shimadzu DT-30 apparatus. Fresh samples (18.5 mg of Pt–SG or Pt–XG; 10.5 mg of Pt–SG–Imp) were placed in the Pt cell and then heated in a N_2 flow (10 ml s^{-1}), at a rate of 20 K min^{-1}, from room temperature to 1000°C. The gas evolved during these experiments was not analyzed.

2.2.2. *FTIR spectroscopy*

The solids were characterized by FTIR spectroscopy with a 170-SX Nicolet spectrometer. Pressure was applied to the solid powder until the pellet was transparent, and the thickness was assumed to be constant for all samples.

2.2.3. *Pyridine adsorption*

To determine acidity experimentally, 14 mg sample wafers were used and were heated to 500°C. The heating rate was programmed and the pyridine flux was 2.14 l h^{-1} for 15 min. Before thermal desorption of the pyridine, samples were maintained in a vacuum (1×10^{-3} mm Hg) at room temperature for 1 h to eliminate excess pyridine. Afterwards, the temperature was increased and the FTIR spectra were measured with a 170-SX Nicolet spectrophotometer.

For studying the electronic and structural properties of the platinum particles, studies involving carbon monoxide adsorption could be complementary. As such studies will be presented in subsequent work they are not included here.

3. Results and discussion

3.1. *Appearance*

The external look of the three samples is the same: they are ≈ 2 mm monolithic glasses. The Pt–SG sample is greyish, the Pt–XG is brilliant yellow and the Pt–SG–Imp is brown.

3.2. *DTA and TGA studies*

In Fig. 1 the Pt–SG thermal curve is shown. At 100°C the intense endothermic peak is due to the loss of water and solvent occluded during gel formation. This peak represents a weight loss of 16.75%. During the gelling process, if ultrasound is used as energy source instead of temperature, the resulting colloid is structured in a different way and thus the amount of water plus solvent trapped in the network is larger than in a xerogel. In xerogel synthesis, hydrogen bridges are not formed and thus at 100°C H_2O and EtOH are desorbed. At 200, 220 and 380°C, for the Pt–SG sample, three small exothermic peaks not observed for the xerogel are found. They may be attributed to an in situ reduction of the platinum by the large

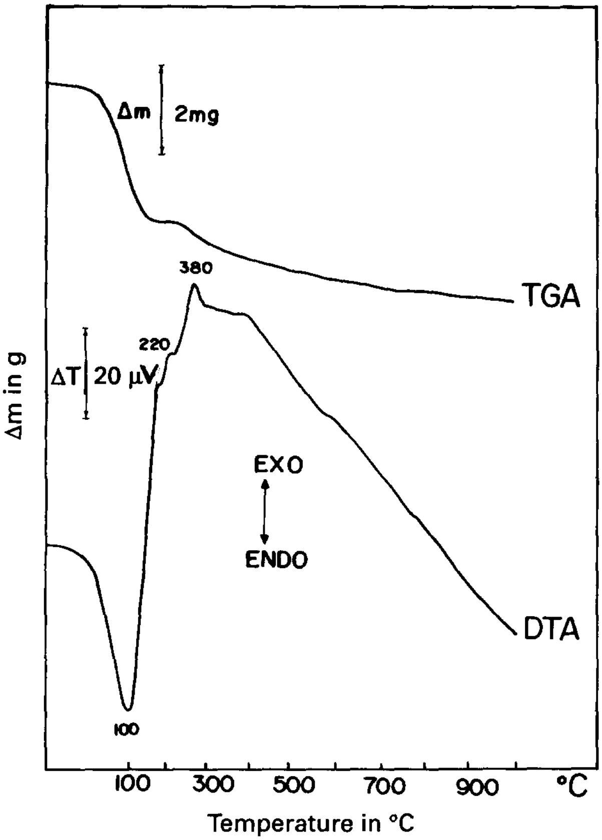


Fig. 1. DTA and TGA of the Pt-SG catalyst.

amount of OH radicals in the solid and to the temperature effect. The 9% weight loss is due to dehydroxylation in the range 380-700°C.

In the thermal curve of the Pt-XG xerogel, Fig. 2, an intense endothermic peak at 100°C is observed. This peak may be attributed to water and solvent desorption, and corresponds to a 14% weight loss. At 190°C a low intensity exothermic peak, due again to a partial in situ reduction of platinum by the temperature effect, is present. At higher temperatures the 9% weight loss is assigned to a partial dehydroxylation of the solid.

The thermal curve of Fig. 3 (Pt-SG-Imp) is different from the other two. In the Pt-SG-Imp sample, the weight loss is very small during the entire heating process (25-700°C) and amounts to only 6%. Water and solvent have already been desorbed during support stabilization and the remaining OH groups are strongly bonded to the silica. As expected, the thermal curve of the catalyst shows only a small exothermic shoulder at 225°C. Platinum is slightly reduced in this sample and the weight loss is due to a small amount of dehydroxylation.

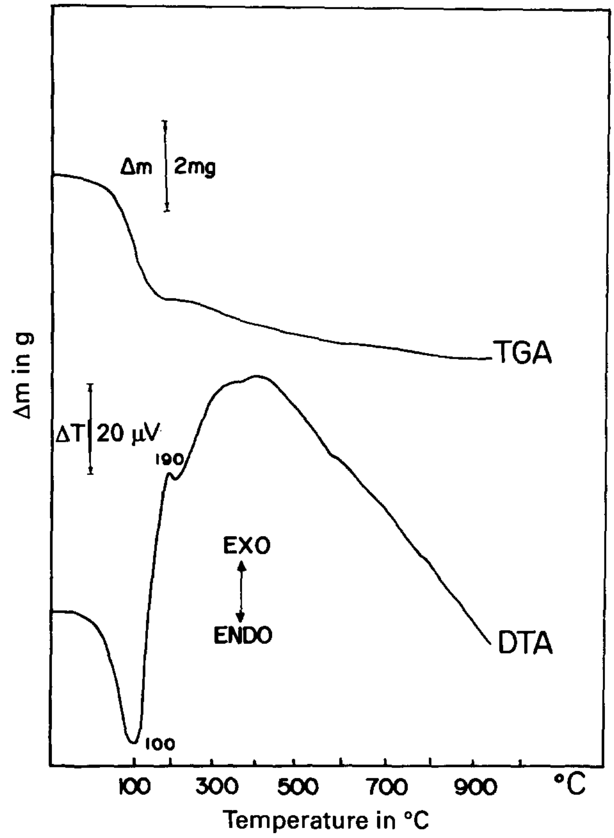


Fig. 2. DTA and TGA of the Pt-XG catalyst.

3.3. *FTIR studies*

In the Pt-SG catalyst the intensity of the band at 3386 cm^{-1}, Fig. 4, due to the OH groups diminishes with increasing temperature and disappears at 800°C. At higher temperatures the solid is highly dehydroxylated. A very small band (1632 cm^{-1}) due to the H_2O hydroxyls present into the gel disappears at 400°C. At 1100 cm^{-1}, the vibration of the O-Si bond, which forms $^-O-Si-O^-$ bridges in silica, is not altered with temperature. Instead, the band at 942 cm^{-1} is not found at temperatures higher than 400°C. The vibrations at 801 and 447 cm^{-1} are attributed to characteristic ring Si-O bonds present in the silica network [14,15]. A flexion of the $^-O-Si-O^-$ bond may explain the small shoulder present at 562 cm^{-1}.

In Fig. 5, the spectrum of the Pt-XG catalyst in shown. It is similar to the Pt-SG (sonogel) spectrum but the bands are shifted to slightly higher energies. The dehydroxylation is probably slower than that of Pt-SG.

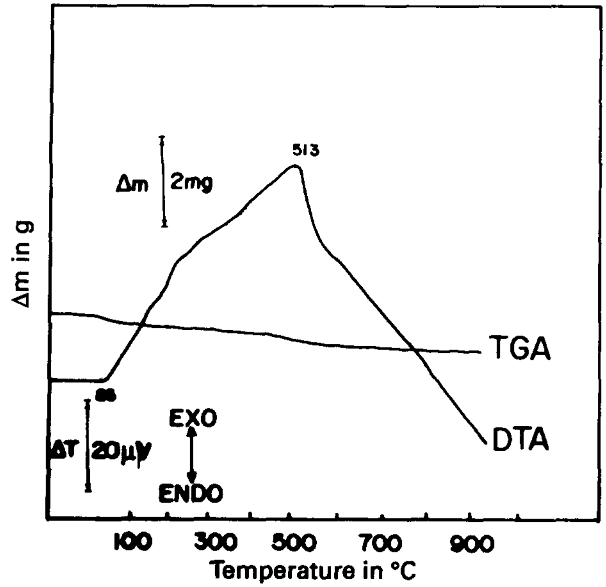


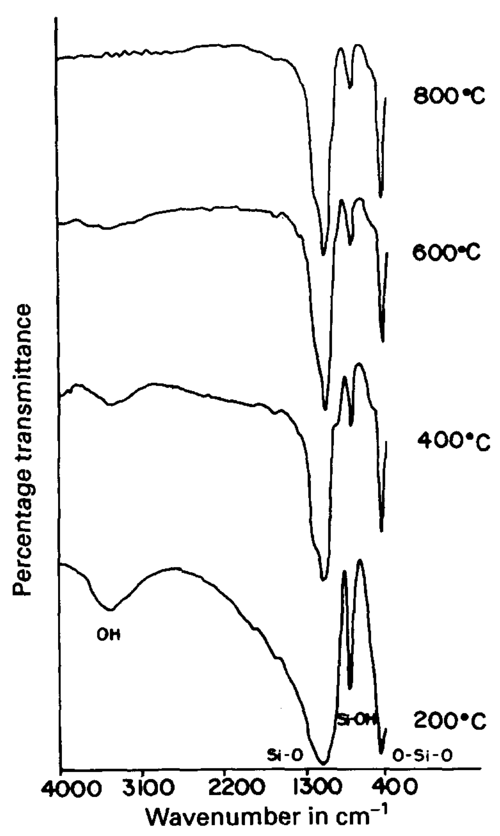
Fig. 3. DTA and TGA of the Pt–SG–Imp catalyst.

The Pt–SG–Imp catalyst is not dehydroxylated, even at 800°C. In the spectrum shown in Fig. 6, a broad band at 3422 cm^{-1} is found, together with a small shoulder at 3647 cm^{-1}. This band disappears at 600°C, showing that the sample is highly hydroxylated and that the Si–OH bonds are strong. Acidity should therefore be stronger. The 1632 cm^{-1} band does vanish with increasing temperature and is more intense than in the other samples. Instead, the band characteristic of silanols at 963 cm^{-1} is not found at temperatures higher than 800°C. Therefore a partial dehydroxylation of the solid can be proposed, as suggested by the previously discussed DTA–TGA results. At 801 and 424 cm^{-1} two intense bands due to Si–O vibrations are observed. These Si–O bonds define the silica structure.

3.4. Pyridine adsorption (acidity studies)

The nature of acidity in catalysts has been studied over many years. One of the more accurate methods for determining acid sites is the adsorption of pyridine or ammonium at variable temperature [16,17]. Our purpose is to differentiate Brönsted (proton acidity) from Lewis (aproton acidity) sites through formation of the pyridinium ion pyH^+, the presence of which may be determined by infrared spectroscopy.

If pyridine is adsorbed on the Pt–SG sample, two low intensity bands are observed at 1590 and 1445 cm^{-1}, showing that this catalyst is barely acid. These bands correspond to Lewis sites (Fig. 7(a)); the relative intensity of the 1590 cm^{-1} band is 0.68 at 80°C, and it falls to 0.52 at 450°C, and to zero at 500°C. The other



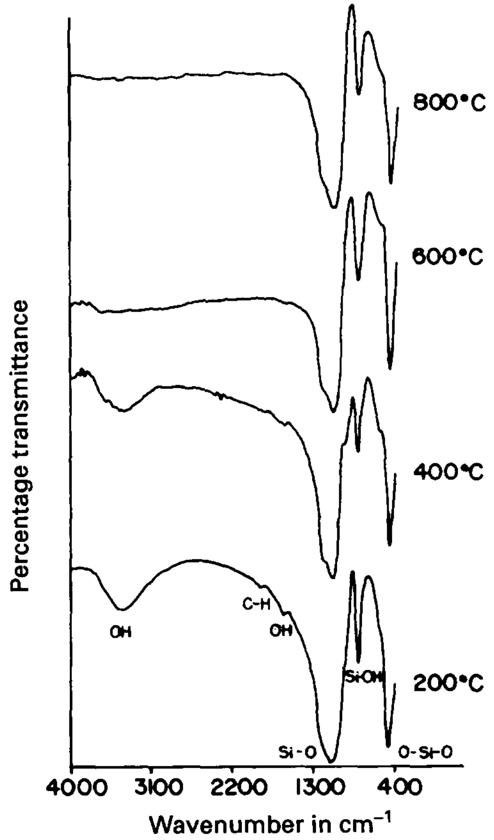
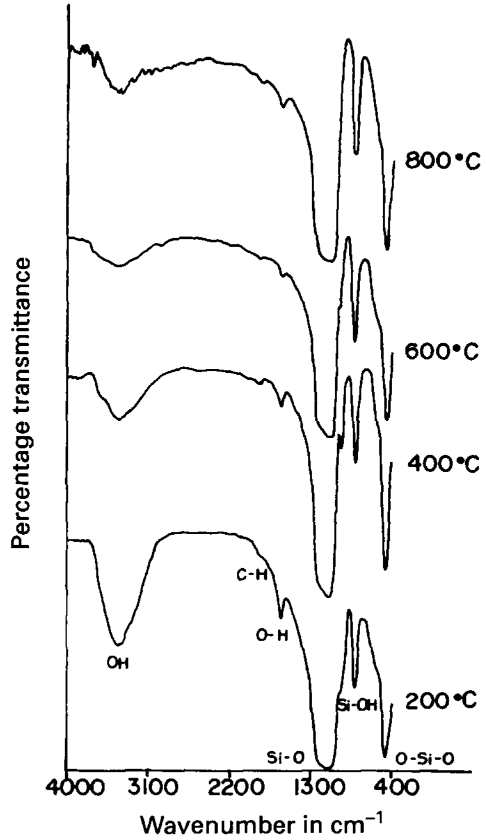


Fig. 4 (left). FTIR spectrum of Pt–SG treated at several temperatures.

Fig. 5 (right). FTIR spectrum of Pt–XG treated at several temperatures.

band (1445 cm^{-1}) has a lower relative intensity (0.31), and it remains constant up to 200°C and then decays (Fig. 8). These results indicate that the platinum sonogel has no noticeable acidity variation.

The 1590 and 1445 cm^{-1} bands of the Pt–XG spectrum, Fig. 7(b), are more intense. These bands are characteristic of Lewis acidity. However, surprisingly, a low intensity band at 1545 cm^{-1} typical of Brönsted acidity is also observed. As shown by the DTA–TGA results, this solid presents a high degree of dehydroxylation, which may be the origin of the various acid sites. The band at 1590 cm^{-1} has a relative intensity of 1.8, more than twice the value for Pt–SG. This band disappears completely at 300°C as the surface is dehydroxylated. It is well known that this vibration is typical of the hydrogen–pyridine bond. Pyridine is thus rather weakly bonded, and indeed is desorbed at 300°C. The band at 1445 cm^{-1} is due to coordinately bonded pyridine if Lewis acidity is present; the relative intensity is 2.2, twice that observed for the Pt–SG sample. This band involves a flexional vibration



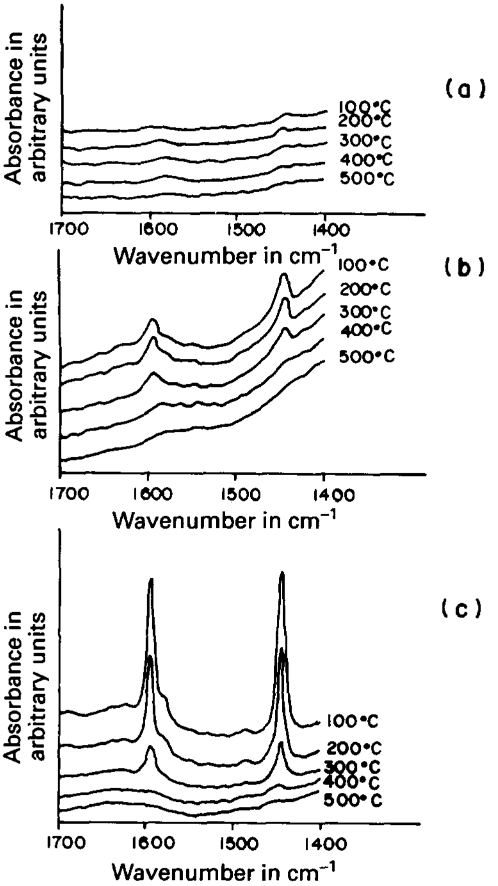


Fig. 6 (left). FTIR spectrum of Pt–SG–Imp treated at several temperatures.

Fig. 7 (right). FTIR spectrum of pyridine adsorption at several temperatures: (a) Pt–SG; (b) Pt–XG; (c) Pt–SG–Imp.

of the N^+–H bond, and the corresponding relative intensity decreases with increasing temperature, Fig. 9. The band disappears at 400°C. This catalyst has a much higher Lewis acidity than the Pt–SG. The band attributed to Brönsted sites (proton acidity) has a very low intensity but remains stable up to 500°C.

If the catalyst is prepared by impregnating silica sonogel (Pt–SG–Imp), the Lewis acidity increases. In the spectrum of Fig. 7(c), the intensity of the bands is much higher than in the spectra of the other catalysts. At 100°C three bands are present, at 1596, 1487 and 1445 cm^{-1}. The first has a relative intensity of 10, the second, one of 1, and the third, 12. Note that these values are 15 times and 6 times higher respectively than the corresponding bands obtained for Pt–SG and Pt–XG. Thus the Pt–SG–Imp catalyst has a very high Lewis acidity. In this sample, no

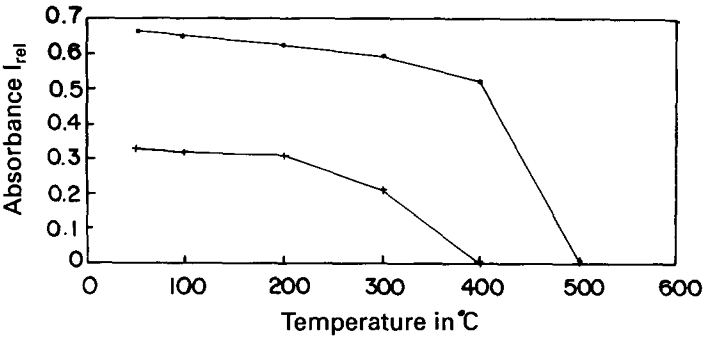


Fig. 8. Relative intensity versus the temperature of Lewis site bands of the Pt-SG catalyst.

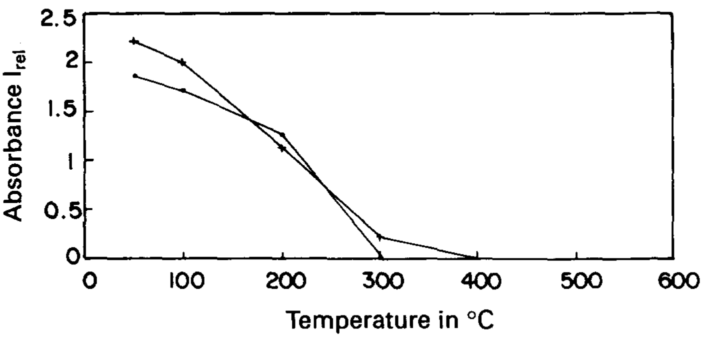


Fig. 9. Relative intensity versus the temperature of Lewis site bands of the Pt-XG catalyst.

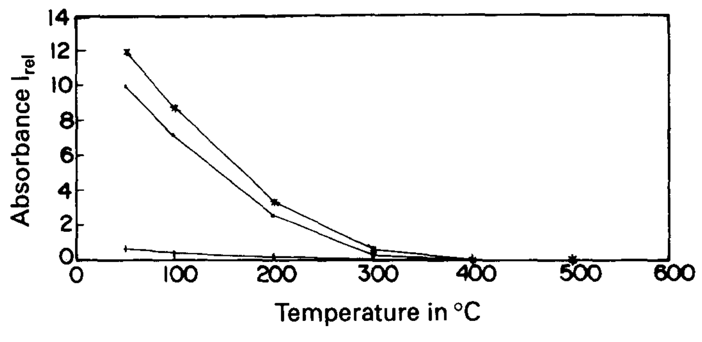


Fig. 10. Plot of relative intensity versus the temperature of Lewis site bands of Pt-SG-Imp.

Brönsted acid sites were detected, Fig. 10. Such properties could be correlated with the ultrasound treatment. This preparation technique seems to alter the acid properties of the solids, as Pt-SG sonogel exhibits the lowest acidity and the Pt-SG-Imp has the highest Lewis acidity. The mechanism of formation of these acid sites may probably be determined by the initial OH group content.

4. Conclusions

The sonication of mixtures during Pt/SiO_2 synthesis alters the colloid structure. The resulting solids have, first, a large amount of occluded water and, second, a high content of OH radicals. With increase in temperature, these OH radicals reduce platinum. Such is not the case if the sample is prepared by impregnation. In the xerogel sample, the platinum is only partially reduced.

If the acidity has to be modified, sonication of the gels inhibits the formation of Lewis acid sites. In the sonogel sample almost no Lewis acid sites were found and the acidity value remained constant with temperature. In the xerogel, Lewis and Brönsted acidity can be explained as resulting from the high dehydroxylation. The impregnated sample did not show any Brönsted acidity but the Lewis acidity was very high.

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