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Pt/SiO$_2$ Sonogels: Synthesis and Characterization

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Ultrasound can be used in sol–gel synthesis as a source of energy which may modify the structural and chemical properties of the resulting gels. Pt/SiO$_2$ sonogel catalysts were obtained and characterized by X-ray diffraction and small angle X-ray scattering. It was found that the aging and polymerization mechanisms are altered by ultrasound. The catalysts were then tested in phenylacetylene hydrogenation, showing a high selectivity toward styrene.

Introduction

In material synthesis, the sol–gel preparation technique is recommended if the synthesis variables have to be controlled. Such is the case of many compounds to be used as catalysts.[1,2] For instance, to obtain supported metal catalysts, the conventional preparation technique is the incipient wetness impregnation of the support with a solution containing the metal precursor. In this case, the sol–gel procedure can be useful to synthesize support materials with improved textural and surface chemical properties.

Alternatively, it is possible to start from reactive mixtures containing both metal and support precursors. After reaction, these mixtures can lead to the formation of gels in which the metal species may be bonded to the support matrix. Thus, the environment of the metal atoms can be chemically modified with regard to the impregnated catalysts. The properties of the dispersed metals prepared in this way can be quite different from those of the samples prepared by impregnation.[3,4]

Ultrasound can be used in sol–gel synthesis as a source of energy which may modify the strucutral and chemical properties of the resulting gels.[5] It is recognized that ultrasound may modify the chemical reactivities in a different way than other conventional energy sources such as heat, light, or high pressure. The collapse of microbubbles generated by sonicating a reactive mixture with ultrasound produces local increases of pressure and temperature as high as several thousand kelvin.[6] The gels obtained in this way are generically called sonogels.

The reactions that occur are the following:

hydrolysis

$$\mathrm{Si(OEt)_4 + H_2O \rightarrow Si(OEt)_3(OH) + EtOH} \qquad (1)$$

$$\mathrm{Si(OEt)_3(OH) + H_2O \rightarrow Si(OEt)_2(OH)_2 + EtOH} \qquad (2)$$

condensation

$$\mathrm{\equiv SiOH + \equiv SiOEt \xrightarrow{H_2PtCl_6} [SiO_2]^{OH}_{Pt} + EtOH} \qquad (3)$$

Hydrolysis occurs when the alkoxide and the water are mixed, using ethanol as solvent (reactions 1 and 2). During the polymerization process (reaction 3), ethoxy and hydroxy groups react, forming siloxanes. The primary structure of the gel, as well as its properties, are determined at this stage. The metal interacts with the silicon nucleophiles formed in the medium during the polymerization stage, causing electrostatic repulsion in the reaction. The resulting gel is homogeneous, with the metal totally dispersed on the support. This process is analogous to the one proposed by Yermakov[7] for the preparation of highly dispersed metallic catalysts.[8-10]

In the present work, Pt/SiO$_2$ catalysts prepared by three different methods have been compared. The sonogel support has been selected in view of the higher specific surface areas and narrower pore size distributions than other gels prepared by "classic" methods.[5] Samples SGI and SGII have been obtained by gelling reaction mixtures containing tetraethoxysilane and hexachloroplatinic acid. In the case of the SGI sample the mixture of starting components was exposed to the action of high power ultrasound. The SGIII sample has been obtained by incipient wetness impregnation of a silica sonogel with hexachloroplatinic acid aqueous solution. These three catalysts can be compared, and the differences, if any, can be correlated with the differences in the preparation method.

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[1] Pajonk, G. M. *Appl. Catal.* **1991**, *72*, 217.

[2] Cauqui, M. A.; Rodríguez-Izquierdo, J. M. *J. Non-Cryst. Solids* **1992**, *147, 148*, 724.

[3] Mason, T. J., Ed. *Sonochemistry: the uses of ultrasound in Chemistry*; The Royal Society of Chemistry: Cambridge, 1990.

[4] Cauqui, M. A.; Calvino, J. J.; Cifredo, G.; Esquivias L.; Rodríguez-Izquierdo, J. M. *J. Non-Cryst. Solids* **1992**, *147, 148*, 758.

[5] Calvino, J. J.; Cauqui, M. A.; Cifredo, G., Esquivias, L.; Pérez, J. A.; Ramírez del Solar, M.; Rodríguez-Izquierdo, J. M. *J. Mater. Sci.* **1993**, *28*, 2191.

[6] Suslick, K. S.; Hammerton, D. A.; Cline, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 5641.

[7] Yermakov, Yu. I. *Catal. Rev.* **1976**, *13*, 77.

[8] Carturan, G.; Facchini, G.; Gottardi, V.; Navazio, G. *J. Non-Cryst. Solids* **1984**, *63*, 73.

[9] Cocco, G.; Schiffini, L.; Strukul, G.; Carturan, G. *J. Catal.* **1980**, *65*, 348.

[10] Carturan, G.; Cocco, G.; Schiffini, L.; Strukul, G. *J. Catal.* **1980**, *65*, 359.

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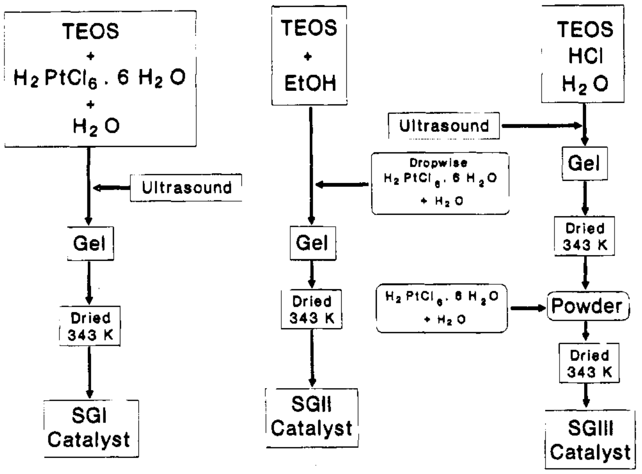
Scheme 1



The catalysts were characterized by X-ray diffraction, and phenylacetylene hydrogenation was used to test them.

Experimental Section

Tetraethoxysilane (TEOS) has been used as the SiO$_2$ precursor in all the preparations. The water used for the hydrolysis of the alkoxide was previously acidified with HCl up 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 sonifier from Vibracell Sonics Materials, operating at 20 kHz, with a titanium transducer of 1.3 mm diameter. The tip of the sonifier was introduced for 10 min in the reactive mixtures contained in 50 mL glass beakers. The power irradiated to the liquid was 1.5 W mL^{-1}.

SGI Sample. The SGI catalyst was prepared by sonicating a mixture of 25 mL of TEOS and 8.1 mL of H$_2$PtCl$_6$ solution; see Scheme 1. The resulting gel obtained at 298 K was dried in air, at 343 K, for 170 h.

SGII Sample. The SGII catalyst was prepared by dropwise addition, under constant stirring, of 8.1 mL of H$_2$PtCl$_6$ 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 get a homogeneous mixture of the reactants.[5] After gelling at 298 K this sample was dried at 343 K as the previous catalyst; see Scheme 1.

SGIII Sample. The silica sonogel support used for the preparation of the SGIII 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$_2$PtCl$_6$ solution was further used to impregnate the silica support. The impregnated catalyst was further dried overnight in an oven at 343 K; see Scheme 1.

Characterization

X-ray Diffraction. X-ray diffraction (XRD) patterns were obtained with a Siemens D500 diffractometer coupled to a copper anode tube. The K$\bar{\alpha}$ radiation was selected with a diffracted beam monochromator. From the platinum peak profile, recorded with step scanning and long counting times, the platinum crystallite size distributions were obtained as shown by Alvarez et al.[11,12]

X-ray diffractograms were also measured with a molybdenum anticathode X-ray tube. The Mo K$\bar{\alpha}$ radiation was selected using a zirconium filter. In this way, it was possible to reach the recommended high values of the angular parameter ($s = 4\pi \sin \theta/\lambda$, where θ is the Bragg angle and λ the wavelength). The intensity values, read at intervals $\Delta 2\theta = (1/8)°$ from $2\theta = 4°$ to $2\theta = 130°$, were the input data for the Magini and Cabrini program.[13] In our diffractometer, the angle of the sample with the incident beam was equal to the angle between the sample and the reflected beam; hence, the angle 2θ is the angle between the incident beam and the reflected beam. The radial distribution function was then obtained and interpreted in terms of the reported interatomic distances.

Small Angle X-ray Scattering. The small angle X-ray scattering (SAXS) intensities were measured with a Kratky camera by step scanning. The samples were mounted on a beryllium window sample holder; no pretreatment was necessary. The experiments were performed using a Mo K$\bar{\alpha}$ radiation selected with a filter. The collimation system (infinite slit type) was such that the beam fulfilled the requirements to be considered as "infinitely high". It is known that desmearing the data is not necessary,[14,15] as the correlation function can be computed directly. With these operating conditions, the resolution obtained for the very large agglomerates is not optimum, but the very small particles (~10 Å) could be resolved. The intensity was registered with a scintillation detector using electronic step scanning for values of $s = 2\theta/\lambda$ varying from 0 to 0.95 Å^{-1}, where 2θ is the scattering angle and λ the wavelength. In SAXS the definition of s is different from that definition of s given previously for XRD measurements.

Our metallic supported catalysts are composed of SiO$_2$ onto which the desired amount of metal was deposited, i.e., a "three-phase system".[16] Although silica does not present microvoids, three experiments were performed for each sample: first, the direct beam, second, the support scattered beam, and third, the supported metal catalyst scattered beam were measured. The Espinat[15] method requires, indeed, calculation of the correlation functions $\gamma^{(2)}$ and $\gamma^{(3)}$ from the scattering of support and catalyst, respectively. As correlation functions are sensitive to oscillations in the intensity data, smoothing was performed. Fourth degree polynomials were used, fitted by a least-squares procedure to seven points. Then, $\gamma^{(2)}$ and $\gamma^{(3)}$ are used to calculate $P_{33}(r)$ (the probability of finding both ends of r in phase 3); from P_{33}, a function $\bar{\gamma}(r)$ is calculated, which is inverted to give $Fv(D)$:

$$Fv(D) = -\frac{D}{3}[\bar{\gamma}''(D) - D\gamma'''(D)]$$

It has to be noted that the value used for n_3, the metal electron density, was, in all cases, the platinum density. In our unreduced samples platinum may be (or may be not) present as PtO.

Brumberger et al.,[17] studying the SMSI catalyst Pt/TiO$_2$ by SAXS, have compared the metal area obtained with different electron densities ($n_{\mathrm{Pt}} = 8.576$ mol mL^{-1}; $n_{\mathrm{PtO}} = 6.070$ mol mL^{-1}, and $n_{\mathrm{PtO2}} = 4.222$ mol mL^{-1}) from the same SAXS curve. The metal surface area was three times larger if the metal compound was PtO$_2$ instead of Pt. Furthermore, it is known, from EXAFS studies,[18] that very small platinum clusters undergo rapid oxidation when exposed to oxygen at 300 K. Thus, the smallest particles may form a liquid-like layer at the surface of support. For these reasons, the SAXS metal surface areas

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(11) Alvarez, A. G.; Bonetto, R. D.; Guerin, D. M. A.; Plastino, S.; Rebollo-Neira, L. *Powder Diffract.* **1987**, *2*, 220.

(12) Bonetto, R. D.; Viturro, H. R.; Alvarez, A. G. *J. Appl. Crystallogr.* **1990**, *23*, 136.

(13) Magini, M.; Cabrini, A. *J. Appl. Crystallogr.* **1972**, *5*, 14.

(14) Brusset, H.; Donati, J. R. *J. Appl. Crystallogr.* **1969**, *2*, 55.

(15) Espinat, D.; Moraweck, B.; Larue, J. F.; Renouprez, A. J. *J. Appl. Crystallogr.* **1984**, *17*, 269.

(16) Goodisman, J.; Brumberger, H.; Cupelo, R. *J. Appl. Crystallogr.* **1981**, *14*, 305.

(17) Brumberger, H.; DeLaglio, F.; Goodisman, J.; Phillips, M. G.; Schwarz, J. A.; Sen, P. *J. Catal.* **1985**, *92*, 199.

(18) Renouprez, A.; Fonilloux, P.; Moraweck, B. In *Growth and Properties of Metal Clusters*; Elsevier: Amsterdam, 1980; p 421.

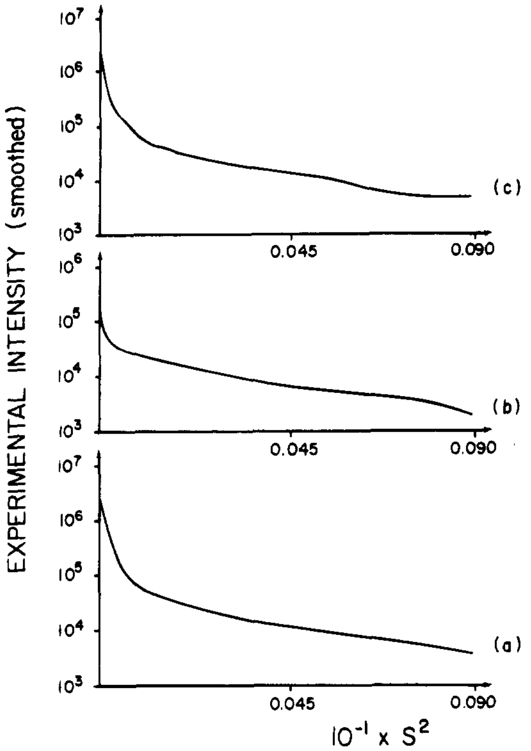

Figure 1. Experimental SAXS intensities as a function of the squared angular parameter s ($s = 2\theta/\lambda$): (a) SGI, (b) SGIII, (c) support (silica).

are not presented here as the composition of the platinum particles is not clear.

However, as it is well established, the small angle X-ray scattering depends only on the size of the particles.[19] Therefore, the different electron densities will only increase the size of the distribution peaks. But, the position of these peaks should remain the same. Thus, the particle size distributions determined here, even with an electron density equal to 8.576 mol mL^{-1} are reliable. Following the method of Espinat et al.[15] the metal distribution function was determined assuming spherical particles.[20-22] If the particles were not spherical, the distribution curve would reflect the distribution of the small dimensions.

Catalytic Test

Phenylacetylene (Aldrich, 99.9%) hydrogenation activity curves were obtained at low conversion (less than 25%). Catalysts samples were first reduced in hydrogen at 673 or 1023 K. The activity was then measured at 303 K (reaction temperature) for 5 Torr hydrocarbon partial pressure and 755 Torr hydrogen partial pressure. The identified products were styrene and ethylbenzene.

Results and Discussion

External Appearance. The reduced synthesized materials looked different depending on the preparation method. The SGI sample was gray, the SGII turned out to be yellow, and the SGIII was pink. The three samples were vitreous.

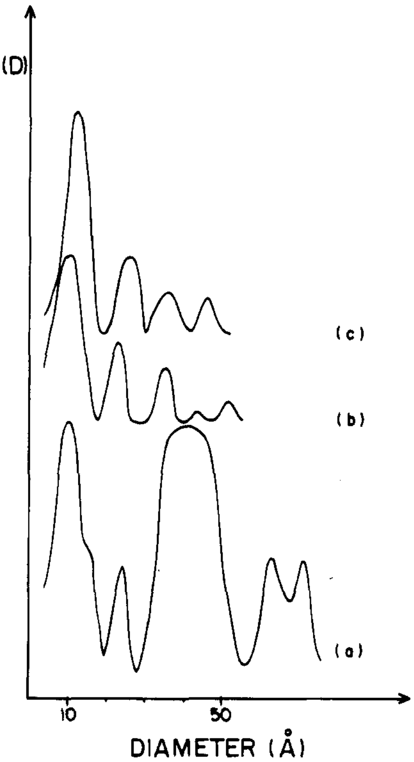

Figure 2. Volume size distribution of the unreduced catalysts (SAXS): (a) SGI, (b) SGIII, (c) SGII.

Table 1. Peak Position in the Radial Distribution Function Compared with Some Selected Interatomic Distances

interatomic distances, (Å)			
catalysts			
SGI	SGII	SGIII	assigned
1.58	1.79	1.94	Si–O = 1.62 (in SiO_2) O–O = 2.69 (in SiO_2)
2.70	2.78	3.01	Pt–O = 2.71 (in PtO) Pt–Pt = 2.78 (in Pt)
	3.40	3.57	Si–Si = 3.24 (in SiO_2)
3.83	3.93	4.05	O–O = 3.83 (in PtO) Pt–Pt = 3.93 (in Pt)

X-ray Diffraction. *(a) Unreduced Samples.* The diffractograms of the three unreduced catalysts did not show peaks of platinum or any other platinum compound. The volume particle size distributions of the solids, extracted from the SAXS experimental intensities shown in Figure 1 (catalysts SGI and SGIII only as SGIII and SGII were very similar), are reported in Figure 2. The main maximum was found for 8–12 Å particle size, but in addition, several small peaks appeared up to 50 Å, Figure 2. The SGI catalyst showed some large inhomogeneities ($D \approx 40$ Å) which were not found in the other samples. These distributions, as they were determined by SAXS on the unreduced catalysts, correspond to platinum species whose nature is not clearly established. They correspond, and this is the interesting point, to the approximate size of the probable precursor agglomerate of the platinum particles present in the reduced samples.

To determine if the structure of the materials was different from one preparation to the other, the electronic radial distribution function (RDF) should be helpful. It measures indeed the short range order of the studied materials. In Table 1, the position of each peak in the radial distribution function is presented, Figure 3. The first peaks at values less than 1.40 Å are parasites. This part of the curves should be as flat as possible. In these catalysts the composition, which is an important param-

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[19] Guinier, A. *Théorie et Technique de la Radiocristallographie*; Dunod: Paris, 1964; p 639.

[20] Renouprez, J. A.; Imelik, B. *J. Appl. Crystallogr.* **1973**, *6*, 105.

[21] Renouprez, J. A.; Hoang Van, C.; Compagnon, P. A. *J. Catal.* **1974**, *34*, 411.

[22] Dartigues, J. M.; Chambellan, A.; Corolleur, S.; Gault, F. G.; Renouprez, A.; Moraweck, B.; Bosch, P.; Dalmai-Imelik, G. *Nouv. J. Chim.* **1979**, *3*, 591.

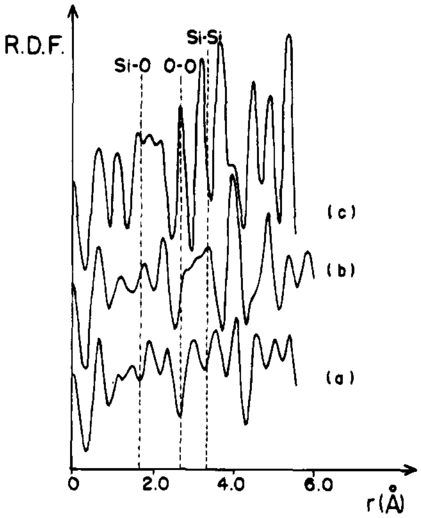

Figure 3. Radial distribution function of the unreduced catalysts (XRD): (a) SGIII, (b) SGII, (c) SGI.

eter for an accurate radial distribution function, is approximate. The sol–gel samples may contain, for instance, organic impurities, or chlorine atoms may be present still bonded to platinum. However, the distances for silica reported by Klug and Alexander[23] are reproduced in the SGI sample, and clear peaks at 1.58 and 2.70 Å may be attributed to Si–O and O–O distances, respectively. If the Si–O–Si bond was linear a peak at 3.24 Å should appear; such is not the case. The platinum or platinum oxide peaks should be found at 2.71, 2.78, 3.83, and 3.93 Å, which are Pt–O in platinum oxide, Pt–Pt in platinum, O–O in platinum oxide, and Pt–Pt in platinum. Unfortunately, the small difference between 2.71 and 2.78 Å as well as between 3.83 and 3.93 Å is not resolved in our radial distribution functions; hence, it is not possible to distinguish between these two compounds. Only a clear peak at 3.83 Å is observed, which may be attributed to a platinum bond whose length is the same in the three preparations. The 2.71–2.78 peak overlaps with the O–O silica bond length (2.69 Å).

In SGII preparation the Si–O (1.79 Å) distance is slightly larger as well as the O–O distance (2.78 Å) due to the SiO$_2$, but in this case, the expected peak at around 3.24 Å is present, showing that Si–O–Si bonds are rather linear (the experimental value is 3.40 Å). Again, first neighbor distances in platinum or platinum oxide overlap with the silica peaks.

First peaks in the radial distribution function of the impregnated sample SGIII are shifted 0.3 Å from the previously discussed sample (SGI), Si–O peak is now at r = 1.94 Å and O–O at r = 3.01 Å. The Si–Si distance appears to be 3.57 Å. Nevertheless, the peak at 4.05 Å is clearly resolved as in the other preparations, and it is found in the same position as in the other samples.

Hence, the two sonogel preparations (SGI and SGIII) differ on the Si–O bond length and on the mean structure of the silica. The angle between silica tetrahedra is almost 180° in conventional sol–gel synthesis (SGII). The impregnated sample (SGIII) reproduces the main features of the shape of the (SGII) preparation although the peaks are shifted.

(b) Reduced Samples. Figure 4 compares the X-ray diffraction peaks of platinum which were used to estimate the crystallite size distribution, Figure 5, in 1023 K reduced sample. In SGI preparation a broad crystallite size distribution was obtained whose maximum was found at 58 Å. In SGII and SGIII a bimodal platinum crystallite size was found. The impregnated sample SGIII has a higher amount of small (D = 22 Å) than large (D = 122 Å) crystallites. In the conventional sol–gel preparation (SGII) the ratio of the amount of small (D = 30 Å) to large (D = 122 Å) crystallites is lower. This effect has been reported in previous works;[24,25] therefore, it seems that the sonogel method provides a broad crystallite size distribution but that the amount of crystallites whose diameter is larger than 110 Å is insignificant. The other two preparations provide smaller crystallite sizes, but the amount of large particles (~122 Å) is considerable. These distributions have to be attributed, of course, to Pt^0 as they are estimated from the corresponding X-ray diffraction peak. Unfortunately, these Pt^0 peaks were not present in the unreduced samples, showing that the platinum crystallites are too small or that platinum constitutes other species which are, also, too small to be observed in X-ray diffraction. Therefore, in the unreduced catalysts the crystallite size distribution could not be determined. However, the distribution of inhomogeneities

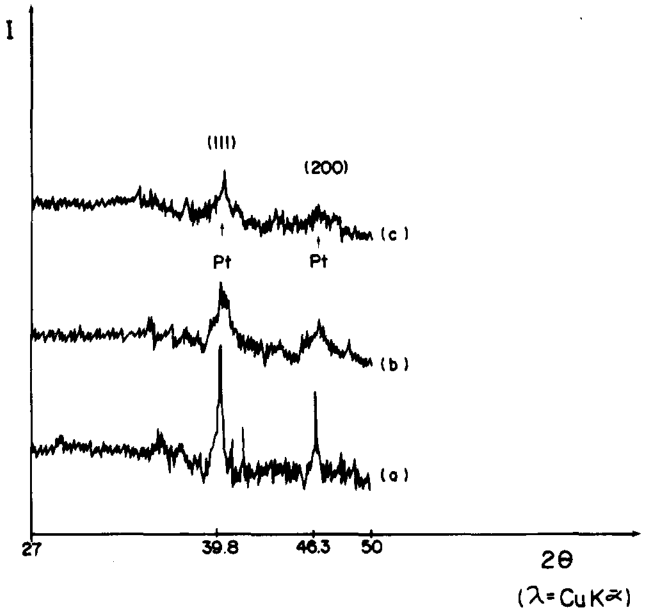

Figure 4. X-ray diffraction (XRD) platinum peaks observed in the catalysts reduced at 1023 K: (a) SGI, (b) SGII, (c) SGIII.

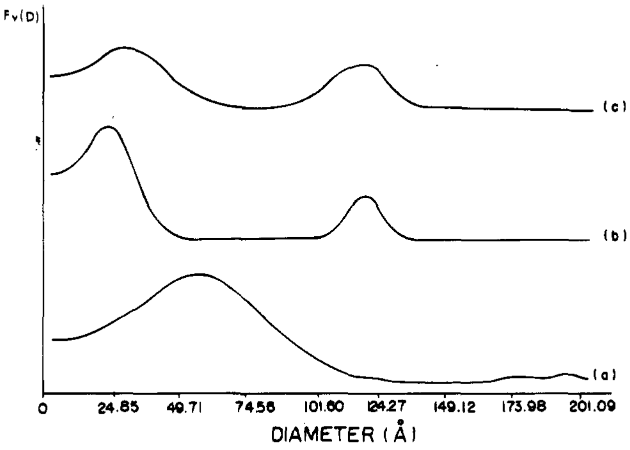

Figure 5. Crystallite size distributions of the reduced catalysts at 1023 K (XRD): (a) SGI, (b) SGIII, (c) SGII.

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[23] Klug, H.; Alexander, L. *X-ray Diffraction Procedures*; Wiley: New York, 1954.

[24] Lopez, T.; Bosch, P.; Moran, M.; Gomez, R. *J. Phys. Chem.* **1993**, *97*, 1671.

[25] Bosch, P.; Lopez, T.; Lara, V. H.; Gomez, R. *J. Mol. Catal.* **1993**, *80*, 299.

Table 2. Activity and Selectivity of the Pt/SiO$_2$ Catalysts for the Phenylacetylene Hydrogenation

catalyst	temp (K)	specific rate 10^5 mol/g·s	selectivity (%) to styrene
SGI	673	1.37	93
SGII		0.48	94
SGIII		0.25	95
SGI	1023	0.91	97
SGII		1.27	98
SGIII		0.69	98

(platinum species) obtained by SAXS showed that the SGI preparation is at this step (before reduction) different, but the other two preparations are similar.

Catalytic Test

Specific rate and selectivity to styrene depending on reduction temperature are presented in Table 2. If the reduction temperature is 673 K and SGI activity is three times higher than the activity of the SGII and SGIII samples ((0.48 and 0.25) × 10^5 mol/g·s). It seems then that the sonogel preparations favor a higher activity. If the reduction temperature is 1023 K the activity of the catalysts are of the same order.

In Figure 6 and Table 2 the selectivity values after 30 min are between 88 and 98% for all catalysts reduced at 673 or 1023 K. However, it seems that increasing temperature treatment favors a higher selectivity to styrene. For short reaction time (less than 30 min) the SGIII (impregnated) is less selective than the two others. It is clear that this catalyst is structurally modified during the first 30 min. Such is not the case for the SGI and SGII samples. Therefore, the sonogel preparation provides samples with a constant selectivity.

Conclusions

Structurally differing catalysts were obtained depending on the preparation method. It was found that in unreduced catalysts the structure of the resulting powder is such that, only in the sonogel, the Si–O–Si bond is not linear. The aging and polymerization mechanism is, therefore, altered by ultrasound. This network seems to favor platinum atom migration so that larger platinum crystallites were obtained in the resulting reduced catalyst.

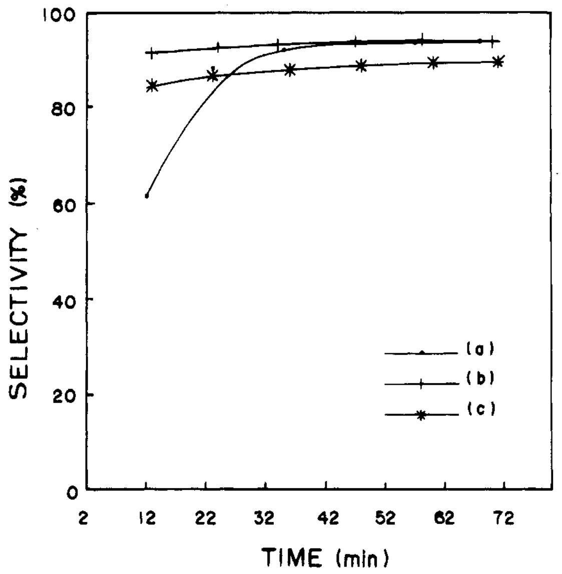

Figure 6. Selectivity to styrene curves as a function of time: (+) SGI, (∗) SGII, (●) SGIII.

It seems, therefore, that ultrasound treatment of the SiO$_2$ support provides structure which differs from the conventional SiO$_2$. If the metal is incorporated to the silica sonogel during preparation, the activity is the highest if the sample is reduced at 673 K. Selectivity toward styrene was constant with time in sonogels.

Treatment of the gel with ultrasound seems, then, to be an adequate method to alter structural features and, hence, catalytic properties.

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