Journal of Non-Crystalline Solids 147&148 (1992) 758–763
North-Holland

JOURNAL OF
NON-CRYSTALLINE SOLIDS

Preparation of rhodium catalysts dispersed on TiO_2–SiO_2 aerogels

M.A. Cauqui [a], J.J. Calvino [a], G. Cifredo [a], L. Esquivias [b] and J.M. Rodríguez-Izquierdo [a]

[a] *Department of Inorganic Chemistry and* [b] *Department of Structure and Properties of Materials, University of Cadiz, Apartado 40, Puerto Real 11510, Spain*

TiO_2–SiO_2 aerogels have been used as supports to disperse rhodium. Three different ways have been followed for the preparations: (a) a classic TiO_2–SiO_2 aerogel, obtained from a mixture of alkoxides and water dissolved in ethanol, was impregnated with a rhodium nitrate solution; (b) a TiO_2–SiO_2 sonogel, obtained by hydrolysis of alkoxides in the absence of alcohol, under the action of ultrasound, was impregnated with a rhodium nitrate solution; and (c) a mixture of alkoxides and water, including rhodium nitrate in the reaction vessel, was exposed to the action of ultrasound, thus leading to a ternary Rh–TiO_2–SiO_2 sonogel. The behaviour of these three catalysts has been compared with that of a Rh/TiO_2–SiO_2 system (d), obtained by conventional impregnation methods, starting from a commercial silica support. The samples prepared by impregnation of aerogels (a,b) present high levels of rhodium dispersion and show an increase of the catalytic activities in parallel with the pretreatment temperature in flow of hydrogen. On the contrary, the sample prepared including rhodium before gelling (c) presents a poor metallic dispersion, is not active for benzene hydrogenation, and has the capability of uptaking large amounts of hydrogen at ambient temperature. Both patterns of behaviour are greatly different from that characteristic of conventional Rh/TiO_2–SiO_2 catalyst (d).

1. Introduction

Sol–gel methods have been used by different authors working on catalyst preparation [1]. The advantages of these methods have been already described in the literature [1,2]. Pajonk [2] focussed on the review of the applications of the aerogel routes to the design of catalytic materials, and pointed out the potential use of a new type of aerogels, the sonogels [3,4], as heterogeneous catalysts.

The aim of the present work is to report some results on the use of sonogels in catalysis.

The main characteristic of the sonogel route is that hydrolysis and polycondensation of alkoxides takes place in the absence of a solvent. The use of a high-power ultrasound source allows atomic level mixing of the reactants and leads to the production of homogeneous gels. This technique has been applied to the preparation of SiO_2 [3,4], TiO_2–SiO_2 [5] and P_2O_5–SiO_2 [6] glasses from sonogels.

The catalysis literature shows that interest in TiO_2–SiO_2 materials is growing. The applications of this type of solid are quite diverse, including the roles of supports for dispersed metals [7,8], supports for catalytically active oxides [9,10], and the possibility of being active materials by themselves [11]. Additional evidence of interest in TiO_2–SiO_2 related systems in catalysis are recent publications dealing with their fundamental structural and surface chemical characterization procedures [12–14].

In this paper, we study the use of TiO_2–SiO_2 aerogels prepared by: (a) the classic sol-gel method (with alcohol as a solvent), and (b) the sonogel method, as supports of dispersed rhodium phases. These results are compared with those of a Rh–TiO_2–SiO_2 sample prepared by the sonogel technique (c), in which the rhodium was added before gelling took place. A sample prepared by traditional methods (d), starting from a commercial silica support, is used as a reference. The work includes characterization measurements and

0022-3093/92/$05.00

catalytic activity tests for the benzene hydrogenation reaction.

2. Experimental

Tetraethoxysilane (TEOS) and tetrabutylorthotitanate (TBOT) were used as precursors to prepare aerogels containing 10 mol% TiO_2. Since TBOT is much more reactive towards hydrolysis than TEOS, it was modified by the addition of acetic acid [15]. Water/Alkoxides molar ratio was 4 for all the preparations. The pH of water was adjusted to 1.4 by addition of HCl.

The classic TiO_2–SiO_2 gel was prepared mixing equal volumes of TEOS and ethanol with the hydrolysis water and the solution of the modified titanium alkoxide. This mixture was kept in an hermetic glass container, at 323 K, for 1 week, before drying.

The sonogel was prepared in the absence of ethanol, by irradiation of the TEOS–water mixture with ultrasound and further mixing with the solution containing the TBOT precursor. Aging time was 1 week, at 323 K. The classic gels and sonogels were dried in a 1 l autoclave, filled with 300 cm^3 of ethanol, at 200 bar and 573 K. Additional details on the preparation of these gels can be found elsewhere [5]. The resulting aerogels were calcined in air at 723 K for 1 h in order to eliminate organic residues. Following calcination, these gels were impregnated with rhodium nitrate solutions and dried in air, overnight at 363 K, to obtain the (a) conventionally and (b) sono-dispersed rhodium catalysts. The rhodium content was in both cases 2.5 wt%.

One alternative method of preparation was the addition of the rhodium nitrate in the hydrolysis water; in such case the mixture of TEOS with an aqueous rhodium nitrate solution was exposed to ultrasonic stirring before mixing with the modified TBOT precursor in order to obtain a ternary Rh–TiO_2–SiO_2 gel. This gel was aged and dried in the autoclave as described above, thus leading to catalyst c. The rhodium and TiO_2 contents of this sample were the same of those prepared by impregnation with rhodium nitrate solutions.

A reference sample was prepared by impregnation of a commercial silica gel, Davisil grade 644, with a solution of TBOT in hexane. After drying in vacuum for 2 h at ambient temperature, it was calcined in a flow of nitrogen for 2 h at 473 K, and finally calcined in air for 2 h at 773 K. This led to a 10 mol% TiO_2 support which was further impregnated with a rhodium nitrate solution to obtain a 2.5 wt% rhodium catalyst, d.

The characterization of the four catalysts (a,b,c,d) was carried out by N_2 adsorption for surface area measurements, temperature programmed reduction in flow of hydrogen, volumetric hydrogen chemisorption of catalysts reduced at different temperatures, temperature-programmed desorption of hydrogen, and transmission electron microscopy.

Benzene hydrogenation was selected as test reaction in order to check the catalytic behaviour of the different samples. The reaction was run at 303 K, with a mixture of 6.5 kPa of benzene and 94.5 kPa of hydrogen, flowing at 1 cm^3 s^{-1}. Conversion of benzene to cyclohexane was always kept below 10%, thus allowing us to assume differential operating conditions. It was checked that, under reaction conditions, diffusion was not the rate limiting step.

3. Results

The Brunauer, Emmet and Teller (BET) surface area of the catalysts, obtained from N_2 adsorption experiments at 77 K, are shown in table 1. These values did not change with reduction treatments in flow of hydrogen between ambient temperature and 773 K. The sol–gel methods used for the preparation resulted in surface areas

Table 1
BET surface area of the catalysts and H/Rh chemisorption ratios after reduction at different temperatures

Sample	Surface area (m^2 g^{-1})	Reduction temperature (K)		
		473	623	773
a	675	0.98	0.97	0.95
b	623	0.65	1.0	1.0
c	560	0.00	0.00	0.45
d	292	0.82	–	0.50

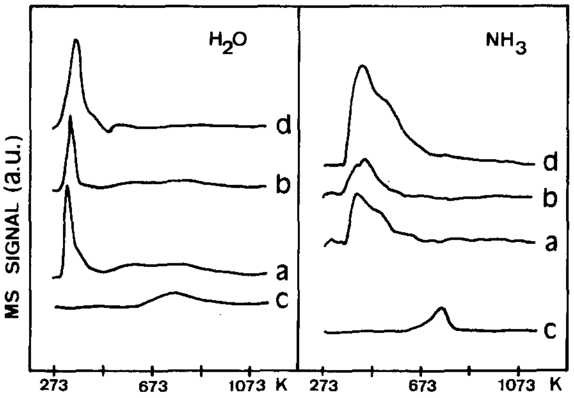

Fig. 1. Temperature-programmed reduction results, showing water and ammonia signals detected by mass spectrometry, as a function of the reduction temperature. Catalysts: (a) rhodium dispersed by impregnation on a classic TiO_2–SiO_2 aerogel, (b) rhodium dispersed by impregnation on a TiO_2–SiO_2 sonogel, (c) ternary Rh–TiO_2–SiO_2 aerogel prepared under the action of ultrasound, and (d) rhodium dispersed by impregnation on a TiO_2–SiO_2 support prepared from commercial silica. (Flow of hydrogen: 1 cm^3 s^{-1}. Heating rate: 0.17 K s^{-1}.)

of about 600 m^2 g^{-1}. According to the *t* method, micropores (pore radii lower than 1 nm) do not represent a significant fraction of the surface area of the catalysts.

The results shown in fig. 1 were obtained by temperature-programmed reduction of the catalysts in a flow of hydrogen. The analytical device used for the experiments was a mass spectrometer. The signal corresponding to an m/e ratio of 18 gave direct information about the evolution of water, and traces representing the evolution of ammonia can be drawn from the comparison of the signals of $m/e = 18$ and 17.

All the samples prepared by impregnation show strong water features, centered at 370 K, corresponding to weakly retained water introduced during wetting of the TiO_2–SiO_2 support with rhodium nitrate solutions. The low intensity signals observed at higher temperatures (473–973 K) can be understood in terms of dehydroxylation of the supports, although some contribution associated to the partial reduction of TiO_2 cannot be ruled out. However, the sample c, in which the rhodium was added before gelling, shows a single water feature centered at 773 K.

Ammonia is the main product of the reduction of nitrate species, coming from rhodium nitrate, with hydrogen. For the samples prepared by impregnation (a,b and d) the NH_3 signals show up between 400 and 650 K as several overlapping features with the most intense peak near 440 K. The behaviour of sample c is again quite different from the others, showing a single peak centered at 773 K.

Table 1 includes hydrogen chemisorption data, at room temperature (293 K), for the catalysts reduced in a flow of hydrogen at 473, 623 and 773 K. These data are presented in the usual form of H/Rh apparent ratios. Although there is some debate in the literature concerning the stoichiometry of hydrogen adsorption on rhodium [16], it is in principle accepted that an H/Rh ratio of 1 is indicative of the existence of reduced metal with a good metallic dispersion. It can be observed that samples a and b, prepared by impregnation of TiO_2–SiO_2 aerogels, show high chemisorption uptakes. For the sample prepared by traditional methods starting from silica (d), the chemisorption uptake decreases with the reduction temperature. The sample c, prepared from a ternary Rh–TiO_2–SiO_2 gel, only showed hydrogen adsorption capability after reduction at 773 K.

The temperature-programmed desorption experiments give information complementary to the chemisorption uptakes. Following reduction at 773 K the sample was cooled to room temperature and a flow of hydrogen was allowed to contact the catalyst. When the sample was further heated in a flow of inert gas, the hydrogen evolved was detected by a catharometric detector as a function of the desorption temperature. Thus, it is possible to obtain information about the type of interaction between the hydrogen and the catalyst surface.

For catalysts a and b, prepared by impregnation of sol–gel derived TiO_2–SiO_2 supports, it can be observed that there are significant amounts of hydrogen desorbing below 673 K. These hydrogen forms can be ascribed to adsorption on the dispersed metal phase. On the contrary, the catalyst c prepared from the Rh–TiO_2–SiO_2 aerogel desorbed large amounts of hydrogen at temperatures higher than 773 K. Such behaviour is characteristic of hydrogen adsorption on the support, and its existence prevents use of the H/Rh ratio of this particular sample (table 1) in order to obtain information on the metallic dispersion.

In fig. 2, the trace corresponding to a sample of catalyst c reduced at 773 K and cooled without further treatment with hydrogen is shown. In this case a signal peaking at the same temperature as that for the sample treated with hydrogen at 293 K was observed (and is designated as c*). This means that significant amounts of hydrogen are retained by the sample during the reduction treatment, although in this case it is less than 10% of the total amount desorbed after treatment with hydrogen at ambient temperature.

The catalyst samples were observed by transmission electron microscopy (TEM). Samples a and b, prepared by impregnation of TiO_2–SiO_2 aerogels, showed excellent dispersion and a high degree of particle size homogeneity. The average metal particle size for both samples was 1.8 nm. The traditional sample, d, prepared starting from commercial silica, showed similar levels of dispersion; whereas, following reduction at 773 K, most of the metal particles become covered by a thin layer of material. Such coverage effects following high-temperature reduction treatments have been formerly proposed on metals dispersed on titania containing supports [17]. Sample c showed a quite different aspect when observed by TEM; large metallic aggregates, with sizes ranging from 10 to 40 nm, have been detected, small rhodium particles being absent in this preparation.

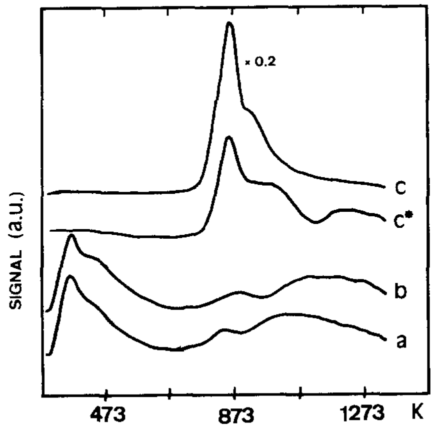

Fig. 2. Temperature-programmed desorption of hydrogen after reduction of samples a, b and c at 773 K, cooling under flow of argon, and treatment with a flow of hydrogen (1 cm^3 s^{-1}) at ambient temperature. c* corresponds to the signal recorded for sample c, reduced at 773 K and cooled under flow of argon without further treatment with hydrogen. Note that signal c has been divided by a factor of 5. (Heating rate: 0.17 K s^{-1}.)

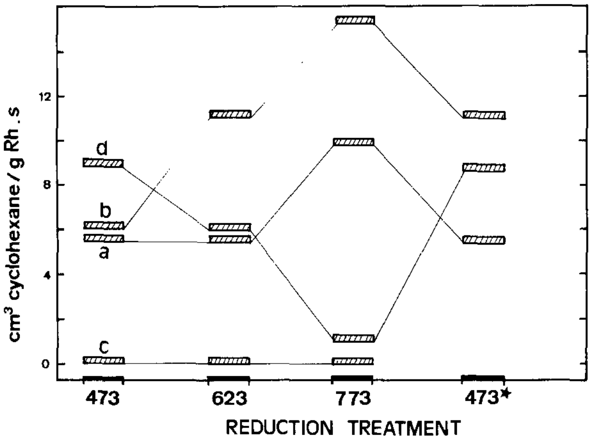

Fig. 3. Catalytic activities, corresponding to catalysts a, b, c and d, for the benzene hydrogenation reaction, after reduction at different temperatures (473, 623 and 773 K). 473* represents the catalytic activities observed for the samples reduced at 773 K, reoxidized in air at 673 K, and further reduced in hydrogen at 473 K.

The catalytic activity data for the benzene hydrogenation reaction, measured at 303 K, for catalysts reduced at 473, 623 and 773 K are shown in fig. 3. A fourth type of treatment, consisting of reoxidation in air and further reducing, at 473 K, samples previously reduced at high temperature (773 K), is also considered. Catalysts a and b, prepared by impregnation of TiO_2–SiO_2 aerogels, showed an increase in catalytic activity with the reduction temperature. On the contrary, sample d showed a decrease in activity with reduction temperature. It has to be remarked that the sample prepared with ultrasound (b) reduced at 773 K is the most active of all the series. The sample c, prepared by addition of the rhodium before gelation, did not show activity at any of the reduction temperatures tested.

4. Discussion

The first point to be considered is the state of reduction of rhodium as a function of treatment temperature in flow of hydrogen. If it is assumed that the reduction of nitrates to ammonia takes place in parallel with the reduction of the metal, the ammonia traces shown in fig. 1 give indirect information about the state of reduction of rhodium. For the case of the samples prepared by impregnation, a, b and d, it can be concluded that at 473 K most of the metal is in the reduced state, and after treatment of 1 h in flow of hydrogen at 623 K all the metal would be reduced. This is in good agreement with the chemisorption uptake data given in table 1, which reveals that the catalysts adsorb hydrogen at room temperature. Sample c requires treatment in hydrogen at 773 K for the elimination of ammonia, in good agreement with the absence of hydrogen adsorption after reduction at lower temperatures.

Transmission electron microscopy gave direct evidence on the state of dispersion of rhodium. For the samples prepared by impregnation (a,b,d) the state of dispersion of rhodium is high, showing small average particle sizes (1.8 nm). It can be observed that the metal particles did not exhibit sintering effects between 473 and 773 K. The chemisorption uptake for samples a and b, prepared by impregnation of conventional and sono-TiO_2–SiO_2 aerogels, is in good agreement with the metal dispersions observed by TEM. For the sample prepared by traditional methods, d, the decrease in the H/Rh apparent ratios with the reduction temperature can be understood on the grounds of the coverage effects observed for the metal particles by TEM.

The low metallic dispersion of the catalyst, c, prepared including the rhodium before gelling, and the fact that the reduction of the sample took place at high temperature (fig. 1), explains why this catalyst did not adsorb significant amounts of hydrogen after reduction at temperatures < 773 K. Hydrogen adsorption of catalyst c at ambient temperature after reduction at 773 K deserves to be specially mentioned. There are important differences between the H/Rh apparent ratio determined by chemisorption, 0.45, and that which can be drawn by integration of the corresponding trace in fig. 2 ($H/Rh = 10$). Such difference reveals that this type of hydrogen is very sensitive to the experimental adsorption conditions. Another interesting feature is the fact that this type of adsorption takes place on the support. The role of the reduced metal is to dissociate the molecular hydrogen which can further migrate to the support. This type of phenomena has been described in the catalysis literature as 'spillover' effect [18]. The spillover effect on this catalyst is remarkable both for the high amount of hydrogen transferred to the support and by taking place at ambient temperature. Thermal activation is usually required in order to allow migration of H-spillover species from the metal to the support.

The catalytic activity data must be discussed on the ground of the former characterization results. Thus, the samples a and b which are completely reduced at 623 K show an increase in activity when the reduction temperature is increased up to 773 K. This effect can be reversed by oxidation and further reduction at low temperature. Such behaviour is opposite to that of the catalyst prepared by traditional methods, d. The properties of sample d are similar to those extensively described in the literature for metal catalysts dispersed on TiO_2 supports, and known as strong metal–support interaction effects (SMSI) [17,19,20]. The most accepted explanation for these phenomena is that, following high-temperature reduction (773 K), the metal becomes covered by patches of partially reduced support, thus inhibiting the chemisorptive and catalytic properties of the metal [17,19], although the participation of electronic interactions in the SMSI effects cannot be ruled out [20]. This type of coverage effects has been evidenced by TEM for catalyst d reduced at 773 K, whereas, for understanding the increase in activity with the reduction temperature for the catalysts prepared by impregnation of TiO_2–SiO_2 aerogels (samples a and b), it is necessary to consider the role played by other types of metal–support interactions which lead to a type of behaviour opposite to that characteristic of the SMSI effect.

It is noteworthy that the catalyst b, prepared from a TiO_2–SiO_2 sonogel, after reduction at 773

K, presents the highest activity of all the series. The specific activity of this catalyst is four times that of other rhodium catalysts highly dispersed on conventional supports [21]. This suggests that the use of ultrasound in the preparation of the support may be a factor to modulate its properties and improve catalytic behaviour.

Concerning the catalytic behaviour of catalyst c, it is worth noting that the hydrogen forms adsorbed by spillover on a support can create active centers on its surface with properties which are characteristic of metal catalysts [18]. Although sample c was inactive for the reactions and conditions tested in this work for other experimental conditions and/or for other catalytic reactions, this material can become an interesting catalyst.

5. Conclusion

The results presented in this paper demonstrate that the Sol–gel methods allow preparation of dispersed metal catalysts with rather singular properties.

Catalysts obtained by impregnation with rhodium nitrate solutions of classic and sono-titania–silica aerogels present a pattern of behaviour opposite to that of a catalyst prepared by traditional methods from a commercial silica. The sono-supported sample, prepared using ultrasound, leads to the highest specific activity in the benzene hydrogenation reaction.

Strong hydrogen spillover effect was observed at ambient temperature for a ternary Rh–TiO_2–SiO_2 aerogel prepared with high-power ultrasonic stirring. This type of adsorbed hydrogen can generate active sites for other reactions or in different conditions of those tested in the present work.

Sol–gel methods in general, and the use of ultrasound in particular, can be fruitfully used in order to modulate the properties of catalytic materials.

The authors thank the CICYT (project PB90-0671) and the Junta de Andalucía for financial support.

References

[1] M.A. Cauqui and J.M. Rodríguez-Izquierdo, these Proceedings, p. 724.
[2] G.M. Pajonk, Appl. Catal. 72 (1991) 217.
[3] N. de la Rosa Fox, L. Esquivias and J. Zarzycki, Rev. Phys. Appl. 24 (1989) 233.
[4] N. de la Rosa Fox, L. Esquivias, A.F. Craievich and J. Zarzycki, J. Non-Cryst. Solids 121 (1990) 211.
[5] M. Ramírez del Solar, N. de la Rosa Fox, L. Esquivias and J. Zarzycki, J. Non-Cryst. Solids 121 (1990) 84.
[6] L. Esquivias, C. Fernández-Lorenzo and J.M. Rodríguez-Izquierdo, Riv. Staz. Sper. Vetro 20 (1990) 85.
[7] E.I. Ko, J.P. Chen and J.G. Weissman, J. Catal. 105 (1987) 511.
[8] J.S. Rieck and A.T. Bell, J. Catal. 99 (1986) 262.
[9] E.T.C. Vogt, A. Boot, A.J. Van Dillen, J.W. Geus, F.J.J.G. Janssen and F.M.G. van den Kerkhof, J. Catal. 114 (1988) 313.
[10] R.A. Rajadhyaksha and H. Knözinger, Appl. Catal. 51 (1989) 81.
[11] S. Imamura, H. Tarumoto and S. Ishida, Ind. Eng. Chem. Res. 28 (1989) 1449.
[12] C.U. Ingemar Odenbrand, S.L.T. Anderson, L.A.H. Anderson, J.G.M. Branchin and G. Busca, J. Catal. 125 (1990) 541.
[13] A. Fernández, J. Leyrer, A.R. González-Elipe, G. Munuera and H. Knözinger, J. Catal. 112 (1988) 489.
[14] M.G. Reichmann and A.T. Bell, Langmuir 3 (1987) 111.
[15] S. Doeuff, M. Henry, C. Sánchez and J. Livage, J. Non-Cryst. Solids 89 (1987) 206.
[16] A. Crucq, L. Degols, A. Frennet and G. Lienard, Catal. Today, 5 (1989) 91.
[17] G.L. Haller and D.E. Resasco, Adv. Catal. 36 (1989) 173.
[18] W.C. Conner, G.M. Pajonk and S.J. Teichner, Adv. Catal. 34 (1986) 1.
[19] S.J. Tauster, S.C. Fung and R.L. Garten, J. Am. Chem. Soc. 100 (1978) 170.
[20] A.R. González-Elipe, A. Fernández, J.P. Espinos and G. Munuera, J. Catal. 131 (1991) 51.
[21] S. Fuentes and F. Figueras, J. Catal. 61 (1980) 443.