Tuned Pd/SiO_2 aerogel catalyst prepared by different synthesis techniques

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Abstract

Pd nanoparticles have been embedded on silica aerogel by using three different techniques. In each of them the metal was loaded in the matrix at different steps of the production: the direct synthesis, the wet impregnation and the supercritical impregnation of the previously dried aerogels. The resultant materials have been characterized to analyze the differences depending on the applied technique for its impregnation. Atomic absorption, nitrogen physisorption, X-ray diffraction, infrared spectroscopy and transmission electron microscopy where performed. In all the techniques the concentration of metal has been varied (from 0.13 to 1.61 % wt.) by modifying the concentration of the suspension (Pd-polyvinylpyrrolidone nanoparticles used in the direct synthesis) or of the solution of the metallic precursor (palladium acetylacetonate), both in the organic solvent and the supercritical media. The characterization had generally shown a good distribution of the metallic particles in the matrix, and the negligible effect of the metal on the textural properties. Finally, considerable variations where observed on the silanol groups on the surface of the catalysts. These materials were tested in D-glucose hydrogenation, observing significant

differences on the performance of the catalyst depending on the synthesis technique employed.

Keywords aerogel; silanol; tuned selectivity; palladium catalyst; nanoparticles; supercritical CO_2

1. INTRODUCTION

Effective routes to obtain more valuable products require the design of efficient catalysts. Novel catalytic structures are therefore needed to overcome the present challenges. These novel structures require the integration of support active sites in a way that preserves their advantages and capabilities. Therefore the development of novel catalytic structures achieved by the integration of metallic nanoparticles evenly distributed in a mesoporous and high-surface aerogel appears as a promising alternative.

Silica aerogels present remarkable properties which make them suitable materials to overcome these new challenges: high pore volumes, favorable transport properties, stability and surface activity. What is more, their properties can be easily tuned: their textural properties can be tailored by changing the ratios of precursor [1]; the chemistry of their surface can be controlled by using different alkyl-alkoxy/chloro silanes allowing to govern their grade of hydrophobicity [2]; in addition, the option of creating hybrid aerogels make almost all properties requirements achievable [3].

By constrast, due to its breakability special techniques must be applied for the metal impregnation before or after the drying in order to avoid the capillarity forces which could damage the structure of the matrix. Cogelled aerogel and Impregnated Aerogel Catalysts were already produced [4], concluding that the cogelled ones showed better resistance to sintering. Also Ni and Pd nanoparticles were embedded on aerogels by impregnation of the gels followed by supercritical drying [5]. Ionic liquids have also been considered as a possible route [6]. Finally supercritical CO_2 has been used as

impregnation media and 1,1,1,5,5,5-Hexafluoro-2,4-pentanedione-palladium (2:1) as metal precursor [7]. Furthermore, the solubility of Palladium(II) acetylacetonate in supercritical CO_2 has been already studied, providing another Pd precursor which could be used in the supercritical impregnation (SCI) technique[8].

Therefore, different preparation techniques have been proposed for incorporating Pd catalytic nanoparticles in a silica matrix, showing different results depending on the technique employed. But to our knowledge, a systematic study of the variation of the final properties of the materials depending on the techniques and solvents used for the metal impregnation has not been done. What is more, this variation of properties could be translated into differences on the functionality of the final catalysts.

Catalytic hydrogenation of D-glucose into sorbitol seems to be a simple reaction, but in fact D-glucose can follow different reaction pathways instead of being converted into sorbitol. In essence, D-glucose can isomerize into D-fructose by Lobry de Bruyn Alberda – Van Ekenstein reaction [9] and its subsequent hydrogenation allows to obtain mannitol / sorbitol mixture[10]. In addition, byproducts such as glycolaldehyde and glyceraldehyde could appear as a result of retro aldol condensation reaction [11], which are hydrogenated into smaller sugar alcohols like ethylene glycol and glycerol respectively. Ru-based catalysts demonstrated to be the most effective for catalytic hydrogenation into sorbitol. However, metals such as Ni, Pt, Pd and Rh have been used for similar purposes due to their lower price in comparison with Ru [12]. Bizhanov et al. reported that the combination of Pd and Ni in the hydrogenation of D-glucose was very effective in comparison with other bimetallic catalysts [13].

In this work, Pd nanoparticles have been embedded on silica aerogel by using three different techniques. In each of them the metal was loaded in the matrix at different steps of the production: the direct synthesis (DS), the wet impregnation (WI), and the

SCI of the previously dried aerogels. Kinetic tests of D-glucose hydrogenation into sugar alcohols were carried out in order to check the catalytic behavior of the catalysts. The influence of the preparation technique in the activity of each catalyst was reported.

2. EXPERIMENTAL

2.1 Reagents

Tetramethoxysilane (TMOS, 98%), Palladium(II) acetylacetonate ($Pd(acac)_2$, 99%), Polyvinylpyrrolidone (PVP) average mol wt 10,000, Borane-ammonia complex (97%) and D-(+)-glucose (≥99.5%) were purchased from Sigma–Aldrich. Methanol (99.8%) and ammonium hydroxide (25%) were obtained from Panreac. CO_2 (>99.95 mol%) and technical H_2 were supplied by Carburos Metálicos S.A. Deionized water was used in all experiments.

2.2 Aerogels synthesis:

Hydrophilic silica alcogels were produced following the single step sol–gel process [14]. The molar ratio was TMOS:CH_3OH:H_2O:NH_4OH, $1:2.3:3.8:1.2 \times 10^{-2}$.Then the alcogels were dried by using supercritical CO_2. The drying took place in a closed circuit where the CO_2 at 10.5 MPa and 45ºC was recirculated till the solvent was completely removed. Three loads of fresh CO_2 where needed. A detailed description of the setup can be found elsewhere [15].

2.2.1 Palladium impregnation

Three different techniques were used to impregnate Pd into the silica matrix by using the same metal precursor.

The first one was the traditional WI method, which consisted on adding $Pd(acac)_2$ into the aging solvent. That was followed by the supercritical drying with CO_2. Two solvents were used: methanol and acetone. Acetone one was chosen because of the higher solubility of the precursor. The solutions were saturated at 20, 40 and 50ºC.

The second one was the SCI. It is based on the dissolution-precipitation principle. After the supercritical drying of aerogels, the supercritical CO_2 was also used as solvent media for the $Pd(acac)_2$. The precursor was placed in excess in a batch reactor where the samples stayed at 25 MPa and 60ºC for a long time to secure the solubilization till saturation conditions and diffusion of the metal precursor. Then the solubility of the precursor was decreased to force its precipitation into the aerogels pores by reducing temperature till room temperature. Finally the system was decompressed at a rate of 0.3 MPa/min.

The third one, the DS, was made by suspending metallic Pd nanoparticles in the methanol of the alcogels synthesis. These nanoparticles were produced by taking as reference the methodology described by other authors, which reduces the metal precursor with ammonia borane in a methanol solution [16]. Then the samples were calcinated at 400°C during 3 hours in order to eliminate the surfactant.

Finally, in all the cases, the aerogels were milled during 60 minutes at 100 rpm with a Planetary Ball Mill PM 100 (Retsch) and the powder was treated with a flow of 2 Nl/min of pure H_2 at 150°C during 30 minutes to activate the catalyst.

2.2.2 D-glucose hydrogenation:

The reaction was performed in batch in an experimental set-up with a commercial stainless steel high pressure reactor (Berghof BR-25) with an internal volume of 25 cm^3, agitated with a magnetic stirring bar 1400 rpm and fitted up with a proportional–integral–derivative system for temperature control. The hydrogenation reaction was performed by pumping 5 mL of glucose solution (10g/L) and charging 150 mg of the hydrophilic aerogels with different loads of Pd. All the catalytic tests were performed at 120ºC and 2.5 MPa of pure hydrogen during 360 min. A more detailed description of the set-up can be found elsewhere [17]. Activity of the different catalyst (A, $mol_{converted}$

$_{glucose}\cdot mol_{metal}^{-1}\cdot min^{-1}$) and selectivities to the products (S, %) were calculated using Eq. (1) and Eq. (2).

$$A = \frac{n_{glucose\,0} - n_{glucose\,f}}{n_{metal} \cdot min} \qquad (1)$$

$$S\,(\%) = \frac{n_{product}}{n_{glucose\,0} - n_{glucose\,f}} \qquad (2)$$

2.3 Characterization:

The aerogel structure was studied by Fourier transform infrared spectra (FT-IR model TENSOR fromBRUKER, Spain)

Metal loading was determined by atomic absorption (AA) using a VARIAN SPECTRA 220FS analyzer. Digestion of the samples was performed with HCl, H_2O_2 and HF using microwave at 250 ºC.

The crystallinity of the impregnated Pd particles were analyzed by X-ray diffraction (Discover D8-Bruker)

A JEOL field emission microscope, model JEM-FS2200 HRP, operating at 200 kV was used for HR TEM (High Resolution Transmission Electron Microscopy) and EDX (Energy-Dispersive X-ray spectroscopy).

The textural properties of the catalysts were determined by nitrogen isothermal adsorption-desorption. A Surface Area and Porosity Analyzer (ASAP2020-Micrimetrics) was used. The specific surface area was calculated by the BET (Brunauer–Emmett–Teller) method. The specific pore volume is determined by the single point adsorption method. The shown average pore diameter is based on the desorption isotherm of the Barrett-Joynes-Halenda (BJH) method.

Hydrogenation products were analyzed by liquid chromatography (HPLC). The HPLC column used was SUGAR SC-1011 from Shodex at 80 °C and a flow of 0.8 $cm^3 \cdot min^{-1}$ using water Milli-Q as the mobile phase. A Waters IR detector 2414 was used to identify sugars, polyols and their derivatives.

3. Results

3.1 Infrared spectra studies

Fig. 1 shows the infrared spectra of the silica aerogel and the different synthesized catalysts. The untreated support shows some methyl groups on the surface (815, 2862, 2936 and 2974cm^{-1}); these groups are expected to correspond to residual non-hydrolyzed alkoxy groups on the surface of the silica aerogels [18]. The free metal support was also reduced under the same conditions which were used to reduce the catalysts and not important fluctuations where noticed on the spectra. By contrast a significant decrease on the methyl groups followed by an increment of the silanol peak (960 cm^{-1}) was noticed in the samples produced by WI. What is more, comparing the sample prepared at 20ºC and the one at 50ºC, the hydroxylation seems to be related with the temperature of the impregnation. A similar but slighter effect is observed on the sample prepared by SCI. Although the temperature of SCI is 60ºC, the reduction in the methyl groups and the increment at 960cm^{-1} is less pronounced in supercritical CO_2 than in acetone. A different phenomena is observed in the catalyst made by direct synthesis which has completely lost these methyl groups but does not show the higher intensity on the silanol region. This could be explained by the temperatures reached during the calcination of the PVP which allows the loose of the methyl groups but also the initialization of the dihydroxylation [19].

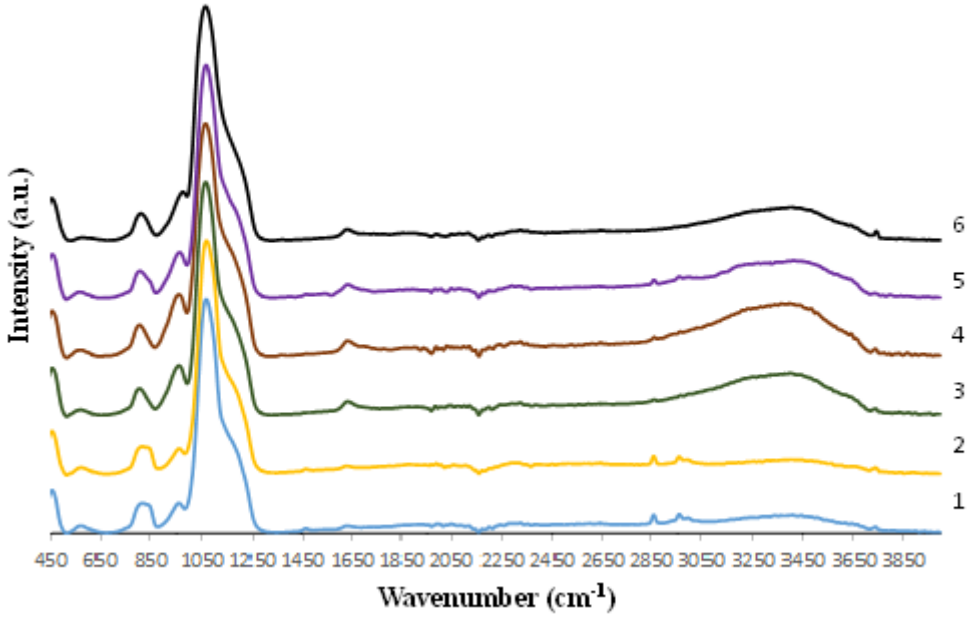

Fig. 1. Infrared spectra of the raw aerogel (1), reduced aerogel (2), reduced WI with acetone at 20ºC (3), reduced WI with acetone at 50ºC(4), reduced SCI (5) and reduced DS (6).

Concerning the OH stretching region, three different bands can be distinguished. The one at 3735cm^{-1} corresponds to the free silanol groups on the silica surface. The broad band at ~3502cm^{-1} belongs to the stretching vibrations of the hydroxyl groups of water physically adsorbed on SiO_2 surface and the surface silanol groups entering into a hydrogen bond. The band at ~3660cm^{-1} can be assigned to the hydroxyls that have formed weak hydrogen bonds [20]. The different catalysts show different intensities in these peaks, which is translated into different chemical properties of the surfaces of the materials.

3.2 Nitrogen physisorption studies

The N_2-adsorption experiment with the raw aerogel and the activated catalyst led to the isotherms illustrated in Fig. 2. The isotherms belongs to "type IV" which is typical for mesoporous materials. The hysteresis loop is wide, and the desorption curve is more precipitous than the adsorption curve. This situation is classified as H2 type loops and usually occurs when the distributions of pore size radius are wide [21]. Like the raw

aerogel, all the catalyst present a unimodal pore size distribution except the DS one, whose distribution is bimodal.

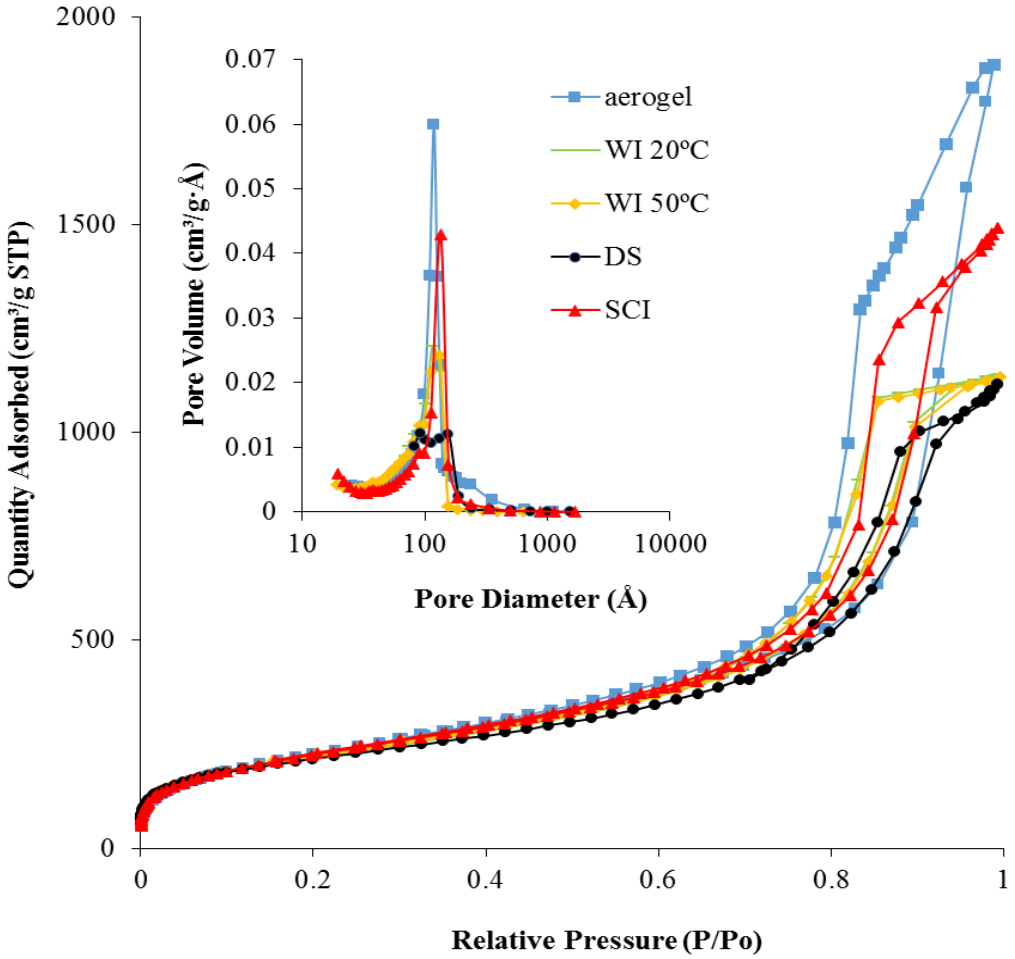

Fig. 2. Nitrogen adsorption isotherms and pore size distribution of the raw aerogel, the WI with acetone at 20°C, the WI with acetone at 50°C, the SCI and the DS

Table 1 BET surface area, pore volume and pore diameter of raw aerogel and activated catalysts

	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore diameter (Ø) (nm)
raw aerogel	845	2.91	11.66
WI 20°C	788	1.76	10.37
WI 50°C	799	1.71	8.86
SCI	825	2.31	11.13
DS	766	1.72	13.67

As shown in Table 1 the impregnated sample which keeps its final properties closer to the ones of the raw aerogel is the one prepared by SCI. Apparently this technique has allowed to block less of the pores than the WI technique because the size of the biggest particles of metal produced by SCI is smaller than the biggest particles produced by WI. Concerning this WI catalyst, the possibility of increasing the Pd loading by increasing the temperature at which the solvent is saturated with the Pd precursor does not seem to increase the number of obstructions because there is not an important effect on the textural properties. With respect to the catalyst prepared with suspended Pd nanoparticles during the sol-gel process, the drop in surface and pore volume is bigger than in the other samples and its pore diameter is the biggest. As said above, this sample is the only one with a bimodal pore size distribution. But in this case, the changes on the properties could be attributed to the thermal treatment of the sample during the calcination in order to remove the surfactant which requires temperatures of 400ºC [22].

3.3 Powder X-ray diffraction studies

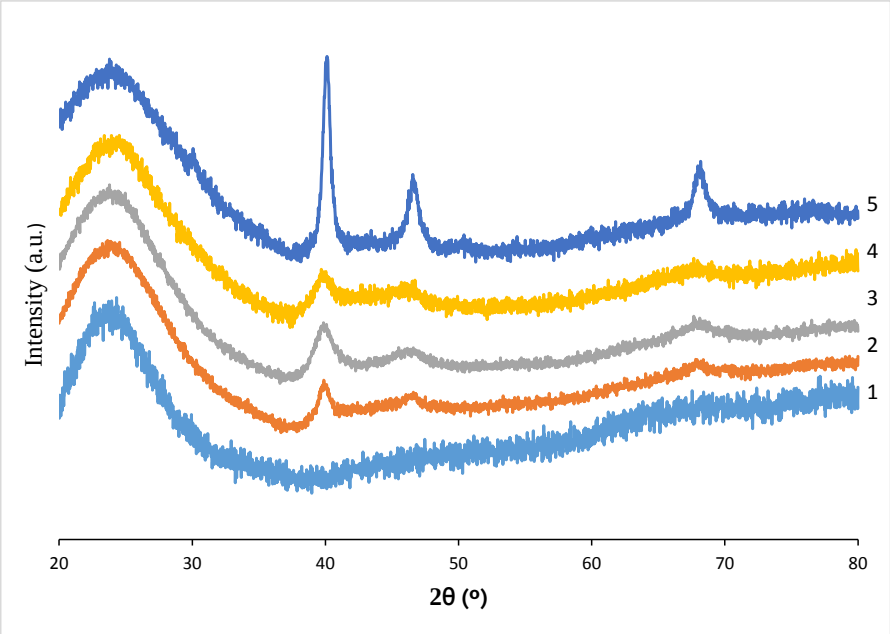

Fig. 3. X-ray diffraction patterns of silica aerogel (1) and palladium containing aerogels; WI with acetone at 20 (2) and 55°C (3), SCI (4) and DS (5) samples.

X-ray diffraction patterns for bare silica aerogel and Pd-based catalysts are shown in Fig. 3. Three characteristic diffraction peaks were detected at 2θ=40º, 46º and 68º (JCPDS 46-1043)) corresponding to the presence of (111), (200) and (220) planes [23]. This information suggested the presence of Face-Centered Cubic (FCC) Pd^0 nanoparticles [24]. The broader base of the peaks in the cases of the WI and SCI indicate a better distribution of the metal inside the matrix[25].No PdO peaks were observed which means that the samples were completely reduced under pure H_2. By applying the Scherrer equation to the samples prepared by WI with acetone at 20 and 50°C, SCI sample and the ones prepared by DS, the calculated crystal size are 4.4nm, 3.72 nm, 5.01 nm and 7.14 nm respectively.

3.4 *Transmision electron microscopy studies*

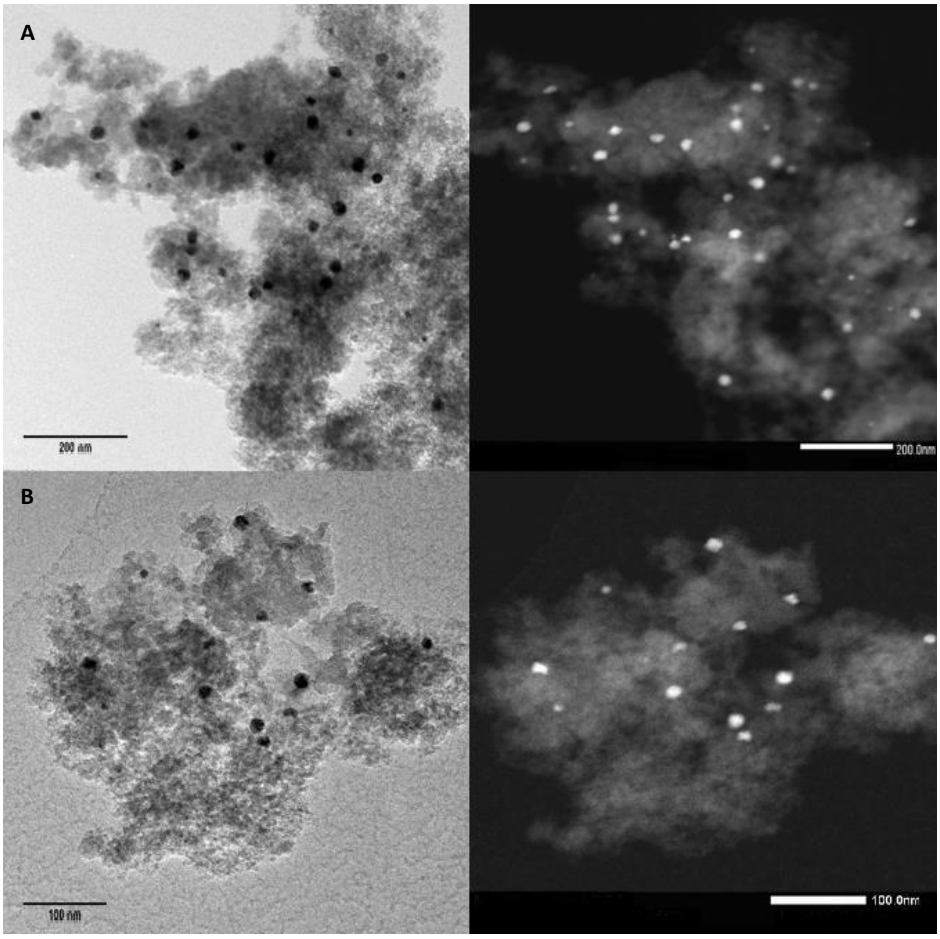

Fig. 4. HR TEM and dark field images of cataltalyst prepared by WI (A) and SCI (B)

Fig. 4 shows the HR TEM and dark field of the catalyst prepared by WI and SCI. Both of them present a homogeneous and well distributed particles, which is in good relation with the small and wide peaks in the X-ray spectra. Nevertheless an important variation on the size of the particles is seem; in the case of the WI, the size varies from 4 to 30nm and in the case of the SCI, from 3 to 20 nm. This variation in the size of the biggest particles could be important; it is similar to the expected pore size of the matrix, which indicates that particles with sizes in this range probably are blocking some of the pores of the aerogel scaffold.

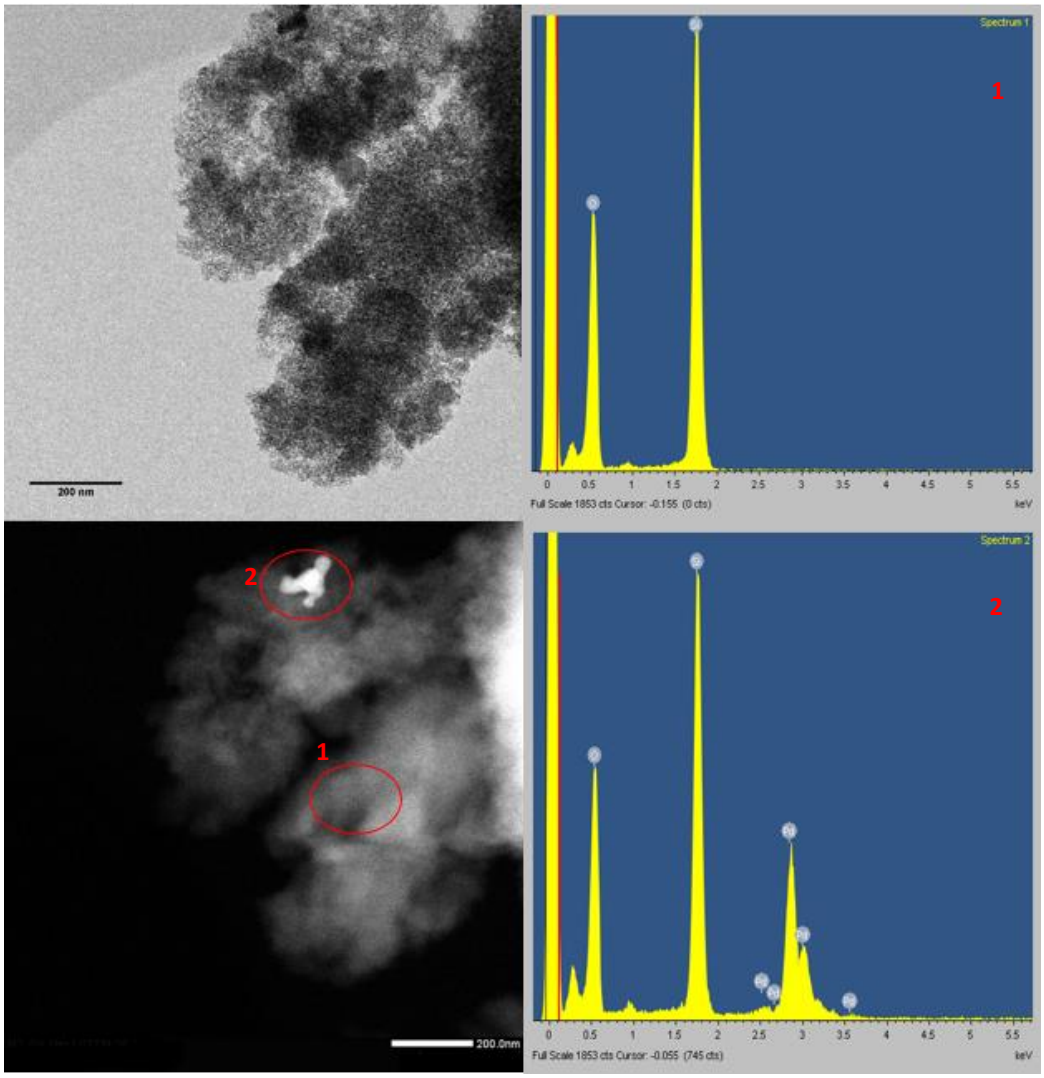

Fig. 5.HR TEM, dark field images and EDX of direct synthesis catalyst.

By contrast the images showed on Fig. 5 demonstrate the agglomeration of the metallic particles in the catalyst prepared by the direct synthesis technique. This bad distribution is also checked by comparing region 1 and 2 in the dark field. Their corresponding EDX show the presence of palladium just in region 1, without presence of palladium in the rest of the scaffold. The agglomerates present a size above 100nm. This result is in good agreement with the highest reduction on the pore volume observed in the BET analysis. This result could be due to the incorrect suspension of the Pd-PVP nanoparticles in the solvent during the sol-gel reaction. Indeed, a correct dispersion of the particles in the gel during ageing is difficult due to the high viscosity of this medium. The use of ultrasounds could be useful to overcome this defect. Another reason could be the formation of PdO during the calcination of PVP promotes the sintering due to the weaker interactions of the metallic particles with the support.

3.5 Atomic absorption studies

As can be seem in Table 2, the catalyst with less metal content was the on impregnated with methanol (0.13%). By contrast, the ones impregnated with acetone present higher concentrations from 0.54 to 1.03%. On the one hand, this gradient was achievable by increments of the impregnation solution temperature and concentration. On the other hand the low ebullition temperature of the acetone limits the maximum operating temperature, and therefore the maximum concentration of $Pd(acac)_2$ in the solution. It can be concluded that two effects govern the final metal content: the solubility of the precursor and the interactions between the silanol groups on the surface and the solvent. Further studies could also be done in order to check the SCI results when using other pressure and temperature conditions, resulting in other solubilities. Finally the amount of Pd on the sample prepared with suspended Pd PVP particles can be controlled by

adding more or less metal in the suspension used for the synthesis of the gels. The amount of metal added to the suspension and the final one is in good agreement.

Table 2 Metallic content on the activated catalysts

	WI				SCI	DS
P (MPa)					25	
solvent	MeOH		Acetone		Supercritical CO_2	
T (ºC)	20	20	40	50	60	
Pd wt %	0.13	0.54	0.65	1.03	0.84	1.61
Particle size (nm)				4-30	3-20	> 100

3.6 Catalytic activity studies

The results of the hydrogenations of D-glucose are summarized in Table 3 in terms of activity and selectivity. On the one hand, the materials have shown different catalytic behaviors depending on the preparation method. The catalysts prepared by WI method (WI 20ºC and WI 50ºC) showed the highest activity during the hydrogenation experiments and the material synthesized by DS presented the lowest one. This fact can be attributed to the different crystallite size calculated from XRD patterns and Scherrer equation, where WI 20ºC and WI 50ºC obtained crystallite sizes around 4 nm while DS achieved 7 nm. In addition the crystals are not just the biggest but also forms agglomerates as shown in HR TEM images (Fig. 5). Small differences in terms of activity were observed comparing both WI 20ºC and WI 50ºC. The higher concentration of the metal in the matrix has not been turned into a higher activity. This could be explained by the size of the particles in the matrix, which is probably bigger in the case of the catalyst with more metal content, reducing the exposed active surface of the metal. Another point to contrast is that the textural properties of the SCI sample are the best, but its activity is lower than those obtained by WI. Therefore, other factors should

be taken into account. First of all, the different concentration and nature of the hydroxyl groups on the surface seem to be playing a role. Secondly, the formation of different types of carbide on the surface due to the direct reduction under hydrogen atmosphere [26] cannot be ignored.

On the other hand, selectivity to sorbitol results presented in Table 3 demonstrated the influence of the preparation method and metal loading in the composition of the final product. Comparing both selectivities to sorbitol for WI 20ºC and WI 50ºC, it was observed that an increase in Pd loading from 0.54 to 1.03 % enhanced selectivity to sorbitol from 54 to 76 %. Low amounts of fructose were detected suggesting retro aldol condensation reaction to produce glyceraldehyde that is subsequently hydrogenated into glycerol which is the main byproduct in both cases. In addition, glycerol was the main compound in the liquid product when hydrogenation of D-glucose was carried out over the catalyst prepared by SCI achieving a selectivity to glycerol around 89 %. In the case of SCI sorbitol was not detected in the final product. As it was explained above, hydroxyl groups and carbide on the surface of the support could decrease the activity of the catalyst and favor glycerol production. Finally, D-glucose is hydrogenated with a selectivity around 47 % to sorbitol over the catalyst prepared by DS and no other products could be identified by HPLC in this case.

Table 3 Catalytic activity, (moles of converted glucose per moles of metal and per minute) and selectivity to sorbitol of the synthesized catalysts at 120 ºC, 2.5 MPa H_2 and 360 min

	WI 20ºC	WI 50ºC	SCI	DS
Activity	$1.42 \cdot 10^{-2}$	$1.07 \cdot 10^{-2}$	$4.45 \cdot 10^{-3}$	$2.27 \cdot 10^{-3}$
$S_{SORBITOL}$ (%)	54.23	75.85	0	47.26
$S_{GLYCEROL}$ (%)	34.71	22.43	88.45	0

4. CONCLUSIONS

Three different routes have been used to impregnate silica aerogels with Pd. The load of the metal could be tuned by controlling the concentration of Pd in the different impregnation media but at the same time the achievable concentration is limited by the solubility of the precursor. Well distributed particles were obtained with WI and SCI but agglomeration was observed on the DS catalyst. The test of the catalysts in the hydrogenation of D-glucose have proved that the influence of the concentration of metal and the size of the metallic particles are important. In addition, the chemistry of the support, which is modified depending on the way in which the support is impregnated, and the presence of carbides, seem to play an important role on activity and selectivity.

Acknowledgments

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