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High specific surface area of SiO_2–C meso- and nanoporous materials textural assessment and surface development

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ABSTRACT

In this work a SiO_2–C system has been prepared on the basis of phenolic resins co-gellification and prehydrolized ethyl silicate. This material was cured at 180 °C and calcinated at 1500 °C in a reducing atmosphere, obtaining a composite material with two different crosslinked frameworks, one of silica and the other of carbon. These frameworks are self-supported and independent, and the carbon structure can be isolated by the elimination of silica network by HF acid attack. SiO_2–C and C materials were characterized and employed as Pt catalytic support. These catalytic systems were studied on hydrogen production by glycerol steam reforming. Pt/SiO_2–C resulted into a more active and stable catalyst due to the effect of low metal sintering and more favorable transport and diffusion of the reactants and products.

1. Introduction

In recent years, materials synthesis with meso- and nanostructures and/or controlled meso- and nano-textures has gained great scientific interest. The field of porous nanostructures has received a great boost due to major technological and environmental implications that they have. Several works have been published regarding the formation of micro- and macro-siliceous compounds generated by gellification of TEOS in the presence of different surfactants and different experimental conditions [1–3].

A material used as a catalytic support has to provide porosity and high specific surface area; both of them play important roles depending on the studied reaction [4–6]. In the particular case of hydrogen production from glycerol, there are searches for a catalyst metal that reaches a high metallic dispersion, with a strong interaction with the support, and that avoids superficial acidity that encourages lateral reactions [7,8]. In this paper SiO_2–C and C catalytic supports were evaluated. These materials were obtained by co-gellification of TEOS and phenolic resin; successive stages of drying, curing and thermal treatment in highly reducing conditions produce nanoporous materials of special characteristic which allows application as catalytic support. Platinum was selected as a catalyst. The materials were characterized by mercury intrusion porosimetry, nitrogen adsorption data from Brunauer–Emmett–Teller (BET), X-ray diffraction (XRD), point of zero charge (PZC), X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), and hydrogen chemisorptions; glycerol steam reforming was selected as a reaction test.

2. Experimental

Materials: The TEOS (SILBOND 40-AKZO Chemicals) used is a partially hydrolyzed mixture of monomers, dimmers, trimers, higher polymers and cyclic polysilicates. Liquid phenol/formaldehyde resin: RL 43003 (ATANOR. Argentina) were used as cogelling agent; a characteristic of this thermo-rigid resin is the high mass of pyrolytic carbon waste generated when it is calcinated at high temperatures in a strong reducing atmosphere [9].

Gel preparation: TEOS (40 g) and RL 43003 (20 g) were mixed on a magnetic stirrer until obtaining an emulsion, to which was gradually added 44 ml of commercial ethyl alcohol (96%) to obtain a translucent ambers colored liquid similar to the resin. Necessary water for TEOS gellification was provided by the alcohol and the liquid resin. Pre-gel liquid was cast on covered cylindrical molds to gellificate at room temperature without solvent evaporation (alcohol and water). After 24 h, the molds, were uncovered; in order to lift the gel in the mold out from the walls, gel contraction by solvents evaporation was employed. On release, it was aerated at room temperature for 24 h, and dried at 50 °C for another 24 h. After that the material was heated until 180 °C with a 10 °C/h heating rate, producing the resin polymerization.

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Obtaining SiO_2–C composites: Cylindrical parts obtained on curing were introduced on covered refractory crucibles, totally covered with petroleum´s carbon waste pre-calcined. The system was calcinated for 3 h on an electrical oven at 1500 °C (at 5 °C/min).

Obtaining C: Composites SiO_2–C were submerged into 20 wt% HF, and taken off from the solution after 30 min. The pieces were washed with distilled water, eliminating the residual H_2F_6Si by heating at 400 °C.

Pt catalysts preparation: These supports (SiO_2–C and C) were used in the preparation of platinum catalysts ($\sim$2 wt%) employing H_2PtCl_6 as the metal precursor following the same procedure as that of Cui et al. [10]. Platinum catalyst supported in commercial SiO_2 (Aerosil 200) was used as reference. These materials were identified as PtC, PtSiO$_2$–C, and PtSiO$_{2comm}$.

Reaction test: The experimental equipment used for reaction tests of glycerol reforming is a fixed-bed quartz reactor operated isothermally at atmospheric pressure [8]. Aqueous solution of glycerol (30 wt%) was injected to the reactor by a HPLC pump with feed flow 0.5 $cm^3\ min^{-1}$. Hydrogen chemisorption measurements were carried out in dynamic equipment with a TCD detector. Samples were reduced in H_2 flow at 700 °C during 1 h, cooled in H2 up to 400 °C, flushed with Ar for 2 h at 400 °C and then cooled up to room temperature in Ar flow. Hydrogen pulses were then injected up to saturation. Dispersions were estimated from the hydrogen amount consumed, assuming an adsorption stoichiometry H/Ni=1.

3. Results and discussion

Solids were characterized by X-ray diffraction (Cu Kα_1 radiation). A sample C diffractogram (Fig. 1) shows the presence of a large band focused on 25.6° and 43.7° of 2θ which corresponds to the basal level of the graphite structure, and to the spaced C–C of the graphitic structure, respectively. For the composite SiO_2–C, it was possible to observe that the bands of carbon are maintained and a new band corresponding to amorphous silica centered at 21.8° of 2θ appeared. These results suggest that SiO_2–C is a composite material with two different crosslinked frameworks, one of silica and the other of carbon. These frameworks are self-supported and independent; the carbon structure can be isolated by the elimination of silica network by HF acid attack, and the silica network by an oxidative calcination.

Results of the characterization of the materials are shown in Table 1. The pore size distributions were determined by mercury intrusion porosimetry, in the radius range of 36–30,000 Å (3.6–3000 nm). SiO_2–C and C present a very narrow pore size distribution centered on 250 Å for SiO_2–C and 200 Å for C.

BET surface area of support C is similar to those of some commercial carbons; most commercial carbons present large pores radius distribution; material C can be distinguished by the presence of mesopores of 200 Å. XPS analysis was carried out in an LHS10 equipment, with Al Kα radiation (1486.6 eV) and it was demonstrated that the treatment with HF did not eliminate completely the silica on material C (C1s/Si2p=25). Deconvolution of C1s peak of SiO_2–C and C samples showed a main peak at 284.6 eV attributed to the C–C bonds of graphite, and at 286.9 eV attributed to C=O bonds (carbonyls, quinone and aldehydes groups).

It is observed also that both materials have a point of zero charge near 7. According to its definition, the PZC of carbon should depend not only on its total surface oxygen but also on the nature and distribution of the surface oxygen sites. Oxidized carbons always contain basic surface sites in addition to the acidic functions. In describing the surface chemistry of carbon, two main types of oxygen surface groups are considered, acidic and basic groups. The analysis by TPD allows the detection of two other categories of surface oxygen groups, those that generate CO_2 and those that generate CO [11]. We performed a quantitative analysis

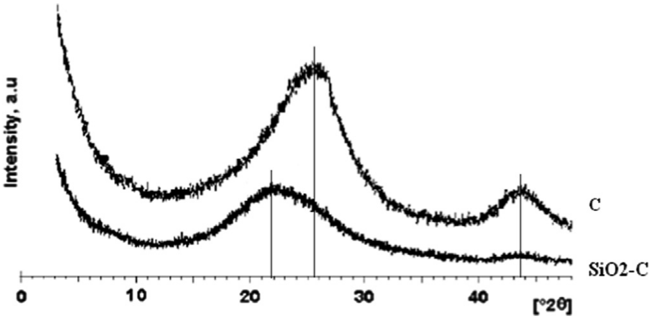

Fig. 1. XRD patterns for SiO_2–C and C materials.

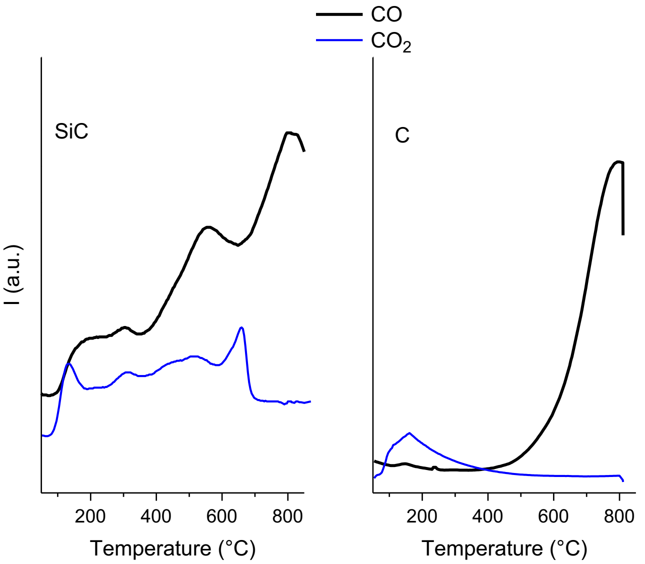

Fig. 2. Temperature programmed desorption (TPD). TPD spectra (in helium flow) of SiO_2–C and C supports: CO (—) and CO_2 (—) released.

Table 1
Structural parameters of SiO_2–C and C materials.

	Hg intrusion porosimetry		Nitrogen adsorption			PZC[a]	XPS[b]
	Max pore vol (mm^3/g)	Max pore rad (Å)	BET (m^2/g)	Pore vol (cm^3/g)	Pore diam (Å)	–	C1s/Si2p (284.6/103.9) (eV)
SiO_2–C	8600	250	255	0.40	63	6–7	10.4
C	760	200	1140	2.0	69	6–7	25

[a] Point of zero charge.

[b] Binding energies (eV) and surface atomic composition.

Table 2
Results of activity test: steam reforming of glycerol.

Catalyst	D (%)	X_G^i (%)	Gas product composition [mol%/mol (dry basis)]				"$a_{20\ h}$"
			H_2	CO	CH_4	CO_2	
PtC	77	98	59	34	2	5	0.5
$PtSiO_2$–C	84	100	59	32	2	7	1
$PtSiO_{2comm}$	60	62	59	28.5	1.2	11.3	0.1

Test at 450 °C, atmospheric pressure. Pt dispersions D (%) are calculated by H_2 chemisorptions data. Glycerol concentration: 30 wt%. X_G^i is the initial glycerol conversion. $a_{20\ h}$ is defined as $X_G^i/X_G^{20\ h}$.

of the amounts of CO and CO_2 released, obtained by integration the areas under the TPD peaks following the procedure described by Fraga et al. [11].

CO_2 is produced at low temperatures by oxygenated groups of pka near 5, while CO comes from groups more stable and less acidic on the carbon surface (pka ~ 8–11). Results are shown in Fig. 2. Both supports present low concentration of superficial oxide groups which is reasonable because most superficial oxygen groups have been removed with previous thermal treatment (1500 °C for 3 h).

TPD analysis of SiO_2–C shows a low concentration of superficial oxide groups corresponding to 0.15 mmol CO_2/g and 0.6 mmol CO/g released, which would be consistent with the method of calcination employed for this material. Regarding the evolution of CO_2, it can be seen that it contains very little amount of acidic groups, mainly carboxylic group at 135 °C, and lactone group at 630 °C [11]. With respect to the evolution of CO, a main peak is observed at 800 °C, which corresponds to the decomposition of the quinone groups [11].

On support C more CO at high temperature (0.2 mmol CO_2/g and 3 mmol CO/g) is released near 800 °C, which may correspond to superficial quinone groups [5]. The results obtained by deconvolution of XPS spectra are consistent with the results obtained by TPD analysis. This should indicate that treatment with HF during preparation steps produces some superficial oxidation that produces carbonyl groups but does not originate carboxylic groups. Moreover these results prove there are no acidic sites on supports C and SiO_2–C.

To study the performance of materials, C and SiO_2–C like catalytic supports were impregnated with Pt ~2 wt% to evaluate them on the glycerol steam reforming reaction. Results are shown in Table 2, which include a $PtSiO_{2comm}$ catalyst as reference. Results of Pt SiO_2–C and PtC confirm that most of the metallic dispersion (D%) reached with these supports, 84 and 77 respectively, and the meso-porosity, which would be favorable to the transport and diffusion of the reactants and products, allows reaching higher initial conversion and selectivity levels to H_2 than those of $PtSiO_{2comm}$.

In this work an activity coefficient ($a_{20\ h}$) was defined that expresses the level of catalytic stability. In Table 2 it is observed that PtC catalyst was more stable ($a_{20\ h}=0.5$) with respect to $PtSiO_{2comm}$ catalyst ($a_{20\ h}=0.1$). For PtC it was determined that the metallic dispersion loss of 40% should indicate that principal deactivation mechanism is sintering.

Finally, $PtSiO_2$–C catalyst was the most stable on 20 h of reaction ($a_{20\ h}=1$), and a metallic dispersion loss of 10% was determined. About the sintering, its highest resistance should be associated with the highest interaction that Pt reaches with this support SiO_2–C [12].

4. Conclusions

SiO_2–C composites were obtained by co-gellification of phenolic resins and TEOS. The materials obtained have a narrow pore size distribution in the meso-porous region, and are suitable to be used as catalyst supports, achieving higher dispersion and more activity than those of commercial SiO_2 in the steam reforming of glycerol. Pt supported on SiO_2–C resulted in a more active and stable catalyst due the effect of having a low amount of metal sintering during the reaction process and more favorable transport and diffusion of the reactants and products.

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