Nanoarchitectures based on layered titanosilicates supported on glass-fibers: application to hydrogen storage

Javier Pérez-Carvajal¹, Pilar Aranda¹, Angel
Berenguer², Diego Cazorla², Joaquin Coronas³,
Eduardo Ruiz-Hitzky^{1*}

¹ Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, 28049, Madrid (Spain)

² Departamento de Química Inorgánica, Universidad de Alicante, Apartado 99, E-03080
Alicante, Spain

³ Departamento de Ingeniería Química y Tecnologías del Medio Ambiente e Instituto de
Nanociencia de Aragón, Universidad de Zaragoza, C/ María de Luna 3. 50018, Zaragoza (Spain)

KEYWORDS: Nanoarchitectures, titanosilicate, glass fiber, hydrogen storage, palladium.

ABSTRACT

This work reports on the synthesis of nanosheets of titanosilicate JDF-L1 supported on commercial E-type glass fibers with the aim to develop novel nanoarchitectures useful as robust and easy to handle hydrogen adsorbents. The preparation of those materials is carried out by primary hydrothermal reaction from the corresponding gel precursor in the presence of the glass support. Due to the basic character of the synthesis media, silica from the silicate-based glass fibers can be involved in the reaction cementing their associated titanosilicate and giving rise to strong linkages on the support with the result of very stable heterostructures. The nanoarchitectures build by this approach promote the growth and disposition of the titanosilicate nanosheets as a house-of-cards radially distributed around the fiber axis. Such open arrangement represents a suitable geometry for potential uses in adsorption and catalytical applications where the active surface has to be well available. The crystalline phase content in the system represents about 12% in weight and this percentage of adsorbent phase fraction can achieve, at 298 K, 0.14% of hydrogen adsorbed in weight referred to the total mass of the system. Following post-synthesis treatments, small amounts of Pd (<0.1% w/w) have been further incorporated into the resulting nanoarchitectures in order to improve the hydrogen adsorption capacity. In this way, Pd-layered titanosilicate supported on glass fibers, has been tested as H₂ adsorbent in solid-gas phase experiments carried out at diverse pressures and temperatures, giving rise to values around 0.46% in weight.

1- Introduction

The possibility to attach at the nanometer range diverse building blocks of different nature could lead to nanoarchitectures^{1,2} provided with multifunctional characteristics by adding the individual properties of each component to the resulting assembled system. Novel nanoarchitectures can be designed using layer-by-layer³ or modifying the interlamellar space of 2D solids giving rise to pillared clays⁴, porous-clay heterostructures⁵ or delaminated clays⁶. Another extended approach consists in the generation of junctions by covalent linking of two independent components previously functionalized⁷. This last strategy applied in the case of zeolites supported on glass and mica can allow orientation control towards the linked surface⁸.

As it is well known, by supporting nanostructured materials on bulk solids, it can be improved certain properties, as for instance the mechanical stability of the resulting systems, increasing also their handling and transport abilities. Supported materials, against fine divided powders, avoids losses in flow systems in applications based on solid-gas interactions. Also this conformation could solve problems associated to health and safety legislation for workers who handle submicrometric particles, especially when nanosized materials are involved. E-type glass fibers have been selected in this work as bulk supporting material because of its high aspect ratio, low cost and relative chemical inertness and thermal stability. Related glass fibers have already been successfully tested as support for other type of nanostructured materials as silicalite-1⁹.

A microporous layered titanosilicate known as JDF-L1^{10,11,12} has been here selected for building the novel type of nanoarchitecture considered in this work. Their inherent nanosheets can *a priori* adsorb very small size species because of the presence of a very narrow porosity (ultramicropores) nearly undetectable by usual nitrogen adsorption techniques, being of potential

interest for the uptake of hydrogen gas. The potential utility of porous titanasilicates as viable hydrogen storage materials has been recently proposed¹³

The JDF-L1 titanasilicate used in this work is an unusual non-centrosymmetric tetragonal layered solid that contains five-coordinated Ti (IV) ions in the form of TiO_5 square pyramids in which each of the vertices of the base is linked to SiO_4 tetrahedra $[\text{TiOO}_4(\text{SiO}_3)_4]$ to form continuous layers. The proposed formula for JDF-L1 is $\text{Na}_4\text{Ti}_2\text{Si}_8\text{O}_{22} \cdot 6 \text{H}_2\text{O}$.

Figure 1. Projection of the JDF-L1 titanasilicate structure along the $[010]$ direction (Si atom, white; Ti atom, dark grey; O atom, light grey)

The clay-like structure of JDF-L1 also allows ion-exchange properties following soft chemistry procedures and therefore diverse metal-ions could be easily incorporated to the system in post-synthesis treatments. In addition, the pentacoordinate titanium centers of the titanasilicate can promote redox reactions with low-potential metals like silver¹⁴, facilitating the surface deposition of metal (nano)particles. In this way, doping of the resulting glass-fiber/titanasilicate nanoarchitectures by metal particles of variable size (from nanometers to several hundreds of nanometers) represents an alternative to improve the hydrogen uptake capacity of these

materials. Theoretical calculations have shown that the thermodynamic properties can change by decreasing the particle size of metallic clusters, allowing better results for the hydrogen desorption¹⁵.

Future energy use must count with hydrogen as an ideal vector for clean energy. So, it is nowadays an enormous interest for the development of viable materials efficient for the hydrogen uptake and storage. Several strategies have been addressed to contribute to solve this crucial problem, as for instance the formation of metal hydrides from metals such as palladium, titanium and magnesium allowing the storage of a relative high amount of hydrogen¹⁶. It is possible that the reversibility of the process limits its direct application because the enthalpy of formation of the hydride is too high and therefore the desorption process requires high temperature for the efficient release of hydrogen gas.

Porous nanostructured solids such as certain carbonaceous based materials¹⁷, can adsorb and desorb hydrogen with low enthalpy values. Metal-organic frameworks (MOFs) combines both characteristics: the high specific surface area, and the presence of coordinated metal atoms that are able to achieve metal hydrides or splitting processes in order to improve the hydrogen uptake. However, MOFs applications for H₂ storage show certain disadvantages mainly related with their low stability to moisture and difficulties for handling as they are present as fine powdered materials^{18,19}.

The aim of this work is the development of new nanoarchitectures based on nanosheets of titanasilicate doped with palladium and supported on a commercial bulk material of high aspect ratio, such as the E-type glass fibers, to contribute in the search of alternative efficient hydrogen storage systems.

2.- Experimental details

2.1.- Materials and reagents

The reagents used for the titanasilicate synthesis are 10.05 g of sodium silicate solution (27 mass % SiO_2 , 8 mass % Na_2O , Merck), 1.65 g of deionized water (resistivity of $18.2 \text{ M}\Omega \text{ cm}$) was obtained with Maxima Ultrapure Water from Elga, 1.43 g of NaOH (pure pellets, Merck) and 8.24 g of TiCl_3 solution (20 mass % in 3 wt.% HCl, Alfa Aesar). The nanoarchitecture is performed by adding 3.2 g of E-Glass fibers supplied by VETROTEX (Alcalá de Henares, Spain). In a post-treatment reaction, Pd nanoparticles were incorporated from a mixture of 0.056 g of Pd(II) acetate (98%, Aldrich) and 0.5 mL of hydrochloric acid (37%, Panreac)-

2.2.-Procedure of preparation of the different materials

(a) *Naked fiber* was obtained heating²⁰ the raw fiber material at 450°C in air atmosphere with a temperature increase from 25 to 450°C at $7^\circ\text{C}.\text{min}^{-1}$ rate. The heated material was kept at this last temperature during 6 hours.

(b) *JDF-L1* and *GF-JDF-L1* titanasilicate were synthesized by a primary hydrothermal synthesis during 16 hours at 230°C in a 35-mL Teflon[®] lined stainless steel autoclave keeping the proportion of 4.2 SiO_2 : TiO_2 : $2.9 \text{ Na}_2\text{O}$: $101 \text{ H}_2\text{O}$ ²¹. In order to form the gel, the titanium source is incorporated to the homogeneous mixture of sodium silicate, sodium hydroxide and water. A vigorous agitation is maintained for one hour. Seven grams of the gel is spread to the naked fiber (GF-JDF-L1) and the other fraction of the gel is kept as blank (JDF-L1), both samples are

sonicated for 15 minutes and then autoclaved at the same temperature and time. GF-JDF-L1 is washed 3 times with 25mL of deionized water and decanted. JDF-L1 is washed 3 times with distilled water and recovered by centrifugation (Beckman Coulter Allegra(R) X-15R centrifuge) at 10,000 rpm for 15 min each. JDF-L1 and GF-JDF-L1 are dried at the air atmosphere at 60°C overnight.

(c) *Pd-GF-JDF-L1*. Hydrochloric acid is gently dropped to $\text{Pd}(\text{OAc})_2$ and shaken till a clear solution is obtained and vapors are removed. The light brown solution is diluted in 50 mL of deionized water and then 0.5 grams of GF-JDF-L1 are added. This system is shaken in a thermostatic bath at 25 °C during 24 hours. The formed Pd-GF-JDF-L1 is extracted from the solution and washed 3 times with 25 mL of deionized water and then dried at 60 °C overnight.

2.3.- Materials characterization

The recovered solids were identified by powder X-ray diffraction (XRD), recorded in a Bruker D8 Advance diffractometer using Cu $K\alpha$ radiation between 5 and 40° 2 θ values, using a lynxeye detector. Supported materials were placed in an agate mortar in order to obtain fine powder samples. Fourier-Transform Infrared (FTIR) spectra were recorded with a FTIR spectrophotometer BRUKER IFS 66v/S. Each sample was placed in the sample holder as KBr pellets and scanned from 4000 to 250 cm^{-1} with 2 cm^{-1} resolution. Surface morphology was observed in a FE-SEM equipment FEI NOVA NanoSEM 230 equipped with an EDAX-Ametek detector that allowed semi-quantitative analysis of elements. Sample preparations were performed by adhering particle samples on a carbon tape without any conductive coating on the surface. The silicon/titanium relationship has been measured using Total X-Ray Fluorescence spectrophotometer TXRF 8030c FEI using in a first step a qualitative method for identify the

approximate concentration of each atom and a quantitative method after including a standard reference. The amount of palladium incorporated to the nanoarchitecture has been measured using ICP-MS Elan 6000 Perkin-Elmer Sciex equipped with autosampler AS 91. Samples were previously dissolved in a mixture of hydrochloric acid and hydrofluoric acid in a microwave oven Milestone ETHOS PLUS at 180 degrees. Nitrogen isotherms at 77 K and CO₂ isotherms at 273 K were obtained using an automatic adsorption-desorption equipment (Autosorb-6, Quantachrome). The samples were previously outgassed at 150 °C under vacuum for 4 h. Apparent BET surface area were calculated by fitting nitrogen adsorption data to BET equations. The micropore volume was determined by application of Dubinin–Radushkevich equation to the N₂ adsorption isotherm at 77 K in an adequate range of linearity. The volume of micropores lower than 0.7 nm was calculated from CO₂ adsorption at 273 K using the Dubinin–Radushkevich equation. Hydrogen isotherms at 77 K and up to 4 MPa were carried out in a Sartorius 4406 DMT high-pressure microbalance. The sample was degassed at 423 K overnight under vacuum. The experimental results were corrected for buoyancy effects related to the displacement of gas by the sample, the sample holder and the pan²². Hydrogen isotherms at 298 K were carried out in an automatic volumetric apparatus designed and built up at the *Departamento de Química Inorgánica, Universidad de Alicante* laboratory to perform hydrogen isotherms up to 20 MPa. The manifold of the apparatus was kept at 308 K. Also, the sample cell was refrigerated at 298 K by means of a liquid bath. Manifold volume was calibrated with a standard volume, carrying out helium isotherms. In order to assure that the apparatus was leak-free, hydrogen leak test was executed at 9 and 15 MPa during 28 h, the leak rate resulted below 10⁻⁶ s⁻¹. The bulk gas amounts have been calculated by the equation of state of Modified-Benedic–Webb–Rubin²³ and the cell volume has been calculated taken into account the

correction described in the literature²⁴. Previous to the adsorption isotherm, the sample was degassed at 523 K during 4 h under vacuum. After that, the sample was located in the sample holder, and then evacuated at 403 K during 4 h in vacuum. Sample weight was about 1000 mg. Hydrogen and helium gases used in the experiments were 99.9995% pure.

RESULTS AND DISCUSSION

The starting commercial E-type glass fiber contains an organic coverage on the fiber surface as revealed by the presence of C-H stretching bands in the 2800-3000 cm^{-1} range observed in the corresponding FTIR spectra (Fig. 1S). After the heating treatments these bands are completely eliminated indicating that the organic coating has been fully removed giving rise to the naked glass fibers used as JDF-L1 titanosilicate support to generate the inorganic heterostructured materials. The synthesis of this type of nanoarchitectures is carried out under hydrothermal conditions as reported in detail in the Experimental Section. The reaction media is strongly alkaline, as sodium silicate is involved as a precursor, and therefore it should be admitted that silica from the glass fiber surface is incorporated to the synthesis media during the hydrothermal process. This fact favors the robustness of the junctions between the support and the titanosilicate of the resulting nanoarchitectures. However, a control of the adopted experimental conditions is absolutely necessary to preserve the partial integrity of the support as the naked glass fibers are progressively degraded during the synthesis due to their dissolution in the strong alkaline media. In this way, the silicon atoms from the silicate composition of the glass fibers can be considered as a secondary source of silica giving rise to a total dissolution for long reaction times within the high pH media.

The FE-SEM images of the synthesized titanasilicate show the typical platelet-like morphology (Fig. 2b) already reported for JDF-L1²⁵. The images corresponding to the supported titanasilicate (named as GF-JDF-L1) show a continuous and uniform coverage by the JDF-L1 layers with a radial distribution around the fiber surface (Fig. 3). It can be admitted that the silica afforded from the fiber is being delivered to the reaction in a low rate compared to the silica present in the solution, that promotes the crystal growth from the fiber to the solution direction, giving rise to a preferential radial distribution of the titanasilicate layers on the glass fiber. Such arrangement will be of great interest for the surface availability of the synthesized materials. For reaction treatments of the glass fiber inferior than 24 h, the fiber integrity is almost preserved as observed in the FE-SEM images of a cross-section, where the glass fiber core is clearly revealed (Fig. 2a). For experiments adopting longer reaction times, the synthesis leads to materials practically composed by the titanasilicates in which the glass fiber has been completely dissolved in the alkaline media. Interestingly, a “memory effect” is observed with the titanasilicate layers organized in the same manner than in the presence of an imaginary fiber (Fig. 2d). However, the resulting solids are mechanically weak and are easily reduced to fine powder evidenced the interest to control the reaction time to find supported titanasilicates with suitable mechanical stability.

X-Ray diffraction (XRD) patterns of the resulting titanasilicate obtained after 16 h of reaction (Fig. 4) clearly indicates the predominant formation of the JDF-L1 crystalline phase that coexists with a phase assigned to the ETS-4 titanasilicate present in minor extent²⁶. Supported JDF-L1 sample (noted as GF-JDF-L1) shows lower intensity diffraction peaks compared to the pristine titanasilicate, which are superposed to the large diffusion band associated to the amorphous silica phase of the glass fiber support. Slight shift of diffraction peaks with respect to the pure

titanosilicate could be tentatively related with some structural distortions due to internal tensions that are not present in the isolated solid. It can be assumed that this circumstance is imposed by the anchorage of the titanosilicate sheets to the rigid surface of the fibers avoiding their perfect parallel stacking.

After the post-synthesis treatment in acidic media used to prepare Pd-doped samples (Pd-GF-JDF-L1) it is observed a partial dissolution of the titanosilicate phases, which affects in particular to the smallest crystals as well as to the low-crystalline phases. However, the composition of the supported titanosilicate is maintained as the Ti/Si ratio is almost preserved compared to the one of the pristine GF-JDF-L1 sample (Table 1). It is observed that the XRD peaks of the resulting Pd-GF-JDF-L1 sample are modified after the Pd doping, probably due to the alteration of the titanosilicates by the acidic media that provokes the Na^+ exchange by H^+ species²⁷.

The presence of Pd nanoparticles cannot be distinguished in the X-ray diffractograms because they are present in a very low proportion in the nanoarchitecture (<0.1% w/w). However, the presence of Pd nanoparticles is clearly observed by FE-SEM. In this way, Figure 5 shows the assembling of Pd nanoparticles of size in the range of 75-300 nm. Lower size particles cannot be distinguished due to the limited resolution of this microscopy technique. The Pd content in the Pd-GF-JDF-L1 sample was quantitatively measured leading to values of $90 \pm 0.1 \mu\text{g/g}$, which represent less than 0.1% of its total weight.

Sample	GF	JDF-L1	GF-JDF-L1	Pd-GF-JDF-L1
Si/Ti	>5000	3.9 (4.0)*	33	32

Table 1- Estimation of the Si/Ti relationship obtained by TXRF for naked glass fiber (GF), layered titanosilicate (JDF-L1), supported layered titanosilicate on glass fiber (GF-JDF-L1) and Pd-doped material (Pd-GF-JDF-L1). * Theoretical value from the titanosilicate formulae.

Table 1 shows the estimated relationship between silicon and titanium per atom present in each sample deduced from Total X-Ray Fluorescence (TXRF) technique. The relationship in Si/Ti estimated in the titanosilicate (JDF-L1) is 3.9, which agree with the value deduced from the formulae. The dilution effect produced by supporting the titanosilicate provokes the increase of the Si/Ti ratio. From these data it is possible to estimate that 12% of crystalline titanosilicate phase is present in both GF-JDF-L1 and Pd-GF-JDF-L1 nanoarchitectures.

Fig 6- Nitrogen adsorption-desorption isotherms at 77 K of the JDF-L1, GF-JDF-L1 and Pd-GF-JDF-L1 samples

Sample	S_0 BET (m^2/g)	V_{up} (cm^3/g)	V_{meso} (cm^3/g)	* V_{sp} (cm^3/g)
JDF-L1	1 (1.2)	0.0006 (0.0005) <1·10 ⁻³	0.0010 (0.0095)	0.0011 ---
GF-JDF-L1	8 (7.8)	0.00304 (0.003) 3·10 ⁻³	0.0221 (0.022)	0.0023 ---
Pd-GF-JDF-L1	2 (2.15)	0.0009 (0.00081) <1·10 ⁻³	0.0041 (0.0035)	0.0065 (0.014)

* V_{sp} obtained using CO_2 isotherms at 273K

Table 2- S_0 specific surface area (BET), volume of micropore (V_{up}) and mesopore (V_{meso}) determined from the adsorption-desorption isotherms at 77 K (N_2) and ultramicropore volume (V_{sp}) determined from the adsorption isotherm at 273 K (CO_2) for the JDF-L1, GF-JDF-L1 and Pd-GF-JDF-L1 samples. Note: No reliable V_{sp} data could be obtained for samples JDF-L1 and GF-JDF-L1 due to the almost negligible amount of CO_2 adsorbed

Nitrogen adsorption-desorption isotherms present very low specific surface area values and low micropore volume with presence of meso- and macro-porosity (Table 2 and Fig. 6). These isotherms can be ascribed to adsorption phenomena on 2D solids, where their lamellar structure provides the effect of mesopores and macropores to which the nitrogen molecules can access. The hysteresis loop can be mainly associated to a type H3 loop according to the de Boer classification. These loop types are characteristic for aggregates of platy-like particles²⁹. Interestingly, the titanosilicates supported on the glass fiber samples (GF-JDF-L1) show higher values of specific surface area and pore volume than the non-supported pristine materials. This is surprising taking into account that the JDF-L1 adsorbent phase is present only as a 12% (w/w) on a support (glass fiber) whose specific surface area is practically zero. It can be assumed that the stacking of the sheets once the titanosilicate is anchored allows an easier access of the adsorbate gases to the adsorbent material as, above mentioned, they are built up as a house-of-cards radially distributed around the fiber axis.

When the Pd-nanoparticles are incorporated to the supported titanosilicate it is observed a modification of the textural behaviors of the sample. In this case, the specific surface area and the pore volume is reduced with respect to that of GF-JDF-L1 precursor samples. However, these values are still higher than “pure” (non-supported) pristine titanosilicates. It can be tentatively admitted that a fraction of the pore volume is blocked by the Pd nanoparticles avoiding the access of the adsorbate gases. However, the main factor affecting the reduction of surface area and pore volume could be directly related to structural modification originated by the acidic media used for the Pd-doping. In fact, it is known that acidic media provokes a dramatical decrease of BET values in titanosilicates²⁹.

Figure 7.- Hydrogen adsorption isotherms at 77 K for GF-JDF-L1 and Pd-GF-JDF-L1 samples.

Figure 7 shows the adsorption isotherms of hydrogen at 77 K obtained by a gravimetric method from 1 to 4 MPa. At low pressure the isotherms show a significant difference, suggesting a higher affinity between adsorbent and adsorbate once the palladium is incorporated to the nanoarchitecture. A pseudo-plateau is achieved in GF-JDF-L1 and Pd-GF-JDF-L1 suggesting narrow porosity in the nanoarchitectures³⁰. The percentage of H₂ adsorbed by GF-JDF-L1 in this range of pressure is almost 0.7 in weight and rise to 0.9 once is doped with Pd.

Figure 8.- Hydrogen adsorption (filled symbols)-desorption (void symbols) isotherms at 298 K for JDF-L1, GF-JDF-L1, GF-JDF-L1 MS and Pd-GF-JDF-L1 samples.

Figure 8 shows the H_2 adsorption-desorption isotherms at 298 K determined by a volumetric method at variable pressure, from 1 to 20 MPa. It is observed that the incorporation of Pd strongly increases the hydrogen uptake capacity, reaching a value of 0.46% in weight. It is observed that the corresponding values obtained for the two (JDF-L1, GF-JDF-L1) non-doped samples do not present significant differences during the H_2 adsorption-desorption process, reaching a value of 0.14% in weight at 298 K and 20 MPa. The same behavior is observed for the GF-JDF-L1 sample after the first adsorption-desorption cycle exposed to a sonomechanical treatment, and then submitted to a second adsorption-desorption cycle (noted as GF-JDF-L1 SM). The obtained values are relatively low, but they represent a valuable amount comparing to other solids exhibiting much higher values of specific surface area, total micropore volume or ultramicropore volume^{31,32}.

DIEGO: aqui podria incluirse algo sobre las razones de que el doping con Pd aumente tanto la capacidad de adsorcion de H₂. No parece que este relacionado con la masa de Pd (muy pequeña) para justificarlo como formación de hidruros, quizás pudiera invocarse un efecto catalítico pero también pudiera ser que el proceso de incorporación del Pd haya cambiado las propiedades de superficie del material (se nos ocurre que el efecto del tratamiento acido para depositar Pd puede ser el responsable de la creación de ultramicroporos que favorecerian la retención de H₂) ¿????

Conclusion

This work opens the way for the preparation of new full inorganic nanoarchitectures based on the assembling of active porous solids to glass-fiber substrates operating in alkaline media. This approach result in materials easy to handle compared with the non-supported porous solids, with assumable thermal, mechanical and chemical stabilities for practical applications. Layered titanosilicates have been selected in this first set of nanoarchitectures preparation because they are synthesized in alkaline media, which at the same time promotes the partial dissolution of the glass fibers as well as the cementation of the resulting porous materials assuring it robustness.

The titanosilicate-glass fiber nanoarchitectures have been tested as new hydrogen storage materials obtaining in this preliminary study modest adsorption values, which can be probably improved in further research by increasing and modulating the porosity of the nanoarchitecture. Other related heterostructured materials could be envisaged, as for instance those based on layered alkaline silicates promoters of layered silicic acids (magadiite, octosilicate, etc.) (Preparation and characterization of silylated-magadiites Okutomo, S; Kuroda, K; Ogawa, M

1999, App. Clay. Science 15, 1-2, 253-264)) or diverse zeotypes, with the potential interest in adsorption and catalytic applications.

Acknowledgments

Authors thank to the CICYT (projects MAT2009-09960 and MAT2012-31759) for financial support. The authors also thank Mr. A. Valera and Mr. C. Sebastian (ICMM-CSIC) for technical assistance in the FE-SEM studies and to Mr. T. García-Somolinos (ICMM-CSIC) and to Mr Mirko Kunowsky (University of Alicante) for the support in the gas-adsorption measurements. JPC thanks a PhD grant (FPI, BES-2010- 038410) from the Spanish Ministerio de Ciencia e Innovación.

REFERENCES

- (1) Katsuhiko, A. Manipulation of Nanoscale Materials: An Introduction to Nanoarchitectonics,. Roy. Soc. Chem. Cambridge, 2012.
- (2) Katsuhiko, A; Ajayan, V; Yusuke, Y; Qingmin, J; Jonathan, H. Nanoarchitectonics for Mesoporous Materials. Bull. Chem. Soc. J.,2012, 85, 1-32
- (3) Ruiz-Hitzky, E; Aranda, P; Darder, M; and Ogawa, M. Hybrid and biohybrid silicate based materials: molecular vs. block-assembling bottom–up processes. Chem. Soc. Rev., 2011,40, 801-828
- (4) Ariga, K; Hill, J; Ji, Q. Layer-by-Layer Assembled Films Composed of “Charge Matched” and “Length Matched” Polysaccharides: Self-Patterning and Unexpected Effects of the Degree of Polymerization. Chem. Phys. 2007, 9, 2319–2340
- (5) Galarneau, A; Barodawalla, A, Pinnavaia, T. Porous clay heterostructures formed by gallery-templated synthesis. Nature, 1994 374, 529 - 531
- (6) Belver, C; Aranda, P; Martin-Luengo, MA; Ruiz-Hitzky, E. New silica/alumina-clay heterostructures: Properties as acid catalysts. Micropor. Mesopor Mat. 2012, 147, 157-166
- (7) Ha, K; Lee, J; Lee, J; Yoon, K. Facile assembly of zeolite monolayers on glass, silica, alumina, and other zeolites using 3-halopropylsilyl reagents as Covalent Linkers. Adv Mat. 2000, 12,15,1114–1117.
- (8) Kulak, A; Lee, Y; Park, Y; Yoon, K. Orientation-Controlled Monolayer Assembly of Zeolite Crystals on Glass and Mica by Covalent Linkage of Surface-Bound Epoxide and Amine Groups Angew. Chem. Int. Edition. 2000, 39, 5, 950-953.
- (9) Tosheva, L; Valtchev, V. Silicalite-1 crystallization on glassfiberfilter discs. Mic. Mes. Matt. 2005, 81,1-3, 11-18

- (10) Ferdov, S; Kolitsch, U; Lengauer, C; Tillmanns, E; Lin, Z; Ferreira, Ra. Refinement of the layered titanosilicate AM-1 from single-crystal X-ray diffraction data. *Acta Cryst.* 2007, E63, i186
- (11) Lin, Z; Rocha, J; Brandao, P, Ferreira, A; Esculcas, A; Pedrosa de Jesus, A. Synthesis and structural characterization of microporous umbite, penkvilksite, and other titanosilicates. *J. of Phy. Chem. B.* 1997, 101, 7114–7120.
- (12) Rocha, J; Anderson, M. Microporous Titanosilicates and other Novel Mixed Octahedral-Tetrahedral Framework Oxides. *Eur. J of Inorg. Chem.* 2000, 2000, 5, 801–818.
- (13) Humble, J. The Synthesis and Characterization of Novel Titanosilicates for Next Generation Hydrogen Storage. 2012. University of Tennessee Honors Thesis Projects. http://trace.tennessee.edu/utk_chanhonoproj/1545 (accessed on October 30th, 2012).
- (14) Perez-Carvajal, J; Lalueza, P; Casado, C; Tellez, C; Coronas, J. Layered titanosilicates JDF-L1 and AM-4 for biocide applications. *Appl. Clay Science.* 2012, 56, 30-35
- (15) Baldé, C; Hereijgers, B; Bitter, J; Jong, K. Facilitated Hydrogen Storage in NaAlH₄ Supported on Carbon Nanofibers. *Angw. Chem. Int. Ed.* 2006, 45, 21, 3501–3503.
- (16) Buchener, H; Povel, R. The daimler-benz hydride vehicle project. . *Int. J. Hydrogen Energy.* 1982, 7, 259.
- (17) Casa-Lillo, M; Lamari-Darkrim, F ;Cazorla-Amorós D; Linares-Solano, A. Hydrogen Storage in Activated Carbons and Activated Carbon Fibers. *J. Phys. Chem. B.* 2002, 106 (42), 10930–10934
- (18) Murray, L; Dincă M; Long, J. Hydrogen storage in metal–organic frameworks. *Chem. Soc. Rev.*, 2009, 38, 1294–1314
- (19) Suh, M; Park, H; Prasad, K; Dae-Woon, L. Magnesium Nanocrystals Embedded in a Metal–Organic Framework: Hybrid Hydrogen Storage with Synergistic Effect on Physi- and Chemisorption. *Chem. Rev.* 2012, 112, 782–835
- (20) Olmos, D; Gonzalez-Benito, J. Composites Formed by Glass Fibers and PS-Modified Matrix. Influence of the Glass Fibers Surface on the Morphologies and Mechanical Properties of the Interphases Generated.
- (21) Rubio, C; Casado, C; Uriel, C; Tellez, C; Coronas, J. Seeded synthesis of layered titanosilicate JDF-L1, *Mater. Lett.* 2009, 63, 113.
- (22) Agarwal, R; Schwarz, J. Analysis of high-pressure adsorption of gases on activated carbon by potential-theory. *Carbon.* 1988, 26, 6, 873–87.
- (23) Zhang C, Lu XS, Gu AZ. How to accurately determine the uptake of hydrogen in carbonaceous materials. *Int J Hydrogen Energy.* 2004, 29(12), 1271-1276.
- (24) Kiyobayashi, T; Takeshita, HT; Tanaka, H; Takeichi, N; Zuttel, A; Schlapbach, L; Kuriyama, N. Hydrogen adsorption in carbonaceous materials. *J Alloys Compd.* 2002, 330, 666–669.
- (25) Roberts, M; Sankar, G; Thomas, J; Jones, R; Du, H; Chen, J; Pang, W; Xu, R. Synthesis and structure of a layered titanosilicate catalyst with five-coordinate titanium. *Nature.* 1996. 381, 401 – 404
- (26) Nair, S; Jeong, H ;Chandrasekaran, A ;Braunbarth, C; Tsapatsis, M ;Kuznicki, S. Synthesis and Structure Determination of ETS-4 Single Crystals *Chem. Mater.* 2001, 13 (11), 4247–4254.
- (27) Rubio, C; Casado, C; Gorgojo, P; Etayo, F; Uriel, S; Tellez, C; Coronas, J. Exfoliated Titanosilicate Material UZAR-S1 Obtained from JDF-L1. *Eur J Inorg. Chem.* 2010. 1(1) 159-163
- (28) Rouquerol, F; Rouquerol, J; Sing, K. Adsorption by powder and porous solids. 2004 Chapter 4. Elsevier Ltd

- (29) Kyeong-Won, P; Jong Hwa, J., Jong, K; Sung-Kyu, K; Oh-Yun, K. Preparation of mesoporous silica-pillared H⁺-titanosilicates Microp. Mesop. Mat.2009. 118:100-105.
- (30) Wang, Q; Johnson, K. Molecular simulation of hydrogen adsorption in single walled carbon nanotubes and idealized carbon slit pores. 1999, J. of Chem Phys. 110, 577-586
- (31) Thomas, K. Adsorption and desorption of hydrogen on metal-organic framework materials for storage applications: comparison with other nanoporous materials. Dalton Trans. 2009,1487-1505.
- (32) Jordá-Beneyto, M; Suárez-García, Lozano-Castelló, D; Cazorla-Amorós, D. Hydrogen storage on chemically activated carbons and carbonnanomaterials at high pressures. Carbon. 2007. 45,2,293-303.

Figure 4. X-Ray diffractogram of the following materials (from bottom to top: A) primary 16 hours synthesis (JDF-L1), B) Primary synthesis in glass-fiber presence (FV-JDF-L1) and C) Post treated Pd-FV-JDF-L1 where palladium is already incorporated.

Figure 2.- FE-SEM images of a) GF-JDF-L1 cross-section of glass fibers where it is observed the radially growth of the titanate crystals. b) as-made JDF-L1, c) naked glass fiber, d) GF-JDF-L1 after 4 days of reaction

Fig 3.- FE-SEM images of a general view of GF-JDF-L1.

Fig 5- FE-SEM images of a) Pd-GF-JDF-L1 b)Pd-GF-JDF-L1 detail and onset of one of the spots associated to Palladium particles.

SUPPLEMENTARY INFORMATION

Figure 1S

IR spectra of pristine E-glass fiber before and after (naked fiber) thermal treatment.