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A comparative study on porous solid acid oxides as catalysts in the esterification of glycerol with acetic acid

Antonio B. S. Neto<sup>1</sup>, Alcineia C. Oliveira<sup>1\*</sup>, Enrique Rodriguez-Castellón<sup>2</sup>, Adriana F. Campos<sup>3</sup>, Paulo T. C. Freire<sup>4</sup>, Francisco F. F. Souza<sup>4,5</sup>, Josué M. Filho<sup>4</sup>, Jesuina C. S. Araujo<sup>6</sup> and Rossano Lang<sup>7</sup>

<sup>1</sup> Universidade Federal do Ceará, Campus do Pici-Bloco 940, Departamento de Química Analítica e Físico-Química, Fortaleza, Ceará, Brazil. Phone/fax: 55 85 3366 90 08. \*Email: alcineia@ufc.br

<sup>2</sup> Universidad de Málaga, Departamento de Química Inorgánica, Facultad de Ciencias, 29071, Spain.

<sup>3</sup> CETENE, Av. Prof. Luz Freire n.1, Cidade Universitária, 50740-540, Recife, Pernambuco, Brazil.

<sup>4</sup> Universidade Federal do Ceará, Departamento de Física, Campus Pici-922, Fortaleza, Ceará, Brazil.

<sup>5</sup> Universidade Federal do Sul e Sudeste do Pará, Campus Universitário de Marabá, 68505-080 Marabá, Pará, Brazil

<sup>6</sup> Universidade Federal do Espirito Santo, Centro Universitário Norte do Espírito Santo, São Mateus, Espirito Santo, Brazil.

<sup>7</sup> Instituto de Ciência e Tecnologia - ICT, Universidade Federal de São Paulo UNIFESP, 12231-280, São José dos Campos, SP, Brazil.

#### Highlights

- Esterification of glycerol into acetins studied over two series of SiAl-based solids.
- Acid SiAl with a defined hierarchy of pores was synthesized
- Molybdophosphoric heteropolyacid supported SiAl nanotubes
- A 50 wt% of molybdophosphoric on nanotubes lead to selectivity towards the acetins.
- Acidity, stability structure and porosity of the MPA on nanotubes gave best results.

#### Abstract

Acid catalysts comprising of porous SiAl, as well as molybdophosphoric heteropolyacid, supported SiAl nanotubes were synthesized. The characterizations were through scanning electron microscopy coupled to energy-dispersive X-ray spectroscopy (SEM-EDS), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), termoprogrammed ammonia desorption (NH<sub>3</sub>-TPD) and Fourier transform infrared spectroscopy (FTIR). Esterification of glycerol into acetins reaction was evaluated over two series of SiAl-based solids. Both series displayed very good activity as well as selectivity towards the acetins within a short reaction time. However, porous SiAl deactivated due to acid sites leaching in long-term catalytic runs. The tuning of the loadings of the molybdophosphoric amount on SiAl halloysite nanotubes leads to an increase in the selectivity towards the mono, di, and triacetins. These catalysts were also recycled up to three times, and a 17 % of conversion and 100 % selectivity for triacetin were obtained due to the combination of acidity, stable structure and porosity of the molybdophosphoric supported SiAl nanotubes.

Keywords:

SiAl catalysts; porosity; nanotubes; acetylation; glycerol; molybdophosphoric.

#### 1. Introduction

Acetylation of glycerol with acetic acid (AG) is a promising reaction to convert crude glycerin from Biodiesel production preferably to acetylated glycerol derivatives [1-3]. This transformation consists of an esterification reaction to form esters of glycerol such as monacetin (MAG), diacetin (DAG) and triacetin (TAG), as shown in scheme (I):



The esters of glycerol (acetins) produced by the reaction (I) are important intermediates for fuel additives and valuable chemicals [4]. For instance, MAG is of great interest for manufacturing of explosives and tanning agent as a solvent for dyes, whereas DAG is applied as a plasticizer, softening agent and biodegradable polyesters [3,5]. The TAG is used as an emulsifying agent, fuel additive for reducing knocking in a gasoline engine and antimicrobial agent in pharmaceutical products [3,6].

Thus, AG reaction can be considered as a potential route for the transformation of low-cost compounds found in biorefinery wastewaters such as crude glycerin into value-added products. However, a very challenging task within the AG research is finding an active and stable catalyst under the demanding reaction conditions, as a request to attain the process. In general, high activity and acetins selectivity have typically been achieved in AG reaction through the use of acid catalysts, especially those possessing Lewis and/or Brønsted sites [6].

In this sense, several solid acid-based catalysts have been reported to be effective for the reaction including transition metals oxides, ion exchanged-resins, molecular sieves, supported heteropolyacids, zeolites, sulfated materials dispersed on active carbon, Al<sub>2</sub>O<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>, ZrO<sub>2</sub>, MCM-41, SBA-15 and USY

zeolites, among others [5-10]. Although these solids show high activity, their acid sites possessing medium to strong acid strength can cause low selectivity to desired products. Another point is that leaching of the acid sites is serious on these acid catalysts, all these factors contributing to their low performance in the AG reaction.

As a promising alternative approach, binary oxides with a porous hierarchy have proved to be also highly active and stable catalysts with elevated monoacetins selectivity in the AG reaction [6]. The obtained results demonstrated that the use of mild acid sites solids tuned with a controlled hierarchy of pores could improve both the selectivity and stability of the catalysts in AG. However, the most active SiAl-based catalyst exhibits limitations in its applicability for AG reaction due to the loss of active acid sites during demanding reaction conditions; consequently, changing of their structures, leaching of the acid sites or textural parameters decay are likely during the reaction [6]. This motivates us to investigate the effect of porosity tuning of the modified SiAl-based solids with distinct acidities to facilitate the interaction between glycerol and acetic acid in the AG reaction.

In the present study, SiAl-based acid catalysts are modified to improve their textural properties and enhance their performance in AG reaction, as well. These solids are expected to have a defined hierarchy pores with mild to high acidity to give more efficient catalysts. It is well known that the acid strength of the solids in AG reaction has a considerable effect on the catalytic activity and selectivity [6,10-12]. Thus, heteropolyacids (MPA) will be dispersed on the SiAl-based halloysite nanotubes (HNT). These materials were selected to be tested as potential stable supports for MPA, in the current paper. Also, the catalytic systems in the study were compared with that of porous SiAl-based catalysts to evaluate their resistance against leaching. They are expected to be an effective esterification catalyst overcoming most of the limitations of the acid solids and helping the active sites to interact with glycerol and acetic acid during the AG reaction.

### 2. Experimental

#### 2.1. Catalyst preparation

Two groups of mesoporous SiAl catalysts were considered in this work: the porous SiAl-based solids and the molybdophosphoric heteropolyacid dispersed on SiAl nanotubes.

#### 2.1.1. Synthesis of the porous SiAl-based solids

The SiAl-based solids were synthesized by the sol-gel method adopting the procedure described elsewhere [6,13], with minor modifications. The synthesis consisted of preparing three solutions. The first one was a 20 % aqueous solution of cetyltrimethylammonium bromide (CTAB). The second solution is composed of a 0.01 mol of aluminum tri-sec-butoxide dissolved in 5 mL of isopropanol at 60 °C and this mixture was constantly stirred, resulting in a sol of pH 5.0. The third solution was prepared by dissolving 0.01 mol of tetraethylortosilicate in ethanol and distilled water at pH 6.4.

The aforesaid solutions were then mixed through a peristaltic pump to obtain a gel and aged for 30 min. Subsequently, the gel was placed into a Teflon-lined autoclave at 80 °C for 48 h. Finally, the formed white precipitate was filtered off and washed with distilled water until pH = 7. After drying overnight the powder, about 2 g of the as-synthesized solid was placed in a rotatory evaporator in 25 mL of ethanol to remove the CTAB template at 60 °C. The solid was labeled as SAE. The letters S, A and E describe the Si, Al and the as-synthesized materials obtained by extraction treatment, respectively. The same procedure was applied by refluxing the as-synthesized solid, and the obtained sample was denoted as SAR. Another sample was prepared by calcinating the as-synthesized solid at 600 °C for 2 h, under air flow atmosphere giving the SAC sample.

#### 2.1.2. Preparation of the molybdophosphoric heteropolyacid supported SiAl nanotubes

The SiAl-based halloysite nanotubes (HNT) possessing formula  $Al_2Si_2O_5(OH)_4.2H_2O$  were purchased from Aldrich. The HNT nanotubes had a BET surface area of 64 m<sup>2</sup>g<sup>-1</sup>, a pore volume of 1.3 cm<sup>3</sup>g<sup>-1</sup> and pore diameter of 1.9 nm. In addition, the nanotubes have 30-70 nm × 1-3 µm, in terms of dimensions. Prior to use, the HNTs were pretreated by calcination at 400 °C in air for 2 h. Although the heating treatment caused a reduction in the BET surface area from 64 to 30 m<sup>2</sup>g<sup>-1</sup>, the thermal stability of the SiAl-based HNT support was improved.

The molybdophosphoric heteropolyacid (MPA) supported on HNT nanotubes namely *x*-MPA/HNT were prepared by the classical wet impregnation method, with modifications [11,13]. The methodology consisted of mixing 1.0 g molybdic heteropolyacid (Sigma Aldrich, H<sub>2</sub>MoO<sub>4</sub> with 88 % of MoO<sub>3</sub>) in 20 mL of distilled water, under stirring at room temperature. After that, the aforesaid aqueous solution was added to 2.5 mL of phosphoric acid (Sigma Aldrich, H<sub>3</sub>PO<sub>4</sub>, 85 %) keeping the stirring for 30 min. to obtain the solution molybdophosphoric heteropolyacid (MPA, H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>) [13]. Afterward, a certain amount of the MPA aqueous solution was impregnated on 1.0 g of the calcined HNTs. The mixture was allowed to be stirred and evaporated at 70 °C during 2 h, and the excess of water was removed by vacuum filtration. The produced pastes were dried at 60 °C overnight and calcined in air for 4 h at 400 °C, before use.

A series of samples with different wt.% loadings of heteropolyacid (MPA) were obtained. The catalysts are referred to as molybdophosphoric heteropolyacid supported SiAl nanotubes, *x*-MPA/HNT: 10-MPA/HNT, 25-MPA/HNT, and 50-MPA/HNT, where *x* represents the 10, 25 and 50 wt.% loading of MPA impregnated on HNTs.

Table 1 includes a summary of the main features of the porous SiAl-based solids obtained by the solgel method.

Table 1

### 2.2. Characterizations of the solids

X-ray diffraction (XRD) measurements were carried out at room temperature by using a Bruker D8 Advance diffractometer with Cu-K $\alpha$ 1 (1.5406 Å) radiation at 40 kV and 40 mA. The diffraction patterns were obtained in the 2 $\theta$  range between 5 and 80° with steps of 0.02° and acquisition time of 2 seconds. The patterns were indexed by comparison with the Joint Committee on Powder Diffraction Standards (JCPDS).

Surface area and pore size distributions were measured by nitrogen adsorption-desorption isotherms at –196 °C in a Micromeritics ASAP 2420 instrument. Previously, samples were degassed under vacuum for 24 h at 90 °C. The surface area was estimated from Brunauer-Emmett-Teller (BET) model. The micropore and mesopore size distributions were obtained using Barrett-Joyner-Halenda method (BJH).

The scanning electron microscopy (SEM) observations were recorded on an FEI, Quanta 200 FEG electron microscope equipped with an energy dispersive X-ray spectroscopy (EDS) system coupled. SEM

samples were prepared by directly spreading the powder materials over a conducting carbon double-sided tape (mounted on a microscope stub) and coated with a thin carbon film.

The Fourier-transformed infrared spectroscopy (FTIR) measurements of the solids were performed on a Brucker, FT-IR VERTEX 70 spectrophotometer. Samples were prepared with dilution in KBr, and the spectra were recorded in the 400 - 4000 cm<sup>-1</sup> range.

Transmission electron microscopy (TEM) images were performed on a transmission electron microscope (JEOL JEM-2100) with an acceleration voltage of 200 kV. TEM samples were prepared by dropping isopropanol sample suspensions (previously dispersed in an ultrasonic bath) on 200 mesh copper grid coated with a colloid on film.

The acidity of the catalysts was characterized by termoprogrammed ammonia desorption (NH<sub>3</sub>-TPD) followed by thermogravimetry (TG) measurements using a TGA/DSC Mettler Toledo equipment coupled to an SDT 2960 (TA Instruments).

The chemical states of the studied elements were determined by X-ray photoelectron spectroscopy (XPS) measurements. Physical Electronics PHI 5700 apparatus was used for the analyses applying the non-monochromatic Mg-K $\alpha$  line at 1253.6 eV as the excitation source. High-resolution multi-region spectra were recorded with a pass energy of 23.5 eV. The binding energies were referenced to the C-1*s* peak at 284.8 eV.

### 2.3. Catalytic testing the acetylation of glycerol with acetic acid

The acetylation of glycerol with acetic acid (AG) reaction was carried out in a batch reactor at atmospheric pressure using a temperature of 80 °C. About 75 mg of the catalysts were loaded in the reactor, under vigorous stirring using glycerol to the acetic acid molar ratio of 1:3 under nitrogen flow. The later parameter was also varied to better understand the effects of the composition on the catalytic performances. After the tests, aliquots were withdrawn from the reactor at a certain interval of time and analyzed by gas chromatography in an Intercrom Geracao 8000 apparatus. Ortho-xylene was used as an internal standard. Reaction products were identified by gas chromatography coupled to mass spectroscopy (GC-MS) from Shimadzu (QP 5050 Plus). Blank runs showed that without the catalysts the reaction takes place with conversions lesser than 3 %.

Recyclability studies were conducted at 80 °C using 150 mg of catalyst and glycerol to the acetic acid molar ratio of 1:9. After the first cycle with the fresh catalysts, the reaction was allowed to settle, and the catalyst was removed from the reactor, washed with chloroform and dried at 35 °C for 6 h. The subsequent runs were continued by adding the aforesaid catalyst to perform three runs of 24 h. The catalytic activity was measured as the glycerol conversion and product selectivities, according to the previous studies [6,14].

#### 3. Results and discussion

#### 3.1. Textural properties and acidity

The main physicochemical features of the porous SiAl-based solids obtained by sol-gel method are shown in Table 2. The textural properties of the solids are obtained from nitrogen adsorption-desorption isotherms. The modified SiAl-based solids synthesized by the sol-gel method have IV-type isotherms (not shown), which may be attributed to mesoporous materials. Accordingly, SAE, SAR and SAC samples have higher surface area and mesopore volumes than those of the heteropolyacid dispersed on SiAl-based HNT nanotubes.

#### Table 2

As shown in Table 2, SAE and SAR possess the highest parameters among the solids studied. This is attributed to the extraction and reflux procedures removing the free impurities from the solid surface and producing accessible porosity [6]. As expected, the calcination procedure eliminates the organics from the pores of the as-synthesized solids, resulting in large pore size for SAC sample. Accordingly, the textural parameters of the SiAI-based samples obtained by sol-gel are summarized in Table 2. The pore diameters range of the modified SiAI samples ranges from 6.4 - 10.4 nm indicating the macro-mesoporous and micro-mesoporous presence.

The MPA heteropolyacid supported SiAl nanotubes exhibits similar isotherms at the relatively low pressures (Fig. 1a), which indicates that they have some micropores. However, these samples display hysteresis loops typical of II-type isotherms with micro to mesoporous structures, as indicated in the high relative pressure region. All samples depict their hysteresis loops with the general form of type H<sub>3</sub>, which

means that the samples have slit-shaped pores [6], with 10-MPA/HNT being an exception. It is interesting to note that a widening of the hysteresis loop between the adsorption and desorption branches at high relative pressure is observed for 50-MPA/HNT, which indicates a shift of the pore sizes for micro to mesopore range. Moreover, the pore size distribution curve of 10-MPA/HNT is narrow whereas the other solids have broad pore size distributions confirming the existence of micro and mesoporous solids (Fig. 1b).

### Fig.1

A more detailed analysis (Table 2) reveals the textural properties of the MPA heteropolyacid supported SiAl nanotubes. For instance, the dried MPA powder heteropolyacid is not a porous sample whereas the bare calcined HNT support has a surface area of  $30 \text{ m}^2\text{g}^{-1}$  and pore volume of  $0.15 \text{ cm}^3\text{g}^{-1}$ . A slight increase in the BET surface area as well as in the pore volume is observed after impregnating the HNT with 10 or 25 wt.% of MPA heteropolyacid, respectively for 10-MPA/HNT and 25-MPA/HNT samples. This can strongly assert the interaction between the heteropolyacid and HNT nanotubes producing stable solids with a pore size of ca. 1.7 nm, which is indeed a feature of micro to mesoporous materials.

It is noted that the increasing the MPA loading up to 25 wt.% results in an increment in the surface characteristics, being the 50-MPA/HNT sample with a surface area of 75 m<sup>2</sup>g<sup>-1</sup> and pore volume of ca. 0.28 cm<sup>3</sup>g<sup>-1</sup>. This can be attributed to the MPA producing an additional surface porosity to the solids. The pore diameters of the three SiAl-based heteropolyacid samples differ slightly, as a consequence of the absence of pores blockage of the support with the HPA component, even at high MPA loadings on HNT as in the case of the 50-MPA/HNT sample.

The total acidity values obtained through the NH<sub>3</sub>-TPD measurements are shown in Tab. 2. As a general trend, all samples display an acid character, regardless of the nature of their Brønsted and Lewis acidic sites. The HNTs are tubular nanoclays with cylindrical and open-ended particles possessing an electron-transparent central lumen [15]. Indeed, the Al-OH hydroxyl groups are located inside the tubes, while only a few hydroxyl groups (Al-OH and Si-OH) are found to be on the edges of the external tube surfaces. Thereby, the HNTs nanotubes support holds the lower total acidity among the SiAl-based solids studied (Table 2). Specifically, the porous SiAl-based solids have acidity comparable to that of HNT, except for SAR that has acidity comparable to that of heteropolyacid supported on SiAl samples. This suggests that

the reflux treatments submitted to the as-synthesized solid eliminate the surfactant from their pores giving porosity and accessible acid sites (Table 2).

Moreover, the total acidity increases from 0.18 to 0.33 µmolg<sup>-1</sup>, when comparing the acidities of bare HNT with that of 10-MPA/HNT. This can possibly be attributed to the MPA heteropolyacid intrinsic acidity in stronger interaction with the HNT support, in line with the other heteropolyacids supported solids [16-20]. In contrast to the 10-MPA/HNT, the total acidity greatly raised with increasing the concentration of the MPA heteropolyacid up to 10 wt.%, most likely due to the acidity of the isolated MoO3 species formation [21]. This results in the creation of acid sites with relatively high acid strength and in weak interaction with the HNT support, as in the case of the 25-MPA/HNT and 50-MPA/HNT samples. Importantly, the textural properties of these solids are not affected by using 10 to 25 wt.% of MPA loadings, and the accessibility to acid sites might not decrease, as well.

The total acidity of the solids can be ranked as 50-MPA/HNT > 25-MPA/HNT > 10-MPA/HNT > SAR > SAE > HNT > SAC, with the heteropolyacid impregnated on the SiAl-based solids holding the highest acidities.

### 3. 2 XRD and FTIR structural characterizations

All the porous SiAl-based solids have a broad reflection at a 20 value of  $24^{\circ}$  [6], being representative of amorphous silica nanocomposites (Table 1). Therefore, the XRD patterns are not shown here. In contrast, the XRD pattern of the MPA sample depicts the characteristic of well crystallized molybdophosphoric heteropolyacid (H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>), as shown in Fig. 2a. On the other hand, the HNT has a semicrystalline structure (Fig. 2b), typical feature of 7Å-halloysite corresponding to the JCPDS n° 29-1487. As documented elsewhere, the halloysite nanotubes may undergo a dehydration process at around 450 °C to form an amorphous phase, while a tubular morphology will be maintained at this stage [22]. It is expected that some peaks from crystalline SiO<sub>2</sub> appear in the XRD pattern of the HNT due to the dehydration of the halloysite [15]. Nevertheless, only a very weak peak around 26.7° is identified in the diffractogram. This reflection peak appears slightly more pronounced in the patterns of the other samples.

The incorporation of the MPA heteropolyacids on HNT gives rise solids with low crystallinity due to high dispersion of the MPA on the support, with the predominance of the halloysite and amorphous  $SiO_2$ 

phases. Peaks of the7Å-halloysite,  $\alpha$ -MoO<sub>3</sub> and  $\beta$ -MoO<sub>3</sub> appear in the diffractograms (Fig. 2b). It should be observed that the diffraction patterns of the *x*-MPA/HNT samples also present reflection peaks that characterize the contributions of the constituent elements. For example, the orthorhombic structured  $\alpha$ -MoO<sub>3</sub> molybdate phase arises mainly at 2 $\theta$  value equal to12.3° (020), in accordance with n JCPDS n° 05-0508. However, the contributions of the reflections from (011), (200) and (211) lattice planes of the monoclinic  $\beta$ -MoO<sub>3</sub> phase at 2 $\theta$  values of 23.0 and 35.0 and 54.3°, respectively (JCPDS n° 47-1081) cannot rule out. Probably,  $\beta$ -MoO<sub>3</sub> species are formed from the decomposition of heteropolyanions due to the calcination, as reported elsewhere [17].

Moreover, the MPA heteropolyacid might be loaded either in the lumen or on the surface of the nanotubes, and thus, the halloysite nanotubes walls are preserved and thereby, no further transformation to other structures is observed.

Fig. 2

Fig. 2c depicts the FTIR spectra of the MPA, HNT and x-MPA/HNT samples. The HNT sample exhibits the IR absorptions at about 690, 754 and 794 cm<sup>-1</sup>, which can be attributed as the symmetric stretching vibrations of the Si-O-Si in the structural siloxane bond and O-H bonds from Al-OH translational vibrations, as well [23]. Moreover, the band at 912 cm<sup>-1</sup> is reported to be associated with the presence of inner O-H deformation vibrations. Important is to note that broadband at about 1037 cm<sup>-1</sup> (in the rectangle) can be attributed to the anti-symmetric stretching vibrations of the structural siloxane bond (Si-O-Si) from the SiO4 tetrahedron [15,23]. Additionally, the bending deformation vibration in physically adsorbed water is observed at around 1625 cm<sup>-1</sup> while the interlayer water O-H stretching vibration is seen in 3560 cm<sup>-1</sup> [23]. At around 3400 - 3600 cm<sup>-1</sup>, the inner-surface O-H stretching vibrations and in-phase and out-of-phase stretching vibrations are observed [23]. The broadband at about 1565 cm<sup>-1</sup> is due to symmetric stretching of carboxylate groups. These descriptions match well with the geometrical features of the HNT, which consists of gibbsite octahedral sheet (Al-OH) groups with a positive surface charge on the internal surface. Moreover, the external surface is composed of tetrahedral sheets of siloxane groups (Si-O-Si) with a negative electrical potential [15].

The FTIR spectrum of pristine MPA depicts typically four major FTIR bands located at 1067, 975, 870 and 810 cm<sup>-1</sup>. These bands may be assigned to anti-symmetric stretching vibrations of P-O, stretching of

Mo=O, corner-sharing Mo-O-Mo, and edge-sharing Mo-O-Mo bonds, respectively. All of these assignations are due to absorption modes of the  $[PMO_{12}O_{40}]^{3-}$  Keggin ion [24]. Besides, the bands appearing at 1625 and 3560 cm<sup>-1</sup> are respectively due to the bending deformation vibration and O-H stretching vibration in physically adsorbed and interlayer water. It should be noted that the incorporation of the MPA to the HNT nanotubes does not affect the FTIR curves, significantly. Indeed, some peaks typical of the Keggin structures of MPA are superimposed or partially overlapped with the peaks of the HNT framework, indicating that the MPA impregnation on HNT keeps the Keggin structure. Moreover, the presence of isolated  $\beta$ -MoO<sub>3</sub> on HNT surface in the *x*-MPA/HNTs (XRD results) cannot be ruled out, since the IR bands are close to that reported in the literature [25].

Through the correlation of the XRD and FTIR investigations, it is observed that the incorporation of the MPA to the HNTs maintains the structural features of the solids. FTIR measurements of the porous SiAlbased samples namely, SAE, SAR, and SAC were previously published [6], and these amorphous samples have similar FTIR features as those of the HNTs.

#### 3.3. Morphological aspects by SEM-EDS and TEM analysis

The morphological aspects of the HNT, MPA and *x*-MPA/HNTs were evaluated by SEM-EDS analysis. Fig. 3 shows SEM images and EDS mappings of the powders. The micrograph of HNTs demonstrates the typical tubular feature of halloysite. Moreover, EDS analyses illustrate the existence of Si and Al well distributed on the solid surface. The morphology of MPA reveals the formation of irregular shape particles, mostly agglomerated. Also, EDS analysis depicts the presence of Mo, P and O elements on MPA. There are no specific variations within a particular nanotube such as nanotube length or shape with low amounts of MPA on HNT, as in the case of 10-MPA/HNT. This result is in full agreement with textural properties, SEM and FTIR measurements that show no changes in the textural and structural features of the solids with loading a 10 wt.% of MPA on HNT. Accordingly, EDS analysis shows a homogeneous distribution of Mo, probably from  $\alpha$ -MoO<sub>3</sub> and  $\beta$ -MoO<sub>3</sub> nanoparticles (XRD results) on 10-MPA/HNT surface, which does not exclude the possibility that the Keggin anion is located inside the HNT pores.

On the contrary, separate particles of the bulk phase of MPA are found in the supported 25-MPA/HNT sample. The nanotubes are indeed tangled together with agglomerates formed of small spherical

particles of MPA. Similar results are also observed in the literature reports with loading SiAl-based compounds with high amounts of heteropolyacids [24]. From SEM image of 50-MPA/HNT, one can observe that the nanotubes have their length reduced with some instances of partially agglomerated around the MPA particles. It is observed a heterogeneous Mo species distribution on the solid surface, as a result of the high MPA heteropolyacid loading in 50-MPA/HNT.

### Fig. 3

The characterization results through TEM and SEM-EDS of the SiAl-based samples obtained by the sol-gel method have been presented and discussed in our earlier report [6]. The SAC sample shows the presence of nanocrystalline particles exhibiting uniform macropores whereas SAE and SAR ones display interstitial voids between their nanoparticles.

Fig. 4 exhibits TEM images of the HNT halloysite nanotubes. As it can be seen, the HNTs are predominantly a hollow tubular structure, and both ends are open. The lengths of the tubes range from 50 to 5000 nm, and their outer diameter is in the 20 - 200 nm interval whereas the inner ones vary in the 5 - 70 nm range, in agreement with the findings [26]. Also, the empty lumens of the tubes are clearly seen. The introduction of 10 wt.% of MPA on the HNT preserves the well-defined tubular morphology compared with the pristine HNTs, indicating that the MPA layers exist on both the inner and the outer surfaces of HNTs. This corroborates the XRD, FTIR, SEM-EDS and textural properties that strongly suggest a good dispersion of the MPA on HNTs in 10-MPA/HNT. Furthermore, the findings state that a periodic multilayer scroll-like structure of halloysite wall, which indicates the existence of the aluminol (Al-OH) and external siloxane (Si-O-Si) surfaces is expected for halloysite-based samples [15,22]. However, the high magnification image of 10-MPA/HNT does not reveal such kind of morphology most probably due to dehydration process, when calcining the 10-MPA/HNT sample.

### Fig. 4

Clearly, incorporation of MPA loadings superior to 10 wt.% tends to provoke a progressive collapse in the tubular structure, as in the case of 25-MPA/HNT. The high magnification image of 25-MPA/HNT suggests that increased incorporation of MPA on HNT also promotes the entanglements of the tubes with segregation of MPA polyanions nanoparticles. At an MPA content of 50 wt.%, the nanotubes are all

agglomerated with the heteropolyacids nanoparticles mostly included in the inner diameter, as shown by the high magnification micrograph.

Although no appreciable change of the structural features is observed for MPA loading up to 10 wt.%, the morphological aspects of the samples are affected. This is especially seen in 25-MPA/HNT and 50-MPA/HNT samples.

#### 3.4. Surface composition by XPS measurements

The oxidation states of the element present in the solids are investigated by XPS analyses. The Si-2p, O-1*s*, Al-2p, P-2p and Mo-3d core levels spectra are identified in the solids studied, and the results are summarized in Tab. 3. As expected, HNT possesses Si, Al and O elements with the binding energies (BE) of 102.7, 74.4 and 531.9 eV, respectively for Si-2p, Al-2p and O-1*s* core levels. The Si/Al ratio of ca. 1.14 indicates that the outer surface of the HNTs has a chemical structure similar to that of silicon dioxide while its inner surface is similar to that of alumina [27,28]. Carbon is a contaminant detected in low amount in reason of the presence of some organic contaminants adsorbed on the surfaces (about 2 - 5 %). Traces of other elements such as iron commonly found in HNTs are not seen [27].

### Table 3

For MPA, the binding energy of Mo-3 $d^{5/2}$  at about 232.6 eV (Fig. 5) suggests that Mo is comprised mainly of the [PMO<sub>12</sub>O<sub>40</sub>]<sup>3–</sup> Keggin ion as found elsewhere [28]. This is in close agreement with XRD and FTIR measurements. Besides, the binding energy for P-2*p* core level is at around 133.5 eV, which can be ascribed to phosphorous as P<sup>5+</sup> of phosphate [29]. In addition, the O-1*s* has two components with binding energies of 530.6 and 532.1 eV for MPA sample. As the PMo<sub>12</sub>O<sub>40</sub><sup>3–</sup> Keggin ion structure has PO<sub>4</sub> tetrahedron surround by four Mo<sub>3</sub>O<sub>13</sub> formed by edge-sharing octahedra; these groups are connected each other by corner-sharing oxygen. Thus, the oxo-molybdenum species displays BE at around 530 eV due to the OH group in Mo-OH species [16,30]. This assignment is supported by the fact that the electron density in the OH group in Mo-based compounds is substantially lower than that in the lattice oxygen, according to the findings [25,29-32].

The same range of binding energies is found with Al-2p and P-2p levels for all *x*-MPA/HNT. On the contrary, variations of the Si-2p and O-1*s* binding energy versus the amount of MPA on HNT is observed,

especially for MPA loading amounts superior to 10 wt.%. This change of BE is a result of charging effects as the BE of Mo varies when the MPA are dispersed on HNTs. Accordingly, BE for Mo-3*d* are 230.2, 232.4, 233.3 and 235.6 eV for 10-MPA/HNT as exhibited in Fig. 5. The major peaks around of 232.2 and 235.6 eV correspond to the doublet Mo-3 $d^{5/2}$  and Mo-3 $d^{3/2}$ , respectively. These contributions indicate Mo presence on the carbon HNT support is in the fully oxidized VI state [33]. In line with these results, XRD measurements suggest a high dispersion of  $\alpha$ -MoO<sub>3</sub> and  $\beta$ -MoO<sub>3</sub> over the *x*-MPA/HNT. Moreover, the contributions appearing at 230.2 and 233.3 eV are assigned to the partially reduced V state [34], which may be bonded to Si or O. Based on the variations in the BE of the Si-2*p* and O-1*s*, the charge transfer among these species and Mo are likely.

### Fig. 5

The BE for 25-MPA/HNT shifts towards lower binding energies by a factor of 0.4, which indicates Mo may interact more strongly with the support compared to 10-MPA/HNT. Moreover, the Mo/Al and Mo/Si atomic concentrations are kept in 0.006 for 10-MPA/HNT and 25MPA/HNT, which means that the fraction of highly oxidized Mo is on the surface.

With increasing the MPA content to 50 wt.%, BE related to Mo<sup>6+</sup> species increases whereas that of Mo<sup>5+</sup> remains constant when compared with those data from 10-MPA/HNT. This is consistent with the fact that lowering the MPA heteropolyacid loading from 50 to 10 wt.% gives to a decreased surface area (Tab. 2). This is understandable when looking at the fact that pore volume and size of 50-MPA/HNT is not plugged with the heteropolyacids as the Keggin units are small enough (diameter  $\approx 1.2$  nm) to enter even micropores [32]. Thus, a fraction of Mo<sup>6+</sup> species may be weakly interacting with the support without blocking the pores. In accordance, the Mo/Al and Mo/Si atomic concentration are 0.0017 for 50MPA/HNT as compared with the 0.006 value of 10-MPA/HNT and 25-MPA/HNT. This may be attributed to the fact that a fraction of highly oxidized Mo is free of interaction on the surface as  $\beta$ -MoO<sub>3</sub> in the former sample.

Consistent with that observation, the hydroxyl groups of silanols present on HNT surface become protonated as  $SiOH^{2+}$  when dispersing the heteropolyanion  $(HMPAn)^{-1}$  to form  $(SiOH^{2+})(HMPAn)^{-1}$  [35]. In the case of interaction with the hydroxyl groups of the  $Al_2O_3$  present in the lumen of HNT, the protonation of  $Al_2O_3$  yields  $MoOH^{2+}$  resulting in a surface with a positive charge that can interact strongly with  $(HMPAn)^{-1}$ forming (HMPAn), which is indeed distorted. Therefore, these interactions lead to the charge transfers, as

suggested by XPS. Moreover, the formation of active intermediates with different strength of Brønsted acid sites and stabilized structures are suggested, as emphasized in previous studies on heteropolyacids dispersed on carbon nanotubes [34].

#### *3.5. Catalytic performance*

### 3.5.1. Catalyst screening

Table 2 summarizes the catalytic performance for some preliminary tests in the acetylation of glycerol with acetic acid reaction carried out at 80 °C, glycerol to the acid acetic molar ratio of 1 and 75 mg of catalyst mass. As it can be seen, pure halloysite HNT nanotube possessing low acidity achieves meaningless conversion. On the other hand, pure MPA used for comparison has itself a stronger acidity than HNT, but the conversion of the former is of ca. 6 %. Moreover, the AG reaction system is strictly homogeneous due to the dissolution of MPA catalyst in a polar substance such as glycerol, as commonly found for other heteropolyacids [36].

The glycerol conversions over the porous SiAl-based solids only display conversions between 7 and 16 %, being the lowest conversion achieved with SAC. Although SAR and SAE exhibit high textural properties and acidity compared to SAC, the former catalysts have a modest performance in the reaction. It is noteworthy that the acid sites of these solids may not be fully accessible to the reactants during the reaction, leading to modest conversions. Also, their porosity (Table 2) does not give more molecules diffusivity inside their meso-macro or micro-mesopores, as reflected by the poor performances.

The glycerol conversions over the molybdophosphoric heteropolyacid supported SiAl nanotubes demonstrate that an effect of MPA loading on the conversion is observed in the *x*-MPA/HNT catalysts. For instance, 10-MPA/HNT possessing a 10 wt.% of MPA with a high amount of active acid sites give the lowest activity compared to other catalysts. This may be explained based on the fact that the MPA anions might have been easily oxidized to  $\beta$ -MoO<sub>3</sub> oxide strongly interacting with the support, as suggested by XRD and XPS. Thus, it can result in the MPA Keggin structure change, and the glycerol conversion over the 10-MPA/HNT is significantly lower when compared with the others *x*-MPA/HNT catalysts.

The favorable effects in terms of improvement of glycerol conversion are seen by incorporation of MPA on HNT with loadings from 25 to 50 wt.%. Despite the expectations that the incorporation of high

loadings of MPA on HNTs gives best catalytic results due to the very high dispersion of active, poor glycerol conversion is observable over 10-MPA/HNT. It can be asserted that most MPA anions are still located in the mesopores of the 25-MPA/HNT catalyst even for loading of 25 wt.%, resulting in a glycerol conversion of 25 % in 6 h of reaction. Thus, no evident blockage of the HNT pores by MPA particles takes place when loading the solids with MPA loading up to 10 wt.%. In agreement, the introduction of MPA heteropolyacid on silica results in a very regular arrangement of channels of siliceous samples with very homogeneous openings [36,37]. In the case of 50-MPA/HNT, a considerable amount of MPA anions may be located on the pores and the other part on the external the surface of the support, as suggested by both SEM and TEM images. Therefore, the 50-MPA/HNT catalyst has a high amount of active acid sites available to the reactants that yield the best catalytic results in terms of glycerol conversion.

The selectivities toward the mono-, di- and tri-derivates are also shown in Table 2. All solids depict the formation of the three main products, as indicated by reaction (I). The solids exhibit selectivities towards MAG of ca. 19 - 27 % overall solids whereas the selective formation of DAG surpasses 45 %. This is due to the consecutive oligomerization of MAG by forming DAG in 6 h of reaction [6]. The findings state that the acidity of the solids and the reaction time are crucial to forming TAG from the consecutive reaction of DAG, in line with our results [38].

### 3.5.2. Recyclability and glycerol conversion in function of the time studies

The recyclability studies were performed with all solids. The reaction conditions used in the recyclability experiments are at 80 °C, catalyst mass of 150 mg with glycerol to acetic acid to a molar ratio of 1:9. The reaction mixture was allowed to react for 24 h for each run. Afterward, the catalyst was recovered from the reaction mixture by centrifugation, dried and reused in the subsequent run at regular 24 h intervals. The reaction progress was monitored by GC.

All porous SiAl-based samples are inactive for 24 h of reaction due to leaching of the acid sites occurred during the reaction, after the first use. Moreover, pure HNT and MPA are inactive along of 24 h of AG reaction. The liquid filtrate from these samples is used instead of the solid catalyst for the further reaction, and no glycerol conversion is observed. However, the *x*-MPA/HNT catalysts are actives for the first time of use with the 50-MPA/HNT affording 98 % of triacetin and glycerol conversion of 38 % (Fig. 6a).

Indeed, triacetin is the main product obtained overall solids. However, the successive uses under the standard experimental conditions illustrate that both 10-MPA/HNT and 25-MPA/HNT deactivate after third uses. This is a consequence of the changes in the textural properties, phase transformations, and acid sites leaching. Figs. 6

The 50-MPA/HNT catalyst displays good reusability during the three cycles with a glycerol conversion of 17 %. Moreover, 50-MPA/HNT sample has some catalyst losses during the third use step; thus, a limited amount of fresh catalyst (< 4 % of the total weight) was also added to the reaction medium. Importantly, the selectivity to triacetin remains practically unchanged during the recyclability studies. The liquid filtrate analysis after the recycling experiment indicates that the metal is not completely leached over 50-MPA/HNT. This is a clear indication that 50-MPA/HNT may preserve its structure intact avoiding leaching of its acid sites and being stable after the reuses, as well.

Effects of the glycerol to acetic acid molar ratios on the glycerol conversion and triacetin selectivity are investigated over 50-MPA/HNT (Fig. 6b). The glycerol conversions increases in the first 6 h of AG reaction, independently of the glycerol to acetic acid molar ratios tested. No changes in terms of selectivities to the triacetin are observed, as a result of the increased nucleophilic attacks of the remaining hydroxyl groups of the MAG moiety on the acid site-acetic acid complex on the catalyst surface [11]. As the reaction time is prolonged to 70 h, the glycerol conversion greatly dropped achieving 4.8 % for glycerol to the acetic acid molar ratio of 1:9. Thus, an increase in the concentration of acetic acid gives a drastic change in the conversion due to significant blockage of mesopores by the products and inaccessibility of reactants to the active Mo sites within pores of 50-MPA/HNT.

The beneficial effects of dispersing MPA heteropolyacid on HNT could be seen in the performance of the catalysts during glycerol conversion. The selectivities to acetins are enhanced and some solids are resistant to deactivation by leaching.

#### 4. Conclusions

Several acid catalysts comprising SiAl and molybdophosphoric heteropolyacid supported SiAl nanotubes were characterized by the XRD, FTIR, XPS, SEM, EDS and TEM techniques. The objective was to understand the textural, morphological and catalytic properties of these materials. The molybdophosphoric supported SiAl nanotubes have acid sites of high strength dispersed on HNT resulting in porous solids with

elevated acidity. Although SiAl-based solids synthesized by the sol-gel method have a great porosity and mild to moderate acidity, the leaching of the acid sites was the landing cause of their deactivation. Dispersing 50 wt.% of molybdophosphoric on HNT nanotubes gave the formation of a porous and stable solid with  $Mo^{6+}$  and  $Mo^{5+}$  species evidently promoting a superior catalytic performance and reusability at the best reaction conditions of 80 °C.

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### Figures

Fig. 1. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distributions for the MPA heteropolyacid supported SiAl nanotubes.

**Fig. 2. (a)** XRD patterns of the dried MPA heteropolyacid and (b) bare HNT support and *x*-MPA/HNT samples. (c) FTIR spectra of the bare HNT support and *x*-MPA/HNT samples.

Fig. 3. SEM-EDS images of the pure HNTs, dried MPA heteropolyacid and x-MPA/HNT solids.

Fig. 4. TEM images of the pure HNTs, MPA heteropolyacids, and x-MPA/HNT solids.

**Fig. 5.** Mo-3*d* core level spectra of the SiAl-based samples modified with the MPA heteropolyacid: MPA, 10-MPA/HNT, 25-MPA/HNT and 50-MPA/HNT.

**Fig. 6. (a)** Recyclability studies on *x*-MPA/HNT solids. Reaction conditions: glycerol to the acetic acid molar ratio of 1:9, temperature of 80 °C and 150 mg of catalyst mass. The numbers in parenthesis indicate the selectivity to triacetin value. (b) Catalytic performance of 50-MPA/HNT in 70 h of reaction time by varying the glycerol to acetic acid molar ratios. Reaction conditions: temperature of 80 °C and 150 mg of catalyst mass by varying the glycerol to the acetic acid molar ratios.

Fig. 1.





Fig. 2.









Fig. 3.



Fig. 4.



Fig. 5.



Fig. 6.



| Catalyst | XRD and<br>FTIR | RD and         TEM         Textural properties         Acid propertie           FTIR         FTIR <t< th=""><th>Acid properties</th><th>References</th></t<> |  | Acid properties   | References |
|----------|-----------------|--|--|---|------------|
| SAE      | Amorphous       | Nanostructured<br>solid  | High surface area;<br>Macro-mesoporous | Mild acidity<br>Presence of<br>Brønsted and<br>Lewis acid sites | [6]        |
| SAR      | Amorphous       | Nanostructured<br>solid  | High surface area;<br>Micro-mesoporous | Mild acidity<br>Presence of<br>Brønsted and<br>Lewis acid sites | [6]        |
| SAC      | Amorphous       | Nanoparticles  | High surface area;<br>Micro-mesoporous | Mild acidity<br>Presence of<br>Brønsted and<br>Lewis acid sites | [6]        |

**Table 1.** Summary of the main features of the porous SiAl-based solids obtained by sol-gel method.

**Table 2.** Physiochemical properties of catalysts in acetylation of glycerol with acetic acid in 6 h of reaction. Reaction conditions: temperature 80°C, glycerol to acetic acid molar ratio of 1:3 and catalyst mass of 75 mg.

| Catalysts | <sup>a</sup> S <sub>BET</sub> | $\begin{array}{ccc} ^{a}S_{BET} & Pore & ^{b}Pore \\ (m^{2}.g^{-1}) & volume & size \\ (cm^{3}.g^{-1}) & (nm) \end{array}$ | <sup>b</sup> Pore | e %<br>Glycerol<br>conversion | % Selectivity |     |     | <sup>c</sup> Total acid<br>sites<br>amount |
|-----------|-------------------------------|--|-------------------|-------------------------------|---------------|-----|-----|--|
|           | $(m^2.g^{-1})$                |  | (nm)              |                               | MAG           | DAG | TAG | $(\mu mol NH_3.g^{-1})$                    |
| SAE       | 398*                          | 1.12*  | 6.4*              | 16                            | 27            | 68  | 5   | 0.21*                                      |
| SAR       | 292*                          | 0.95*  | 8.4*              | 10                            | 23            | 66  | 12  | 0.31*                                      |
| SAC       | 198*                          | 0.64*  | 10.4*             | 7                             | 19            | 63  | 18  | 0.12*                                      |
| MPA       | 2                             | 0.01   | -                 | 6                             | 24            | 68  | 8   | 0.29                                       |
| HNT       | 30                            | 0.15   | 1.8               | 1                             | -             | _   | -   | 0.18                                       |
| 10MPA/HNT | 37                            | 0.18   | 1.7               | 5                             | 25            | 45  | 30  | 0.33                                       |
| 25MPA/HNT | 38                            | 0.19   | 1.7               | 25                            | 26            | 58  | 16  | 0.38                                       |
| 50MPA/HNT | 75                            | 0.28   | 2.0               | 45                            | 20            | 55  | 25  | 0.48                                       |

<sup>a</sup> BET surface area <sup>b</sup> BJH method from the desorption branch of the isotherm.

<sup>c</sup> Measured by TPD of ammonia. \*Data taken from reference [6].

Legend: MAG = monoacetin; DAG diacetin; TAG=triacetin.

| Samples   | Binding energy (eV) |       |       |       | % Concentration |       |       |       |
|-----------|---------------------|-------|-------|-------|-----------------|-------|-------|-------|
| Samples   | O 1s                | Si 2p | Al 2p | Р 2р  | Mo <i>3d</i>    | Si/Al | Mo/Al | Mo/Si |
| HNT       | 531.9               | 102.7 | 74.4  | -     | -               | 1.13  | -     | -     |
| MPA       | 530.6               | -     | -     | 133.5 | 232.6           | -     | -     | -     |
|           | 532.1               |       |       |       |                 |       |       |       |
| 10MPA/HNT | 532.1               | 103.0 | 74.7  | 133.4 | 230.2           | -     | 0.006 | 0.007 |
|           |                     |       |       |       | 232.4           |       |       |       |
|           |                     |       |       |       | 233.3           |       |       |       |
|           |                     |       |       |       | 235.6           |       |       |       |
| 25MPA/HNT | 531.8               | 102.6 | 74.2  | 133.4 | 229.7           |       | 0.006 | 0.007 |
|           |                     |       |       |       | 232.1           |       |       |       |
|           |                     |       |       |       | 232.8           |       |       |       |
|           |                     |       |       |       | 235.2           |       |       |       |
| 50MPA/HNT | 531.3               | 102.5 | 74.3  | 133.4 | 230.8           | -     | 0.017 | 0.017 |
|           |                     |       |       |       | 232.4           |       |       |       |
|           |                     |       |       |       | 233.9           |       |       |       |
|           |                     |       |       |       | 235.6           |       |       |       |

Table 3. XPS data of the solids studied. The accuracy on the BE values is of ca.  $\pm 0.1$  eV.