Sustainable Microwave-assisted solketal synthesis over sulfonic silica-based catalysts

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Abstract

Sulfonic and propylsulfonic silica-based catalysts were synthesized, characterized and tested in the acetalization of glycerol (G) by a sustainable, solvent-free and fast procedure, under microwave irradiation, to produce solketal (S). The catalysts were prepared by different grafting procedures and their surface and structural properties were investigated by means of N_2 adsorption isotherms, Thermogravimetric Analysis (TGA), X-ray Photoelectron Spectroscopy (XPS) and X-Ray Fluorescence Spectroscopy (XRF). Under the optimized reaction conditions (Temperature 40 °C, microwave power <100W, time 2 min and 1:12 glycerol/acetone molar ratio) the sulfonic materials, produced by the hydrothermal grafting, showed excellent performance in terms of activity, selectivity and stability, with no leaching of sulfonic groups after several cycles. By the correlation of the structure properties of the materials and their activity, the performance of the catalysts was shown strictly correlated both to the acidity and the surface density of the active sites.

Keywords: Glycerol, Microwaves, Sulfonic silica materials, Solketal, Sustainability.

1. Introduction

Biomass represents one of the most abundant materials on the earth and fulfils the requirements of sustainability since it is a stable, renewable, biocompatible, biodegradable, low-cost and low-impact material [1,2]. These characteristics make its exploitation, as renewable font of chemicals and energy, one of the most interesting alternatives to the fossil fuel [3,4]. Biomass conversion can produce several valuated chemicals and platform molecules, applied as renewable starting materials in different manufacturing processes. One of the most exploited platform molecules is glycerol (G) thanks to its abundance as by-products materials in different processes (synthesis of fatty acids, soaps, fatty alcohols and biodiesel production) [5] and, also, to its eco-compatible characteristics towards both human and environment. Due to its chemical structure, it can be used as a smart building block to produce different fine chemicals and added value products, as oxygenated fuel additives and solvents [6–9]. In particular, various chemical reactions, such as dehydration, etherification, oxidation, esterification, were considered for the glycerol conversion [10–14]. In the last decades, several scientific research reported the glycerol transformation into solketal, a versatile molecule very useful as fuel additive since it reduces the particulate emission and improve both the flow properties and the oxidation stability of liquid fuels [15–18]. Due to its low toxicity [19], solketal is also applied as green solvent in several industrial procedures involved in pharmaceutics, polymers, cleaning products, pesticides [20,21]. The glycerol conversion into solketal is a significant acid-catalyzed route (Figure 1) in which the 5-membered ring (1,3-dioxolane or solketal) is thermodynamically favored with respect to the corresponding 6-membered ring (1,3-dioxane) [22].

(Figure 1 near here)

Several studies on the use of homogenous acid catalysts (p-toluenesulfonic acid, sulfuric acid, Brønsted acids ionic liquid, methane sulfonic acid or $FeCl_3.6H_2O$) are till today reported in the literature [22–24]. Despite the high activity of these catalysts, they cannot be separated and reused

resulting very inefficient in terms of environmental and economic sustainability. In order to make greener and more sustainable the synthetic approaches, many efforts are being made not only for the use of heterogeneous catalysts as replacement of the more common homogeneous ones, but also on the reaction parameters as for working on solvent-free methodologies, reagents ratio and thermal source.

A large number of acid materials, including zeolite, acid exchange resins, metal-based materials, heteropoly acids, acid modified montmorillonite have been studied during the last years and recently published in the literature [5,25,26]. In most of the reported synthesis the acid functionalization of the materials occurs through a simple impregnation approach with the possibility of leaching of the active sites and low stability of the catalysts [5].

Silica supports have several advantages over other inorganic materials since they possess high surface area, they are structurally stable in a large range of temperatures, and they can be easily chemically modified by covalent functionalization procedures. High surface acid silica-based catalysts have already proved the advantages of efficiency and high stability in the glycerol conversion to solketal. In particular, Vicente et al. [27] showed, for the first time, the efficiency of different sulfonic functionalized mesoporous silicas both in terms of glycerol conversion (80-90%) and solketal selectivity (81%). After the optimization of experimental parameters, the reaction was carried out in two step batches of 30 min, under conventional heating at 70 °C, over arenesulfonic acid functionalized SBA-15, as best catalyst. Recently, Li et al. [28] tested propylsulfonic functionalized SBA-15 and KIT-6 in glycerol acetalization with formaldehyde and 1,3,5-trioxane achieving more than 90% yield of cyclic acetals with a ratio between the two isomers of 42:58. The reaction was carried out under conventional heating at 90 °C during 8 h. Metal (ZrMo) doped KIT-6 showed high catalytic performance (conversion of glycerol was 85.8% and selectivity of solketal was 97.8%) and stability in conventional heating at 50 °C during 4 h reaction [12].

The variation of the reaction parameters can significantly improve the catalytic performance of the materials. Moreover, in view of the efficiency and the sustainability of the chemical processes, the reaction conditions should be oriented to those more environmentally friendly. Taking into account these considerations, nowadays, the catalytic acetalization of glycerol is often carried out in a solvent-free system by using an excess of acetone (A) that allows to shift the equilibrium of the reaction towards the synthesis of solketal (Figure 1) [5,16,24]. As for the thermal source, the majority of published studies are conducted in a conventional heating from 50 °C to 90 °C. Despite the operating temperatures are not high, the process results inefficient in terms of energy transfer from source to reactants. To overcome this drawback, very recently, microwave (MW) assisted procedures are being applied to the synthesis of chemicals. In fact, the use of microwave irradiation allows a rapid and uniform internal heating, leading to a considerable energy and time saving and to a sustainable process. To the best of our knowledge, very few and recent studies were published involving in the use of microwave assisted synthesis of acetals (in particular solketal) starting from glycerol. Pawar et al. [29] investigated the MW-assisted acetalization of glycerol and carbonyl compounds in high yields under both catalyst- and solvent-free conditions. Different aromatic aldehyde reacted with glycerol at 140 °C, 600 W during 15 min achieving high glycerol conversion (90%) but low selectivity to five- (60%) and six- (40%) membered acetal. At the same reaction conditions, the use of cyclic ketones (cyclohexanone) allows to maintain same glycerol conversion (90%) improving the selectivity towards 5-membered acetal (98%). Priya et al. [30] studied the synthesis and application of metals (Fe, Co, Ni, Cu, Zn) impregned Mordenites catalysts in the solvent-free MW-assisted solketal synthesis. In particular, the screening of the materials was carried out at 100 °C, 500 W of MW power during 15 min with a glycerol/acetone molar ratio of 1:3. The reaction achieved 95% of glycerol conversion and 98% selectivity to solketal by using Cu-Mordenite as best catalyst. The reusability of the materials showed a deactivation, after the 4th cycles probably due to the blockage or the leaching of active sites.

Recently, aluminumphosphates solid acid catalysts [31] achieved a high solketal selectivity (96%) and glycerol conversion (94%) during 30 min at 60 °C in MW irradiation. Filho et al. [23] compared the conventional heating and microwave irradiation in the catalytic performance of homogeneous sulfuric acid, p-toluenesulfonic and $FeCl_3$ catalysts, at 65 °C, 600 W during 15 min with 1:6 glycerol/acetone molar ratio. Among them, only two mentioned studies investigate the use of heterogeneous catalysts.

Moreover, considering the studied reaction conditions, the MW-assisted production of solketal need to be still investigate and optimized. In fact, all the few already mentioned published papers still present some inconvenience, as the use of homogeneous [23] or metal-based catalysts [30], the low solketal selectivity with the formation of isomers [29], high temperature [29,30], high watt power [29,30] and/or long time [31].

In a view of a sustainable MW-assisted process, here metal-free acidic materials are chosen to catalyze solketal production, optimizing the procedures towards low values of temperature, as well as low power and short reaction time.

On these premises and as a continuation of our interest on the application of sulfonic acid catalysts in the MW-assisted glycerol conversion into valuated chemicals [32,33], this study deals with the synthesis of sulfonic acid-functionalized hybrid silicas both amorphous and with ordered mesoporosity of the KIT-6 and SBA-15 types, and their catalytic evaluation in the MW-assisted acetalization of glycerol into solketal.

For the synthesis of catalysts, different synthetic approaches as grafting and hydrothermal grafting were considered. By using these procedures, both propylsulfonic and sulfonic groups were covalently linked onto the silica surface and the functionalized materials were evaluated in their catalytic activity. The surface and structural properties of the fresh and spent catalysts were investigated by means of N_2 adsorption isotherms, Thermogravimetric Analysis (TGA), X-ray Photoelectron Spectroscopy (XPS) and acid capacity measurements by X-Ray Fluorescence

Spectroscopy (XRF). The catalytic performance of the sulfonic silicas was evaluated comparing conventional heating and MW irradiation, optimizing the reaction parameters such as temperature and time. Finally, recycling experiments were performed over the most active catalysts.

2. Experimental

2.1 Catalyst synthesis

Amorphous and mesoporous silica supports. Different types of silica, herein after referred to as Am, KIT-6 and SBA-15, were synthesized by sol–gel techniques according to previously described procedures [34,35].

In the synthesis of the Am support [34], 30 mL of tetraethoxysilane (0.135 mol TEOS, ≥99.0% Sigma-Aldrich) was dissolved in 20 mL of dry ethanol (VWR Chemical) and stirred at 45 °C for 15 minutes. Then, 19 mL of aqueous solution of acetic acid at pH 5 was added to the mixture. The temperature was increased to 80 °C until the formation of the gel. The obtained wet gel was dried at 100 °C overnight and then, calcined in air at 450 °C for 4 h (heating ramp of 5 °C/min).

For the synthesis of the KIT-6 silica [35], 6 g of copolymer Pluronic P123® (Sigma-Aldrich) was dissolved in a mixture of 217 mL deionized H_2O, 11.8 mL HCl conc. (Supelco) and 7.4 mL of butanol (≥99.0%, Sigma-Aldrich) in a polypropylene bottle, and stirred at 35 °C for one hour. Then, 13.8 mL of TEOS was added and left stirring overnight. The mixture was aged at 100 °C for 24 h without stirring, in the sealed bottle. The obtained wet gel was filtered under vacuum and washed with hot water and ethanol. The resulted solid product was calcined in air at 550 °C for 6 h (heating ramp of 2 °C/min).

The SBA-15 support [34] was prepared by using a non-ionic amphiphilic triblock polymer, Pluronic P123, as surfactant. The polymer (8.1 g) was dissolved in deionized water (146.8 mL) and 4.4 g of HCl conc. (37%, Supelco) and stirred overnight at 35 °C. Then, 17.1 mL of TEOS (0.077 mol) was quickly added to this solution and the resulting mixture was kept under stirring for 24 h at

35 °C. The milky suspension was aged at 100 °C for 24 h in a closed polypropylene bottle. The solid product was filtered, washed with a HCl/water mixture and calcined in air at 500 °C for 5 h (heating ramp of 2 °C/min).

Sulfonic acid catalysts. Sulfonic (KIT-SO_3H, SBA-SO_3H, Am-SO_3H) and propylsulfonic (KIT-$PrSO_3H$, SBA-$PrSO_3H$ and Am-$PrSO_3H$) silica based materials were prepared according to grafting procedures [33,36] In order to compare the functionalization procedures, propylsulfonic silica based materials were also synthesized by hydrothermal grafting [37] and labelled as KIT-$PrSO_3H$ HT, SBA-$PrSO_3H$ HT and Am-$PrSO_3H$ HT.

Grafting procedure for the synthesis of the sulfonic catalysts KIT-SO_3H, SBA-SO_3H and Am-SO_3H. In a typical synthetic procedure [33], 0.25 mL (3.6 mmol) of $ClSO_3H$ (99.0% Sigma-Aldrich) was added dropwise to a suspension of the corresponding silica (1.0 g, 1.2 mmol) in 10 mL dry CH_2Cl_2 (99.0% Sigma-Aldrich) at 0 °C with stirring for 2 h until the HCl gas evolution stopped. The temperature increased to room temperature and the mixture was stirred for an additional 2 h. Then, the mixture was filtered and washed with ethanol and finally, dried at room temperature.

Thermal grafting procedure for the synthesis of the propyl sulfonic catalysts KIT-$PrSO_3H$, SBA-$PrSO_3H$ and Am-$PrSO_3H$. In a typical synthesis [36], 1 mL (5.67 mmol) of (3-Mercaptopropyl) trimethoxysilane (MPTMS) (95%, Sigma-Aldrich) was added to 1 g of silica support suspended in 35 mL of dry ethanol and the mixture was refluxed overnight. The obtained product was filtered, washed with ethanol and dried at 100 °C overnight. Thereafter, the recovered product was oxidized with 18 mL (by gram of catalyst) of H_2O_2 solution (35% wt.% in H_2O, Sigma-Aldrich) at room temperature overnight. After filtration, the solid was dried at 100 °C overnight.

Hydrothermal grafting procedure for the synthesis of the propyl sulfonic catalysts KIT-$PrSO_3H$ HT, SBA-$PrSO_3H$ HT and Am-$PrSO_3H$ HT. In a typical synthesis [37], 1 g of support and

1 mL (5.67 mmol) of MPTMS was mixed in a polytetrafluoroethylene (PTFE) vessel by adding 3 mL of methanol (≥99.9% Sigma-Aldrich) dropwise until to obtain a homogeneous paste. The PTFE vessel was inserted in a steel autoclave which was heated at 180 °C for 18 h. The obtained product was washed with distilled water, ethanol, and dried at 100 °C overnight. Thereafter, the recovered product was oxidized with 35% hydrogen peroxide solution (18 mL by gram of catalyst). The mixture was left stirring at room temperature for 24 h. After filtration, the solid was dried at 100 °C overnight.

For comparison purposes, commercial 22% H_2SO_4 coated silica gel (Supelco) was also included in the tests for the conversion of glycerol into solketal. According to the safety sheet of the product, the presence of sulfuric acid on silica gel is in the range $30>H_2SO_4>20\%$.

2.2 Catalyst Characterization

The textural properties of the materials were measured using a Micromeritics ASAP2020 Plus 1.03 (Micromeritics, Ottawa, Canada). The fully computerized analysis of the N_2 adsorption isotherm at 77 K allowed us to obtain, through the BET method in the standard pressure range 0.05–0.3 p/p0, the specific surface areas of the samples. The total pore volume, Vp, was evaluated on the basis of the amount of nitrogen adsorbed at a relative pressure of 0.998, while mesopore size distribution values and mesopore volumes were calculated by applying the BJH model in the range of p/p0 of 0.1–0.98.

The thermogravimetric analysis of the samples was performed in air using the TGA 1 Star System of Mettler Toledo (Mettler Toledo, Schwerzenbach, Switzerland). About 10 mg of sample was heated from room temperature to 100°C, left at this temperature for 30 min and then heated to 1000°C at a rate of 10 °C/min in 40 mL/min of air.

Acid capacity of catalysts was determined from the content of sulfur in the materials using X-ray fluorescence (XRF). The measurements were carried out on a ZSX primus IV instrument from Rigaku (Tokyo, Japan), using fundamental parameters in a semi- quantitative analysis. Each

measure was done twice and the final result is the average of both measurements. The estimated error was ≤ 6%.

X-ray diffraction patterns were measured with a Bruker vertical goniometer using Ni-filtered Cu K radiation. A proportional counter and 0.05° step sizes in 2 were used. The assignment of the various crystalline phases was based on the JPDS powder diffraction file cards of the Inorganic Crystal Structure Database (ICSD); FIZ Karlsruhe: Karlsruhe, Germany, 2019.

X-ray photoelectron spectroscopy analysis were performed with a VGMicrotech ESCA 3000 Multilab (VG Scientific, Sussex, UK), equipped with a dual Mg/Al anode. The spectra were excited by the unmonochromatized Al_K source (1486.6 eV) run at 14 kV and 15 mA. The analyser operated in constant analyser energy (CAE) mode. For the individual peak energy regions, a pass energy of 20 eV set across the hemispheres was used. Survey spectra were measured at 50 eV pass energy. The sample powders were analysed as powder mounted on a double-sided adhesive tape. The pressure in the analysis chamber was of the order of 10-8 Torr during data collection. The constant charging of the samples was removed by referencing all the energies to the Si 2s set at 154.7 eV used as internal standard. The invariance of the peak shapes and widths at the beginning and end of the analyses ensured the absence of differential charging. Analyses of the peaks were performed with the Casa XPS software Version 2.3.18PR1.0. Atomic concentrations were calculated from peak intensity using the sensitivity factors provided with the software. The binding energy values are quoted with a precision of ± 0.15 eV and the atomic percentage with a precision of ±10%.

2.3 Glycerol Acetalization

Microwave-assisted acetalization of glycerol (≥99.5%, Sigma- Aldrich) with acetone (≥99.5%, Sigma-Aldrich) was carried out in a CEM-DISCOVER apparatus (Model 2.0). The amount of glycerol (0.241 g), the molar ratio acetone/glycerol (12) and the catalyst loading (5 %w/w, referred to initial glycerol mass) were selected in accordance with the results obtained in a

previous study about the reaction parameters optimization by an ANOVA statistical test [38]. Vessels are made of Pyrex glass and the total volume is 10 mL. Temperature is measured by IR temperature sensor, employing the iWave® method. The magneton frequency was 2.45 GHz. Before each test, the mixture was stirring for 1 min at room temperature and then, irradiated under a maximum power of 50-100 W to reach a reaction temperature of 40 °C. Usually, the time to reach the reaction temperature is less than 20 seconds. To reach the reaction temperature, the microwave induces the power needed. Once the reaction temperature is reached, the power is alternated from ON to OFF, or vice versa, in order to keep the temperature stable. Different experiments at other times and temperatures of reaction were performed under the same conditions. For comparative purposes, the reaction between glycerol and acetone was also carried out using conventional heating at the same experimental conditions in a Syrris-Orbit Multi-reactor. In both cases, after time of reaction, under magnetic stirring at autogenous pressure, the reactor vessel was cooled down in an ice bath and the sample was filtered off and subsequently analysed. The quantitative analysis was carried out by Gas Chromatography in an Agilent Technologies 7890A GC System, equipped with a Supelco 25357 NukolTM capillary column and a Flame Ionization Detector (FID), using N,N-dimethylformamide (≥99.9% Sigma-Aldrich) as an internal standard. The analysis program was: 60 °C for 6 min, heating rate of 20 °C·min−1 until 240 °C which was held for 10 min. The identification of the products was confirmed by Mass Spectrometry.

The glycerol conversion (X_G) and solketal selectivity ($S_{solketal}$) were determined by means of the equations 1 and 2:

$$X_G\,(\%) = \frac{\text{mmol of products}}{\text{starting mmol of G}} \times 100 \qquad \text{(Equation 1)}$$

$$S_i\,(\%) = \frac{\text{mmol of compound i}}{\text{mmol of products}} \times 100 \qquad \text{(Equation 2)}$$

Blank experiments under either conventional or microwave heating showed any conversion of glycerol in the absence of catalyst at the studied experimental conditions.

Recycling experiments were performed over the most active catalysts. In this case, at the end of the reaction, the catalyst was recovered, washed with ethanol (99.5%, PanReac AppliChem) and dried at 80 °C. Afterwards, it was tested again under the same reaction conditions following the above-mentioned procedure.

3. Results and Discussion

3.1 Catalyst characterization

Different sulfonic functionalized amorphous (Am) and mesoporous (KIT-6 and SBA-15) silica were prepared by using different grafting procedures and well characterized by previously reported techniques.

(Figure 2 and Table 1 near here)

Initially, in order to verify the ordered structure in the mesoscale of the synthesized supports, small angle X-ray diffraction analyses were performed on bare KIT-6 and SBA-15 (Figure 2). The KIT-6 silica exhibits the typical pattern with the two well defined peaks at 1.5° and 1.8° that, in the case of SBA-15 are shifted at 1.8° and 2.0°, respectively. They are indexed as (110) and (200) Bragg reflections of the hexagonal (p6 mm) KIT-6 and SBA-15 and confirms the ordered structure of the mesoporous. Bare silica supports were, then, functionalized with sulfonic and propylsulfonic groups through different grafting approaches depending on both the acid groups and the used temperatures. In fact, according to the used procedures, -SO_3H is grafted onto the silica supports through a mild condition by using chlorosulfonic acid as font of -SO_3H (Table 1, entry 1-3), while when -$PrSO_3H$ functions were used, a thermal (Table 1, entry 4-6) or hydrothermal (Table 1, entry 7-9) grafting procedure, involving the hydrolysis and condensation of trimethylmercaptopropyl silane, was carried out. Table 1 summarizes the characterization results of all the synthesised samples. The crystal structure of the mesoporous materials was not significantly influenced by the insertion of the organic groups, as already evidenced by previous studies [36]. The

incorporation of sulfur in the silica-based materials was corroborated by different techniques.

Thermogravimetric analyses allow not only to confirm the thermal stability of the catalysts but also to quantify the incorporation of the sulfonic acid groups, by the calculation of the weight loss between 300 °C and 800 °C. TGA profiles of the bare supports (data not shown) did not evidence any significant loss. The loading of acid groups linked to the silica supports is associated to the synthesis procedure, as evidenced by TGA results (see Table 1 and Figure 3). Thus, those solids synthetized by means of a mild grafting, incorporated the lowest amount of sulfonic group, 0.5 mmol SO_3H/g onto the amorphous and KIT-6 silica, and 0.7 mmol SO_3H/g when SBA-15 is used as support. The higher insertion of sulfonic groups, in the latter case, is probably due to the higher surface area of SBA-15 in comparison to that of amorphous and KIT-6 silicas (Table 1). The thermal grafting procedure refluxing ethanol, leads to a comparable loading (about 0.7 mmol SO_3H/g) of propylsulfonic groups for all considered silica (Table 1, entry 4-6). Due to the stronger reaction conditions (autoclave at 180 °C), when propylsulfonic groups were grafted into the SiO_2 materials by using the hydrothermal approach, the loading of acidic groups results higher (around 0.9 mmol/g) with respect to the previous procedures (Table 1, entry 7-9). These solids exhibit a very similar TGA profile with weight losses between 10.9 and 12.2%. In particular, Figure 3 allows evidencing the effectiveness of hydrothermal procedure with respect grafting one of the higher insertions of propylsulfonic groups.

(Figures 3 and 4 near here)

Figure 4 shows the nitrogen adsorption-desorption isotherms and the pore size distribution (in the insert) of the propylsulfonic catalysts prepared by the hydrothermal procedure. All these solids showed type IV isotherms, characteristics of mesoporous materials. For KIT-PrSO_3H HT (Figure 4a) and SBA-PrSO_3H HT (Figure 4b) materials, a

type H1 hysteresis loops with narrow relative pressure range ($p/p^0 = 0.6–0.7$) is revealed, indicating that the pores system in these two solids is highly uniform. In fact, both catalysts present very similar volume pore (0.6 cm^3/g) and a narrow pore size distribution (5 nm). This hysteresis loop is typical of materials with a cylindrical pores system [39]. The amorphous silica derivate (Figure 4c) showed H4 hysteresis loops, which is often associated with narrow slit-like pores. Thus, the Am-PrSO_3H HT is characterized by very small pore volume (0.1 cm^3/g) and wider pore size distribution centered at lower pores size (4.5 nm) in relation to the corresponding KIT and SBA derivatives. In general, all solids preserved a high surface area in a range 458-697 m^2/g except for Am-PrSO_3H HT (Table 1, entry 7), whose area decreased from 610 to 131 m^2/g, i.e., a 79% lower. Conversely to the corresponding KIT and SBA materials, the Am-PrSO_3H HT synthesized by the hydrothermal approach presents a higher surface density of acid sites, due to a combination of a higher insertion of the sulfonic groups along with a strong decrease in the surface area (Figure 3 and Table 1, Entry 7-9). In all cases the functionalized catalysts exhibit smaller surface area and pore volume, maintaining the pore size around 5 nm (Table 1), indicating that the decrease of the surface area is proportional to the higher insertion of acidic groups while there is any effect on the mesoporosity of silica after the insertion of sulfonic groups.

(Figure 5 near here)

In all cases, the successful oxidation step for the production of sulfonic groups was revealed by the XPS analysis. As example, Figure 5 reported the spectra of mercaptopropyl KIT-6 and the corresponding oxidized -SO_3H groups synthesized by both thermal and hydrothermal grafting. All sulfonic samples exhibited the S2p photoelectron peak centered at 170.5 ± 0.3 eV typical of SO_3= indicating that the H_2O_2 treatment allowed complete oxidation of mercapto- to sulfonic groups as confirmed also by the absence of the S2p component, typical of a mercapto group, lying at ca. 164 eV [40]. The S/Si atomic ratio

derived by XPS confirm the order of the -SO_3H loading. The values are slightly higher indicating a surface localization of the groups, and hence a good availability of the acidic function for catalysis.

Since the XPS analyses confirm that all the sulfur is in sulfonic form, the amount of sulfur determined by XRF analysis can be evaluated equivalent to the acidity of the materials. As it can be observed in Table 1, the acidity values of the solids are in agreement with the results obtained by TGA. Accordingly, the materials synthetized by using the hydrothermal method gave rise to the best acidity values (0.8-0.85 mmol S/g, Table 1 entry 7-9), while their counterparts synthetized by the thermal grafting yielded solids with acidities around 0.41-0.53 mmol S/g (Table 1 entry 4-5). The lowest acidity was obtained when the mild grafting was employed as synthetic approach. In this case, the solids containing either KIT or Am as support, showed the lowest incorporation of S, 0.18 and 0.29 mmol S/g respectively, and therefore, the lowest acidity (Table 1 entry 1, 2). Exceptionally, SBA-SO_3H exhibits an acidity value of 0.73 mmol S/g (Table 1 entry 3).

3.2 Glycerol Acetalization

Figure 1 shows the acetalization reaction of glycerol and its conversion into acetals at 5- (solketal) and 6-membered cycles, the only products detected in this study. The reaction was studied in the presence of the sulfonic silica catalysts and the catalytic behavior of the materials was evaluated in terms of conversion of glycerol and selectivity towards solketal. The influence of temperature (25-80 °C) and time of reaction (2-60 min) on the glycerol conversion and selectivity to solketal under both conventional heating and microwave irradiation was, firstly, studied, in order to obtain the optima experimental conditions. This study was carried out on the synthetized silica, SBA-SO_3H, and on the commercial one, 22% H_2SO_4 coated silica. Table 2 summarizes the reaction results obtained.

As can be seen, for both catalysts and under conventional heating at T ≥ 40 °C and a time of reaction ≥ 7 min, the values of glycerol conversion hardly changed (88-92%). Considering that the estimated experimental error in the calculation of the values of glycerol conversion is < 4% (the final value is the average of at least three values), it can be assumed that the equilibrium of the reaction is reached at 40 °C and 7 min. Under microwave irradiation (< 100 W), the equilibrium conversion and selectivity were reached in 2 min. This fact could be related to a faster and more homogeneous heating of the reaction medium under microwave irradiation. Likewise, the microwave energy would promote a faster activation of the reactant molecules and therefore, the time to reach the reaction equilibrium decreases. In this sense, the role of the dielectric properties of reaction mixtures on the absorption grade of the microwave energy, allowing to reduce the reaction times compared to those of conventional heating has been recently reported [41]. The evolution of the solketal selectivity values, as a function of the reaction time, (see Table 2) shows an increase until reaching the equilibrium value (from 66% to 98%). This result has again verified that the 5-membered ring ketal is thermodynamically more stable than the expected six-ring ketal, according to Ozorio et al. [41], unlike other glycerol ketals and acetals [5,8,22]. In this regard, the isomerization of the six-membered ring to solketal by the action of Brønsted acid sites has been described [42]. Similar values of conversion have been reported, but at higher values of temperature (T ≥ 50 °C) and time of reaction under conventional heating [12,27,43], as well as under MW irradiation [30,31]. Comparing the reaction carried out under microwave irradiation, the sulfonic silica catalysts resulted more performant in terms of both activity and reaction conditions. In fact, as described in the introduction, Pawar et al. [29] investigate the acetalization in a both, catalytic and solvent-free system, but the used experimental conditions (T = 140 °C, t = 15 min, 600 W) were certainly stronger of those found in this study (T = 40 ºC, t = 2 min, <100W), whereas a poor solketal selectivity was

obtained in that research (60%). Priya et al. [30] studied metal doped mordenite in a strong reaction conditions (T = 100 °C, t = 15 min, 500W) achieving both high glycerol conversion and solketal selectivity. Analogously, aluminumphosphate [31] resulted very good catalysts even if the reaction was carried out during 30 min at 60 °C in MW irradiation.

(Table 2 near here)

Under the optimization of the reaction conditions, the obtained results, represented in this study, showed important advantages of microwave heating with respect to conventional one. In fact, the microwave irradiation rapidly activates acetone favouring the interaction with the catalysts and leading to the glycerol conversion towards the solketal formation. With so fast and efficient reaction, the process could be considered sustainable in terms of energy, time and economy savings. Similar results were achieved in other works carried out by our research group in the etherification of glycerol with tert-Butyl alcohol [14,33,45,46].

3.3 Catalytic behaviour of all the studied sulfonic silicas

The values of glycerol conversion and selectivity to solketal obtained with all the catalysts at the optimized reaction conditions, T = 40 °C and t = 2 min, under microwave irradiation (< 100 W) are shown in Table 3.

All the prepared materials brought about a very high (>90%) solketal selectivity, whereas the glycerol conversion is rather influenced by the characteristics of each catalyst. In particular, on amorphous and SBA sulfonic silica (Table 3, entry 1 and 3) glycerol conversion values of 74% and 90%, respectively, were attained, whereas such values fell to 55% in the case of KIT-SO_3H. Likewise, the propylsulfonic-based catalysts synthesized by thermal grafting, allowed a glycerol conversion in a range 72-78% (Table 3, entry 4-6). Nevertheless, the use of hydrothermal grafting procedure allowed producing highly active materials, regardless of the type of silica. In fact, in all cases, the materials showed the best catalytic behavior, achieving both high glycerol conversion (around 90%) and high solketal

selectivity (96-98%) (Table 3, entries 7-9). These results were equivalent to that of the commercial 22% H_2SO_4 silica coated both in terms of glycerol conversion and solketal selectivity and yields (Table 3, entry 10).

The catalytic performance of the sulfonic material showed a strict correlation not only to the employed synthetic procedure, but also to the acidity. In general, with the increase of the acidity, a higher glycerol conversion, as well as solketal yield was achieved, as can be seen in Figure 6 that shows the catalytic activity of the studied materials as function of their own acidity, calculated by the XRF analysis.

(Figure 6 near here)

As above-mentioned, the represented results showed a linear correlation between acidity and catalytic activity of the used materials. As for amorphous and KIT silica, the three grafting approaches lead to a rising acidity, while in case of SBA support, a lower mmol S/g was found when the -$PrSO_3H$ function was linked by thermal grafting. Anyway, also in this case, the activity of SBA-$PrSO_3H$ was correlated with its acidity value. To better explain the behavior of these sulfonic materials, another parameter to consider is the density of sulfonic groups that takes into account also the textural properties of the materials (see Table 1). In fact, those catalysts that showed a higher density of acid sites revealed a better performance in terms of both glycerol conversion and solketal yield. These materials are Am-$PrSO_3H$ HT, Commercial H_2SO_4 Silica, KIT-$PrSO_3H$ HT, SBA-$PrSO_3H$ HT, SBA-SO_3H, listed in decreasing order of density of acid sites. A higher density, in fact, directly influences the activity of the catalysts, promoting a better accessibility of the reactants to the acid sites. As evident, the higher acidity and the higher density of active sites of the sulfonic silica, prepared by the hydrothermal procedure, confirms, to a greater extend, the efficacy of this synthetic approach in the insertion of catalytic active sites.

The stability of the HT-sulfonic acid functionalized silica catalysts and the commercial 22% H_2SO_4 silica coated, exhibiting the best catalytic performance, was investigated in several recycling runs (Figure 7). Despite the high value of acidity (1.56 mmol SO_3H/g) as well as the density of acid sites (53 mmol S/m^2x10^{-4}, Table 3, entry 10), commercial material totally lost its activity already after the first reuse, proving the very weak link of the acidic sites on the silica. This fact is confirmed by the analysis of the surface by XPS indicating the total loss of sulfur after the first cycle pointing to a massive leaching. As for the synthesized sulfonic materials, all the three catalysts showed an almost constant activity for all the studied cycles. The analysis of the sulfur on the surface of the catalysts after three catalytic cycles shows a good stability of the acidity moieties. All samples show a S2p peaks at 170.5 eV typical of S(VI) moreover they maintain the same S/Si ratio as the fresh samples, confirming that no leaching occurs during the reaction cycles. Figure 8 shows the Si2s and S2p region of fresh and recycled Am-PrSO_3H HT sample as example.

(Figures 7 and 8 near here)

The comparison of the results here obtained with the recent studies of Priya [30] and Pratap [31], carried out under microwave methodology using heterogeneous catalysts, shows as sulfonic silica catalysts exhibited good efficiency and repeatability at more convenient reaction conditions. In particular, Pratap studies the use of Fe-aluminophosphate at 60 °C during 30 min time reaction, while Priya investigates Cu-Mordenite materials at 100 °C, 500 W and 15 min time reaction. In both cases the glycerol conversion and solketal selectivity are comparable to the results obtained in the present study. According to both studies, as concern the stability, a deactivation of the materials occurred at the fourth cycles probably due to the metal leaching [30] or chemisorption of species on catalytic acid sites [31].

Conclusions

Amorphous and mesoporous silica modified by sulfonic acid groups have been synthesized by different grafting procedures (mild, thermal and hydrothermal grafting) and tested in the microwave-assisted synthesis of solketal. The hydrothermal (HT) synthetic approach allowed to insert higher amount of acidic functions leading to an increasing performance of the catalysts with respect to the materials produced with the other grafting procedures. Under the optimized reaction conditions (temperature 40 °C, microwave power <100 W, time 2 min and 1:12 glycerol/acetone molar ratio) the HT sulfonic materials efficiently catalyzed the glycerol acetalization achieving 90% of glycerol conversion and 96-98% of selectivity to solketal. Furthermore, to show a high thermal stability (up to 300 °C), the reuse of the catalysts on consecutive reaction cycles was very effective not leading to a significant loss of activity. This was also confirmed by the XPS and XRF characterization of the spent catalysts that revealed no leaching of the sulfonic groups. By the correlation of the structural properties of the materials to their activity, the performance of the catalysts is strictly correlated both to the acidity as well as the surface density of the active sites. For both parameters the hydrothermal synthetic approach turned out to be the key to obtain materials not only with a high acidity but also with high density of sulfonic groups.

Finally, this study presents huge advantages with respect the related few already mentioned published papers, since metal-free stable sulfonic silica-based materials have been developed to catalyze solketal production by using a sustainable, green and fast (2 min) procedure in mild reactions conditions under microwave irradiation.

The results, obtained in this study, showed the real effectiveness of the microwaves with respect to the conventional heating. In fact, as already evidenced, the microwave irradiation allows a rapid and uniform heating of the reaction mixture obtaining the same results in a lesser time. All these experiments were carried out in laboratory scale. Nevertheless, if an industrial plant is

considered, the time saving implies an important energy savings, so essential during this historical period, that results also in a significant economic and sustainable process.

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Table 1. Surface and structural properties of synthetized sulfonic silica-based materials.

Entry	Catalyst	TGA		N_2 adsorption–desorption			XRF		XPS		
		SO_3H wt.%	mmol SO_3H/g	S_{BET} m^2/g	Vp cm^3/g	Dp nm	Acidity[a] mmol S/g	mmol Si/g	S/Si ($\times10^{-2}$)	S/Si ($\times10^{-2}$) molar ratio	Density of acid sites mmol S/m^2 x 10^{-4}
1	Am-SO_3H	4.1	0.5	508	0.4	3.5	0.3	12.8	2.3	1.7	5.7
2	KIT-SO_3H	4.4	0.5	603	0.9	5.5	0.2	12.8	1.4	2.1	2.9
3	SBA-SO_3H	5.9	0.7	559	0.8	5.9	0.7	11.1	6.6	12	13
4	Am-PrSO_3H	8.1	0.7	665	0.5	3.7	0.5	12.2	4.1	6	7.5
5	KIT-PrSO_3H	7.4	0.6	589	0.8	5.8	0.5	12.4	4.3	9	8.9
6	SBA-PrSO_3H	8.3	0.7	697	0.8	5.5	0.4	12.3	3.3	2	5.9
7	Am-PrSO_3H HT	12.2	1.0	131	0.1	4.5	0.8 (0.8)[b]	11.7 (10.9)[b]	7.1 (7.1)[b]	12 (12)[b]	64
8	KIT-PrSO_3H HT	11.2	0.9	458	0.6	5.7	0.8 (0.7)[b]	12.0 (10.6)[b]	7.0 (6.9)[b]	7.5 (7.5)[b]	19
9	SBA-PrSO_3H HT	10.9	0.9	526	0.7	5.4	0.8 (0.6)[b]	12.0 (9.6)[b]	6.6 (6.3)[b]	9 (6)[b]	15
10	Commercial 22%H_2SO_4 Silica coated [c]	-	-	291	0.6	5.9	1.6	10.2	15.3		53
11	Am[d]			610	0.5	4.1					
12	KIT-6[d]			785	0.9	6.0					
13	SBA-15[d]			988	1.0	6.0					

[a] Acidity calculated from XRF, considering that all the sulfur measured is in sulfonic form, as determined by XPS, [b] After 4 reaction cycles, [c] Commercial catalyst used for comparison purpose. [d] BET values of support silica are reported

Table 2. Optimization of reaction conditions in the glycerol acetalization over SBA-SO_3H and commercial 22%H_2SO_4 silica coated by using different heating source.

Experimental conditions			SBA-SO_3H		Commercial 22%H_2SO_4 Silica coated	
Heating mode	time (min)	T (°C)	X_G (% mol)	$S_{solketal}$ (% mol)	X_G (% mol)	$S_{solketal}$ (% mol)
Conventional	7	80	92	98	92	98
	15		92	98	92	98
	30		90	98	88	98
	60		90	98	89	98
	7	25	90	97	80	98
		40	92	98	89	98
		60	91	98	89	98
		80	92	98	92	98
Microwave	2	40	90	97	92	98
	5		90	98	90	98
	5*		92	98	92	99
	7		89	97	89	98
	10		89	97	91	98
Conventional	2	40	59 (16)**	66 (50)**	59	66
vs Microwave	2	40	90	97	92	98

Solvent-free acetalization with a G:A molar ratio 1:12 and 5% w/w catalyst. *T=60°C; ** T= 25 ºC (Room Temperature)

Table 3. Catalytic performance of sulfonic acid catalysts under MW irradiation.

Entry	Catalyst	X_G (% mol)	$S_{Solketal}$ (% mol)	$Y_{Solketal}$ (% mol)
1	Am-SO_3H	74	92	68
2	KIT-SO_3H	55	87	48
3	SBA-SO_3H	90	97	87
4	Am-PrSO_3H	78	94	73
5	KIT-PrSO_3H	74	93	69
6	SBA-PrSO_3H	72	98	71
7	Am-PrSO_3H HT	89(82)[a]	96(93)[a]	86(76)[a]
8	KIT-PrSO_3H HT	91(90)[a]	98(92)[a]	89(80)[a]
9	SBA-PrSO_3H HT	90(85)[a]	98(96)[a]	88(82)[a]
10	Commercial 22%H_2SO_4 Silica coated	92(0)[b]	98 (0) [b]	90 (0)

[a] Data after 4 reaction cycles. [b] Data after 2 reaction cycles. Solvent-free acetalization with a G:A molar ratio 1:12, 5% w/w catalyst (referred to initial glycerol mass), T=40°C, t=2min

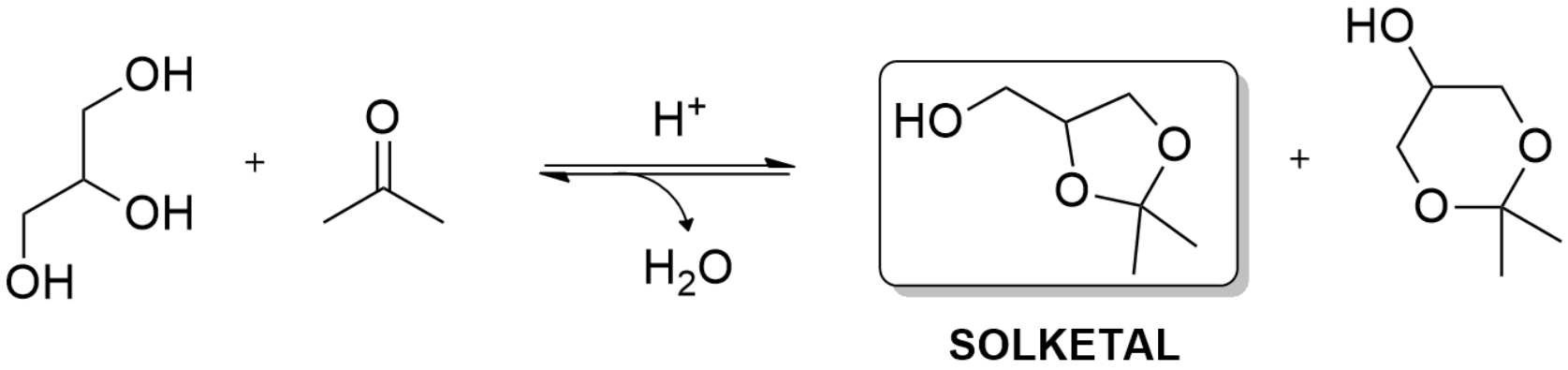

Figure 1

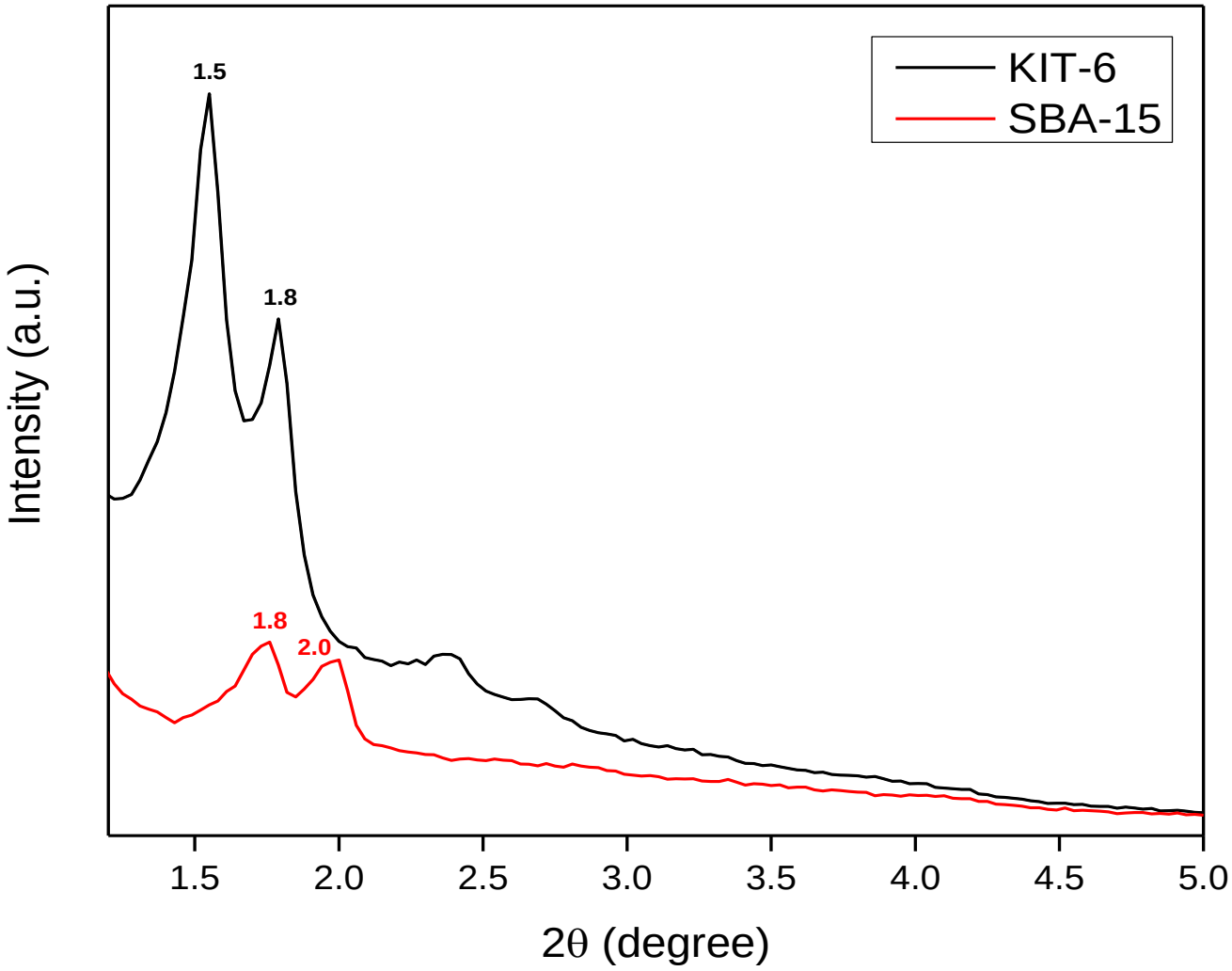
KIT-6
SBA-15
1.5
1.8
1.8
2.0
Intensity (a.u.)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
2θ (degree)

Figure 2

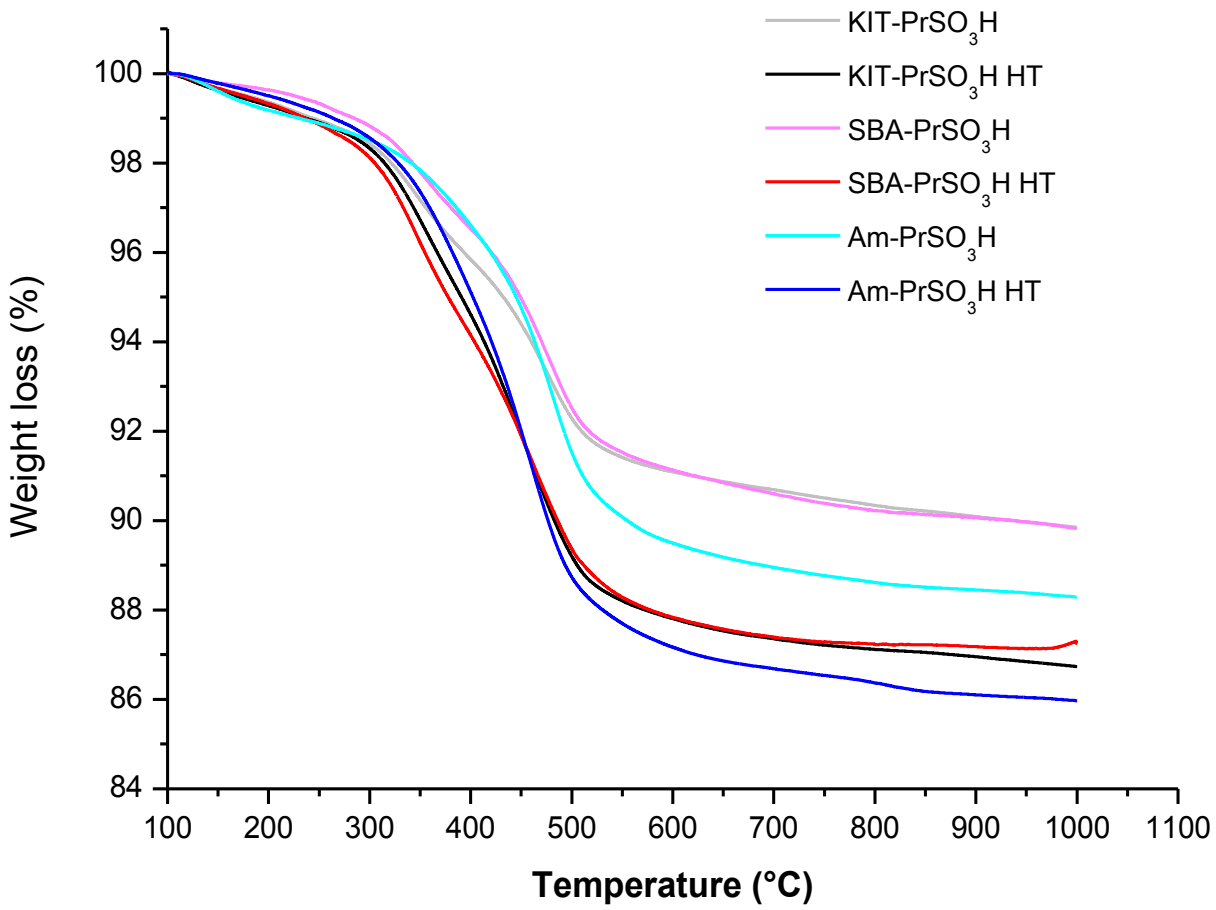
KIT-PrSO3H
KIT-PrSO3H HT
SBA-PrSO3H
SBA-PrSO3H HT
Am-PrSO3H
Am-PrSO3H HT
Weight loss (%)
100
98
96
94
92
90
88
86
84
100
200
300
400
500
600
700
800
900
1000
1100
Temperature (°C)

Figure 3

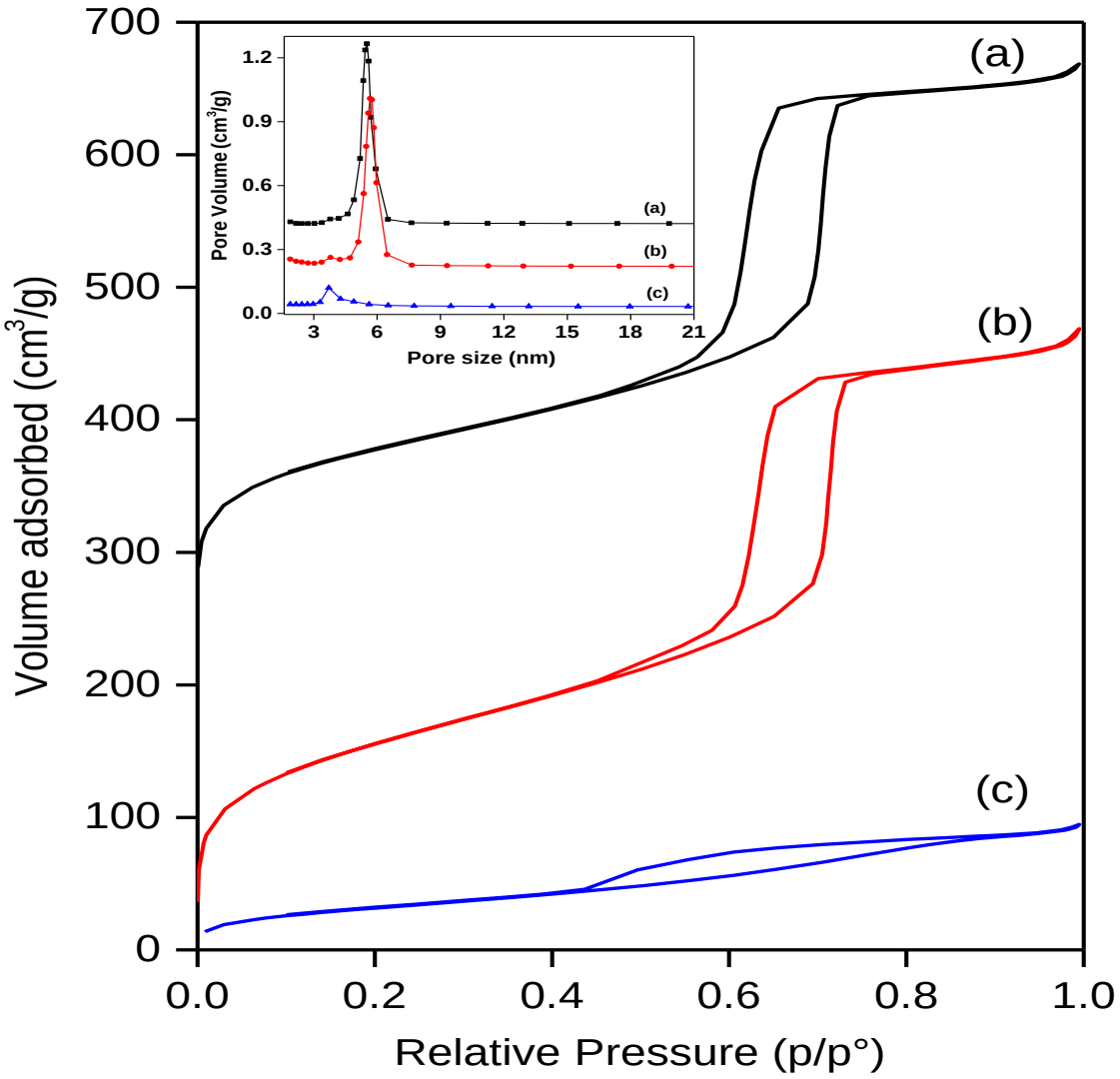
Volume adsorbed (cm3/g)
Relative Pressure (p/p°)
(a)
(b)
(c)
Pore Volume (cm3/g)
Pore size (nm)

Figure 4

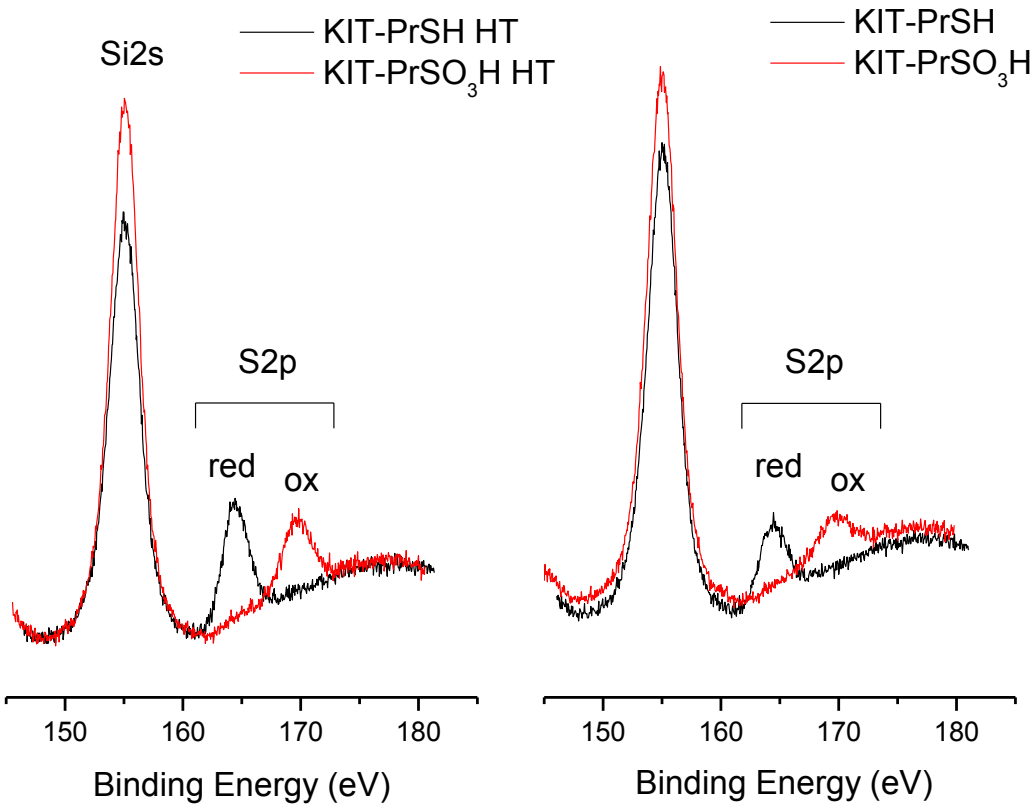
Si2s
KIT-PrSH HT
KIT-PrSO3H HT
S2p
red
ox
150
160
170
180
Binding Energy (eV)
KIT-PrSH
KIT-PrSO3H
S2p
red
ox
150
160
170
180
Binding Energy (eV)

Figure 5

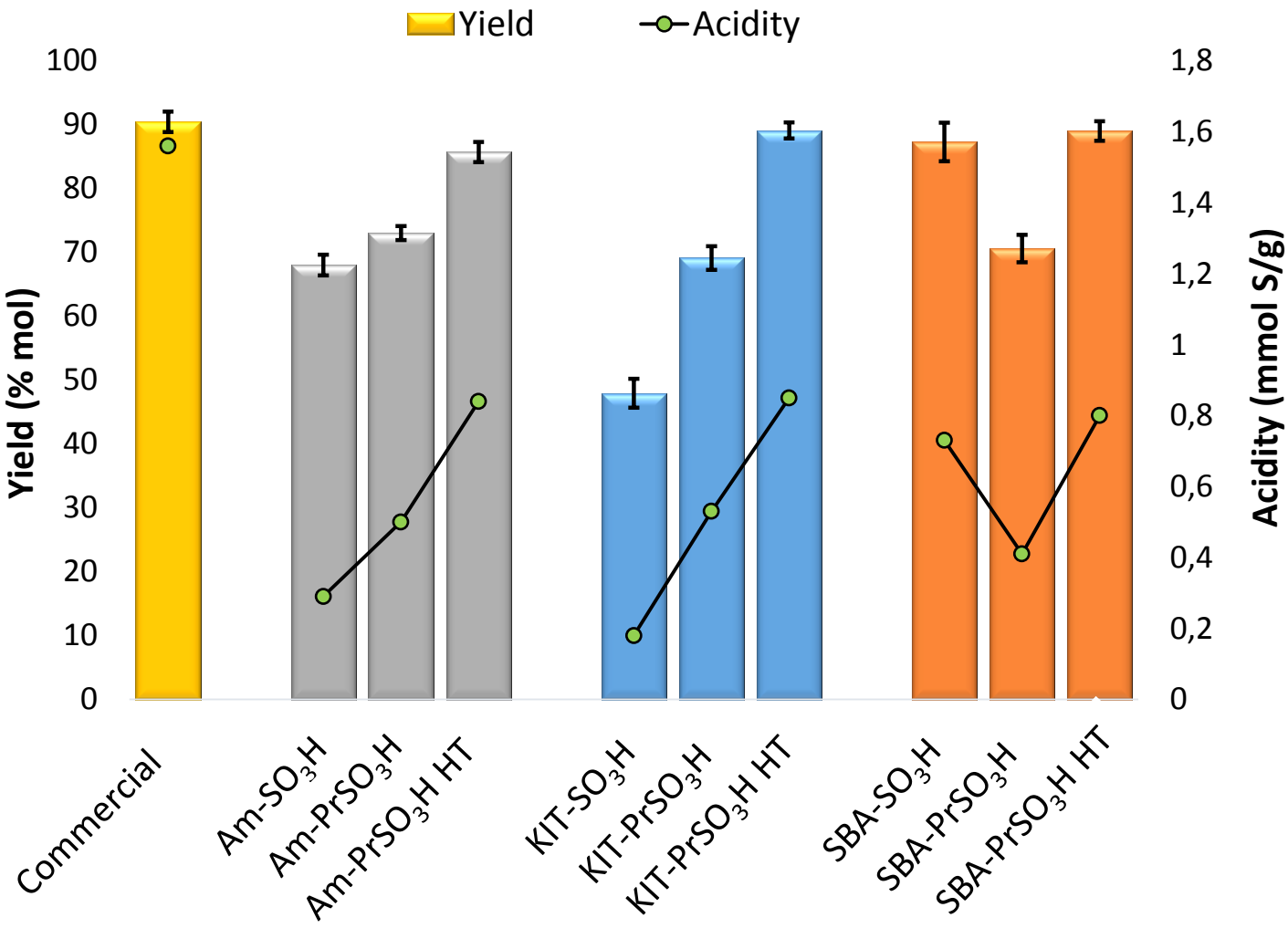
Yield
Acidity
Yield (% mol)
Acidity (mmol S/g)
100
90
80
70
60
50
40
30
20
10
0
1,8
1,6
1,4
1,2
1
0,8
0,6
0,4
0,2
0
Commercial
Am-SO3H
Am-PrSO3H
Am-PrSO3H HT
KIT-SO3H
KIT-PrSO3H
KIT-PrSO3H HT
SBA-SO3H
SBA-PrSO3H
SBA-PrSO3H HT

Figure 6

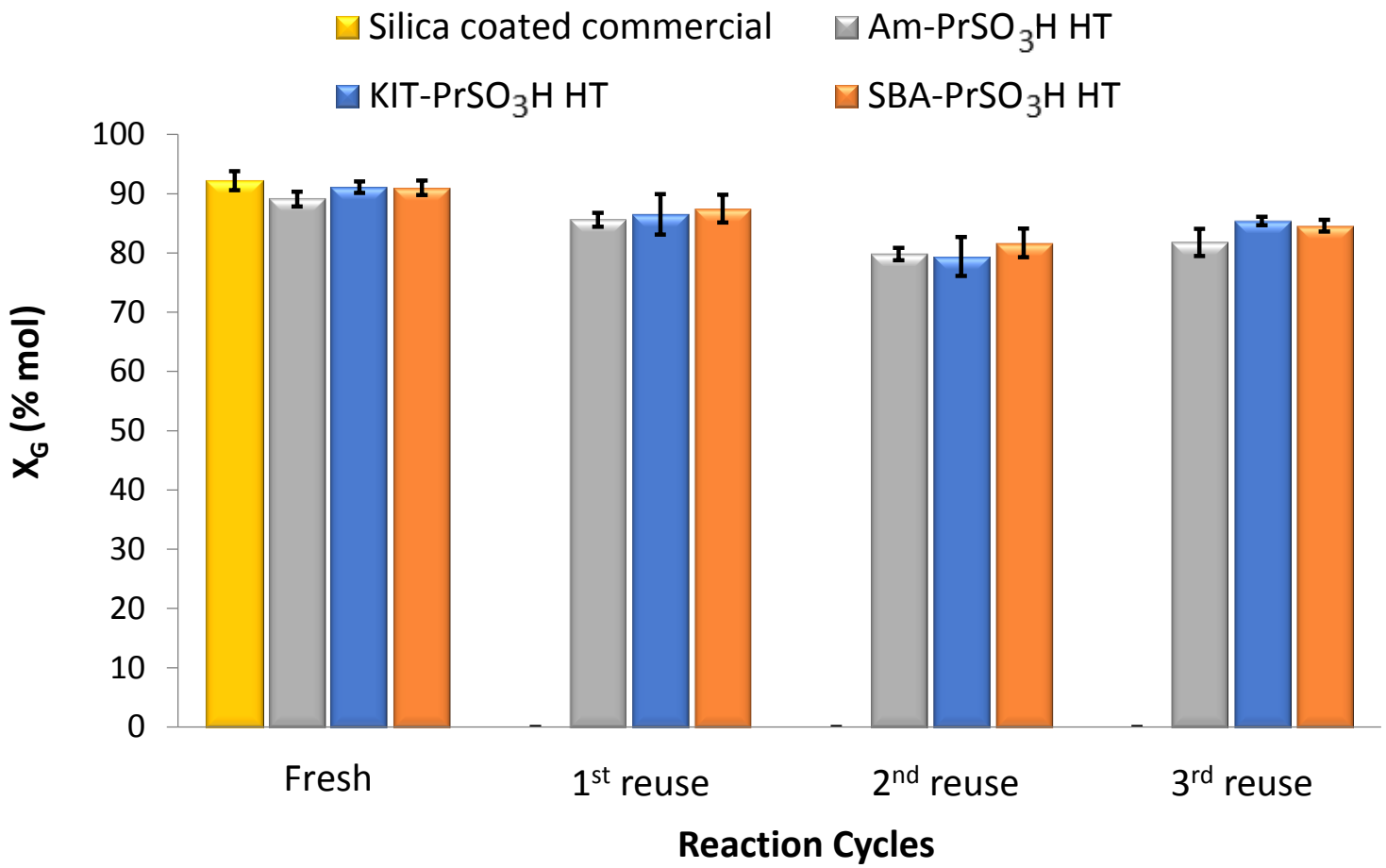
Silica coated commercial
Am-PrSO3H HT
KIT-PrSO3H HT
SBA-PrSO3H HT
100
90
80
70
60
50
40
30
20
10
0
XG (% mol)
Fresh
1st reuse
2nd reuse
3rd reuse
Reaction Cycles

Figure 7

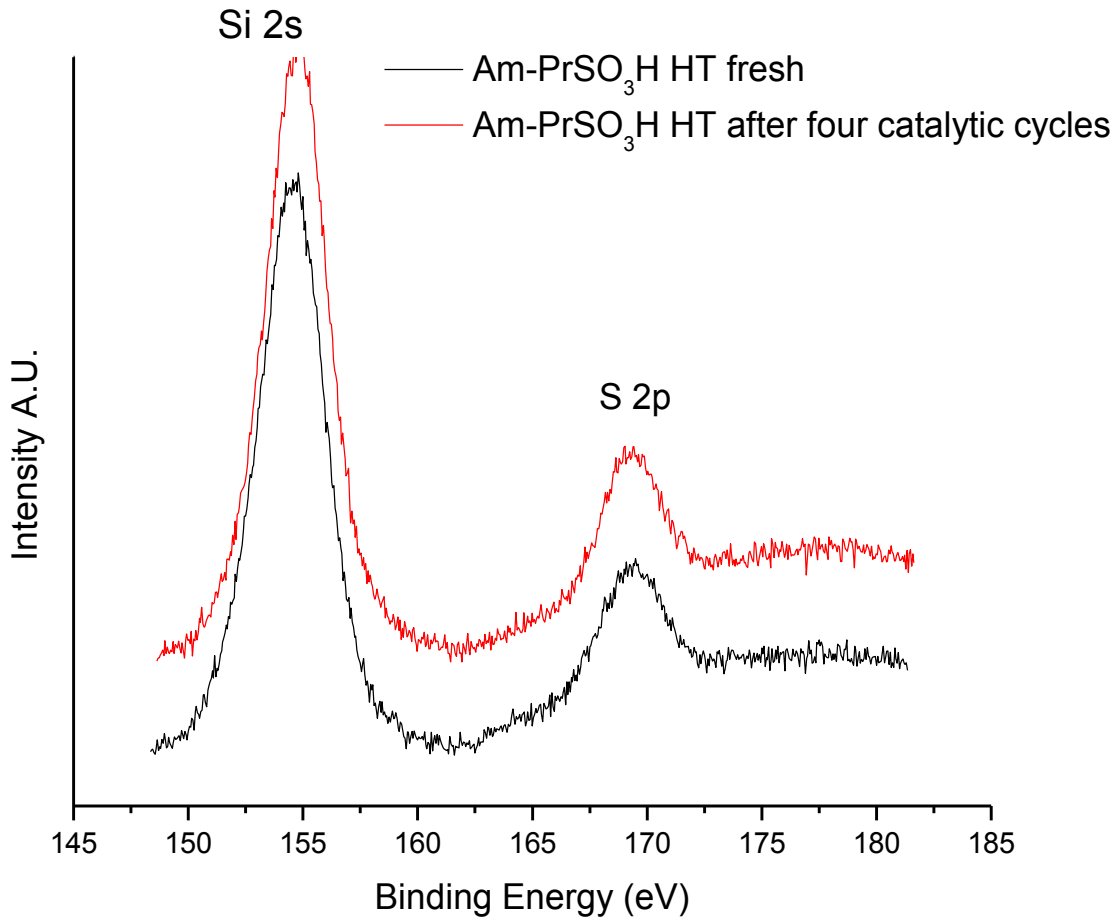
Si 2s
Am-PrSO3H HT fresh
Am-PrSO3H HT after four catalytic cycles
S 2p
Intensity A.U.
145
150
155
160
165
170
175
180
185
Binding Energy (eV)

Figure 8

Figure Legends

Figure 1. Acetalization of glycerol with acetone.

Figure 2. XRD patterns of mesoporous bare silica KIT-6 and SBA-15.

Figure 3. TG analysis of the materials synthesized by hydrothermal method.

Figure 4. Nitrogen adsorption-desorption isotherms of KIT-PrSO_3H HT (a), SBA-PrSO_3H HT (b) and Am-PrSO_3H HT (c). The curves are shifted along y-axis for sake of clarity. In the inset the pore size distribution as calculated by BJH method.

Figure 5. XPS Si2s and S2p region KIT-PrSO_3H and its precursor KIT-PrSH prepared by both, thermal and hydrothermal grafting.

Figure 6. Correlation between the values of acidity from XRF analysis (mmol S/g) and of solketal yield (% mol) obtained with all the studied catalysts

Figure 7. Recycling runs on the glycerol acetalization over commercial and HT-sulfonic materials under MW irradiation. Experimental conditions as in Table 3

Figure 8. Si2s and S2p XPS region of Am-PrSO_3H HT fresh and after four catalytic cycles