

Acidic Mesoporous Silica for the Acetylation of Glycerol: Synthesis of Bioadditives to Petrol Fuel

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Expected increasing biodiesel production during the next few years will lead to an overproduction of glycerol, which is the main byproduct. The use of glycerol-based additives to improve petrol fuel properties is one of the possibilities currently being explored to utilize this renewable feedstock. In this context, sulfonic acid functionalized mesostructured materials have demonstrated an excellent catalytic behavior in the esterification of glycerol with acetic acid to yield acetylated derivatives. Diacetylglycerol (DAG) and triacetylglycerol (TAG, also called triacetin) have been shown to be valuable petrol fuel additives leading to either enhanced cold and viscosity properties when blended with diesel fuel or antiknocking properties when added to gasoline. The activities and selectivities achieved using sulfonic acid functionalized mesostructured materials as catalysts are comparable or even superior to those displayed by conventional acid catalysts, providing values up to 90% of glycerol conversion and over 80% of combined selectivity toward DAG and TAG after 4 h of reaction. The acid strength of the sulfonic acid site has also been found to be an important factor affecting the catalytic performance of these materials. Moreover, these sulfonated mesostructured materials have been reused in repeated catalytic runs after a mild solvent-washing regeneration step yielding similar catalytic performance to that of the fresh catalyst.

1. Introduction

Biofuels for transportation have the potential to displace a substantial amount of petroleum-based fuels around the world over the next few decades. The Directive 2003/30/EC of the European Union recently stated that, by the end of the year 2005, member states should ensure a biofuels proportion of 2% calculated on the basis of energy content for all the petrol fuels used for transportation purposes. This figure rises up to 5.75% by the end of the year 2010.¹ Other countries including the U.S., Canada, Australia, and Japan have already adopted policies that will result in much higher biofuels use over the next decade. Bioethanol and biodiesel are currently the commercial biofuels for transportation worldwide. Ethanol is by far the most widely used biofuel. However, biodiesel production is higher in Europe where more biodiesel is produced than ethanol. The adopted policies will lead to a global increase of both biofuels. If the target of the European Directive is achieved, the European biodiesel demand could increase up to 10 million tons per year by 2010.²

Biodiesel is a mixture of fatty acid methyl esters (FAME) manufactured by the transesterification of triglycerides with methanol, typically in the presence of homogeneous acid or base catalysts. Glycerol is the main byproduct, whose production is equivalent up to approximately 10 wt % of the total FAME product. Therefore, the predicted increase of biodiesel produc-

tion will result in the accumulation of glycerol and create a glut in the market.³ This situation has prompted a search for new glycerol uses. To date, glycerol is too expensive to be used as a fuel, but as the biodiesel production increases, its availability could exceed the demand for traditional use (synthesis of fine chemical products), and hence its price will decrease, making it a cost-effective raw material for the preparation of fuels. Among different alternatives, the use of glycerol-based additives to improve properties of biodiesel is being explored.⁴ This approach not only makes good use of the reaction product but also could increase the fuel yield in the overall biodiesel process. Glycerol ethers have been prepared using isobutene over Amberlyst-type acid catalyst.^{5–11} These compounds can be directly blended with diesel fuel⁴ or can be added to the transesterified triglycerides to yield an improved biodiesel before being blended with the diesel fuel.^{6–8} Different studies have shown that di- and tri-tert-butylethers (monoderivates are highly water soluble and thus are not suitable as diesel-blending agents) added in different proportions to diesel fuel result in an improvement of cold properties^{7–8} and a reduction of contaminant emissions⁴ and viscosity. Likewise, these derivatives can be also used as octane boosters as an alternative to commercial

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Table 1. Cold Properties Improvement when Mixing Triacetyl glycerol with Biodiesel (Data from ref 14)

parameter	biodiesel ^a	biodiesel + 1% of triacetin	biodiesel + 5% of triacetin	biodiesel + 10% of triacetin
density (g cm ⁻³)	0.859	0.862	0.869	0.881
mp ^b (°C)	-7	-16	-16	-17
viscosity at -10 °C (cSt)			931.2	453.9

^a Fatty acid methyl esters from rapeseed oil. ^b Melting point of the mixture.

Table 2. Triacetyl glycerol Properties as Fuel Additive (Data from ref 12)

density (g cm ⁻³)	boiling pt. (°C)	solubility in fuels			
		gasoline	diesel	FAME	
1.10	259	+	+	+	
engine test					
MON ^a		RON ^b		CN ^c	
gasoline	10% mix	gasoline	10% mix	diesel	10% mix
85.3	88.0	97.0	98.3	50.5	45.0

^a Motor octane number. ^b Research octane number. ^c Cetane number.

tertiary alkylethers (MTBE and ETBE).¹² However, this approach has a serious drawback with regard to the availability of isobutene feedstock. On the other hand, some work has been described in the literature dealing with the preparation of ketals of glycerol by reaction with acetone or aldehydes over Amberlyst-15.^{12–13} Likewise, glycerol has also been esterified with acetic acid or transesterified with methyl acetate to yield glycerine triacetate (commonly called triacetin).^{12–14} These compounds have been introduced in biodiesel formulation, resulting in a final fuel having enhanced cold and viscosity properties.¹⁴ Table 1 shows data revealing the improvement in cold properties in biodiesel (comprising fatty acid methyl esters from rapeseed oil) when mixed with small amounts of triacetin. Likewise, triacetin has also been used as an antiknock additive for gasoline (see Table 2).¹²

The purpose of this contribution is the esterification of glycerol with acetic acid to yield these glycerine acetates as valuable transportation fuel additives. Yadav and Mehta¹⁵ reviewed several synthetic routes for obtaining organic esters, the direct esterification of carboxylic acids with alcohols in the presence of acid catalysts being the most-used methodology for ester synthesis, considering equilibria limitations that control the esterification reaction. Currently, for example, the esterification of fatty acids with alcohols is achieved commercially using liquid acid catalysts, such as sulfuric acid, hydrochloric acid, and *para*-toluenesulfonic acid. However, the use of conventional homogeneous acid catalysts must be limited in the future to comply with the increasingly strict environmental regulations. In this context, scientific literature contains a growing amount of reports on the use of heterogeneous acid catalysts for esterification reactions. The most-used solid acids for the production of esters have been ion-exchange organic resins, such as Amberlyst-15,¹⁶ zeolites,¹⁷ and silica-supported heteropoly acids.¹⁸ Nevertheless, they have been shown to

exhibit limitations in applicability for catalyzing esterification due to low thermal stability (resins), mass transfer resistance (zeolites),¹⁹ or loss of active acid sites due to high solubility in a polar medium (heteropoly acids).¹⁸ Moreover, the presence of water can seriously affect the catalytic behavior of these solid acid catalysts due to their highly hygroscopic nature,²⁰ the practice of removing product water from reaction media as the reaction proceeds being common. As a promising alternative approach, silica-supported Nafion SAC-13 has been shown as an effective esterification catalyst overcoming most of the limitations of resins.^{21–22}

In connection with this, the incorporation of organosulfonic groups over mesostructured materials (MCM-41,^{23–24} HMS,²⁵ and SBA-15²⁶ materials) have generated effective solid acid catalysts with enhanced catalytic properties as compared with conventional homogeneous and heterogeneous acid catalysts in several acid-catalyzed reactions.^{27–28} These sulfonated mesostructured silicas lead to materials with high surface area, narrow pore size distributions with high accessibilities to acid sites, and relatively high acid strength. Specifically, some sulfonic acid modified mesostructured materials from the MCM-41 family have been successfully used in the esterification of glycerol with bulky fatty acids to yield monoglycerides which are valuable chemical products in the food, pharmaceutical, and cosmetic industries.^{29–30} Herein, we describe the application of this kind of mesostructured silica-based solid acid catalyst to the production of fuel additives from glycerol. Thus, a multivariate analysis has been used to assess the conditions (acetic acid/glycerol molar ratio and temperature) that yield the best catalytic results in terms of glycerol conversion and yield toward the di- and tri-derivates. Finally, their catalytic performance has been benchmarked with other commercial acid catalysts.

2. Experimental Section

2.1. Catalysts Preparation. Propylsulfonic acid functionalized mesostructured silica (Pr-SBA-15) was synthesized following a procedure described elsewhere.³¹ Synthesis molar composition of

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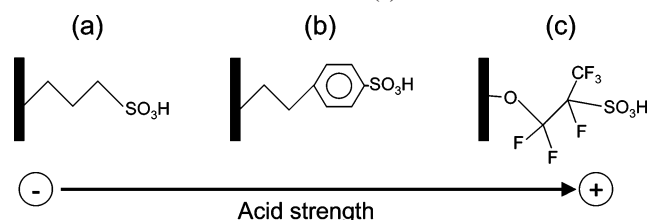
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Table 3. Physicochemical, Textural, and Acidity-Related Properties for Sulfonic Acid Modified Mesostructured Materials

sample	textural properties				acid properties	
	d_{100}^a (Å)	pore size ^b (Å)	BET area (m ² /g)	pore volume ^c (cm ³ /g)	acid capacity ^e (meq/g)	organic incorporation ^f (%)
Pr-SBA-15	111	82	666	1.19	1.15	91
Ar-SBA-15	103	80	720	1.03	1.04	99
F-SBA-15	109	96	404	0.83	0.30	16

^a d (100) spacing, measured from small-angle X-ray diffraction. ^b Mean pore size (D_p) from adsorption branch applying the BJH model. ^c The pore volume (V_p) was taken at $P/P_0 = 0.975$ single point. ^d Average pore wall thickness calculated by a_0 pore size ($a_0 = 2d(100)/\sqrt{3}$). ^e Acid capacities defined as meq of acid centers per gram of catalyst (obtained either directly by titration or indirectly from sulfur content by elemental analysis). ^f Organic incorporation estimated from sulfur content after synthesis and maximum theoretical content.

Scheme 1. Sulfonic Acid Moieties in the Functionalized Mesostructured Samples: Propyl- (a), Arene- (b), and Perfluoro- (c)



the mixture for 4 g of templating copolymer was 0.0369 tetraethylorthosilicate (TEOS, Sigma-Aldrich); 0.0041 mercaptopropyltrimethoxysilane (MPTMS, Sigma-Aldrich); 0.0369 H₂O₂; 0.24 HCl; and ≈ 6.67 H₂O. Likewise, arenesulfonic acid functionalized mesostructured silica (Ar-SBA-15) was synthesized as described before.³¹ In this case, the molar composition of the mixture for 4 g of copolymer was 0.0369 TEOS; 0.0041 chlorosulfonyl-phenyl-ethyltrimethoxy-silane (CSPTMS, Gelest); 0.24 HCl; and ≈ 6.67 H₂O. The amount of sulfur precursors in both materials (MPTMS and CSPTMS) has been established to be 10% of the total moles of silicon.

Fluorosulfonic Acid Functionalized Mesostructured Silica (F-SBA-15). This sample was prepared adapting the procedure published by Corma et al.³² First, the pure silica SBA-15 support³³ was prepared with the following molar composition for 4 g of pluronic 123: 0.0410 TEOS; 0.24 HCl; and ≈ 6.67 H₂O. After calcination for complete surfactant removal, a grafting procedure was used: 2 g of SBA-15 silica were dried at 120 °C for 8 h and functionalized with 1 g of the precursor 1,2,2-trifluoro-2-hydroxy-1-trifluoromethylethane-sulfonic acid sultone (FluoroChem) in 50 mL of dry toluene under a nitrogen atmosphere. The precursor reacts with the surface silanol groups of the mesoporous silica by opening up the sultone ring and forming a covalent bond. The final solid product is vacuum-filtered and washed thoroughly with toluene and finally dried at 100 °C overnight.

Other Commercial Acid Catalysts. Sulfuric acid (H₂SO₄), Nafion-SiO₂ composite (SAC-13), and Amberlyst-15 were supplied by Sigma-Aldrich.

2.2. Catalyst Characterization. Nitrogen adsorption and desorption isotherms at 77 K were measured using a Micromeritics TRISTAR 3000 system. The data were analyzed using the Bopp-Jancso-Heinzinger (BJH) model, and the pore volume was taken at $P/P_0 = 0.975$ single point. X-ray powder diffraction (XRD) patterns were acquired on a PHILIPS X'PERT diffractometer using Cu K α radiation. The data were recorded from 0.6 to 5° (2 θ) with a resolution of 0.02°. Cation-exchange capacities corresponding to the sulfonic acid mesostructured materials were determined using aqueous solutions of sodium chloride (NaCl, 2 M) as a cationic-exchange agent. In a typical experiment, 0.05 g of solid was added to 15 g of aqueous solution containing the sodium salt. The resulting suspension was allowed to equilibrate and thereafter was titrated

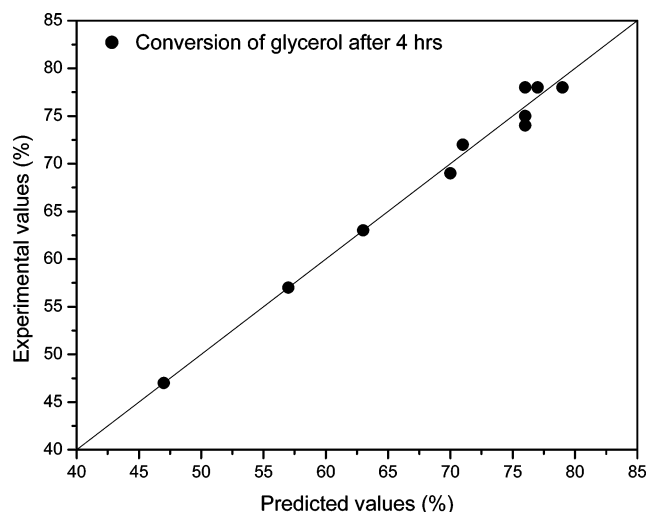


Figure 1. Accuracy of the predicted data relative to the experimental data for the conversion of glycerol (catalyst: Pr-SBA-15).

Table 4. Physicochemical and Textural Properties for Commercial Acid Catalysts

catalyst	BET area (m ² /g)	pore size (Å)	acid capacity ^a
sulfuric acid			20.4
Amberlyst-15	45	macroporous	4.8
SAC-13 (Nafion-SiO ₂)	200	> 100	0.12

^a Millimoles of acid centers per gram of catalyst.

potentiometrically by the dropwise addition of 0.01 M NaOH (aq). Sulfur and organic contents were determined by means of an elemental analysis (HCN) in a Vario EL III apparatus and by means of a thermogravimetry analysis (SDT 2960 Simultaneous DSC-TGA from TA Instruments). Table 3 summarizes the most relevant physicochemical properties for the sulfonic acid modified mesostructured materials. Data from XRD and nitrogen adsorption isotherms evidence high mesoscopic ordering of the different sulfonic acid modified mesostructured SBA-15 materials. Likewise, high surface areas along with narrow pore size distributions around 8–9 nm are obtained (size enough to avoid the steric constraints imposed by the pore size when relatively bulky substrates such as glycerol derivatives are considered). It is important to note that Pr-SBA-15 and Ar-SBA-15, prepared through a cocondensation technique, display high incorporation yields for the sulfonic acid moieties (over 90%). In the case of F-SBA-15, since the preparation proceeds via a reactive-grafting method,³² the organic incorporation is much lower (16%). In this way, mesostructured materials with different acid strengths of the sulfonic acid groups by close attachment of different functionalities have been prepared (see Scheme 1). Finally, characterization data (textural properties and acid capacities) corresponding to the commercial acid catalysts also assessed in this particular reaction are depicted in Table 4.

2.3. Reaction Procedure. Scheme 2 is a representation of the esterification of glycerol with acetic acid, showing the main acetylation products: mono-acetyl-glycerol (MAG), di-acetyl-glycerol (DAG), and tri-acetyl-glycerol (TAG). Among them, DAG

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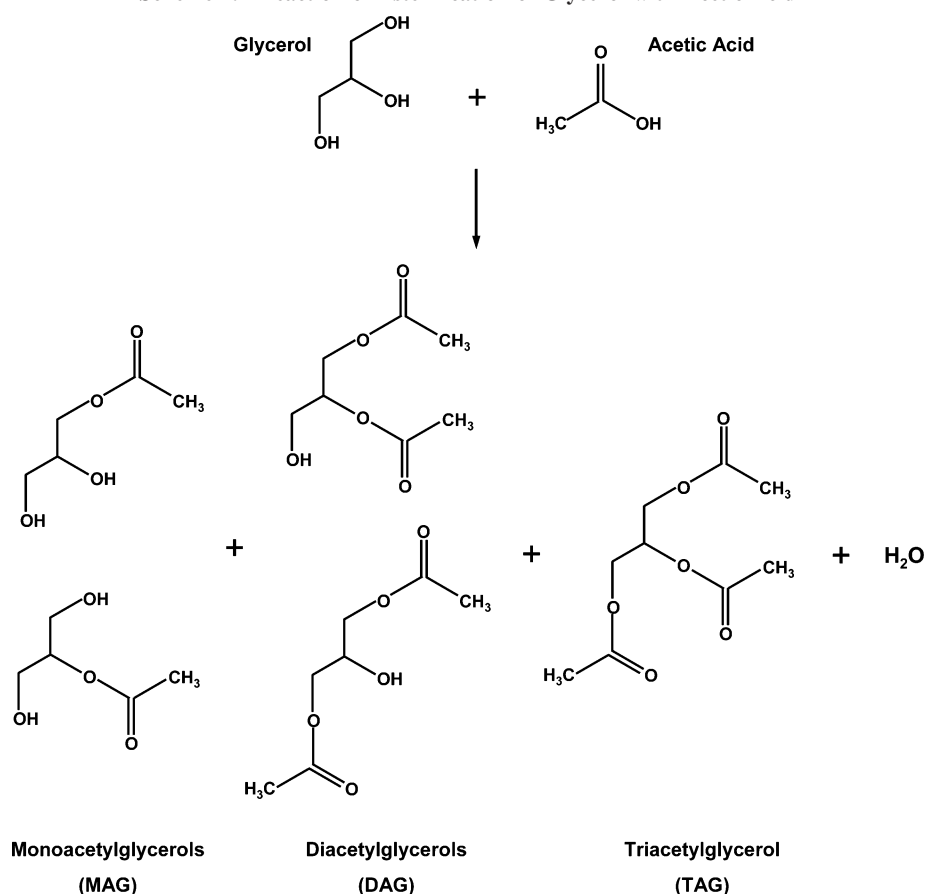
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Table 5. Experimental Results of the Factorial Design for the Esterification of Glycerol with Acetic Acid over Propylsulfonic Acid Modified Mesostructured Catalyst, Pr-SBA-15 [Glycerol/Catalyst Weight Ratio = 25; Reaction Time = 4 h]

run	acetic acid/glycerol (molar ratio) (X)	T (°C) (Y)	x_{glycerol}^a (%) (Z_1)		S_{MAG}^b (%) (Z_2)		S_{DAG}^b (%) (Z_3)		S_{TAG}^b (%) (Z_4)	
			exptl ^c	calcd ^d	exptl ^c	calcd ^d	exptl ^c	calcd ^d	exptl ^c	calcd ^d
1	3:1 (−1)	100 (−1)	63	63	45	48	42	40	13	13
2	3:1 (−1)	125 (0)	57	57	58	53	33	36	9	9
3	3:1 (−1)	100 (−1)	47	47	49	41	40	38	11	11
4	6:1 (0)	100 (−1)	78	76	37	34	41	44	22	22
5	6:1 (0)	125 (0)	75	76	26	30	50	45	24	25
6	6:1 (0)	125 (0)	78	76	28	30	47	45	25	25
7	6:1 (0)	125 (0)	74	76	31	30	44	45	25	25
8	6:1 (0)	150 (+1)	72	71	22	19	48	51	30	29
9	9:1 (+1)	100 (−1)	78	79	20	31	52	51	28	28
10	9:1 (+1)	125 (0)	78	77	17	17	44	47	39	39
11	9:1 (+1)	150 (+1)	69	70	7	7	50	48	43	43

^a Conversion of glycerol. ^b Selectivities toward the different acetylated products (MAG, DAG, and TAG). ^c Experimental values. ^d Calculated values according to eqs 1–4, Table 6.

Scheme 2. Reaction of Esterification of Glycerol with Acetic Acid



and TAG are the most interesting products from a fuel-application point of view, since they can be formulated with petrol-derived fuels to improve either cold and viscosity properties (biodiesel)¹⁴ or antiknocking properties (gasoline).¹² It must be noted that MAG and DAG can include several isomers depending upon the acetylation position within the glycerol molecule. Hence, herein, the terms MAG and DAG are intended to embrace all the possible mono- and di-acetylated products, respectively. Additionally, the presence of MAG in the final reaction product is not desired due to its relatively high solubility in water. Thus, the reaction conditions have to be established with the purpose of maximizing the production of the di- and tri-derivatives.

Acetylation runs were performed in the liquid phase at temperatures ranging from 100 to 150 °C in a stirred Teflon-lined stainless-steel autoclave under autogenous pressure (with an initial nitrogen pressure of 4 bar in order to ensure the liquid phase for both

reactants). The reaction temperature was controlled using a thermocouple immersed in the reaction mixture. In order to monitor the reaction, samples were withdrawn periodically at time intervals ranging from 0 to 4 h. Typically, the weight composition of the reaction mixture was 5 g of glycerol, from 9.78 to 29.34 g of acetic acid (which acted also as a solvent), that is, from a 3:1 to 9:1 molar ratio of acetic acid/glycerol, and a constant catalyst loading of 0.2 g. Reaction samples were analyzed by gas chromatography (GC; Varian 3900 chromatograph) using a CP-SIL 8 CB column [30 m × 0.25 mm, film thickness (DF) = 0.25] and a flame ionization detector. Acetylation products were the only reaction products detected by GC. Catalytic results are shown either in terms of absolute conversion of glycerol or in terms of selectivities toward the different derivatives. In order to distinguish among the catalytic activity of different acid groups from different surface microenvi-

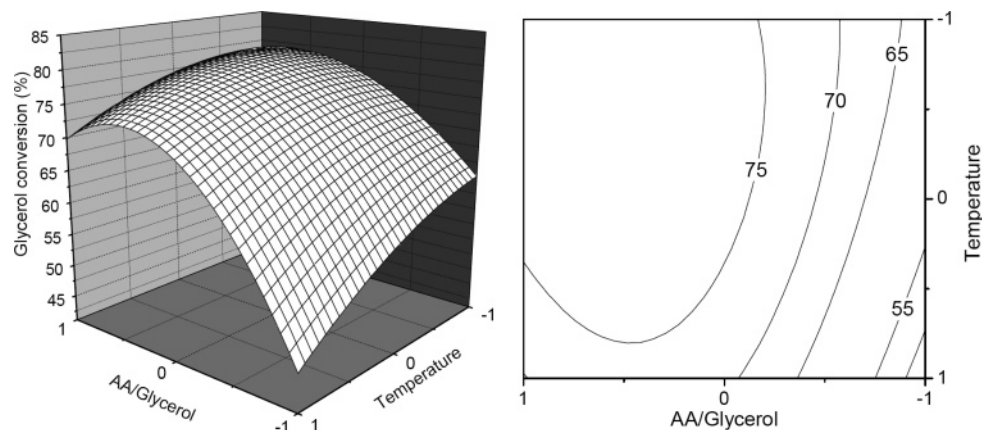


Figure 2. Response surfaces for glycerol conversion after 4 h of reaction (catalyst: Pr-SBA-15).

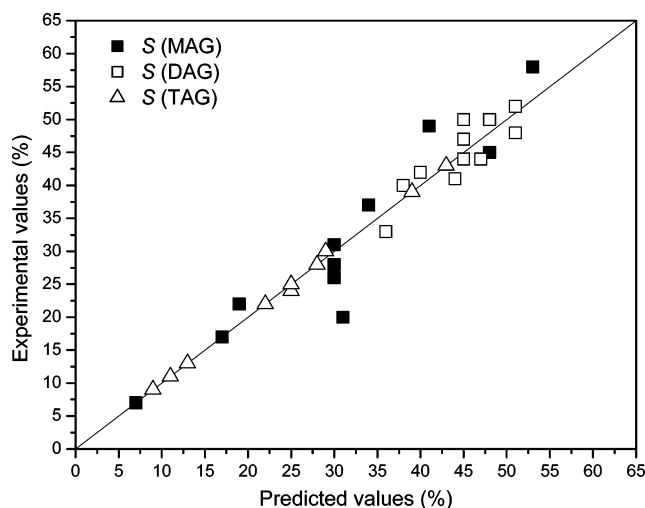


Figure 3. Accuracy of the predicted data relative to the experimental data for the selectivities to MAG, DAG, and TAG (catalyst, Pr-SBA-15; reaction time, 4 h).

Table 6. Predictive Equations Obtained by Factorial Design of Experiments

$$\begin{aligned}
 x_{\text{glycerol}} &= 76.35 + 9.78X - 2.8Y + 1.8XY - 9.22X^2 - 2.67Y^2 - 3.5YX^2 \\
 S_{\text{MAG}} &= 29.84 - 18X - 7.5Y - 4.25XY + 4.89X^2 - 3.1Y^2 + 5.25YX^2 \\
 S_{\text{DAG}} &= 44.95 + 5.33X + 3.5Y - 3.37X^2 + 2.63Y^2 - 4.75YX^2 \\
 S_{\text{TAG}} &= 25.2 + 15X + 3.5Y + 4.25XY - 1.37X^2 - 3.25YX^2
 \end{aligned}$$

ronments, a specific rate per acid site has also been utilized (millimoles of reacted glycerol per millimole of acid sites).

3. Results and Discussion

3.1. Design of Experiments. This part of the work will deal with the optimization of the reaction conditions to reach high conversions of glycerol and high selectivities to the most valuable products (DAG and TAG, Scheme 2). Preliminary experiments showed that sulfonic acid modified mesostructured materials display an acceptable catalytic performance in the esterification of glycerol with acetic acid. Thus, in order to establish the influence of the most significant reaction variables, Pr-SBA-15 (Table 3) was chosen as the system catalyst. The optimization was achieved by means of an experimental design methodology, leading to a study which has been mainly focused on the influences of the acetic acid to glycerol molar ratio and temperature (variables) on the glycerol conversion and selectivity to the different acetylated derivatives (response factors). The

selection of these two variables responds to the belief that they are the most influential parameters on an equilibrium-mediated process such as the esterification of glycerol, regardless a priori of the solid acid catalyst used.

Thus, a factorial experimental design based on 3^2 considering three different levels for each factor (X , acetic acid to glycerol molar ratio; Y , temperature) was carried out.³⁴ Low and high levels for the acetic acid/glycerol molar ratio were at a stoichiometric ratio of 3:1 and three times said stoichiometric ratio (at 9:1) for temperatures of 100 and 150 °C, respectively. Table 5 describes the factorial design of the experiments, including the codified and real experimental values selected in this work. Low and high levels are denoted as -1 and $+1$, respectively, whereas the central point is 0. The conversion of glycerol (%) and the selectivities to MAG, DAG, and TAG (%), after 4 h of reaction, were chosen as the response factors. The central point experiment (125 °C and 6:1 acetic acid/glycerol molar ratio) was repeated three times in order to check the reproducibility and obtain the standard deviation of the experimental response: glycerol conversion, $75.6\% \pm 2.1\%$; selectivity to MAG, $28.3\% \pm 2.5\%$; selectivity to DAG, $47.0\% \pm 3.0\%$; selectivity to TAG, $24.7\% \pm 0.6\%$. Therefore, it can be concluded that the experimental error corresponding to the reaction parameters shown in Table 5 is acceptable and not excessively significant.

The experimental values of the response factors, as well as the calculated values obtained from the model, are also incorporated in Table 5. From the matrix generated by the experimental data and assuming a second-order polynomial model, eqs 1–4 were obtained (Table 6) for different reaction conditions using a Levenberg–Marquard algorithm for nonlinear regression, where X and Y represent the glycerol to acetic acid molar ratio and the temperature, respectively. The magnitude of the interaction between the variables is related to the value of the coefficients of the polynomial expression used to fit the experimental data.

Values of glycerol conversion after 4 h of reaction were selected for the study of the activity of the system. Figure 1 shows the relationship between experimental and predicted values (eq 1, Table 6). As can be observed, values calculated with the predictive eq 1 are very close to those obtained experimentally. Considering the influence of the variables through the coefficients shown in eq 1, it is remarkable that the acetic acid to glycerol molar ratio (X) is the most influential factor on the glycerol conversion, whereas the temperature (Y)

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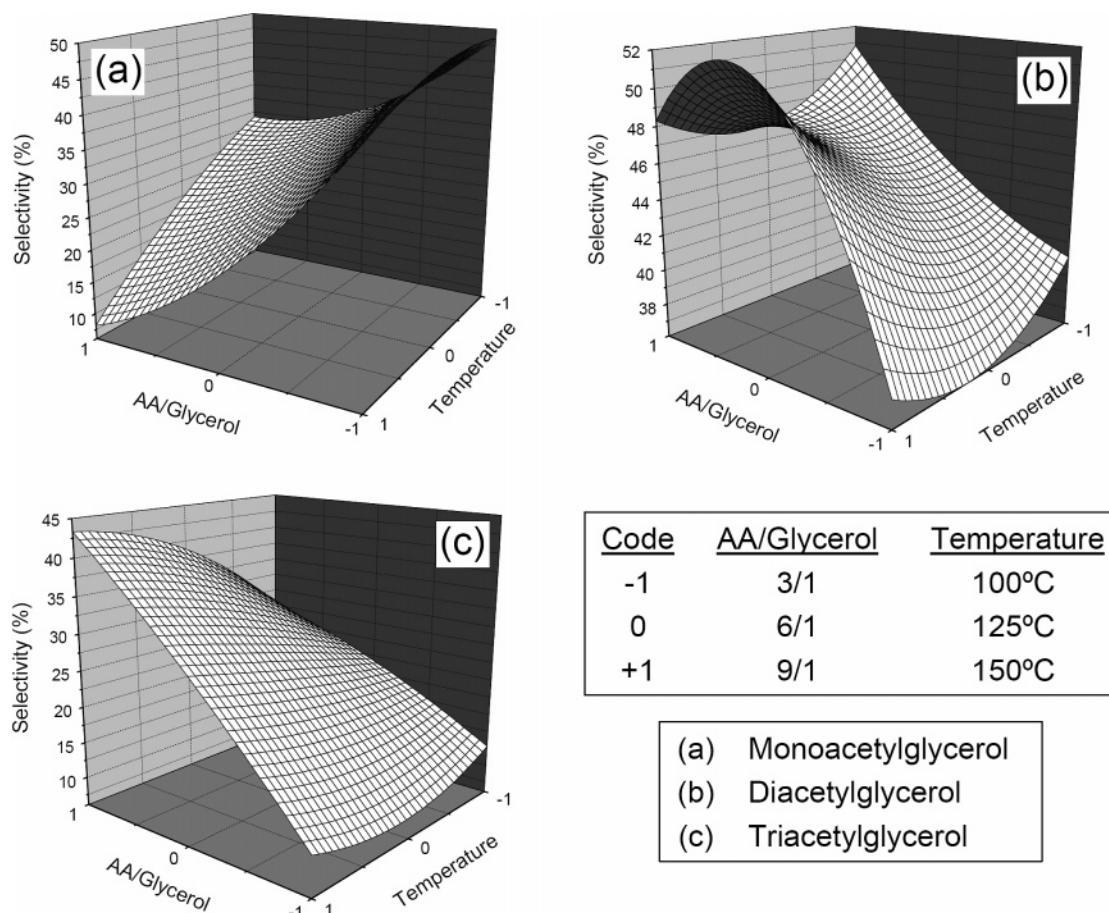


Figure 4. Response surfaces for selectivity toward the different acetylated compounds: MAG (a), DAG (b), and TAG (c) (catalyst, Pr-SBA-15; reaction time, 4 h).

remains less influential and even displays a detrimental effect evidenced by negative coefficients in eq 1. This fact can be explained in terms of thermodynamics, due to the exothermicity of esterification reactions and its effect on the equilibrium. The 3D response surface (Figure 2) clearly shows an enhanced conversion of glycerol with increasing acetic acid loadings for all the temperatures. Likewise, it must be noted that the detrimental effect of increasing the temperature is more pronounced when low acetic acid loadings are used. Thus, from the point of view of glycerol conversion, the optimal values would be the highest acetic acid/glycerol molar ratio (9:1) and low or medium temperature (100–125 °C), that is, points (+1, -1) and (+1, 0) of the experimental design.

The main object of this optimization is not only to reach maximum glycerol conversion but also maximum selectivities to the most valuable acetylated products, di- and tri-acetylglycerol. Tables 5 and 6 show the experimental selectivity values and the fitting equations, respectively, for MAG, DAG, and TAG. Figure 3 shows the relationship between experimental and predicted selectivity values (eq 2–4, Table 6). Again, values calculated with the predictive equations are relatively close to those obtained experimentally, especially in the case of the TAG.

Considering the coefficients from fitting eqs 2–4, the most influential parameters (or interactions thereof) can be deduced. Graphical representation of these equations (Figure 4) readily allows establishment of those influences. Figure 4a displays the 3D response surface corresponding to selectivity toward MAG, showing that high acetic acid to glycerol molar ratios and high temperatures result in lower selectivities to MAG, as could be expected a priori considering that high reaction conversions would favor the formation of the di- and trisubstituted deriva-

tives. Likewise, it can be deduced that the amount of acetic acid is a more influential parameter than the temperature in the formation of MAG. On the other hand, Figure 4b demonstrates that the optimal conditions for DAG production are an intermediate acetic acid to glycerol molar ratio and a high temperature. This shows clearly that both factors have nonlinear behaviors, which results in high selectivity values for both low- and high-temperature levels and for a 6:1 molar ratio. Increasing the amount of acetic acid supposes a negative effect on the selectivity toward DAG, likely due to the transformation into TAG. Finally, the selectivity to TAG is maximized using both high acetic acid to glycerol molar ratios and high temperatures (Figure 4c). Nevertheless, the most influential factor for TAG selectivity is the acetic acid to glycerol molar ratio, evidenced by the coefficients in eq 4 (Table 6). In conclusion, high reaction temperatures and acetic acid/glycerol molar ratios appear to favor the evolution of the final product distribution in equilibrium to the most substituted glycerol acetylated derivatives.

Since DAG and TAG are the most interesting products, the optimized conditions for the selectivity of the system will be those which result in the highest selectivity to these compounds. Hence, it is interesting to study the influence of reaction conditions on the selectivity toward the sum of both compounds at the same time. Equation 5 represents the experimental data fitting corresponding to the combined selectivity to DAG and TAG.

$$S_{\text{DAG+TAG}} = 69.95 + 18.17X + 7.5Y + 4.5XY - 4.87X^2 + 3.13Y^2 - 5.5XY^2 \quad (5)$$

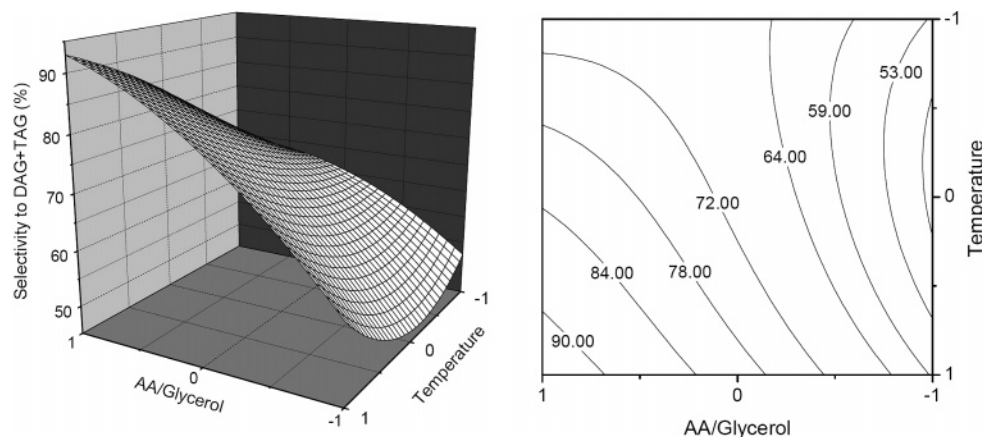


Figure 5. Response surfaces for combined selectivity toward DAG and TAG after 4 h of reaction (catalyst: Pr-SBA-15).

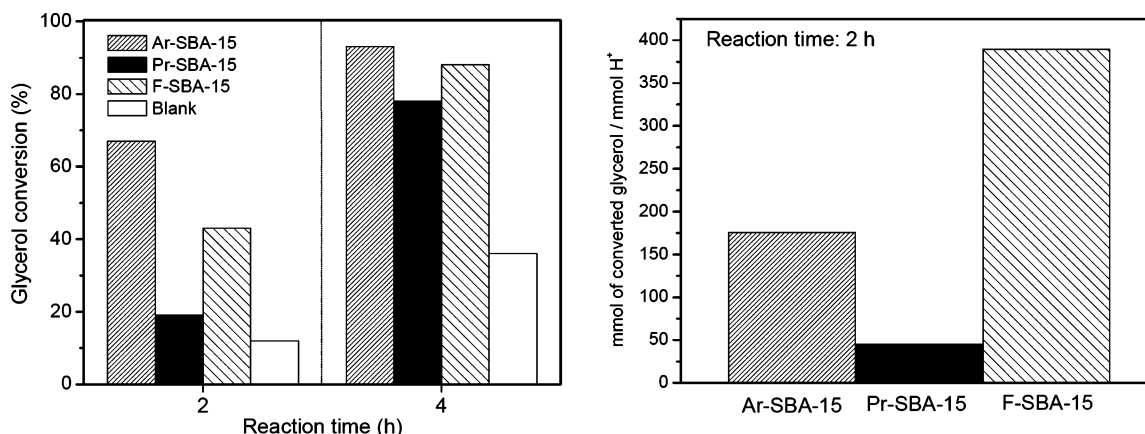


Figure 6. Glycerol conversion after 2 and 4 h of reaction (left) and specific activity per acid site after 2 h (right) over sulfonic acid modified mesostructured materials. Blank means in absence of catalyst. Temperature, 125 °C; acetic acid to glycerol molar ratio, 9:1; catalyst mass, 0.2 g.

In this case, both experimental factors (temperature and acetic acid loading) have a positive influence on the combined selectivity to di- and triacetylated products, the acetic acid to glycerol molar ratio being the predominant factor. The 3D response surfaces (Figure 5) clearly demonstrate this trend. Thus, from the point of view of products distribution, optimal reaction conditions should be established in the levels (+1, +1) of the experimental design, that is, a 9:1 molar ratio and a temperature of 150 °C.

3.2. Comparative Study of Sulfonic Acid Mesostructured Catalysts in the Esterification of Glycerol with Acetic Acid.

The feasibility of tuning the acid strength of the sulfonic acid groups incorporated within mesostructured SBA-15-type silicas by the close attachment of different moieties has been reported before.^{27,32,35} Thus, the presence of a more electron-withdrawing moiety close to the sulfonic acid group, such as a phenyl group (sample Ar-SBA-15) or a fluoro-modified group (Sample F-SBA-15), significantly increases the acid strength in comparison to microenvironments such as a propyl chain (sample Pr-SBA-15). It has been reported that this enhancement in the acid strength leads to an improvement in the catalytic activity in several acid-catalyzed reactions.^{31,36–39} Taking this into account, the catalytic performance of propylsulfonic acid modified SBA-15 has been compared with that of arenesulfonic acid modified SBA-15 and fluorosulfonic acid modified SBA-15 in the esterification of glycerol with acetic acid, using optimized reaction conditions chosen after the experimental design, i.e., intermediate temperature (125 °C) and high acetic

acid/glycerol molar ratio (9:1). In order to evaluate the progress of the reaction in the absence of solid catalyst a blank run was also carried out since the presence of a relatively large excess of acetic acid introduces another significant source of potentially catalytic protons to the mixture. As can be concluded from Figures 6 and 7, the esterification reaction occurs even in absence of a solid acid catalyst, although the glycerol conversion remains much lower than when sulfonic acid modified solids are used.

Figure 6 (left) depicts the glycerol conversion after 2 and 4 h of reaction using the three sulfonic acid modified mesostructured materials, along with the blank reaction. Particularly after 2 h of reaction, when the reaction mixture has not yet reached the equilibrium state, Pr-SBA-15 appears to be the less active solid acid catalyst. The three solids are based in well-defined hexagonal mesostructured silicas, as evidenced by their textural properties (Table 3), except for a lower surface area in the case of F-SBA-15. The acid capacities are similar for Pr-SBA-15 and Ar-SBA-15, approximately 1 mmol H⁺/g, whereas for F-SBA-15, it is as low as 0.30 mmol H⁺/g due to synthesis limitations. Thus, the low activity observed with Pr-SBA-15 may be directly attributed to the lower acid strength of propylsulfonic acid groups. Nevertheless, to get a better

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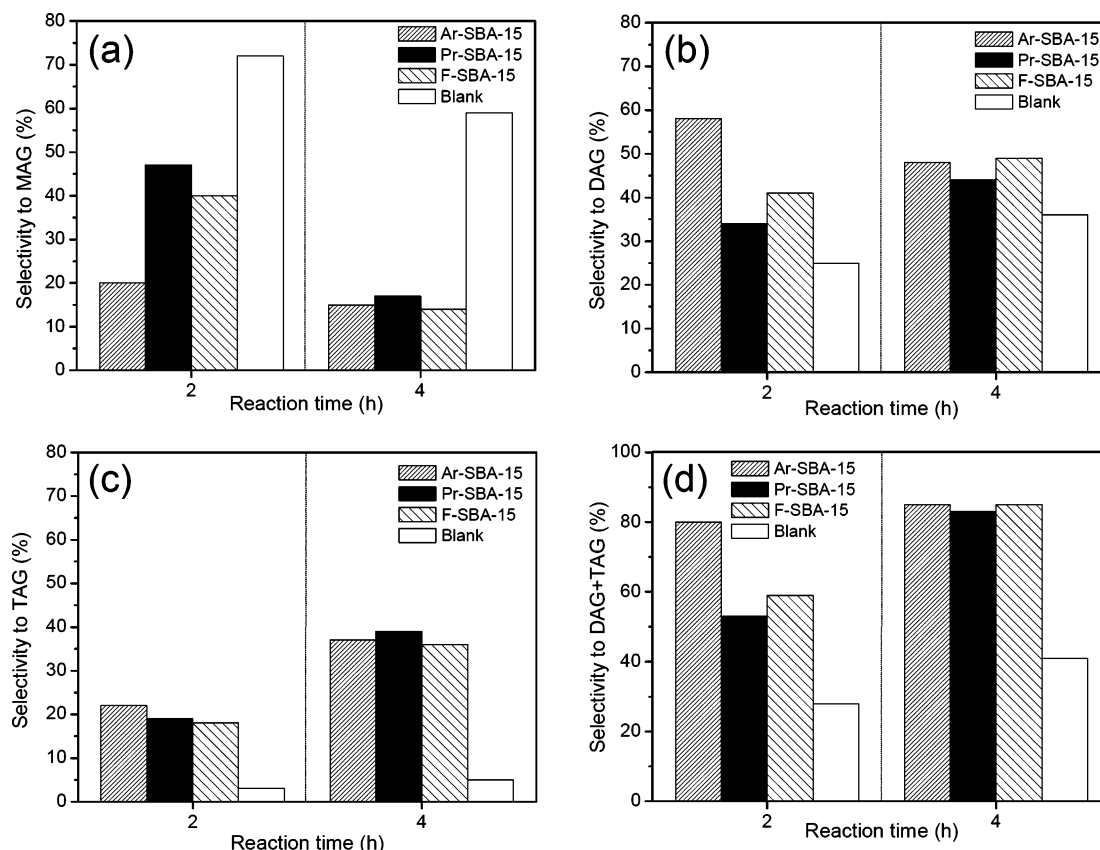


Figure 7. Selectivity toward MAG (a), DAG (b), TAG (c), and DAG + TAG (d) after 2 and 4 h of reaction over sulfonic acid modified mesostructured materials. Blank means in absence of catalyst. Temperature, 125 °C; acetic acid to glycerol molar ratio, 9:1; catalyst mass, 0.2 g.

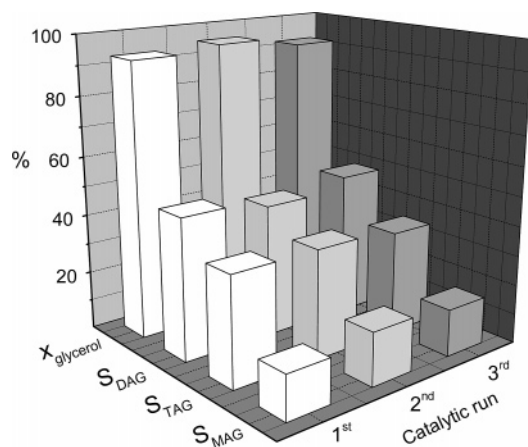


Figure 8. Catalyst reuse: glycerol conversion and selectivity to MAG, DAG, and TAG, after 4 h, in three consecutive catalytic runs reusing catalyst Ar-SBA-15. Temperature, 125 °C; acetic acid to glycerol molar ratio, 9:1; catalyst mass, 0.2 g.

comparison of the catalytic activity, Figure 6 (right) shows the specific activity per acid site during the first 2 h of reaction, that is, the millimoles of glycerol converted per acid site. The observed trend in the activity per acid center agrees with the increasing acid strength of the respective sulfonic acid groups: propylsulfonic < arenesulfonic < fluorosulfonic. In conclusion, in the esterification of glycerol with acetic acid, the acid strength is an important factor affecting the kinetics of the catalyzed reaction.

The evolution of the selectivity toward the different acetylated compounds is shown in Figure 7. It must be noted that the run without a solid acid catalyst preferentially gives the undesired MAG, displaying selectivities to MAG up to over 70% (Figure

7a). In the presence of solid acid mesostructured catalysts, as the reaction progresses, the selectivity toward MAG drastically decreases. Such a reduction is expected since MAG molecules undergo further esterification reactions to provide the di- and triacetylated products. Figure 7b shows the evolution of selectivity toward DAG, evidencing the typical behavior of an intermediate product which will further react to give TAG. Nevertheless, the different catalysts provide different evolutions of the selectivity to DAG at 2 and 4 h, likely due to kinetic phenomena inherent in the different catalytic systems. Ar-SBA-15 appears to be the most active catalyst in the transformation of DAG into TAG, as indicated by its decreasing value of selectivity to DAG with time. On the other hand, selectivity toward TAG (Figure 7c) clearly follows an increasing trend with time for all the catalytic systems, as corresponds to an end product in a serial reaction. Finally, Figure 7d shows the combined selectivity toward the most interesting products. The evolution of this combined selectivity is similar to that of the TAG, reaching high values after 4 h of reaction for the three mesostructured acid materials. At final reaction times, the influence of the type of solid acid catalyst does not seem to be significant, corresponding final selectivity values being very similar (over 80%). Thus, it appears that equilibrium phenomena are controlling the reaction after 4 h, regardless of the catalyst. However, after 2 h of reaction, the most active catalyst toward DAG and TAG is Ar-SBA-15. This enhanced activity is supposed to arise from an optimal combination of acid strength and acid capacity, which makes it a slightly more suitable solid acid catalyst for the esterification of glycerol with acetic acid than Pr-SBA-15 (high acid capacity but low acid strength) and F-SBA-15 (high acid strength but low acid capacity). Likewise, it is very interesting to note the importance of the presence of

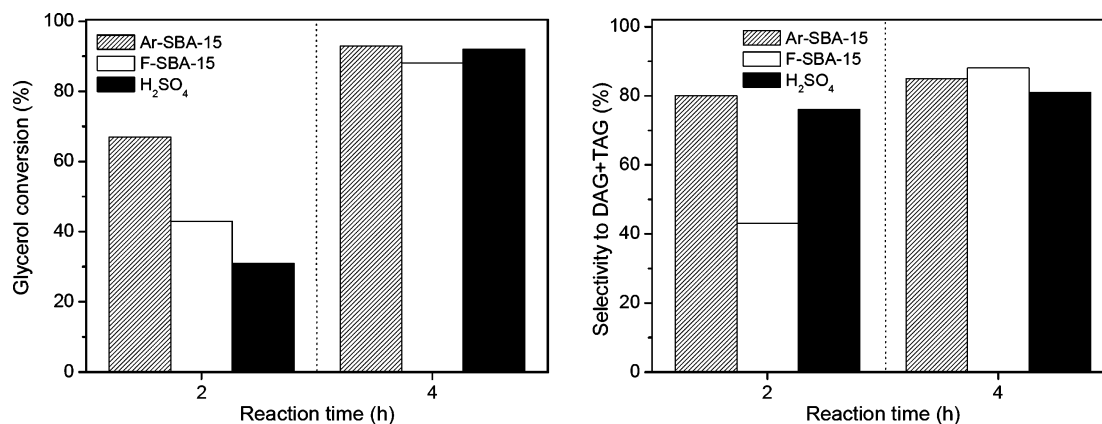


Figure 9. Glycerol conversion (left) and combined selectivity toward DAG and TAG (right) after 2 and 4 h of reaction with sulfuric acid, Ar-SBA-15, and F-SBA-15. Temperature, 125 °C; acetic acid to glycerol molar ratio, 9:1; catalyst mass, 0.2 g.

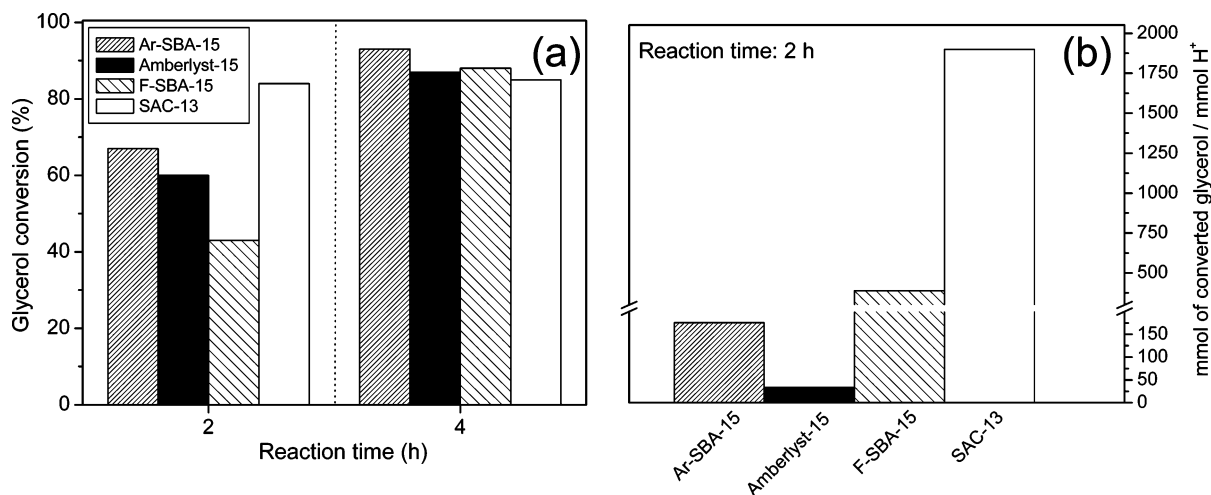


Figure 10. Glycerol conversion after 2 and 4 h of reaction (a) and specific activity per acid site after 2 h (b) over sulfonic acid resins and mesostructured materials. Temperature, 125 °C; acetic acid to glycerol molar ratio, 9:1; catalyst mass, 0.2 g.

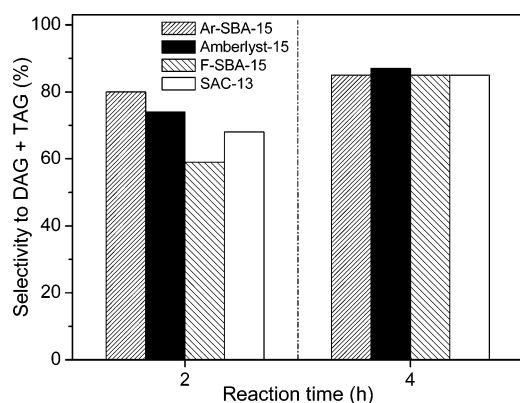


Figure 11. Combined selectivity toward DAG and TAG at 2 and 4 h over sulfonic acid resins, Ar-SBA-15, and F-SBA-15. Temperature, 125 °C; acetic acid to glycerol molar ratio, 9:1; catalyst mass, 0.2 g.

an acid catalyst to maximize the combined selectivity toward the di- and triacetylated derivatives (see blank reaction, Figure 7d).

Catalyst life has also been evaluated for the most active solid acid catalyst, Ar-SBA-15. Figure 8 depicts the results of three consecutive catalytic runs performed reusing the catalyst at the optimal reaction conditions. After each catalytic run, the catalyst was recovered by filtration, washed with ethanol and acetone at room temperature, and air-dried before being used again in a new reaction. From the results shown in Figure 8, no loss of

catalytic performance is observed either in conversion of glycerol or in product distribution after 4 h of reaction.

3.3. Comparative Study Among Sulfonic-Modified Mesostructured Materials and Commercial Sulfonic-Nature Catalysts in the Esterification of Glycerol with Acetic Acid.

Another objective of the present work is to compare the catalytic performance of the synthesized mesostructured catalysts with other sulfonic-nature catalysts, commercially available and conventionally used in acid-catalyzed processes. An effect of the type of catalyst on the reaction is expected to occur due not only to acid strength but also to porosity or pore volume limitations on the intra- and intermolecular esterification and transesterification processes, which ultimately leads to the formation of DAG and TAG.

Thus, activity and selectivity of arenesulfonic acid and fluorosulfonic acid modified SBA-15 samples (Ar-SBA-15 and F-SBA-15, Table 3), as the most catalytically efficient representatives of the synthesized solid acid catalysts, have been compared with those provided by sulfonic acid resin Amberlyst-15, perfluorosulfonic acid resin supported on silica (Nafion SAC-13), and a homogeneous catalyst such as sulfuric acid. Table 4 summarizes the main catalytic properties of these acid catalysts. All the catalytic tests were run in the optimized reaction conditions within the evaluated range (temperature of 125 °C and acetic acid to glycerol molar ratio of 9:1) and keeping a constant mass of the catalyst of 0.2 g (0.6 wt. %).

Figure 9 (left) depicts the evolution of glycerol conversion after 2 and 4 h of reaction using H₂SO₄ as a catalyst, along

with the results from Ar-SBA-15 and F-SBA-15. The liquid acid catalyst has a high acid capacity (20.4 mmolH⁺/g), and its liquid nature allows it to avoid the mass transfer limitations common when using solid catalysts. Yet, its catalytic behavior is not superior to that of Ar-SBA-15 and F-SBA-15, especially after 2 h of reaction. Likewise, selectivity to DAG and TAG after 4 h remains almost identical for the three catalytic systems (Figure 9, right), which indicates that the presence of a solid mesostructure is not hindering the molecular diffusion during the reaction process, leading in all the cases to approximately the same equilibrium distribution. Therefore, Ar-SBA-15 and F-SBA-15 are presented as feasible alternatives to conventional mineral acids in this process. Besides, it is well-known that homogeneous catalysis presents several drawbacks that should be dealt with, mainly those relating to catalyst recovery and environmental issues. On the other hand, the better catalytic performance after 2 h of reaction over Ar-SBA-15 and F-SBA-15 as compared with H₂SO₄ suggests interesting confinement effects when a sulfonic acid group is supported over a mesostructured material, which strongly affects their catalytic performance.

Sulfonic acid resins are used industrially in acid-catalyzed processes, such as the production of ethyl *tert*-butyl ether (ETBE) for gasoline formulation. Thus, they should also be considered in the transformation of glycerol to yield fuel additives. Figure 10a shows the conversion of glycerol obtained using Amberlyst-15 and SAC-13, compared with that from Ar-SBA-15 and F-SBA-15. Amberlyst-15 displays a catalytic behavior similar to that of Ar-SBA-15 and F-SBA-15, and SAC-13 provides high activities especially after 2 h of reaction. When a comparison is made in terms of specific activity per acid site after 2 h of reaction (Figure 10b), SAC-13 shows an outstanding catalytic performance which would agree with the higher acid strength of their fluorosulfonic acid sites and with an improved accessibility due to the use of a silica support. When Ar-SBA-15 is compared with Amberlyst-15, both with phenylsulfonic acid type sites, the mesostructured material clearly presents more active acid sites, mainly attributed to their better dispersion and accessibility arising from the much higher surface area of the support. Therefore, the use of a silica mesostructured framework provides the material with improved catalytic properties beyond the nature of the sulfonic acid site. Catalytic results show that fluorosulfonic acid sites are the most active acid sites among those evaluated. Additionally, when such acid sites are anchored to a resin (Nafion) and supported over high surface area silica, the esterification reaction is specially favored. The advantage of using sulfonic acid modified mesostructured materials as catalyst lies in their improved thermal stability, since at 125 °C (optimized reaction temperature) resins are working at their

thermal limit, especially in the case of Amberlyst-15, thus compromising their recovery and reuse.

Finally, regarding the distribution of products, Figure 11 shows the combined selectivity toward the di- and triacetylated derivatives when using the sulfonic acid resins, along with that of Ar-SBA-15 and F-SBA-15. As can be concluded from the figure, the selectivity of the four catalysts is similar after 4 h of reaction (over 80%), which suggests that for longer reaction times the selectivity is more influenced by the reaction conditions, which ultimately define the equilibrium products distribution, rather than the nature of acid sites.

4. Conclusions

Sulfonic acid functionalized mesostructured materials have demonstrated excellent catalytic behavior in the acetylation of glycerol with acetic acid to yield acetylated compounds with interesting properties as bioadditives for petrol fuels. Their activity and selectivity have been shown to be comparable or even superior to other conventional acid catalysts (homogeneous and heterogeneous) disclosed previously in the literature for these sorts of processes. The experimental design model carried out for different levels of temperature and acetic acid to glycerol molar ratios has shown that it is necessary to use high acetic acid excesses in order to push the equilibrium toward the simultaneous enhancement of the conversion of glycerol and the selectivity toward the most valuable di- and triacetylated derivatives. Likewise, to obtain optimal glycerol conversions, it is advantageous to work with moderate temperatures. Within the studied range, optimal conditions have been found to be a temperature of 125 °C and an acetic acid to glycerol molar ratio of 9:1. Under these reaction conditions, glycerol conversions over 90% and combined selectivities toward di- and triacetyl-glycerol of over 85% were achieved after 4 h of reaction over sulfonic acid-modified SBA-15. The acid strength of the catalytic sites has also been shown to be a determinant parameter in the catalytic performance. The use of stronger acid centers, such as those in arenesulfonic acid and fluorosulfonic acid modified mesostructured materials, provides improved catalytic results both in glycerol conversion and selectivity toward the desired products. Moreover, the catalytic performance of these sulfonated mesostructured materials was completely recovered after a mild solvent-washing regeneration step.

To settle the potential industrial applicability of these solid acid catalysts, and as a continuation of the current research, the use of crude glycerol from FAME production with true plant impurities is already under investigation.

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