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Activation and deactivation characteristics of sulfonated carbon catalysts

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Abstract

Recently, there have been reports in the literature on sulfonated carbon catalysts prepared from sugars exhibiting interesting acid catalytic properties. However, to date, little has been reported about their activation/deactivation characteristics. For this paper, the activation/deactivation behaviors of such sulfonated carbon catalysts were investigated through the esterification of free fatty acids (acetic acid and caprylic acid) and transesterification of triglycerides (triacetin, tricaprylin and soybean oil) with methanol. The catalytic properties of the sulfonated catalysts were compared with those of Nafion® SAC-13 and sulfuric acid, other similar Brønsted acid catalysts. For the liquid-phase esterification of acetic acid and transesterification of triacetin with methanol, the sulfonated carbon catalysts exhibited catalytic site activities comparable to those for sulfuric acid, along with higher (by weight) specific catalytic activities but lower initial TOFs compared with Nafion® SAC-13. Catalyst swelling was critical for catalytic activity of the sulfonated carbon catalysts. Poor swelling in the gas phase of the catalysts led to the appearance of an induction period and inferior catalytic performance in the gas-phase esterification of acetic acid. In the liquid-phase esterification of acetic acid, catalytic activity decreased during the initial reaction batch cycles but reached a plateau after several catalytic cycles at 60 °C. Elemental analysis, ^{1}H NMR results of the liquid reaction mixtures after reaction, and the decreased activity of the catalysts after extensive solvent washing suggest that the initial catalyst deactivation was caused by the leaching of polycyclic aromatic hydrocarbons containing –SO_3H groups. Cycling experiments involving large triglycerides actually showed a cumulative effect of slower catalyst swelling in the less-polar reaction mixtures moderated by deactivation of the catalyst due to leaching, resulting in increased activity in the early cycles followed by a loss of activity in later cycles.

Keywords: Sulfonated carbon catalysts; Esterification; Transesterification; Acid catalysis; Deactivation; Nafion/silica; Sulfuric acid; Swelling effects

1. Introduction

The synthesis of biodiesel from vegetable oils and animal fats through the transesterification of triglycerides (TGs) and esterification of free fatty acids (FFAs) has drawn intense attention due to energy and environmental concerns. The use of solid acid catalysts permits the simultaneous reaction of TGs and FFAs, is more environmentally friendly, and enables the design of more economical continuous processes for biodiesel production [1–3]. Recently, a new class of sulfonated carbons derived through incomplete carbonization of simple sugars has been reported to have better catalytic performance for biodiesel synthesis compared with many other popular solid acids, including Nafion, sulfonated zirconia (SZ), and niobic acid [4–8]. These relatively inexpensive catalysts are prepared using a two-step procedure: first, a natural product such as sugar, starch or cellulose is pyrolyzed in N_2, resulting in a “soft” material composed of polycyclic aromatic hydrocarbons; second, the hydrocarbon precursor is sulfonated to generate a solid with a high density of sulfonic acid sites.

Although reports on the preparation, physicochemical properties, and catalytic activity of sulfonated carbon catalysts are available in the literature, detailed studies dealing with catalyst activation and/or deactivation in acid-catalyzed esterification and transesterification have yet to be reported. In the present work, the catalyst activation/deactivation behaviors of sulfonated carbons prepared by pyrolysis and subsequent sulfonation of glucose were evaluated for the methanol esterifica-

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tion of free fatty acids (acetic acid and caprylic acid) and the transesterification of triglycerides, including triacetin (a synthetic small triglyceride-like molecule, $C_9H_{14}O_6$), tricaprylin, and soybean oil with methanol. The catalytic activities of sulfonated carbon catalysts were compared with those of Nafion® SAC-13 (Nafion resin particles supported on a porous silica matrix [9]) and H_2SO_4, which are similar in chemical functionality to sulfonated carbons [10,11].

2. Experimental

Sulfonated carbon catalysts were prepared according to the procedure described by Toda et al. [5]. Typically, D-glucose (reagent grade, Aldrich) was pyrolyzed under dry N_2 at 300–400 °C for 1–15 h. The resultant solid was ground and then sulfonated using concentrated sulfuric acid (1 g of solid/20 mL of H_2SO_4) at 150–160 °C for 13 h under a dry N_2 atmosphere. The product was then washed at least 7 times with hot distilled water until no sulfate ions were detected in the wash water. In terms of nomenclature, C400 indicates the glucose char obtained after pyrolysis at 400 °C for 1 h, C400–SO_3H indicates a catalyst that was pyrolyzed at 400 °C for 1 h and then sulfonated, and C400(15)–SO_3H indicates a catalyst that was pyrolyzed at 400 °C for 15 h and then sulfonated. The as-prepared sulfonated carbon catalysts consisted of small (<0.2 mm) black lamellar particles.

The sulfur contents of the sulfonated carbon catalysts were determined by elemental analysis using ICP (Galbraith Laboratory, Knoxville, TN). The total acid site concentrations of the catalyst samples were obtained using standard acid–base back-titration [12]. For a typical titration experiment, a 0.1 g sample was dried in air at 100 °C for at least 2 h and then reacted with 30 mL of NaOH aqueous solution (0.004 N) while stirring for 30 min at room temperature. Then a Mettler DL12 automated pH titrator was used to neutralize excess NaOH with 0.02 N HCl. BET surface area was obtained using N_2 adsorption at -196 °C in a Micromeritics ASAP 2020. Before N_2 adsorption, the catalyst samples were degassed for 3 h at 120 °C. A Scintag XDS 2000 θ/θ powder X-ray diffractometer equipped with $\mathrm{Cu}K\alpha_1/K\alpha_2$ ($\lambda = 1.540592$ and 1.544390 Å, respectively) radiation was used to collect X-ray diffraction (XRD) patterns with a step size of 0.03°. IR spectra were recorded using a Nicolet Avatar 360 FTIR spectrometer equipped with a nitrogen-purged chamber and a DRIFT attachment. Thermogravimetric analysis (TGA) was carried out in a Mettler Toledo TGA/SDTA 851 analyzer.

Catalysts were dried at 100 °C for 2 h before reaction. Autocatalysis (esterification reactions can be catalyzed by the carboxylic acid reactant [in this case, acetic acid or caprylic acid] acting as an acid catalyst) was negligible under the experimental conditions used. Initial reaction rates in the liquid phase were determined as described by Liu et al. [11]. No mass transfer limitations were observed for the liquid-phase reactions carried out under the reported reaction conditions. Commercial catalysts used in this work for comparison purposes, Nafion® SAC-13 and concentrated sulfuric acid, were obtained from Sigma–Aldrich.

Liquid-phase reactions were carried out under batch reaction conditions in a shaker reactor at an agitation rate of 225 rpm at 60 °C. Predried solid catalyst or H_2SO_4 was added to the reaction vessels after the reaction mixture reached reaction temperature. A catalyst loading of 0.025 g/mL (0.0005 g/mL for H_2SO_4) was used for the liquid-phase esterification reactions of acetic acid (HAc) (99.7 wt%, Aldrich) and caprylic acid (HCp) (99.0 wt%, MP Biomedicals) with methanol (MeOH) (99.9 wt%, Acros Organics). Tetrahydrofuran (THF, 99.9%, Sigma–Aldrich) was used as an inert solvent to fix the initial carboxylic acid and methanol concentrations at 3 and 6 M, respectively.

A catalyst loading of 0.12 g/mL (0.0005 g/mL for H_2SO_4) was used for the liquid-phase transesterification reaction of triacetin (TAc) (99.5%, Sigma–Aldrich), tricaprylin (TCp) (99%, Sigma–Aldrich), and soybean oil (SBO) (Sigma–Aldrich). THF also was used as an inert solvent to ensure initial reactant miscibility and maintain constant initial triglyceride and methanol molar concentrations (0.64 and 3.81 M, respectively).

Gas-phase acetic acid esterification was carried out in a differential fixed-bed flow reactor (0.7 cm i.d.) at 100 °C and atmospheric pressure [13]. Gaseous acetic acid and methanol were obtained from temperature-controlled liquid saturators by passing through them known flow rates of He. The reactants (acetic acid and methanol) were introduced to the reactor in equimolar ratios with a total flow rate of 120 cc/min and $P_A = P_M = 0.012$ atm ($C_A = C_M = 0.4$ mmol/L).

All the reactants and products were analyzed by gas chromatography (GC). Details of these analysis procedures have been reported elsewhere [10,13,14].

In the reaction cycling experiments, catalysts were recovered after a particular cycle by simply decanting the reaction solution and drying the used catalysts at 100 °C for 2 h between cycles. In order to identify species leached from the catalysts during reaction in the liquid phase, some reaction mixtures after reaction were analyzed using ^{1}H NMR (JEOL ECX 300, 300.5 MHz).

3. Results and discussion

3.1. Characteristics

As shown in Table 1, sulfonated carbon catalysts were prepared at different pyrolysis temperatures (300–400 °C) and pyrolysis times (1–15 h) before sulfonation. All of the sulfonated carbon catalysts exhibited similar BET surface areas, powder XRD results, IR spectra, thermal stabilities and acid site densities. For this reason, only C400–SO_3H was studied in detail for the various reactions, except where indicated. The characteristics of these carbon catalysts were very similar to those reported previously [7,8].

The acid site densities of the catalysts were determined by elemental analysis and acid–base back-titration. The acid site densities calculated from elemental sulfur analysis were 0.5–0.64 mmol H^+/g, assuming that all S atoms in the catalysts were in –SO_3H form, as proposed by Hara's group, who found only a single S 2p peak attributable to SO_3H groups at

Table 1
Preparation conditions and characteristics of sulfonated carbon catalysts

Sample	Pyrolysis temp. (°C)	Pyrolysis time (h)	BET surface area ($m^2\ g^{-1}$)	Powder XRD results	FT-IR results	TGA results (in air)	Acid site density mmol g^{-1}: total[a]/(HSO_3)[b]	HAc conversion (%) 60 °C, 1 h[c]
C400[d]	400	1	<1	Unordered carbon	Aromatic ring, aliphatic CH_3/CH_2, C=O, OH	Stable up to 400 °C	0.2/0	<1
C400–SO_3H	400	1	<1	Unordered carbon	Aromatic ring, C=O, S=O, OH(H_2O)	Stable up to 250 °C	3.7/0.64	42.7
C400(5)–SO_3H	400	5	<1	Unordered carbon	Similar to C400–SO_3H	Stable up to 250 °C	–/0.58	40.6
C400(15)–SO_3H	400	15	<1	Unordered carbon	Similar to C400–SO_3H	Stable up to 250 °C	–/0.60	39.7
C350–SO_3H	350	1	1.4	Unordered carbon	Similar to C400–SO_3H	Stable up to 250 °C	3.8/0.55	39.9
C300–SO_3H	300	1	<1	Unordered carbon	Similar to C400–SO_3H	Stable up to 230 °C	3.4/0.51	36.8

[a] Acid–base back titration. Catalyst reacted with excess 0.004 N NaOH in aqueous solution at room temperature for 30 min before neutralizing. Experimental error: ±5%.

[b] Based on elemental sulfur analysis. Experimental error ±1%.

[c] Liquid-phase esterification of acetic acid with methanol at 60 °C, with $C_{A,0} = 3$ M, $C_{M,0} = 6$ M, catalyst loading 0.025 g/mL. Experimental error ±5%.

[d] D-Glucose char, no sulfonation.

Table 2
Comparison of characteristics and liquid-phase catalytic activities of C400–SO_3H, Nafion® SAC-13, and H_2SO_4

Catalyst	BET surface area ($m^2\ g^{-1}$)	Acid density (mmol $H^+\ g^{-1}$)[a]	HAc[b]		TAc[c]	
			1-h conv. (%)	Initial TOF[d] (min^{-1})	1-h conv. (%)	Initial TOF (min^{-1})
C400–SO_3H	<1	0.64 ± 0.01	40.6	2.8	91.2	0.03
Nafion® SAC-13	221 ± 20	0.131 ± 0.003	29.8	7.3	72.3	0.10
H_2SO_4	NA	10.2[e]	–	22.8	–	0.16

[a] Based on S elemental analysis.

[b] Esterification of acetic acid with methanol at 60 °C, with $C_{A,0} = 3$ M, $C_{M,0} = 6$ M; catalyst loading 0.025 g/mL (0.0005 g/mL for H_2SO_4). Experimental error ±6%.

[c] Transesterification of triacetin with methanol at 60 °C, with $C_{TG,0} = 0.63$ M, $C_{M,0} = 3.8$ M; catalyst loading 0.12 g/mL (0.0005 g/mL for H_2SO_4). Experimental error ±10%.

[d] Based on the average rate during the initial reaction period ($<10\%$ conversion) and the acid site density.

[e] 1 mol H^+/1 mol H_2SO_4 is assumed.

168 eV for all of the sulfonated carbon catalysts in their XPS study [6,7]. The acid titration experiments demonstrated much higher acid site densities than the estimations based on sulfur elemental analysis. The higher estimated acid densities from titration are due to phenolic –OH and –COOH groups originating from incomplete carbonization of glucose [6,7]. The strong sulfonation also may oxidize aliphatic CH_3/CH_2 groups to carboxylic acid groups, which may further explain the significant increase in total acid density after sulfonation. Acid site density based on S content was chosen for TOF calculation because only the –SO_3H groups have sufficient acidity to contribute much to the reaction.

The low surface area ($<2\ m^2/g$) and high –SO_3H density of the dry sulfonated carbon catalysts indicate that most –SO_3H groups were in the bulk of the unswelled catalysts, as opposed to on the outermost surface. Otherwise, there would have been an unreasonable number of S atoms per unit surface area. Taking C400–SO_3H as an example, if all of the sulfonic groups were located on its surface, then 1 $Å^2$ would have to accommodate four S atoms, which is not possible. Thus, the "unfolding" or "swelling" of these materials in the respective reaction mixtures, thereby exposing more acid sites, must have a strong effect on catalyst activity.

3.2. Reaction activities

Table 2 compares 1-h conversions and initial TOFs for the liquid-phase esterification of acetic acid and transesterification of triacetin with methanol catalyzed by C400–SO_3H, Nafion® SAC-13, and sulfuric acid. No pretreatment except drying the solid catalysts at 100 °C was carried out before the catalysts were added into the reaction mixtures. The initial TOF (conversion $<10\%$) calculation for both C400–SO_3H and Nafion® SAC-13 assumed that –SO_3H groups were the only catalytically active sites present and that all of the –SO_3H groups were accessible to reactants. As expected, esterification was faster than transesterification. The TOFs for the esterification and transesterification on these two catalysts were comparable (within a factor of 3–7) to that estimated for sulfuric acid. The sulfonated carbon catalyst exhibited higher activity on a weight basis (% conversion) than Nafion® SAC-13, most likely due to the higher acid site density of the carbon catalyst. However, the initial TOFs of Nafion® SAC-13 were about 1.6 and 2.3 times greater than those of C400–SO_3H for the liquid-phase esterification of acetic acid and the transesterification of triacetin, respectively.

Calculation of TOFs provides a comprehensive way to compare catalysts. However, calculated TOF values are meant only to provide the best form of intrinsic rate available; the reader is cautioned to not attempt to interpret these values as true site activities [15]. The higher initial TOF for Nafion® SAC-13 may have been due to the high acid site strength of Nafion® SAC-13 thanks to the strong electron-withdrawing α-CF_2-polymer moiety. It has been suggested that the Nafion resin has a similar acid strength to H_2SO_4, estimated by Hammett H_0 values ($-H_0 \sim 12$) [16]. The estimated acidity of the sulfonated carbons determined by diffuse reflectance spectroscopy (pKa in the range of -11 to -8) is weaker than that of Nafion but still comparable to that of H_2SO_4 [6]. Another, even more likely reason for the lower initial TOF for C400–SO_3H may be the initial reduced accessibility of the reactants to the acid sites. As mentioned earlier, most –SO_3H groups are in the bulk of the unswelled carbon catalyst, and it is likely that some of the active sites are not available for the reactants at the beginning of the reactions. This is not a problem for Nafion® SAC-13, because the well-dispersed nanoparticles of Nafion require minimal swelling.

3.3. Catalyst activation

To examine the impact of catalyst swelling on initial catalyst activity for sulfonated carbon catalysts, C400–SO_3H and Nafion® SAC-13 was studied for the gas-phase esterification of acetic acid with methanol, because it is known that swelling does not readily occur in a dry atmosphere. Fig. 1 compares the conversion rate of gas-phase acetic acid esterification at 100 °C catalyzed by C400–SO_3H and Nafion® SAC-13. At steady state, the methyl acetate formation rate was 5 times greater on Nafion® SAC-13 than on C400–SO_3H. This result is contradicts what was observed in the liquid phase for acetic acid esterification, where, on a per weight basis, C400–SO_3H demonstrated better catalytic activity than Nafion® SAC-13. The difference in the performance of C400–SO_3H in the liquid phase versus in the gas phase for acetic acid esterification provides evidence that catalyst swelling is important for the catalyst activity of sulfonated carbons. Unlike Nafion® SAC-13 (which consists of nanoparticles of Nafion dispersed on SiO_2), in which sulfonic groups are available for reaction without the need for swelling [11], reactants in the gas phase would appear to have limited access to the active sites in the bulk of the sulfonated carbon catalyst, resulting in its inferior catalytic performance in the gas phase. As can be seen in Fig. 1, the induction period observed for C400–SO_3H should also be taken as an indication that limited swelling occurs with TOS, exposing more sulfonic sites to gaseous molecules, probably by reactant condensation or gradual surface wetting.

The study of gas-phase reaction provides a tool for evaluating the properties of catalysts in a "dry" environment. Sun et al. used the uptake rate of 2-propanol to relate the swelling and acid site accessibilities of Nafion/Silica, Nafion NR-50, and Amberlyst-15 in the gas phase and found that both Nafion NR-50 and Amberlyst-15 reached saturation much slower than supported Nafion [17]. Our gas-phase reaction served the same purpose, and the much lower activity and the induction period for the carbon catalyst indicated poor swelling in the gas phase. Although swelling was much faster in the liquid phase, we must note that the swelling of the sulfonated carbon materials may have affected our calculation of TOFs, because that calculation was based on initial reaction rates and the assumption that all –SO_3H sites were available for reaction at the beginning of the reaction. Since many active sites still may have been blocked in the "bulk" of the catalyst at the beginning of the reaction, it is uncertain how long it took for the "swelling" process to make all of the sites completely accessible to reactants. Thus, the TOF values provided here for C400–SO_3H must be considered a lower-limit estimation. Also noteworthy in this regard is that, whereas the initial TOFs for C400–SO_3H for both liquid-phase esterification and transesterification were lower than those of Nafion® SAC-13 (Table 2), overall conversions of the reactions using C400–SO_3H were significantly greater.

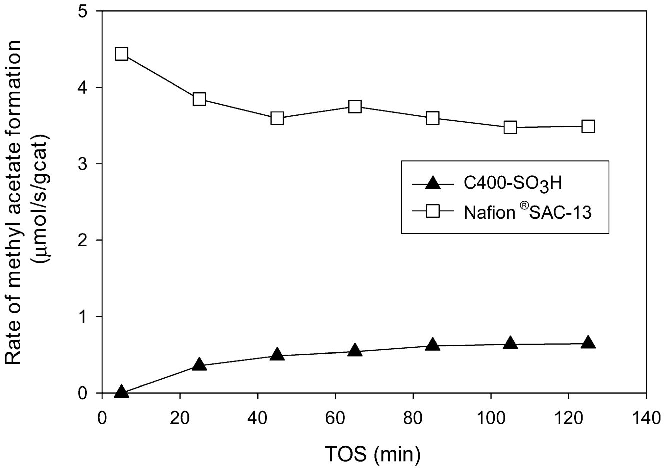
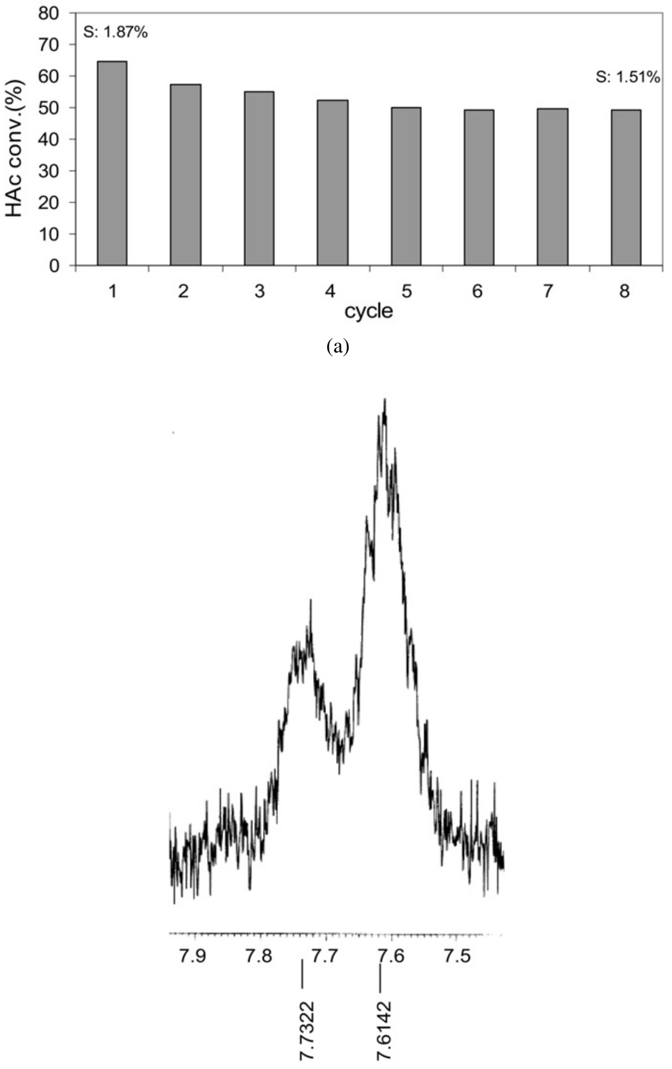


Fig. 1. Rate of methyl acetate formation at 100 °C in gas-phase esterification of HAc with MeOH catalyzed by C400–SO_3H and Nafion® SAC-13 (total flow rate 120 cc/min, $P_A = P_M = 0.012$ atm, $C_A = C_M = 0.4$ mmol/L).

3.4. Deactivation

A series of 3-h acetic acid esterification reaction cycles were carried out in the liquid phase with C400(5)–SO_3H to evaluate catalyst deactivation. Fig. 2a illustrates the acetic acid conversion in each cycle after a 3-h reaction. The figure shows that catalytic activity decreased notably during the first 5 reaction cycles but remained essentially stable thereafter.

To illuminate the causes for catalyst deactivation during the first 5 reaction cycles, ^1H NMR analysis was conducted on the reaction mixture after the first reaction cycle following removal of the catalyst. As shown in Fig. 2b, several weak peaks occurred around 7.4–7.8 ppm, characteristic of polycyclic aromatics [18,19], suggesting dissolution of trace amounts of moieties from the catalyst in the reaction mixture. In addition, elemen-



(a)

(b)

Fig. 2. (a) C400(5)–SO_3H deactivation during multiple 3-h reaction cycles of esterification of HAc with MeOH at 60 °C ($C_{A,0} = 3$ M, $C_{M,0} = 6$ M; catalyst loading = 0.025 g/mL); (b) ^1H NMR spectrum of reaction mixture after the first reaction cycle.

tal analysis of the fresh and used catalysts showed that the weight percent of S in C400(5)–SO_3H decreased from 1.87 to 1.51% after eight 3-h reaction cycles, confirming the leaching of S-containing moieties during reaction at 60 °C. Similar ^1H NMR spectra were also obtained from reaction mixtures after reaction on other sulfonated carbon catalysts studied in the present work (data not shown).

Because preliminary studies suggested that methanol might be the cause of S leaching, fresh sulfonated carbon catalysts were washed using methanol at 60 °C in the shaker reactor at 225 rpm for 1 day. After retrieval by filtration and drying, these catalysts were used for the esterification of acetic acid with fresh methanol. As indicated in Fig. 3, 1-h HAc conversions for all of the methanol prewashed catalysts were 12–20% lower than those for the unwashed fresh catalysts, indicating that deactivation is a common problem for all of the sulfonated catalysts.

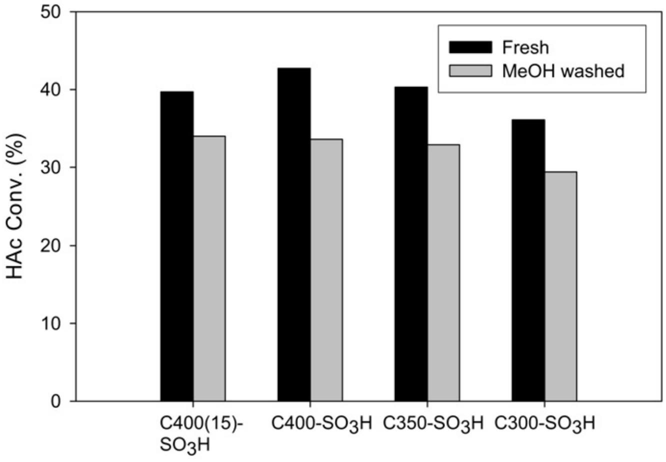


Fig. 3. Catalytic activities of fresh and MeOH-washed sulfonated carbon catalysts for 1-h esterification of HAc with MeOH at 60 °C ($C_{A,0} = 3$ M, $C_{M,0} = 6$ M; catalyst loading = 0.025 g/mL; pretreatment: a mixture of 0.05 g catalyst and 3 g methanol was stirred at 60 °C for 24 h before the catalyst was retrieved).

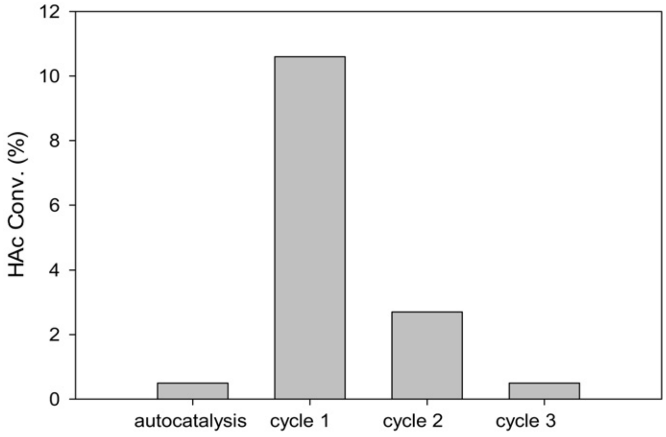


Fig. 4. Conversion of HAc during 1-h esterification with MeOH used previously to wash the C400–SO_3H catalyst at 60 °C ($C_{A,0} = 3$ M, $C_{M,0} = 6$ M; no catalyst added). Autocatalysis measurement was made without preexposure of the methanol to the catalyst.

To determine whether the leached polyaromatic species, as observed by ^1H NMR, had acidic–sulfonic groups-capable of catalysis, C400–SO_3H (0.05 g) was washed with fresh methanol (4 g) for 1 day at 60 °C, after which the catalyst was separated from the methanol by filtration and the recovered methanol saved for the reaction. The washing procedure using the same catalyst was repeated three times, and the methanol saved during these washings was used in a 1-h esterification reaction with acetic acid with no added catalyst. As shown in Fig. 4, the methanol from catalyst washing was active in catalyzing the esterification of acetic acid, indicating that catalytic active species leached into the methanol during the washing procedure. However, the acetic acid conversion with the methanol from the third washing step was close to that for autocatalysis, suggesting that the leaching of the active species of the sulfonated carbon catalyst at 60 °C eventually effectively stopped. This observation is consistent with the trend toward deactivation of the sulfonated carbon catalyst for the esterification of acetic acid (Fig. 2a), with activity becoming stable after 5 reaction cycles. Similar results were obtained from acetic acid esterification reactions with methanol pretreated using other sulfonated carbon catalysts studied in the present work.

Leaching of active sites was also observed in solvents other than methanol (e.g., ethanol, water, hexane). Thus, our findings contradict previous reports claiming that sulfonated carbons as prepared here are insoluble in solvents including water, methanol, ethanol, and benzene [7]. The solubility of solid polycyclic aromatic hydrocarbons (PAH) has been studied extensively in various solvents over a wide range of temperatures and pressures [20–25]. Researchers have suggested that certain PAHs are not totally insoluble in common solvents; for instance, the experimental solubility in water of 2-to-5-ring PAHs at 25–225 °C is about 10^{-11} to 10^{-3} (mol fraction) [20]. It should be expected that functionalization of loosely bonded PAH moieties with highly polar and hydrophilic sulfonic groups would only increase their tendency toward solubility in polar media, where further stabilization in solution can occur through hydrogen bonding. However, it is evident that although initially some leaching of active species occurs, the activity of the sulfonated carbons after several cycles apparently reaches a stable state at 60 °C. Thus, most active sulfonic sites do indeed appear to remain on the solid catalyst phase. In fact, based on calculations of the sulfur content of fresh and used catalysts, and of the catalyst activity for liquid-phase acetic acid esterification before and after extensive solvent washing, we have estimated that around 75–80% of catalytic sites in a freshly prepared sulfonated carbon catalyst remain on the catalyst and are not readily leached out under the reaction conditions used in this study.

3.5. *Combined effects*

Our results using the esterification of acetic acid as a probe reaction for the catalytic characteristics of sulfonated carbons somewhat contradict what has been reported by other authors. For instance, the activity of sulfonated carbon has been reported to remain unchanged and in some instances even increase with reaction cycles for the esterification of oleic and stearic acid with ethanol at 80 °C [5,6]. To investigate these seemingly contradictory results, we studied the effect of molecule size (and hydrophobicity) on the reaction during multiple cycles. Acetic and caprylic acids were used for esterification with methanol, and triacetin, tricaprylin, and soybean oil were used for transesterification with methanol. We observed an activity increase with esterification reaction cycles when using caprylic acid but a decrease when using acetic acid (Fig. 5a). We also found a similar trend to that observed for esterification (acetic acid vs caprylic acid) for transesterification reactions using triglycerides (Fig. 5b). For instance, we found no induction period during three consecutive reaction cycles for reactions using triacetin, finding only a small decrease in conversion; however, when using larger triglycerides, such as tricaprylin and soybean oil, we could clearly see that the activities were higher in the second cycle than in the first cycle. (Note that for the soybean oil case, the induction period for catalytic activity continued into the third reaction cycle.)

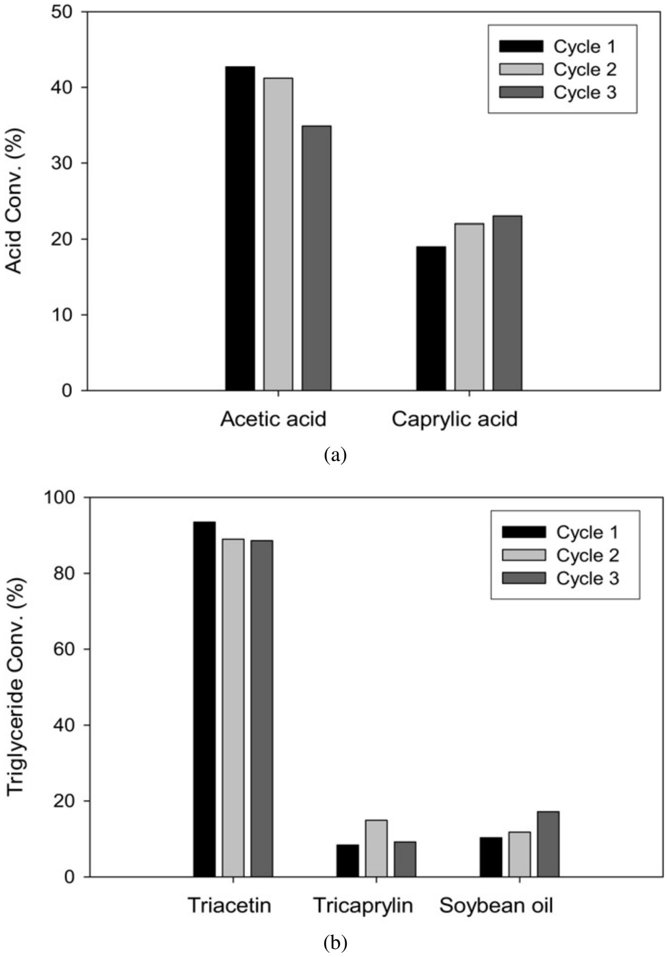


Fig. 5. C400–SO_3H activity during three reaction cycles of (a) esterification of HAc and of HCp, and (b) transesterification of TAc, of TCp and of SBO with MeOH at 60 °C (esterification: $C_{A,0} = 3$ M, $C_{M,0} = 6$ M; catalyst loading 0.025 g/mL; 1 h reaction; transesterification: $C_{TG,0} = 0.64$ M, $C_{M,0} = 3.85$ M; catalyst loading 0.12 g/mL; 10 h reaction).

It is well known that the nature of swelling agents affect their diffusion and swelling efficiency in polymers [26,27]. Similar swelling effects appear to be applicable here for the sulfonated carbon catalysts. Compared with smaller and more hydrophilic molecules like acetic acid and triacetin, larger and more hydrophobic reacting species like caprylic acid and soybean oil seem to be poorer swelling agents, leading to an induction period (requiring several cycles) related to the catalyst "swelling" requirement as discussed earlier for gas-phase reactions. As a result, cycling experiments actually show the cumulative effect of catalyst swelling with consecutive cycles moderated by deactivation of the catalyst due to leaching.

4. Conclusion

A series of sulfonated carbon catalysts was prepared by the pyrolysis of D-glucose followed by sulfonation. Their catalytic nature and deactivation were investigated through the esterification (acetic acid and caprylic acid) and transesterification (triacetin, tricaprylin, and soybean oil) with methanol in the liquid phase, and the esterification of acetic acid with methanol in the gas phase. For the liquid-phase esterification of acetic acid and transesterification of triacetin with methanol, the sulfonated carbon catalyst exhibited comparable catalytic activity during a 1-h reaction cycle to that for sulfuric acid and higher specific (by weight) catalytic activity but lower initial TOF compared with Nafion® SAC-13. Catalyst swelling was critical for the activity of the sulfonated carbon catalysts and appeared to greatly affect their initial activity even in liquid-phase reactions. Poor catalyst swelling in the gas phase led to an induction period and reduced catalyst activity in HAc esterification.

The results of our deactivation studies indicate that leaching of active species substantially affected catalyst activity. Results from our solvent washing experiments, ^{1}H NMR measurements, and elemental analyses suggest that the observed catalyst deactivation was caused by the leaching of polycyclic aromatic hydrocarbon-containing $-SO_3H$ groups, especially in polar media. The cycling experiments for both esterification and transesterification clearly showed the cumulative effect of catalyst swelling moderated by deactivation of the catalyst due to leaching, which for the larger and more hydrophobic reacting species caused an apparent initial increase in activity with reaction cycle, as has been reported previously.

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