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Stability of sulfated zirconia and the nature of the catalytically active species in the transesterification of triglycerides

Kaewta Suwannakarn, Edgar Lotero, James G. Goodwin Jr. *, Changqing Lu

Department of Chemical and Biomolecular Engineering, Clemson University, Clemson, SC 29634, USA

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Abstract

Sulfated zirconia (SZ) exhibits remarkable activity for various hydrocarbon reactions under mild conditions and is of interest for biodiesel synthesis. Nevertheless, to date no detailed study has addressed its activity and stability in liquid polar media such as alcohols, although a number of papers have suggested the possibility for some sulfur leaching. This paper presents an investigation into the activity and stability of a commercial SZ catalyst for the liquid-phase transesterification of triglycerides at 120 °C. The kinetics of tricaprylin (TCP) transesterification with a series of aliphatic alcohols (methanol, ethanol, and *n*-butanol) were investigated at 120 °C and 6.8 atm in a Parr batch reactor. It was found that the catalytic activity for TCP conversion decreased as the number of carbons in the alkyl chain of alcohol increased, most likely as a result of increased steric hindrance. The SZ catalyst exhibited significant activity loss with subsequent reaction cycles. The characterization of used catalysts after their exposure to various alcohols at 120 °C showed that the SO_4^{2-} moieties in SZ were permanently removed. The SO_4^{2-} species were leached out, most likely as sulfuric acid, which further reacted with alcohols to form monoalkyl and dialkyl sulfate species, as demonstrated by ^{1}H NMR studies. This was in essence the main route for catalyst deactivation. Our findings conclusively demonstrate for the first time that in alcoholic-liquid media at higher temperatures, SZ deactivates by leaching of its active sites, most likely leading to significant homogeneous rather than heterogeneous catalysis.

Keywords: Transesterification; Triglycerides; Tricaprylin; Sulfated zirconia; Deactivation; Leaching

1. Introduction

The transesterification of triglycerides, often called alcoholysis, involves the reaction of triesters of glycerol with an alcohol to form alkyl esters and glycerol. This reaction has been the subject of extensive research due to the diverse uses of its products, including in the synthesis of polyester or PET in the polymer industry [1], synthesis of intermediates for the pharmaceutical industry [2], curing of resins in the paint industry [3], and synthesis of biodiesel in the alternative fuel industry [4–7]. The synthesis of biodiesel, for instance, has been a focus of much recent research on triglyceride transesterification, because of the need to replace fossil fuel energy sources with renewable biofuels amid concerns about greenhouse gas emissions. For biodiesel synthesis, transesterification of fats or oils containing mainly triglycerides is performed to reduce the viscosity, producing a biofuel (fatty alkyl esters) that can substitute for petroleum-based diesel fuel without the need for engine modifications.

Transesterification can be catalyzed by both bases and acids. Although the reaction rate of alkali-catalyzed transesterification has been reported to be 4000 times faster than that using acids [5], the use of base catalysts for biodiesel synthesis necessitates refined feedstocks with low content of water (<0.5 wt%) and fatty acids (<1 wt%), which in the long run increases the cost of biodiesel production. This is apparent with the use of virgin vegetable oils (3–6 wt% fatty acids), which forces the use of higher amounts of the homogeneous base catalyst (some catalyst is lost in the neutralization of the free fatty acids), producing additional waste (soap) and complicating product separation. Thus, for feedstocks with high amounts of free fatty acids, acid catalysis is preferable to base catalysis, because it

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* Corresponding author. Fax: +1 864 656 0784.
E-mail address: jgoodwi@clemson.edu (J.G. Goodwin).

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allows for the simultaneous esterification of free fatty acids and transesterification of triglycerides under the appropriate reaction conditions without the formation of soap [7–9].

Industrial processes generally prefer solid catalysts for chemical transformations because of their easy separation from any reaction mixture. In addition, solid catalysts have the potential to be regenerated and are environmentally benign, allowing their multiple reuse with little waste released to the environment.

Among solid acid catalysts, sulfated zirconia (SZ) has received considerable attention over the last 20 years due to its strong acid properties [10–12]. For instance, SZ has demonstrated very high activity for various hydrocarbon reactions at mild temperatures (e.g., alkane isomerization), even though it deactivates rapidly due to coke deposition [11,12]. Much research has been devoted to modifications of SZ to improve its resistance to deactivation in gas-phase reactions [11]. The nature of the active sites on SZ has been extensively studied for hydrocarbon transformations [13–15]; for example, Lercher et al. [16] showed that the covalent sulfate species on SZ responsible for high catalytic activity for *n*-butane isomerization at 100 °C were easily removed by free water at room temperature. However, only limited information exists about the activation–deactivation behavior of SZ for reactions in anhydrous polar liquid media, such as alcohols.

In liquid-phase reactions, SZ has demonstrated significant activity in the esterification of acetic acid with *n*-butanol at 75 °C [17]. According to those authors, SZ could be completely regenerated after a simple calcination at 550 °C. Similar results were reported by Kiss et al. [18] for the esterification of dodecanoic acid with 2-ethyl-hexanol at 160 °C. Those authors showed that catalyst activity dropped to only 90% of its original value after five consecutive runs, but SZ activity could be restored by recalcination at 650 °C. In contrast to these previous reports, Jitputti et al. [19] used SZ for the transesterification of crude palm kernel oil with methanol at 200 °C and obtained remarkably high yields; however, the spent catalyst was fully deactivated and could not be reused. Those authors proposed that catalyst deactivation was due to a combination of catalyst leaching and the blocking of active sites by reactants and/or products. The same conclusion was drawn by Ni and Meunier for the use of SZ in esterification of palmitic acid and methanol at 60 °C [20]; however, they provided no evidence to support this hypothesis.

In the present work, we studied the use of SZ in the acid-catalyzed alcoholysis of triglycerides using a model triglyceride compound, tricaprylin (TCP), and three low-molecular-weight alcohols (methanol, ethanol, and *n*-butanol). Tricaprylin, which has the same chemical functionality as other triglyceride molecules, can be obtained in a pure form, unlike the larger triglycerides. In addition, it has been shown that there is little difference in rates for triglycerides as large as tricaprylin or larger [21]. By using a pure model compound like tricaprylin, we were able to gain some fundamental insight into triglyceride transesterification. For the first time, special attention has been given to the issue of catalyst deactivation in alcoholic condensed media at temperatures above 100 °C, conditions that most likely will be required for the use of solid acid catalysts in biodiesel synthesis.

2. Experimental

2.1. Materials

A sulfated-doped zirconium hydroxide precursor (XZO 1249/01) was kindly provided by Magnesium Electron Inc. (Flemington, NJ). The sulfated zirconia catalyst was prepared by calcining the parent-doped hydroxide under static air at 600 °C for 2 h. After calcination, the solid was kept in a desiccator until further use.

Glyceryl trioctanoate (Tricaprylin, with >99% purity as reported by the supplier) was purchased from Sigma–Aldrich. Anhydrous methanol (99.8%), ethanol (99.5%), and *n*-butanol (99.4%) were purchased from Fisher Scientific. Methyl caprylate (99%, Aldrich), ethyl caprylate (99%, Aldrich), and glycerol (99%, Acros) were used as reference compounds for GC calibration. All analytical chemicals were chromatographically pure and used without further purification. Hexane and ethyl acetate of HPLC grade were obtained from Fisher Scientific. These were mixed in a volume ratio of 1:1 and used as solvent for GC analysis.

2.2. Catalyst characterization

The sulfur content of the fresh calcined and spent SZ samples was analyzed by Galbraith Laboratories, Inc. (Knoxville, TN). Thermogravimetric analysis (TGA) was carried out using a Pyris 1 analyzer (Perkin–Elmer) to characterize sulfur content in the catalyst. Under a nitrogen flow of 20 mL/min, the temperature was first stabilized at 30 °C for 1 min and then ramped to 1000 °C at 10 °C/min. The surface area of the calcined SZ catalyst was determined by N_2 BET analysis using a Micromeritics ASAP 2010. The crystallinity of the calcined SZ powder was analyzed by a Scintag XDS 2000 diffractometer using Cu$K\alpha$ radiation with a wavelength of $\lambda = 1.54$ Å. NH_3 TPD was used to estimate the acid strength and site concentration of SZ, as described previously [22].

2.3. Reaction study

The transesterification of tricaprylin (TCP) with methanol (MeOH), ethanol (EtOH), and *n*-butanol (BuOH) was carried out at 120 °C in a Parr 4590 batch reactor consisting of a stainless steel reactor vessel, a glass liner, a four-bladed pitched turbine impeller, and a thermocouple. To ensure that most of the reactants were in the liquid phase, the reactor was initially pressurized at 6.8 atm (0.68 atm higher than the vapor pressure of methanol at 120 °C). The typical molar ratio of alcohols to tricaprylin was 12:1. The catalyst concentration was 10 wt% based on the weight of the tricaprylin. While the amount of the catalyst and the tricaprylin was kept constant throughout the study, the total volume of the reaction mixture was changed depending on the alcohol used. For the reaction startup, the catalyst was initially charged into the reactant mixture at room temperature, after which the reaction mixture was pressurized and heated to the desired temperature at 120 °C over 7 min. Finally, the stirrer speed was increased to 2138 rpm; this point was taken as time zero for the reaction. The sampling method was described previously [23]. In brief, at particular times of reaction, 0.15-mL sample aliquots were withdrawn from the reaction mixture using a microscale syringe with a pressure-lock button. The reaction sample was immediately mixed with 0.8 mL of solvent (hexane:ethyl acetate = 1:1 v/v) at room temperature, followed by centrifuging to separate out any catalyst particles. Then 40 µL of homogeneous liquid was withdrawn and further diluted in 5 mL of solvent containing a known amount of methyl laurate (an internal standard), followed by GC analysis. Sample analysis using a Hewlett–Packard 6890 gas chromatograph followed the same procedure as described previously [23].

2.4. Catalyst leaching

Because a possible cause of catalyst deactivation is the leaching of active catalyst species (especially sulfur) into the solution, we investigated changes in sulfur content of the catalyst under the experimental conditions described earlier. To estimate the degree of sulfur leaching, because a preliminary study had indicated that the alcohol was the facilitator, a sample of the fresh calcined SZ was contacted with MeOH, EtOH, and BuOH at 120 °C and 6.8 atm under constant stirring. After 2 h, the resulting solutions were centrifuged and filtrated to remove the solid catalyst. Then the solutions were used for reaction without any catalyst. The pH and the acidity of the filtrate were measured by titration with 0.05 M NaOH, using a pH meter combined with phenolphthalein as a colorimetric indicator.

3. Results and discussion

3.1. Catalyst characterization

The fresh calcined SZ contained 1.73 wt% of sulfur (ICP method; Galbraith Laboratories Inc.). This result was consistent with sulfur content (1.74 wt% of sulfur) determined by TGA using N_2. N_2 BET analysis demonstrated a specific surface area (S_{BET}) of 155 m^2/g. Analysis of the N_2 adsorption isotherm at -196 °C showed mesopores of about 4 nm and a pore volume of 0.15 cm^3/g. The acid site concentration determined by NH_3 TPD was 105 ± 12 µmol/g. X-ray diffraction of the SZ powder showed exclusively the tetragonal phase of ZrO_2.

3.2. Reaction studies

All experiments were conducted using a catalyst particle size of 89–104 µm and a stirrer speed of 2138 rpm. Mass transfer limitations could be ruled out, as discussed previously [24,25]; as a result, all of the measured reaction rates can be considered reaction-controlled.

To exclude contributions from potential noncatalytic reactions, blank transesterification reactions of TCP with the three different alcohols were carried out at 120 °C and 6.8 atm in the absence of the catalyst. Negligible activity (<0.6% TCP conversion after 2 h) was observed in all cases. With the catalyst in place, at time zero (after the startup period), about 5% TCP conversion was observed. The evolution of catalytic activity over time for TCP transesterification with MeOH, EtOH, and BuOH at 120 °C is shown in Fig. 1. All reactions demonstrated 100% selectivity to the corresponding ester products. The reaction using MeOH showed the highest activity, with 84% TCP conversion at 2 h. Under the same reaction conditions, the conversions of TCP using EtOH and BuOH were only 45 and 37%, respectively, at 2 h TOS. A similar trend also has been reported for the transesterification of rapeseed oil with various alcohols under supercritical conditions [26], suggesting that the lower reaction rates obtained with EtOH and BuOH are due in part to steric hindrance effects of the larger alkyl chains in these alcohols [27,28]. It should be noted, however, that triglyceride conversion did not decrease proportionately to alkyl chain length; a greater effect on the relative triglyceride conversion was observed when the chain length changed from C_1 to C_2 than when it changed from C_2 to C_4, although for the latter case the chain length increase was also twice as great. Similar observations have been reported for the esterification of carboxylic acids with different chain lengths with methanol using a homogeneous acid catalyst [29]. As suggested for carboxylic acids with different chain lengths, the tendency toward similar conversion profiles with increasing alcohol chain length is probably the result of “conformational leveling” effects wherein large alkyl moieties assume conformations that counteract the contribution of steric hindrance [29].

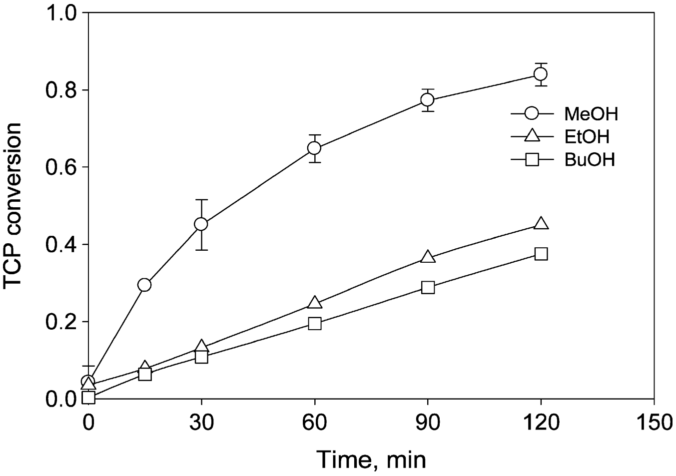

Fig. 1. The catalytic activity profiles for TCP transesterification catalyzed by SZ with (○) MeOH, (△) EtOH, and (□) BuOH at 120 °C, 6.8 atm, molar ratio of alcohol:TCP = 12:1.

Interestingly, faster reaction rates have been reported by Freedman et al. [30] for the acid-catalyzed transesterification of vegetable oils with heavier alcohols. This may be explained by alcohol solubility, with short-chain alcohols (especially methanol) having poor solubility in oils. But under our reaction conditions, TCP and all of the alcohols used were completely soluble; therefore, the lower reaction rates obtained with the heavier alcohols were due in part to steric hindrance, as expected based on fundamental chemical principles.

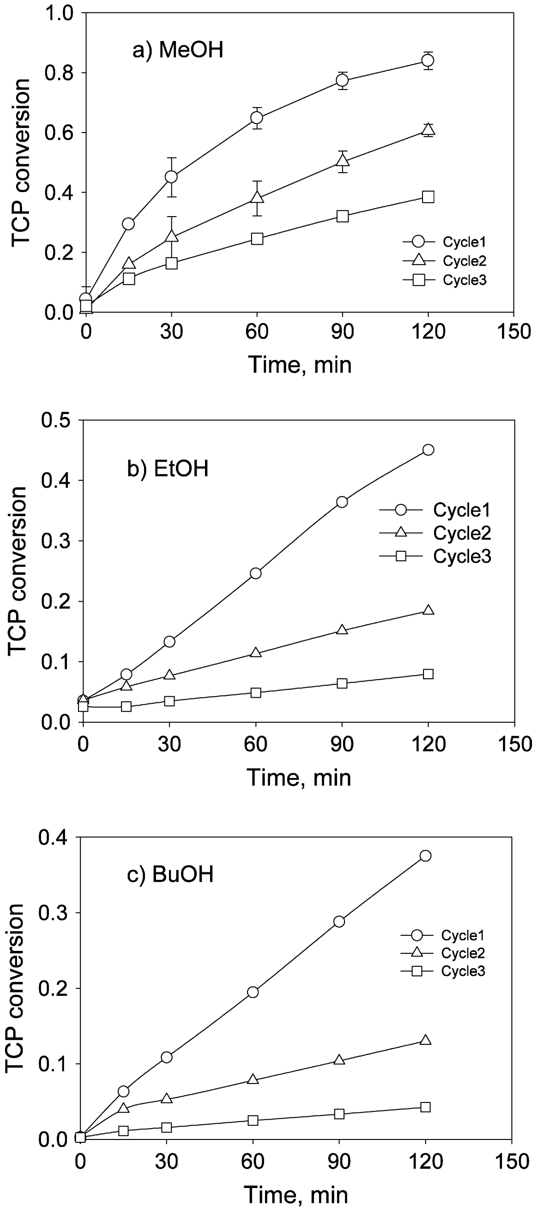

Fig. 2. Reusability of SZ during three reaction cycles of TCP transesterification with (a) MeOH, (b) EtOH, and (c) BuOH using a 12:1 molar ratio of alcohol-to-TCP. ((○) first cycle, (△) second cycle, and (□) third cycle.) $T = 120\,^{\circ}\mathrm{C}$ and 10 wt% catalyst.

3.3. Catalyst recycling

One of the main advantages of heterogeneous acid catalysts over liquid acids is that the former can be easily recovered from the reaction mixture and potentially can be regenerated and reused. In the present study, catalyst recycling studies were carried out by recovering the used catalysts after 2 h of reaction and reusing them (without pretreatment) with fresh reagents in a subsequent reaction cycle. Fig. 2 presents the results for three successive 2-h reaction cycles of TCP alcoholysis with MeOH, EtOH, and BuOH, demonstrating a continuous activity loss for all reactions. To account for the effect of the different TCP and alcohol concentrations used in each case due to the different alcohol volumes used to maintain a molar ratio of 12:1 (alcohol:TCP), our results are presented in terms of relative initial catalytic activity in Fig. 3. As can be seen, the degree of catalyst deactivation was reasonably similar regardless of the alcohol type. We discuss this issue in more depth in Section 3.4.

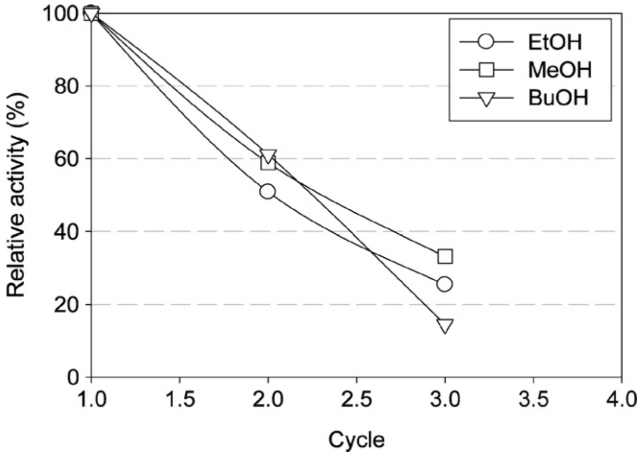

Fig. 3. SZ relative deactivation following multiple reaction cycles with TCP transesterification of MeOH, EtOH, and BuOH at 120 °C, 6.8 atm, molar ratio of alcohol:TCP = 12:1.

As has been reported previously [11,12,31], carbon deposition can be a leading cause of catalyst deactivation with SZ. Consequently, in an attempt to eliminate carbon deposits that may have formed during the first reaction cycle, the recovered solid was dried overnight at 100 °C and recalcined under 20 mL/min of flowing air at 315 °C for 4 h, as was shown to be effective by Suwannakarn et al. [22]. Activities of the recalcined catalyst were comparable to activities obtained for the second reaction cycle where the catalyst was used without treatment, suggesting that formation of carbonaceous deposits was not the cause of catalyst deactivation in this case.

3.4. Catalyst leaching and deactivation

As reported previously, ionic sulfur species supported on the SZ catalyst surface can be modified and successively transformed into H_2SO_4, HSO_4^-, and SO_4^{2-} by the presence of free water in the liquid phase [31], leading to the loss of active sites from the solid surface. Omota et al. [32], for instance, reported that after contacting fresh SZ catalyst samples with water, a rapid drop in the pH of the solution occurred, indicating that acid species likely were being leached out into solution. Other authors also have documented water's capability of leaching out the active catalytic species in SZ [16,32–34]. To the best of our knowledge, however, no one has yet addressed the impact of alcohol on SZ deactivation by site leaching.

To study the effect of alcohols on SZ catalyst deactivation, fresh calcined SZ samples were immersed in the three different alcohols (MeOH, EtOH, and BuOH) at 120 °C and 6.8 atm, under continuous stirring for 2 h. Afterward, the alcoholic solutions were centrifuged and filtrated to remove the solid catalysts. The recovered catalysts were dried overnight and used for the reaction. Fig. 4 shows the activities for TCP transesterification of the recovered catalysts from the three alcohol washes and the activities for TCP transesterification in the ab-

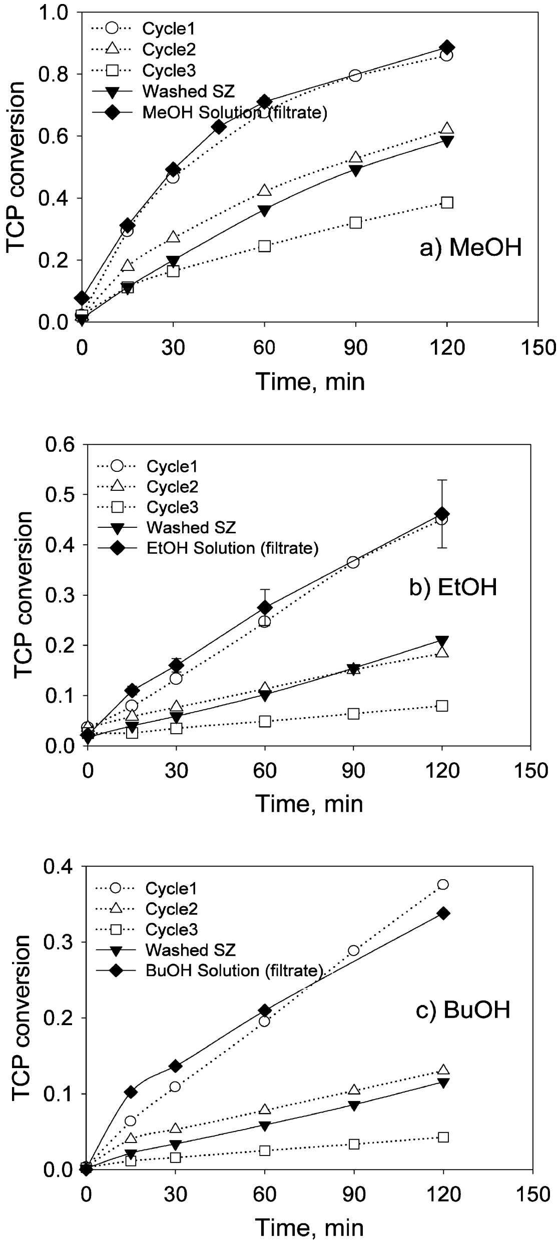

Fig. 4. Activities of alcohol precontacted SZ catalysts and activities of alcohol solutions used in the catalyst washing steps compared to catalyst recycling experiments as shown in Fig. 2 ((a) MeOH, (b) EtOH, and (c) BuOH) in TCP transesterification at 120 °C, 6.8 atm, molar ratio of alcohol:TCP = 12:1.

sence of catalyst using the alcohol solutions (filtrates) obtained after the washing experiments. As can be seen, the alcohol-precontacted catalysts showed activities close to those of the second cycle from the cycling experiments. The small variations in reaction activity can be attributed to differences arising from the previous step (i.e., precontact with the reaction mixture vs. pure alcohol) or to experimental error. On the other hand, the filtrates (i.e., alcohol solutions used in the alcohol precontact pretreatment) showed activities comparable to those of the first reaction cycle, indicating that in-solution (i.e., homogeneous, not heterogeneous) catalytic species are apparently primarily responsible for catalytic activity during the initial reaction cycle at 120 °C.

Table 1
Sulfur content of SZ catalyst samples after washing with fresh alcohol batches multiple times at 120 °C, 6.8 atm, and with continuous stirring

Alcohol	Sulfur content (wt%) after the first wash determined by ICP method[a]	Sulfur content (wt%) determined by N_2 TGA[b,c]		
		After 1 wash[d]	After 2 washes[d]	After 3 washes[d]
MeOH	1.47	1.44	1.27	1.20
EtOH	1.42	1.48	1.33	1.24
BuOH	1.48	1.42	1.30	1.26

[a] Determined by Galbraith Laboratories, Inc.

[b] Sulfur content was determined assuming sulfate moieties desorbed as SO_3 gas.

[c] Experimental error ±0.01 wt%.

[d] Washed for 2 h.

To further explore these phenomena, SZ samples were washed multiple times using fresh alcohol. The sulfur content of the samples pretreated in this manner was then measured using TGA and ICP, the latter carried out by Galbraith Laboratories, Inc. (Table 1). Elemental sulfur analyses by ICP and TGA were in good agreement within an experimental error of ±3%. As shown, after the first alcohol washing pretreatment, SZ samples retained 85% of the original sulfur content (1.73 wt%) regardless of the alcohol used, suggesting that under our conditions, sulfur species were leached out to the same extent regardless of alcohol characteristics (e.g., polarity, nucleophilicity, alkyl chain length). It should be noted that after the catalyst was washed once in pure distilled water under our reaction conditions, it retained 1.30 wt% of sulfur (75% of its original sulfur content). Also note that the amount of sulfur retained in the catalyst after it was washed three times with fresh alcohol was almost identical to that in the catalyst after only a single water wash. As would be expected, water more efficiently removes sulfate species from the catalyst surface, likely due to its higher polarity and stronger hydrogen bonding capacity. Thus, if one assumes that under our conditions, water can remove all of the leachable sulfur, then a single 2-h alcohol wash or (based on the reaction cycle experiments) a single 2-h reaction cycle with a mixture of alcohol and triglyceride effectively removes almost 70% of the leachable sulfate species on the catalyst surface.

The leaching process is fast during the first reaction cycle. As determined by N_2 TGA results, the sulfur content of SZ was 1.47 wt% after washing with methanol for only 15 min under reaction conditions, which is comparable to the result obtained from methanol washing for 2 h under reaction conditions. This finding is further supported by the fact that reactions carried out using the methanol solution recovered after the 15-min washing step exhibited the same reaction profile as reactions carried out using the methanol solution after 2 h of catalyst washing (Fig. 5). Similar results were found for EtOH; however, a longer contacting time (at least 1 h) was required for BuOH. Thus, it seems that alcohols with larger alkyl chain lengths have somewhat slower kinetics for leaching the active sites in SZ.

Another implication of our results is that at temperatures above 100 °C, the ability of sulfate ions to leach from SZ may

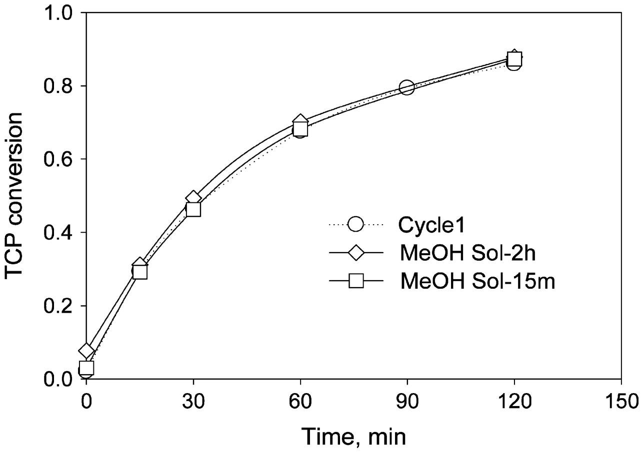

Fig. 5. Activity for methanol alcoholysis of TCP of the alcohol used in washing the catalyst for various lengths of time compared to the first reaction cycle with SZ (120 °C, 6.8 atm).

be related to the presence of the –OH function in the alcohols, imposing a chemical limitation on using SZ for reactions that use or produce compounds with this functionality. Certainly, more research is needed to investigate this issue from a general standpoint in light of the conflicting reports [18].

3.5. Active species in alcohol solution

In an attempt to determine whether sulfate species leached out as H_2SO_4, H_2SO_4 solutions containing concentrations close to those measured in the alcohol washing solutions and catalyst deactivation studies were prepared and their catalytic activity in the alcoholysis of TCP was investigated (Fig. 6). The catalytic activity obtained from low-concentration H_2SO_4 solutions was similar to that obtained from reactions using SZ, suggesting that sulfate ions indeed may have leached from the catalyst surface as H_2SO_4.

To further support this observation, sulfuric acid solutions and filtrates from alcohol washing experiments were titrated using 0.05 mol of NaOH. Our findings were not consistent with the expected molar ratio of $2H^+$:S for H_2SO_4; for instance, a solution of 113 ppm H_2SO_4 in BuOH exhibited a H^+:S ratio of 1.3 value. Similar results (H^+:S ratio $= 0.92$) were obtained for filtrate from BuOH washing experiments. However, as has been reported for H_2SO_4 in aliphatic alcohols [35], H_2SO_4 can undergo esterification with the alcohol to produce mono alkyl-hydrogen and dialkyl sulfate; the latter of which is widely used as an alkylating agent in organic synthesis and chemically induced mutagenesis [36,37]. In fact, dialkyl sulfates are produced commercially by the direct reaction of alcohol and sulfuric acid [36]. In addition, it is known that sulfuric acid can readily react with alcohols to yield dialkyl sulfates even in the gas-phase conditions of the planet's atmosphere [38,39]. The reaction of H_2SO_4 and alcohols has been reported to occur through the following reaction mechanism:

$$H_2SO_4 + ROH \rightleftarrows RSO_3H + H_2O, \tag{1}$$

$$ROSO_3H + ROH \rightleftarrows (RO)_2SO_4 + H_2O. \tag{2}$$

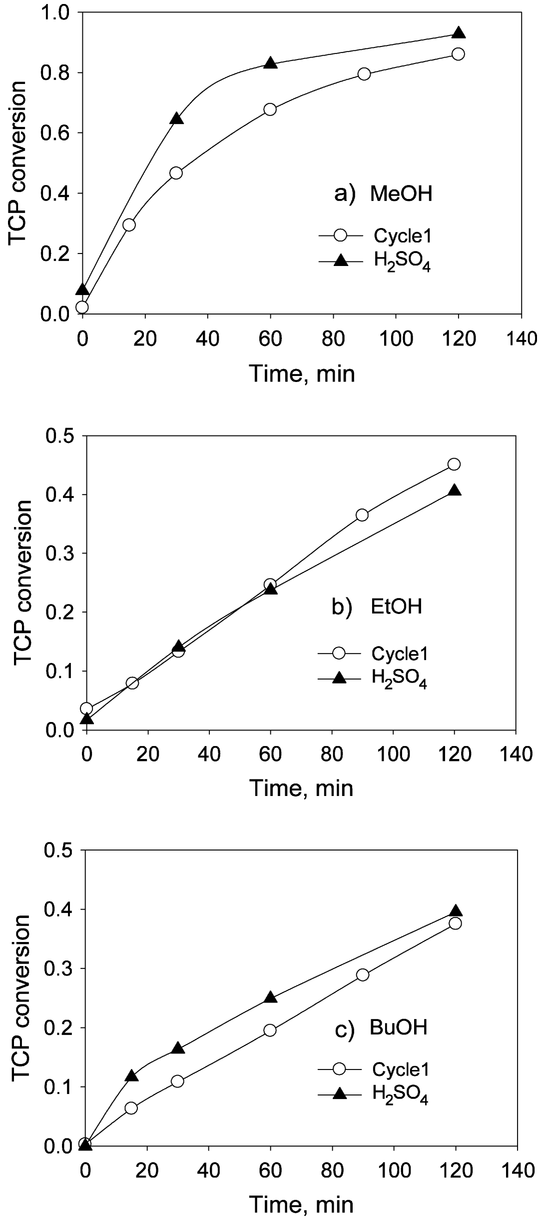

Fig. 6. Sulfuric acid catalyzed TCP transesterification with (a) methanol, (b) ethanol, and (c) butanol at similar sulfur concentrations as in the leachate alcohol and compared to the first of reaction with SZ ($T = 120\,°C$, $P = 6.8$ atm, molar ratio of alcohol:TCP = 12:1).

To corroborate the presence of alkyl-sulfate compounds in our reaction mixtures, residual alcohol solutions after SZ alcohol washing under reaction conditions were analyzed by ^1H NMR (JEOL ECX 300, 300.5 MHz). Fig. 7a shows the ^1H NMR spectrum of a methanol solution obtained from washing SZ at 120 °C and 6.8 atm, with peaks at 3.739 and 3.636 ppm corresponding to monomethyl hydrogen sulfate and dimethyl sulfate, respectively [39]. In addition, control ^1H NMR experiments conducted using trace amounts of dimethyl sulfate in the alcohols showed a strong ^1H NMR peak at 3.636 ppm (Fig. 7b), confirming the presence of this species in the leachate solutions. Consequently, a deactivation pathway for SZ in alcohols at temperatures above 100 °C can be proposed (see Fig. 8).

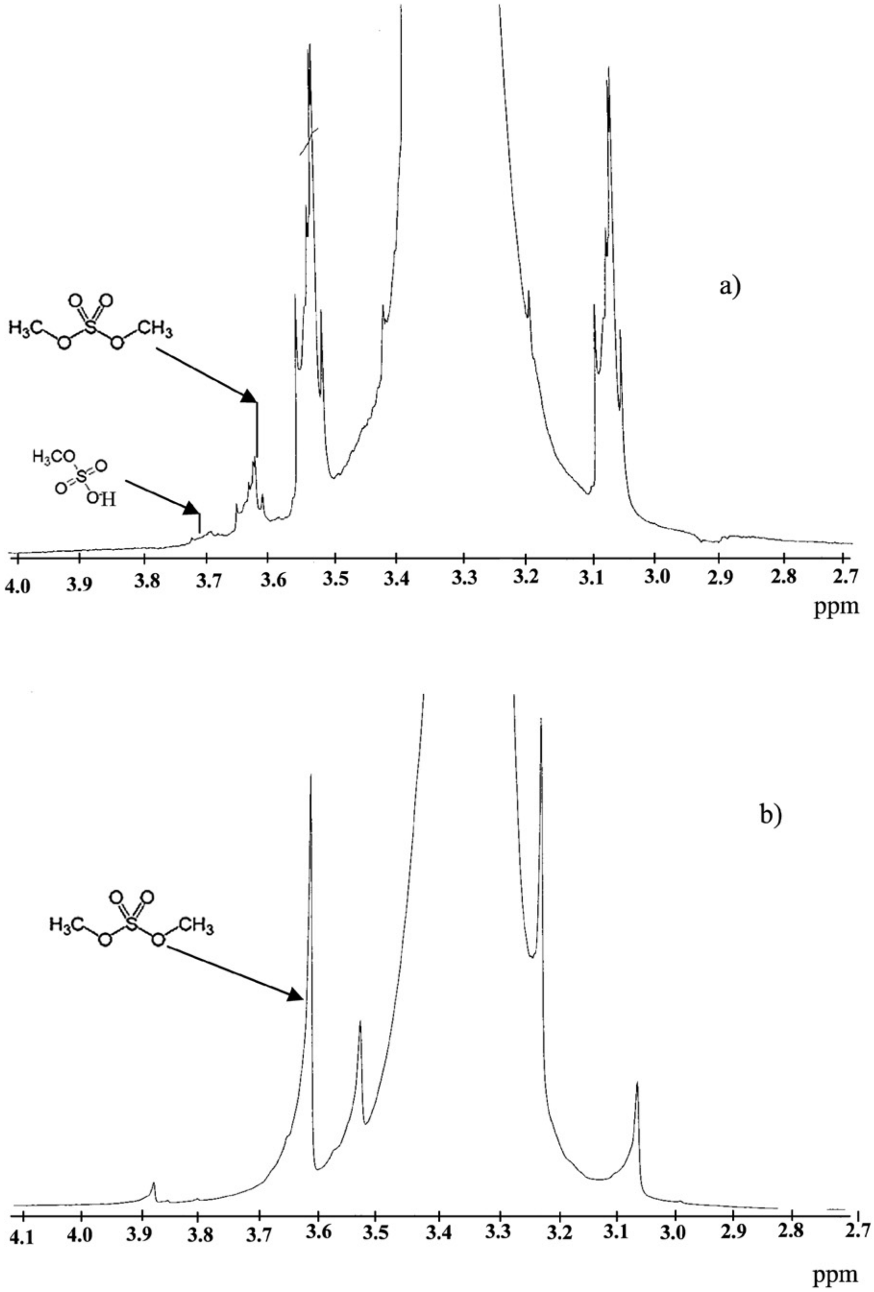

Fig. 7. NMR spectra of (a) the methanol filtrate after washing SZ at 120 °C for 2 h, and (b) methanol solution with a representative concentration of dimethyl sulfate.

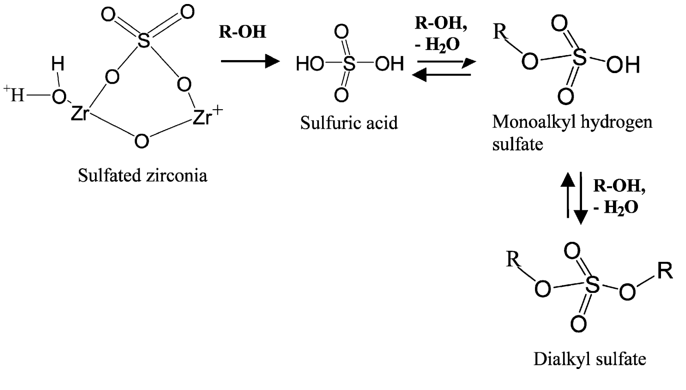

Fig. 8. Schematic representation of possible active site leaching mechanism for SZ.

4. Conclusion

We investigated the activity and stability of SZ for the liquid-phase transesterification of TCP using a series of aliphatic alcohols (methanol, ethanol, and *n*-butanol) at 120 °C and 6.8 atm. The highest catalytic activity was observed in methanolysis, followed by ethanolysis and butanolysis, respectively. The decreased catalytic activity with alcohol size likely was due to increased steric hindrance. The SZ catalyst deactivated with subsequent reaction cycles in all cases due to the leaching of sulfate ion species, most likely as sulfuric acid. Under the reaction conditions used, almost all catalytic activity in the first reaction cycle appeared to be due to homogeneous rather than heterogeneous catalysis, as a result of sulfur leaching. The degree of sulfur removal depended on the alcohol size and contacting time. The proposed catalyst deactivation pathway includes the removal of sulfate ions from the catalyst surface as sulfuric acid, which subsequently reacts with alcohol to form monoalkyl hydrogen sulfate and dialkyl sulfate in solution, as indicated by ^{1}H NMR studies.

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References

[1] U. Meyer, W.F. Hoelderich, Appl. Catal. A 178 (1999) 159.
[2] D. Duran, N. Wu, B. Mao, J. Xu, J. Liq. Chromatogr. Related Technol. 29 (2006) 661.
[3] J. Barrault, Y. Pouilloux, J.M. Clacens, C. Vanhove, S. Bancquart, Catal. Today 75 (2002) 177.
[4] M. Di Serio, M. Ledda, M. Cozzolino, G. Minutillo, R. Tesser, E. Santacesaria, Ind. Eng. Chem. Res. 45 (2006) 3009.
[5] H. Fukuda, A. Kondo, H. Noda, J. Biosci. Bioeng. 92 (2001) 405.
[6] F.R. Ma, M.A. Hanna, Bioresour. Technol. 70 (1999) 1.
[7] E. Lotero, Y. Liu, D.E. Lopez, K. Suwannakarn, D.A. Bruce, J.G. Goodwin Jr., Ind. Eng. Chem. Res. 44 (2005) 5353.
[8] Y. Zhang, M.A. Dube, D.D. McLean, M. Kates, Bioresour. Technol. 89 (2003) 1.
[9] Y. Zhang, M.A. Dube, D.D. McLean, M. Kates, Bioresour. Technol. 90 (2003) 229.
[10] M. Hino, K. Arata, J. Chem. Soc. Chem. Commun. (1980) 851.
[11] G.D. Yadav, J.J. Nair, Microporous Mesoporous Mater. 33 (1999) 1.
[12] X.M. Song, A. Sayari, Catal. Rev. Sci. Eng. 38 (1996) 329.
[13] A. Clearfield, G.P.D. Serrette, A.H. Khazi-Syed, Catal. Today 20 (1994) 295.
[14] C. Morterra, G. Cerrato, F. Pinna, M. Signoretto, J. Phys. Chem. 98 (1994) 12373.
[15] F. Babou, G. Coudurier, J.C. Vedrine, J. Catal. 152 (1995) 341.
[16] X.B. Li, K. Nagaoka, J.A. Lercher, J. Catal. 227 (2004) 130.
[17] T.A. Peters, N.E. Benes, A. Holmen, J.T.F. Keurentjes, Appl. Catal. A 297 (2006) 182.
[18] A.A. Kiss, A.C. Dimian, G. Rothenberg, Adv. Synth. Catal. 348 (2006) 75.
[19] J. Jitputti, B. Kitiyanan, P. Rangsunvigit, K. Bunyakiat, L. Attanatho, P. Jenvanitpanjakul, Chem. Eng. J. 116 (2006) 61.
[20] J. Ni, F.C. Meunier, Appl. Catal. A 333 (2007) 122.
[21] D.E. Lopez, J.G. Goodwin Jr., D.A. Bruce, J. Catal. 245 (2007) 381.
[22] K. Suwannakarn, E. Lotero, J.G. Goodwin Jr., Catal. Lett. 114 (2007) 122.
[23] Y. Liu, E. Lotero, J.G. Goodwin Jr., Appl. Catal. A 331 (2007) 138.
[24] Y. Liu, E. Lotero, J.G. Goodwin Jr., J. Catal. 246 (2007) 428.
[25] Y. Liu, E. Lotero, J.G. Goodwin Jr., J. Catal. 242 (2006) 278.
[26] Y. Warabi, D. Kusdiana, S. Saka, Appl. Biochem. Biotechnol. 113 (2004) 793.
[27] K. Suwannakarn, E. Lotero, J.G. Goodwin Jr., Ind. Eng. Chem. Res. 46 (2007) 7050.
[28] B.R. Jermy, A. Pandurangan, Appl. Catal. A 288 (2005) 25.
[29] Y. Liu, E. Lotero, J.G. Goodwin Jr., J. Catal. 243 (2006) 221.
[30] B. Freedman, E.H. Pryde, T.L. Mounts, J. Am. Oil Chem. Soc. 61 (1984) 1638.
[31] A. Corma, H. Garcia, Catal. Today 38 (1997) 257.
[32] F. Omota, A.C. Dimian, A. Bliek, Chem. Eng. Sci. 58 (2003) 3175.
[33] T. Okuhara, M. Kimura, T. Nakato, Appl. Catal. A 155 (1997) L9.
[34] M. Kimura, T. Nakato, T. Okuhara, Appl. Catal. A 165 (1997) 227.
[35] M. Liler, Reaction Mechanisms in Sulfuric Acid, Academic Press, New York, 1971, pp. 150–152.
[36] S. Theodore, P.S.T. Sai, Can. J. Chem. Eng. 79 (2001) 54.
[37] R. Wolfenden, Y. Yuan, Proc. Natl. Acad. Sci. USA 104 (2007) 83.
[38] N.P. Levitt, J. Zhao, R.Y. Zhang, J. Phys. Chem. 110 (2006) 13215.
[39] Y. Suzuki, M. Kawakami, K. Akasaka, Environ. Sci. Technol. 35 (2001) 2656.