

Highly Promising Sulfate Ion Promoted M–ZrO₂ (M=Al₂O₃ and CeO₂) Heterogeneous Solid Acids for Biodiesel–Derived Glycerol Esterification

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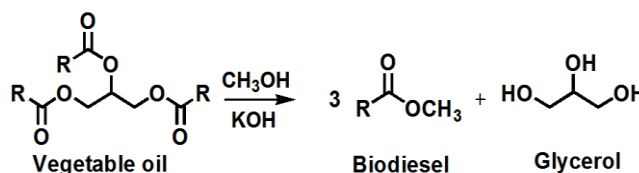
Abstract- Esterification of biodiesel–derived glycerol with acetic acid was investigated over Al₂O₃–ZrO₂, CeO₂–ZrO₂, SO₄^{2–}/Al₂O₃–ZrO₂ and SO₄^{2–}/CeO₂–ZrO₂ solid acid catalysts. The obtained glycerol esters, namely mono–, di– and tri–acylglycerols are versatile chemicals to improve both physicochemical properties of biodiesel as well as its economic profitability. The prepared solid acids were characterized by means of XRD, BET surface area, and ammonia–TPD techniques. It was found that the addition of sulfate ions significantly enhances the surface acidity of mixed oxides. Interestingly, the SO₄^{2–}/CeO₂–ZrO₂ solid acid showed higher amount of super acidic sites, whereas only medium and strong acidic sites were observed in the case of SO₄^{2–}/Al₂O₃–ZrO₂ sample. Among various catalysts investigated, the SO₄^{2–}/CeO₂–ZrO₂ catalyst exhibited excellent catalytic activity (~100% glycerol conversion) with better reusability up to three catalytic runs. The results showed that promoted zirconia–based solid acids are the promising heterogeneous catalysts for esterification of glycerol.

Keywords- Biodiesel; Glycerol; Zirconia; Solid Acids; Esterification; Triacylglycerol

I. INTRODUCTION

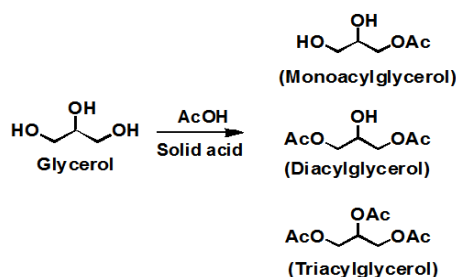
The world has been presently confronted with several energetic and environmental crises due to the rapid escalating oil prices and adverse environmental impacts of fossil fuels. Particularly, combustion of fossil fuels emits various harmful gases that exhibit severe environment and human health problems, such as global warming, acid rain, heart diseases, respiratory troubles, etc [1–3]. Accordingly, there has been significant attention in finding renewable energy sources that must be clean, sustainable and release low carbon dioxide (CO₂) emissions. Amongst, biodiesel is one of the highly potential alternative reserves to conventional petroleum-based diesel fuel that shows various impending advantages. Primarily, biodiesel is a non-toxic, biodegradable, and biocompatible fuel that can be employed directly or as diesel mixture in engines, hence enhances the engine longevity [4]. The closed carbon cycle of biodiesel yields a 78% reduction in CO₂ emissions compared to the diesel fuel. Moreover, biodiesel remarkably reduces the amount of unburned hydrocarbons, carbon monoxide, and particulate matter. The addition of biodiesel to ultra–low sulfur diesel can also improve its lubricating properties [5].

Biodiesel refers to the alkyl esters of long chain fatty acids, which can be synthesized by transesterification of vegetable oil with methanol (Scheme 1). Glycerol is the main by–product in the transesterification reaction that can be obtained ~10 m³ for each 90 m³ of biodiesel produced [6]. Currently, renewable energy contributes only 13.3% of the total global energy. The biodiesel production in 2010 was 20 million tons and it is expected to reach 150 million tons by 2020 [7]. However, there are two major challenges regarding the commercialization of biodiesel production: a) unfavorable physicochemical properties of biodiesel, such as poor oxidation stability and high boiling point and b) high cost of the precursors used for the synthesis of biodiesel. These adverse properties can be reduced by employing different additives, for example, triacylglycerol (TAG, a versatile product of glycerol esterification). Also, TAG can be used to enhance viscosity, cold resistance, and anti–knocking properties of the biodiesel [8–10]. Therefore, synthesis of TAG in high yield from biodiesel–derived glycerol will be a key factor to enhance both economic viability of biodiesel production as well as its physicochemical characteristics.



Scheme 1 Biodiesel production from transesterification of vegetable oil with methanol

As mentioned, TAG including mono–acylglycerol (MAG) and di–acylglycerol (DAG) can be synthesized from the esterification of glycerol with acetic acid (Scheme 2) [6]. These acetylated esters have shown numerous industrial applications ranging from cryogenics to fuel additives. MAG and DAG can be used as building blocks for polyester and cryogenics, and TAG can be added to cosmetics as moisturizer and to diesel fuel as effective fuel additive [11]. They can be also employed in the manufacture of explosives and plasticizers, as solvents for dyestuffs, antiseptics and printing ink, as softening and emulsifying agents, etc [12]. Moreover, TAG is used as filter for cigarettes, as food additive and as an anti–knocking agent for fuel [13].



Scheme 2 Esterification of biodiesel derived–glycerol with acetic acid in the presence of solid acid catalyst

Although esterification of glycerol is carried out by means of homogeneous acids, development of heterogeneous solid acids with desirable characteristics is one of the focuses of the latest research interest [12]. This renewed much attention has been mainly driven by the need to discover ecofriendly catalysts to replace hazardous homogeneous acids. Solid acids significantly differ in acidity, surface area, and cost of production when compared to homogeneous acids. Indeed, they are highly promising because i) they are non-toxic and easy to prepare, ii) they can be easily recovered from the reaction mixture by simple filtration, iii) generation of waste can be minimized and iv) above all, they can be reused multiple times without significant loss of the activity and selectivity, thus making the process economically more viable [14]. Sulfated zirconia is one of the potential solid acids because of its strong acidity and ability to catalyze many reactions, such as cracking, alkylation, isomerization, and esterification. However, sulfated zirconia is known to suffer significant deactivation, probably due to sulfur leaching or transformation of active tetragonal zirconia phase to monoclinic phase, and/or the formation of coke on the surface of catalyst. It was reported that incorporation of metals into the zirconia results in more active and stable catalysts to overcome the above said drawbacks [15–17]. Taking into account these aspects, we prepared zirconia-based mixed oxides, namely $\text{Al}_2\text{O}_3\text{-ZrO}_2$ and $\text{CeO}_2\text{-ZrO}_2$. These mixed oxides are used as active supports for impregnating the sulfate ions. The prepared solid acids were investigated for the esterification of glycerol with acetic acid. By examining various reaction parameters, it was found that sulfate ion promoted $\text{CeO}_2\text{-ZrO}_2$ catalyst exhibits excellent catalytic performance towards the conversion of glycerol and selectivity of TAG. Further, the $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$ solid acid catalyst showed remarkable reusability up to three catalytic runs.

II. EXPERIMENTAL SECTION

A. Catalyst Preparation

The M-ZrO_2 ($\text{M} = \text{Al}_2\text{O}_3$ and CeO_2 ; 1:1 mole ratio based on oxides) mixed oxides were prepared by a co-precipitation method from ultrahigh dilute aqueous solutions. In a typical experiment, to prepare $\text{CeO}_2\text{-ZrO}_2$ the desired amounts of respective nitrate precursors were dissolved separately in double distilled water under mild stirring conditions and mixed together. Upon complete mixing, either a base mixture of 1:1 volume of 2 M NaOH and 1 M Na_2CO_3 or aq. NH_3 solution was added slowly to the mixture solution until the precipitation was complete (pH ~9). The obtained precipitates were thoroughly washed with deionized water, filtered off and oven dried at 373 K for 24 h. The same procedure was extended for the synthesis of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ sample. To impregnate the sulfate ions, an appropriate volume of 0.5 M H_2SO_4 solution was added to the oven-dried support hydroxide. The excess water was evaporated on a water-bath under vigorous stirring for 1 h. The obtained products were oven dried at 393 K for 12 h and calcined at 873 K for 5 h. For convenience, the synthesized solid acids, namely, $\text{Al}_2\text{O}_3\text{-ZrO}_2$, $\text{CeO}_2\text{-ZrO}_2$, $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-ZrO}_2$ and $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$ are denoted by AZ, CZ, SAZ and SCZ, respectively.

B. Catalyst Characterization

X-ray diffraction (XRD) measurements were carried out on a Rigaku Multiflex instrument equipped with nickel-filtered $\text{Cu K}\alpha$ (0.15418 nm) radiation source and a scintillation counter detector. The scattered intensities data were collected from 2θ values of 2 to 80° by scanning at 0.01° steps with a counting time of 1 s at every step. The BET surface area of the samples was determined by nitrogen physisorption at liquid nitrogen temperature on a Micromeritics ASAP 2000 instrument. Prior to analysis, catalysts were pretreated at 623 K for 1 h in helium gas. The NH_3 -TPD measurements were performed on a Micromeritics AutoChem 2910 instrument. A thermal conductivity detector was used for continuous monitoring of the desorbed gas. Prior to TPD measurements, samples were pretreated at 573 K for 1 h and then saturated with ultra-pure anhydrous NH_3 for 1 h, and subsequently flushed with helium to remove the physisorbed gas.

C. Activity Measurements

The catalytic activity of pure and promoted metal oxides for esterification of glycerol was undertaken at atmospheric pressure in the temperature range of 313 to 393 K. In a typical experiment, 2 g of glycerol and 3.9–7.8 mL of acetic acid were taken in 100 mL two-necked round bottom flask. A Dean-Stark trap was attached to the round bottom flask to remove water from the reaction mixture during the reaction process because water is a byproduct, which favors the deactivation of catalyst and reversibility of the reaction. Catalysts were pre-activated at 423 K for 2 h before catalytic runs. Samples were taken periodically and analyzed by GC equipped with BP-20 (wax) capillary column and a flame ionization detector. The conversion

of glycerol and selectivity of the products were calculated as described elsewhere [18].

III. RESULTS AND DISCUSSIONS

A. Catalyst Characterization

Fig. 1a displays the X-ray powder diffraction patterns of $\text{CeO}_2\text{-ZrO}_2$ and $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$ samples. As shown in the Fig. 1a, all the diffraction peaks of $\text{CeO}_2\text{-ZrO}_2$ could be indexed to (111), (200), (220), (311), (400), (331), and (420) crystal faces, which are characteristic of fluorite-type cubic structure of CeO_2 [19]. The absence of reflections corresponding to ZrO_2 suggests the formation of ceria solid solution. The XRD peaks corresponding to the CeOSO_4 phase (PDF # 390515) were noticed in the case of $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$. Additionally, formation of different types of surface zirconium sulphates was noted, such as $\text{Zr}(\text{SO}_4)_2$ (PDF # 722192), $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (PDF # 850703) and $\text{Zr}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$ (PDF # 740542). From the XRD results, it can be concluded that there is a strong influence of impregnated sulfate ions on the $\text{CeO}_2\text{-ZrO}_2$ mixed oxide.

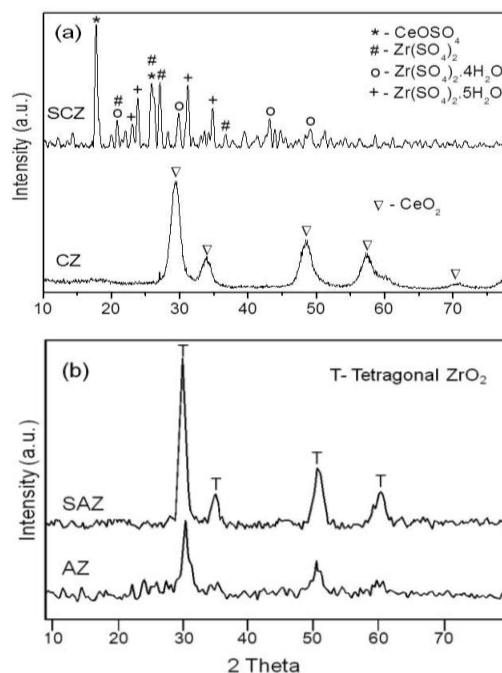


Fig. 1 X-ray diffraction patterns of (a) $\text{CeO}_2\text{-ZrO}_2$ (CZ) and $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$ (SCZ) and (b) $\text{Al}_2\text{O}_3\text{-ZrO}_2$ (AZ) and $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-ZrO}_2$ (SAZ) catalysts

The XRD patterns of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ and $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-ZrO}_2$ catalysts are shown in Fig. 1b. Only broad diffraction lines due to tetragonal zirconia are observed for the $\text{Al}_2\text{O}_3\text{-ZrO}_2$ sample. As per the literature, the XRD pattern of zirconia sample shows both monoclinic and tetragonal phases [12]. Therefore, the absence of monoclinic ZrO_2 demonstrates that alumina acted as a structural stabilizer to zirconia. No XRD peaks due to crystalline alumina were observed which indicates either alumina is homogeneously mixed with zirconia or present in an amorphous state. On the other hand, XRD peaks only due to tetragonal zirconia phase are observed in the case of $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-ZrO}_2$ sample. As observed in the case of $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$ sample, XRD peaks corresponding to surface zirconium and cerium sulfate were not identified.

The BET surface area of CZ, AZ, SAZ and SCZ catalysts are presented in Table I. The CZ and AZ catalysts showed the specific surface areas of 49 and 119 m^2g^{-1} , respectively. However, divergent results were obtained upon impregnation of sulfate ions on the mixed oxides. In the case of SAZ sample, a considerable loss in the BET surface area (33 m^2g^{-1}) is noticed that could be due to the formation of non-porous Al and Zr sulfates at higher calcination temperatures. As can be noted, no XRD lines due to crystalline compounds of the same were obtained. On the other hand, an increase in the surface area of the SCZ (92 m^2g^{-1}) catalyst is noted which can be explained by the formation of porous surface sulfate compounds between the sulfate groups and the CZ support as confirmed by XRD studies.

TABLE I BET SURFACE AREA and XRD PHASES of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ (AZ), $\text{CeO}_2\text{-ZrO}_2$ (CZ), $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-ZrO}_2$ (SAZ) and $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$ (SCZ) CATALYSTS

S. No.	Catalyst	BET Surface area m^2/g	XRD Phases
1	AZ	119	Tetragonal ZrO_2
2	CZ	49	CeO_2
3	SAZ	33	Tetragonal ZrO_2
4	SCZ	92	CeOSO_4 , $\text{Zr}(\text{SO}_4)_2$, $\text{Zr}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ (n = 4,5)

It is well-known that NH_3 is an excellent probe molecule for investigating the acidic properties of solid catalysts [20]. The strong basicity and smaller molecular size of NH_3 allows the identification of acidic sites presented in the narrow pores of the solids. The NH_3 -TPD profiles of CZ, SCZ and AZ, SAZ samples are shown in Fig. 2a and 2b, respectively. The NH_3 -TPD profiles of all samples can be classified as low-temperature (LT) and high-temperature (HT) regions, corresponding to before and after 673 K, respectively [21]. The HT region peaks could be assigned to desorption of NH_3 from strong Brønsted and Lewis acidic sites, whereas the LT region peaks represent the release of NH_3 from weak acidic sites [22, 23]. A closer look at the figure revealed that the CZ catalyst exhibits higher amount of strong acidic sites than that of AZ catalyst. It was reported that the impregnated sulfate ions can generate strong Lewis and Brønsted acidity when adsorbed on the zirconia-based oxides [20]. Upon impregnation of sulfate ions on the AZ support, there is an enhancement in the strong acidic sites (Fig. 2b). On the other hand, SCZ catalyst showed two peaks at around 973 and 1073 K which suggest the formation of two different types of super acidic sites with slight difference in the acidity (Fig. 2a) [18]. It was noticed that SCZ shows large amount of acidic sites than that of SAZ catalyst which could be due to the existence of various types of sulfate phases, namely CeOSO_4 and $\text{Zr}(\text{SO}_4)_2$ (Fig. 1a) associated with high BET surface area of the SCZ catalyst. These acidic sites could be the reason for the observed high catalytic activity of SCZ as discussed in the later paragraphs.

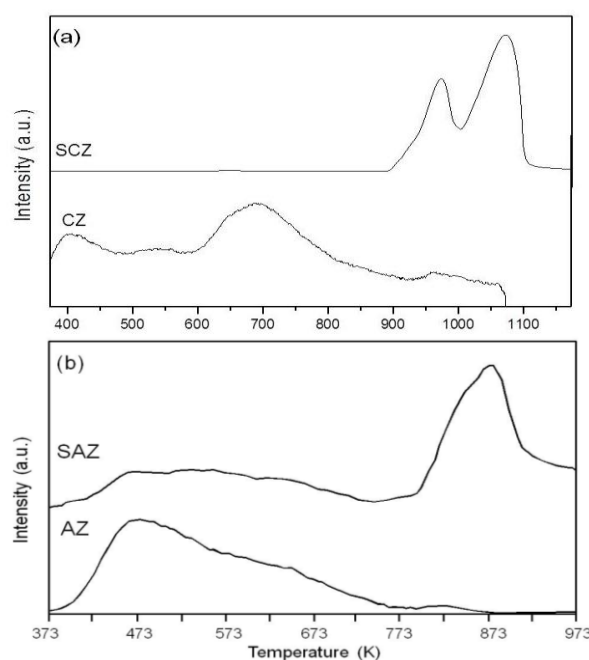


Fig. 2 NH_3 -TPD profiles of (a) $\text{CeO}_2\text{-ZrO}_2$ (CZ) and $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$ (SCZ) and (b) $\text{Al}_2\text{O}_3\text{-ZrO}_2$ (AZ) and $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-ZrO}_2$ (SAZ) catalysts

B. Catalytic Experiments

The conversion of glycerol and the selectivity of products over AZ, CZ, SAZ and SCZ catalysts are presented in Table II. It was found that all the catalysts showed comparable catalytic activity, of which sulfate promoted catalysts exhibited high catalytic activity than the unpromoted catalysts. The better activity of the sulfated catalysts is due to the presence of higher amounts of acidic sites (Fig. 2). Among the promoted solid acids, the SCZ catalyst exhibited excellent catalytic activity attributed to existence of large amount of super acidic sites. The conversion of glycerol was 54, 68, 89 and ~100% over AZ, CZ, SAZ and SCZ catalysts, respectively. Particularly, a high selectivity of DAG (59%) and TAG (16%) was noticed in the case of SCZ catalyst. Conversely, the AZ catalyst exhibited better selectivity of MAG (92%). These interesting results suggest that the existence of higher concentration of super acidic sites is crucial to obtain the TAG in better yields. The catalytic activity of various catalysts follows the increasing order: $\text{AZ} < \text{CZ} < \text{SAZ} < \text{SCZ}$. In order to find the origin of enhanced activity of SCZ catalyst, we have compared the results of SCZ and SAZ catalysts by examining different reaction parameters.

TABLE II GLYCEROL CONVERSION and SELECTIVITY of PRODUCTS in the ESTERIFICATION of GLYCEROL with ACETIC ACID over $\text{Al}_2\text{O}_3\text{-ZrO}_2$ (AZ), $\text{CeO}_2\text{-ZrO}_2$ (CZ), $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-ZrO}_2$ (SAZ) and $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$ (SCZ) CATALYSTS

Catalyst	Glycerol conversion (%)	Selectivity (%)		
		MAG	DAG	TAG
AZ	54	92	8	—
CZ	68	76	22	2
SAZ	89	55	40	5
SCZ	~100	25	59	16

MAG; Mono-acylglycerol, DAG; Di-acylglycerol, TAG; Tri-acylglycerol

Reaction conditions: molar ratio of acetic acid to glycerol = 6:1, reaction time = 1 h, catalyst wt.% = 5 and reaction temperature = 393 K

1) Effect of Reaction Temperature:

Table III shows the effect of reaction temperature on the esterification of glycerol over SAZ and SCZ catalysts. The catalytic experiments were performed by varying the temperature from 313 to 393 K. Both SCZ and SAZ catalysts exhibited insignificant catalytic activity at 313 K, whereas enhanced glycerol conversion was obtained by increasing the temperature that shows the beneficial role of temperature in the glycerol esterification. The conversion of glycerol over SCZ and SAZ catalysts was 9 and 3% at 313 K, while ~100 and 89% of glycerol conversion was observed at 393 K, respectively. Interestingly, the selectivity towards DAG and TAG increased with reaction temperature, whereas the selectivity of MAG was decreased. The selectivity of mono-, and di-acylglycerols was 98 and 2% at 313 K of reaction temperature, whereas 25, 59, and 16% of mono-, di- and tri-acylglycerols were obtained at 393 K for the SCZ catalyst. Conversely, only monoacylglycerol was noted in the case of SAZ catalyst at 313 K.

TABLE III EFFECT of REACTION TEMPERATURE in the ESTERIFICATION of GLYCEROL with ACETIC ACID over $\text{Al}_2\text{O}_3\text{-ZrO}_2$ (AZ), $\text{CeO}_2\text{-ZrO}_2$ (CZ), $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-ZrO}_2$ (SAZ) and $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$ (SCZ) CATALYSTS

Catalyst	Reaction temperature (K)	Glycerol conversion (%)	Selectivity (%)		
			MAG	DAG	TAG
SCZ	313	9	98	2	—
	353	37	94	6	—
	393	100	25	59	16
SAZ	313	3	100	—	—
	353	24	97	3	—
	393	89	55	40	5

MAG; Mono-acylglycerol, DAG; Di-acylglycerol, TAG; Tri-acylglycerol

Reaction conditions: molar ratio of acetic acid to glycerol = 6:1, reaction time = 1 h and catalyst wt. % = 5

These exciting findings demonstrated that the selectivity of products varies with glycerol conversion as well as reaction temperature.

2) Effect of Mole Ratio of Acetic Acid to Glycerol:

The effect of mole ratio of acetic acid to glycerol on the glycerol conversion and the products selectivity was investigated over SCZ and SAZ catalysts and the results are displayed in Figs. 3a and 3b, respectively. Surprisingly, the SCZ catalyst showed remarkable activity even at low acetic acid to glycerol molar ratio (Fig. 3a). The glycerol conversion was 90% at molar ratio of 3:1, and the selectivity of mono-, di- and tri-acylglycerols was 57, 38 and 5%, respectively. On the contrary, the SAZ catalyst exhibited low catalytic activity, and the glycerol conversion at 3:1 mole ratio of acetic acid to glycerol was 59% and the selectivity of mono- and di-acylglycerols were 94 and 6%, respectively and no formation of triacylglycerol was noticed (Fig. 3b). Interestingly, by increasing the concentration of acetic acid, better glycerol conversions and high selectivity of di- and tri-acylglycerols are observed for both SAZ and SCZ catalysts. Indeed, more pronounced results are attained in the case of SCZ catalyst. The availability of more concentration of acetic acid at higher molar ratio of acetic acid to glycerol could be the reason for the better selectivity of di- and tri-acylglycerols.

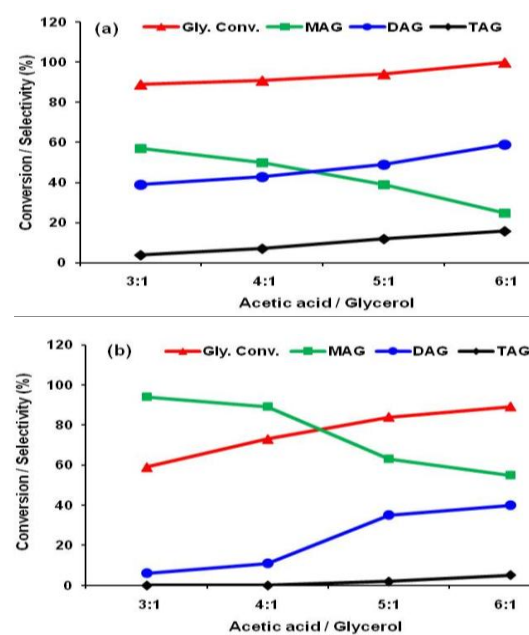


Fig. 3 Effect of mole ratio of acetic acid to glycerol on the glycerol conversion and selectivity of products over (a) $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$ and (b) $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-ZrO}_2$ catalysts

Reaction conditions: reaction time = 1 h, catalyst wt.% = 5 and reaction temperature = 393 K

3) Effect of Catalyst wt. %:

The effect of catalyst wt.% on the glycerol conversion and the selectivity of products over SCZ and SAZ catalysts are shown in Table IV. Other experimental conditions, such as molar ratio of acetic acid to glycerol, reaction time and reaction temperature were remained same. It can be noted that the SCZ catalyst shows better glycerol conversion and selectivity towards mono-, di- and tri-acylglycerols even at low catalyst wt.%. The glycerol conversion at 1 wt.% of catalyst was 94% and selectivity towards mono-, di- and tri-acylglycerols were 63, 32 and 5%, respectively. Conversely, very low glycerol conversion (56%) and selectivity of mono- (87%) and di-acylglycerols (13%) and no formation of triacylglycerol were noted in the case of SAZ catalyst at 1 wt.% of catalyst. Interestingly, the selectivity towards di- and tri-acylglycerols increased with catalyst wt.% for both catalysts that could be due to the availability of more number of active sites. The glycerol conversion of 89 and ~100% were attained, whereas the selectivity of triacylglycerol was 5 and 16% over SAZ and SCZ catalysts at 5 wt.% of catalyst, respectively. However, with further increase of catalyst wt.% there was no significant variation in the glycerol conversion and selectivity of the products (results were not shown).

TABLE IV EFFECT of CATALYST Wt.% in the ESTERIFICATION of GLYCEROL with ACETIC ACID over $\text{Al}_2\text{O}_3\text{-ZrO}_2$ (AZ), $\text{CeO}_2\text{-ZrO}_2$ (CZ), $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-ZrO}_2$ (SAZ) and $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$ (SCZ) CATALYSTS

Catalyst	Catalyst wt.%	Glycerol conversion (%)	Selectivity (%)		
			MAG	DAG	TAG
SCZ	1	94	63	32	5
	2.5	98	39	50	11
	5	100	25	59	16
SAZ	1	56	87	13	–
	2.5	78	68	31	1
	5	89	55	40	5

MAG; Mono-acylglycerol, DAG; Di-acylglycerol, TAG; Tri-acylglycerol

Reaction conditions: molar ratio of acetic acid to glycerol = 6:1, reaction time = 1 h and reaction temperature = 393 K

4) Catalyst Reusability Test:

We investigated the reusability of both SCZ and SAZ catalysts for five catalytic runs and the results are shown in Fig. 4. After each run the catalyst was separated and washed thoroughly with methanol to remove the adsorbed reactants and products. Finally, the washed catalyst was oven dried at 383 K for 1 h followed by activation at 423 K for 2 h for the subsequent run. It was found that the SCZ catalyst shows considerable catalytic performance up to three catalytic runs. The glycerol conversion was ~100 and 96% and selectivity of triacylglycerol was ~16 and 5% for first and three catalytic runs, respectively. Afterward, the activity of SCZ significantly decreased due to repeated usage of catalyst. The conversion of glycerol was 57% and there was no formation of triacylglycerol for the fifth catalytic run. On the other hand, the catalytic activity of SAZ catalyst drastically decreased for the second catalytic run. The conversion of glycerol was ~100 and 96% and selectivity of triacylglycerol was ~16 and 5% for first and second catalytic runs, respectively. At fifth catalytic run, only 5% of glycerol conversion with 100% selectivity of monoacylglycerol and no formation of di- and tri-acylglycerol was noticed. These interesting results suggest that the SCZ catalyst can be recycled multiple times and the activity can be maintained extraordinarily than that of SAZ catalyst. The remarkable catalytic reusability of SCZ catalyst might be due to the existence of higher amounts of super acidic sites.

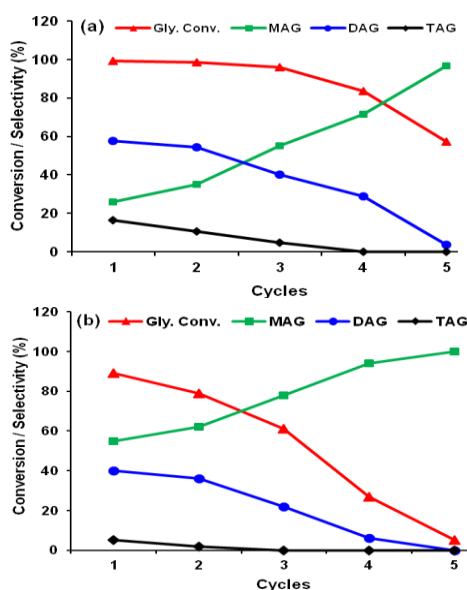


Fig. 4 Effect of catalyst reusability on the glycerol conversion and selectivity of products over (a) $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$ and (b) $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-ZrO}_2$ catalysts.

Reaction conditions: molar ratio of acetic acid to glycerol = 6:1, reaction time = 1 h, catalyst wt.% = 5 and reaction temperature = 393 K.

IV. CONCLUSIONS

The esterification of glycerol with acetic acid was carried out over $\text{Al}_2\text{O}_3\text{-ZrO}_2$, $\text{CeO}_2\text{-ZrO}_2$, $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-ZrO}_2$ and $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$ catalysts. The effect of various parameters such as reaction temperature, molar ratio of acetic acid to glycerol, catalyst wt.% and catalyst reusability were studied to optimize the reaction conditions. It was observed that the $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$ catalyst exhibits excellent catalytic activity (~100% conversion) with better catalyst reusability up to three catalytic runs. The optimized reaction conditions for $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$ catalyst were observed to be 393 K of reaction temperature, 6:1 of acetic acid to glycerol molar ratio and 5 of catalyst wt.%. The selectivity of triacylglycerol in the glycerol esterification was observed to depend on the reaction temperature, acetic acid concentration, catalyst wt.% and the nature of catalyst.

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