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Efficient Esterification of Fatty Acids with Alcohols Catalyzed by $Zr(SO_4)_2 \cdot 4H_2O$ Under Solvent-Free Condition

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Abstract Zirconium sulfate ($Zr(SO_4)_2 \cdot 4H_2O$) was an efficient catalyst for the esterification of fatty acids and alcohols under solvent-free condition. The esterification of fatty acid with branched alcohols using $Zr(SO_4)_2 \cdot 4H_2O$ catalyst gave a good yield of the corresponding ester. The zirconium sulfate Bronsted acid site was suggested to be the catalytically active species in this reaction. In addition, $Zr(SO_4)_2 \cdot 4H_2O$ compound is a potential green catalyst due to its high catalytic activity and low toxicity. This compound is also cost effective, easy to handle, is easily recovered by simple filtration and can be recycled for further reactions.

Keywords Zirconium sulfate · Esterification · Acid catalyst · Green chemistry

1 Introduction

Fatty acid esters have various uses and applications in the chemical and agricultural industry. They can be used as emulsifiers or as oiling agents, lubricants, paints and ink additives, personal care emollients, surfactants, base materials for perfumes, solvent, and oil carriers [1]. They are produced conventionally by esterification of the fatty acids with alcohols. Esterification is usually catalyzed by an acid catalyst donor of protons, such as sulfuric acid, *para*-toluene sulfonic acid or phosphoric acid [2, 3]. However, these homogeneous acid catalysts are toxic, corrosive, environmental hazards and hard to be removed from the reaction medium. Therefore, it is important to replace them with environmental friendly catalysts, which are active under mild conditions, and can be easily recovered and reused. Besides that, the use of large amount of catalysts, condensing reagents, dehydrating agents and activator should be avoided to promote green chemistry.

Solid acid catalysts are environmental friendly with respect to corrosiveness, safety, waste disposal problem and the ease of separation and recovery. Recently, various methods have been explored to find a novel solid acid catalyst. However, esterification reactions have been limited to esters with carbon chain <10 in either carboxylic acid or alcohols [1]. Some commercial available solid acid ion-exchanged catalysts exhibit high activity for water-based reaction but have low thermal stability [4]. For examples, the Amberlyst-15 catalysts are known to be very efficient solid acid ion exchanged catalyst and are commonly used in the industry. However, this acidic resin catalyst is easily deactivated upon heating up to 120 °C for a long period of time and shows poor reusability [5]. The zeolite types solid acid, such as HZSM-5, is also one of the commercial solid acid used for esterification reaction. However, it is limited to applications involving bulky organic molecules reactant, which include fatty acids due to its small uniform pores [4]. The acidic Cs salt of the 12-tungstophosphoric acid is highly active in acid-catalyzed reaction, even in the presence of water, but its low sedimentation poses difficultly to separate it from the reaction suspension [6]. Therefore, the development of a solid acid

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catalyst that not only possesses high activity but also easily separated from the reaction suspension is essential. Some of the other solid catalyst examples for the esterification of long chain aliphatic acids with methanol are tungsten oxide supported on zirconia [7], Ti^{4+} modified with montmorillonite [8], Fe^{3+} modified with montmorillonite [9], and organic sulfonic acid on mesoporous silicas [10, 11].

Studies on the homogeneous and heterogeneous catalysts in the esterification of short chain carboxylic acids with alcohols are widely reported [5, 12–26]. Recently, Yamamoto et al. reported the direct ester condensation of equimolar carboxylic acids and alcohol using Hf^{VI} and Zr^{IV} chlorides [21–23], $ZrOCl_2 \cdot 8H_2O$ and $HfOCl_2 \cdot 8H_2O$ [24], and Zr^{IV}–Fe^{III} complex [24, 25]. Besides that, Sugi et al. investigated the esterification of long chain acids and long chain alcohol using various chlorides salts [27] and $ZrOCl_2 \cdot 8H_2O$ [1, 28] with azeotropic solvent to remove water. Bartoli et al. reported that $Zn(ClO_4)_2 \cdot 6H_2O$ catalyzed condensation of nearly equimolar amount of acids and alcohols with dehydrating agent ($MgSO_4$) [20]. Many other researchers have explored various metal chlorides salts, especially Zr(IV) chlorides salts.

However, little attention was paid on the sulfates compounds, such as zirconium sulfate (ZS) as a potential solid acid catalyst. Other than having high catalytic activity and atom efficiency, green catalysts should also have low toxicity, inexpensive and easy to handle. In general ($Zr(SO_4)_2 \cdot 4H_2O$) or disulfatozirconic acid has low toxicity ($LD_{50} = 3{,}500$ mg kg^{-1}) as compared to that of other Zr(IV) salt, such as $ZrCl_4$ ($LD_{50} = 1{,}688$ mg kg^{-1}) and $ZrOCl_2 \cdot 8H_2O$ ($LD_{50} = 2{,}950$ mg kg^{-1}). In addition, ZS is inexpensive, showed no evidence of carcinogenicity and is considered not poisonous.

Although there large number of literature on acid catalyzed esterifications of carboxylic acid, the "green" synthesis of esters with nearly equimolar amount of long chain fatty acids and various alcohols, which have more than 10 carbon atoms using ZS has not been reported. In addition, the reaction was carried out without additional solvent and dehydrating agents in order to allow a green synthesis procedure.

We report here that ZS is highly effective solid acid catalyst for direct esterification of fatty acid under solvent-free condition. ZS is also easily recovered and recycled to serve for the next reaction.

2 Experimental

2.1 Chemicals

Oleic acid, palmitic acid, lauric acid, linoleic acid, myristic acid, stearic acid, and capric acid were purchased from Sigma–Aldrich Inc. *n*-butanol, *n*-pentanol, *n*-hexanol, *n*-heptanol, *n*-heptanol, *n*-octanol, *n*-dodecanol, *n*-nonanol, isobutyl alcohol, 2-pentanol, 2-nonanol, and 3-nonanol were purchased from Merck. All chemical were used without further purification.

2.2 Catalysts

Zirconium sulfate ($Zr(SO_4)_2 \cdot 4H_2O$) of AR grade was purchased from Beijing Shiji Chemical Co. Other metal salt, such as $MgSO_4 \cdot 7H_2O$, $Na_2SO_4 \cdot 10H_2O$, $CaSO_4 \cdot 2H_2O$, $CdSO_4 \cdot 8/3H_2O$, $MnSO_4 \cdot H_2O$, $CuSO_4 \cdot 5H_2O$, $ZnSO_4 \cdot 7H_2O$, $Al_2(SO_4)_3 \cdot 18H_2O$, $Fe_2(SO_4)_3 \cdot xH_2O$, $FeSO_4 \cdot 7H_2O$, $Zr(SO_4)_2 \cdot 4H_2O$, $ZrCl_4$, $ZrOCl_2 \cdot 8H_2O$, and $Zr(OC_2H_5)_4$ were purchased from Sigma–Aldrich Inc. The Amberlyst-15 and Nafion-H (NR 50, 7–8 mesh) were also purchased from Sigma–Aldrich Inc. Zeolite types solid acid, such as H–Y (Si/Al = 4), HZSM-5 (Si/Al = 38), Hβ (Si/Al = 8), and H-mordenite (Si/Al = 5) were obtained from commercial sources.

2.3 Esterification

The esterification was performed in a three-neck flask at atmospheric pressure equipped with a teflon-coated magnetic stirring bar, a thermometer, a Dean-Strak receiver and a reflux condenser. A nearly equimolar of fatty acid and alcohol were charged into the round-bottomed flask without additional solvent and dehydrating agents. After that, an 5 wt% of catalyst based on the fatty acid, which act as a limiting agent was also charged. For examples, esterification reactant consists of oleic acid (28.2 g, 100 mmol), *n*-butanol (8.9 g, 120 mmol) and fresh catalyst of ZS (1.41 g, 4 mmol) were charged. The reaction temperature was slowly raised to 110–120 °C and maintained at the desired temperature during the specified reaction period. The products were determined by gas chromatography (FID-GC, Agilent 6890) consists of a HP-Innowax column (30 m × 0.25 mm × 0.25 µm). The parameter for the temperature program; started at 120 °C (1 min), ramp at 10 °C min^{-1} to 250 °C (5 min). The amount of the dissolved catalyst after the reaction was estimated by inductively coupled plasma atomic emission spectroscopy (ICP-OES) (Shimadzu ICPE-9000).

2.4 Reuse and Recycling of the Catalysts

The reuse and recycling properties of the catalysts were examined by esterification of the oleic acid with *n*-butanol. The ZS catalyst was recycled to serve for the next reaction without washing or further treatment, such as calcinations. The same amount of reactant and catalyst were used for each of the recycled reaction.

3 Results and Discussion

Table 1 summarizes catalytic activities of some zirconium sulfate (ZS) and other metal sulfate catalysts in the esterification of oleic acid with *n*-butanol. The reaction was carried out without using additional solvent, such as toluene or dehydrating agents in order to promote a more environmental friendly reaction. For the results, ZS (entry 12) demonstrated the highest catalytic activity for esterification of fatty acid. It is arguable that the high catalytic activity of ZS may not contribute from heterogeneous catalyzed reaction but may associate with homogeneous catalyst derived from ZS. It is said that the sulfate ion in ZS may break down and dissociate into sulfuric acid (H_2SO_4) in the presence of water during the reaction. In consideration of sulfuric acid is a strong liquid acid catalyst, the esterification in the presence of ZS might be a homogeneously catalyzed reaction.

In order to further justify this matter, we carried out the same reaction using various metal sulfate salts. It is surprising that a wide range of metal sulfate salts. Cd^{II}, Mn^{II}, Cu^{II}, Zn^{II}, Al^{III}, Fe^{II}, and Fe^{III} sulfate were found to give good to moderate yield of butyl oleate (entries 5–11). However, Mg^{II}, Na^{I}, and Ca^{II} sulfate have relatively low or no catalytic activity for esterification (entries 2–4) as compared to reaction without catalyst. These results led us to believe that catalytic activity is greatly influenced by the cationic metal moiety as the catalyst active species and not due to the sulfate ions. To give a better insight, various zirconium salts have also been investigated under same reaction condition. It was found that zirconium salts are highly efficient catalysts for the esterification as they gave comparable but not the same yield as ZS (entries 12–15). The catalytic activity of these zirconium salts was slightly affected by the anion moiety. However, zirconium salts with sulfate moiety showed the highest catalytic activity among other zirconium salts. We believe that the crystal structure of ZS plays a relevant role as the active species in this reaction and the high catalytic activity is not due to the dissociation of ZS into sulfuric acid. In other words, esterification reaction in the presence of ZS is a heterogeneously catalyzed reaction. The esterification of oleic acid was slow without catalyst (entry 1) only able to achieve 36% yield under the same reaction conditions. Therefore, ZS possesses a heterogeneous catalytic activity rather than homogeneous catalytic activity.

Table 1 A comparison of the esterification of oleic acid with *n*-butanol over various metal salts and solid acid catalysts[a]

Entry	Catalysts	Yield (%)
1	Without catalyst	36.3
2	$MgSO_4 \cdot 7H_2O$	36.1
3	$Na_2SO_4 \cdot 10H_2O$	36.1
4	$CaSO_4 \cdot 2H_2O$	37.1
5	$CdSO_4 \cdot 8/3H_2O$	48.7
6	$MnSO_4 \cdot H_2O$	52.1
7	$CuSO_4 \cdot 5H_2O$	54.8
8	$ZnSO_4 \cdot 7H_2O$	71.2
9	$Al_2(SO_4)_3 \cdot 18H_2O$	73.1
10	$Fe_2(SO_4)_3 \cdot xH_2O$	88.4
11	$FeSO_4 \cdot 7H_2O$	88.0
12	$Zr(SO_4)_2 \cdot 4H_2O$	89.4
13	$ZrCl_4$	85.9
14	$ZrOCl_2 \cdot 8H_2O$	85.3
15	$Zr(OC_2H_5)_4$	82.2
16	Nafion-H[b]	37.5
17	HZSM-5 (Si/Al = 38)[b]	39.1
18	HY (Si/Al = 4)[b]	39.6
19	Hβ (Si/Al = 8)[b]	41.8
20	H-mordenite (Si/Al = 5)[b]	38.3

[a] Reaction conditions: substrates: oleic acid (100 mmol), *n*-butanol (120 mmol); catalysts: 4 mmol; reaction temperature: 120 °C; reaction time: 4 h

[b] Catalyst amount is 5 wt% based on oleic acid as the limiting agent

In addition, Table 1 (entries 16–20) also summarizes the catalytic activity data of various solid acid catalysts. Among these solid acids, ZS still exhibited the highest catalytic activity for esterification. In contrast, Nafion-H known as a strong solid acid catalyst [29], showed low catalytic activity for the above reaction (entry 16). Many zeolite types catalyst, such as HZSM-5, HY, Hβ, and H-mordenite (entries 17–20), were not effective because the reactant cannot enter easily into the small pores of zeolites. It is noteworthy that the small pores prevent the entry of the bulky organic molecules reactant, such as oleic acid, into their acid sites.

The scopes of esterification of the fatty acids of different chain length with alcohols using ZS catalyst are presented in Table 2. The reaction between oleic acid and *n*-butanol under solvent-free condition produced 89% of butyl oleate. The esterification reactions catalyzed by ZS occurred without isomerization at the double bond. The yield of ester with *n*-butanol catalyzed by ZS was in the range of 87–89% (entries 1–7). The catalytic activity of ZS was not significantly influence by the chain length of fatty acids. We further examined the present system in ester reaction with different chain length (C_4 to C_{12}) and branched alcohol. It was observed that the catalytic activity of higher chain alcohol showed a higher catalytic activity as compared to *n*-butanol (entries 8–13). This indicated that yield of ester with oleic acid was slightly influenced by the chain length of alcohols.

The esterification of oleic acid with isobutyl alcohol (entry 14) appeared to give higher yields of esters as compared to *n*-butanol. This means that ZS is highly active for

Table 2 The esterification of different fatty acids and alcohols over ZS catalyst under solvent-free-condition[a]

Entry	Fatty acids	Alcohols	Yield (%)
1	Oleic acid	*n*-Butanol	89.4
2	Lauric acid	*n*-Butanol	88.2
3	Palmitic acid	*n*-Butanol	88.0
4	Linoleic acid	*n*-Butanol	89.1
5	Myristic acid	*n*-Butanol	89.0
6	Stearic acid	*n*-Butanol	86.9
7	Capric acid	*n*-Butanol	89.2
8	Oleic acid	*n*-Pentanol	92.3
9	Oleic acid	*n*-Hexanol	93.9
10	Oleic acid	*n*-Heptanol	93.6
11	Oleic acid	*n*-Octanol	95.9
12	Oleic acid	*n*-Nonanol	93.0
13	Oleic acid	*n*-Dodecanol	92.2
14	Oleic acid	Isobutyl alcohol	91.6
15	Oleic acid	2-Pentanol	79.8
16	Oleic acid	3-Pentanol	58.7
17	Oleic acid	2-Nonanol	85.6
18	Oleic acid	3-Nonanol	61.7

[a] Reaction conditions: substrates: fatty acids (100 mmol), alcohols (120 mmol); catalysts: 5 wt% based on fatty acid; reaction temperature: 120 °C; reaction time: 4 h

Table 3 Effects of reaction variables on the esterification of oleic acid with *n*-butanol over ZS catalyst under solvent-free condition[a]

Entry	Fatty acid:alcohol (mol ratio)	Catalyst amount (wt%)	Time (h)	Yield (%)
1	1:1.2	1	4	81.0
2	1:1.2	2	4	84.8
3	1:1.2	3	4	87.7
4	1:1.2	4	4	88.3
5	1:1.2	5	4	89.4
6	1:1.2	7	4	90.5
7	1:1.0	5	4	83.7
8	1:1.4	5	4	91.0
9	1:1.8	5	4	89.4
10	1:2.6	5	4	73.0
11	1:1.2	5	8	94.5
12	1:1.2	5	16	99.2

[a] Reaction conditions: substrates: oleic acid (100 mmol), *n*-butanol (120 mmol); catalysts: 5 wt% based on fatty acid; reaction temperature: 120 °C

branched alcohol. However, the esterification of oleic acid with 2-pentanol and 3-pentanol (entries 15 and 16) was lower than *n*-pentanol. This phenomenon was also observed with 2-nonanol and 3-nonanol (entries 17 and 18) as compared to that of *n*-nonanol. However, the esterification reaction of this secondary alcohol could be improved by prolonging the reaction time. We conclude that ZS is an active catalyst for long chain and branched alcohols but less active with secondary alcohols. The low reactivity may be due to the blocking of space around the hydroxyl group in the secondary alcohols. Nonetheless, the yield of esters from branched alcohols is rather insensitive to steric factors.

It is impractical to use a large amount of catalyst, and moreover the removal of the adsorbed high molecular weight products, such as butyl oleate from the catalyst is expensive. Hence, we optimized the catalyst loading based on the limiting reactant. The effect of the catalyst loading on the conversion is presented in Table 3. It is observed that the conversion of oleic acid increases in response to the increased of the amount of catalyst (entries 1–6). This finding is expected because the catalyst loading increment is proportional to the availability of the acid sites, which allow accessibility of a large number of reactant to the catalyst active sites. There was no significant catalytic enhancement for catalyst loading above 5 wt% because reaction kinetic mechanism limitation rather than catalyst amount limitation.

In order to achieve better yields of esters with minimum cost, we also varied the fatty acid/alcohol ratios as shown in Table 3 (entries 7–10). Results showed that the yield increases in proportional to the fatty acid/alcohol ratios. By further increase to the mole ratio to above 1:1.8, a decrease in yield was observed. The decrease in yield at mole ratio of 1:2.6 was due to the flooding of active sites with alcohols molecules rather than oleic acids. These results support the findings that were reported by others [12, 13]. It is likely that the increase of mole ratio hinders complete protonation of oleic acid at the catalyst active sites.

When the reaction time of 5 wt% catalyst and fatty acid/alcohol at a ratio of 1:1.2 was prolonged, the yield of butyl oleate increased as shown in Table 3 (entries 11 and 12). For instance, the yield increased from around 89.4% in the first 4 h to around 94.5% 4 h later; upon increasing the reaction time to an additional 8 h, the conversion increased to 99.2%. It was concluded that with the suitable amount of catalyst and fatty acid/alcohol ratios, optimum yield of ester can be obtained by prolonging the reaction time.

The reusability of ZS catalyst for the esterification of oleic acid with butanol is shown in Table 4. An 15% decrease in the yield of butyl oleate was observed and remained for the third and fourth cycle. The decrease of the yield did not affect the selectivity of the catalyst. The selectivity did not alter significantly, which remains the same at more than 99% for the fresh and all recycled catalyst. It is interesting to note that a slight decrease was observed in the second recycle of the esterification of oleic acid with *n*-butanol. There was no further decrease during the third and fourth recycle of the ZS catalyst. It should be

Table 4 The regeneration of ZS catalyst in the esterification of oleic acid with *n*-butanol[a]

Entry	Times of reuse	Yield (%)
1	Fresh	89.4
2	First recycle	75.5
3	Second recycle	74.4
4	Third recycle	74.4
5	Fourth recycle	75.1
6	Fifth recycle[b]	89.0

[a] Reaction conditions: substrates: oleic acid (100 mmol), *n*-butanol (120 mmol); catalysts: 5 wt% based on fatty acid or 4 mmol; reaction temperature: 120 °C; reaction time: 4 h

[b] The catalyst was separated by filtration, washed with dichloromethane, and dried at 100 °C for 2 h

emphasized that the ZS catalyst settled rapidly after the stirring had stopped, which allowed easy recovery of the catalyst by filtration. These results demonstrated that ZS is reusable for esterification of fatty acid without special treatment, such as calcination or acid washing.

Zirconium ion was not detected by ICP-OES in the reaction mixtures during first, second, third and fourth time of reuse. Therefore, it was suggested that there was no dissolution of ZS during the reaction. This further proved that this reaction is heterogeneous catalyzed reaction because ZS did not dissociate into sulfuric acid. Although there was a drop of the catalytic activity after the second time of reuse, the catalyst was recovered after washing with dichloromethane and gave comparable performance as the fresh catalyst.

The crystal structure of ZS was suggested to play an important role as the active species for esterification. The $Zr(SO_4)_2 \cdot 4H_2O$ is known to be an ion exchanger, which has a layered structure [30]. Within the layers, each zirconium (Zr) atom is attached to four sulfate groups, and each sulfate group is attached to two Zr atom [30, 31]. Also, each Zr atom is bind with four water molecules, and each water molecule is bind with one Zr atom.

As shown in Fig. 1, it was suggested that ZS comprised of Bronsted and Lewis acid sites. The Bronsted acid sites are formed the weakening of the –OH bond by the sulfate groups attached to Zr. Meanwhile, the Lewis acid sites are shorts of electrons, at the Zr^{4+} center as electron withdrawn from the sulfate groups [30]. It was suggested that these active species are the active centers for the esterification of fatty acid. Preliminary results showed that the esterification may take place through a ligand exchange reaction with fatty acid on the Bronsted acid sites [30]. We also believe that the zirconium sulfate have many acid sites on its outer surface because the interlayer of ZS was rather small to permit the entry of bulky organic molecules such as fatty acid.

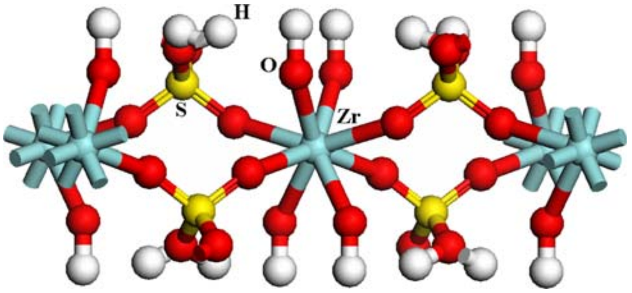

Fig. 1 The structure of zirconium sulfate tetrahydrate ($Zr(SO_4)_2 \cdot 4H_2O$)

4 Conclusion

In conclusion, ZS was an efficient catalyst for the esterification of various fatty acids with long chain and branches alcohols under solvent-free condition. Notably, ZS is a potential green catalyst due to its low toxicity, possesses high catalytic activity, ease of handling, and reusability. Thus, we conclude that ZS can provide a green protocol as a new candidate of solid acid catalyst for the above reactions.

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