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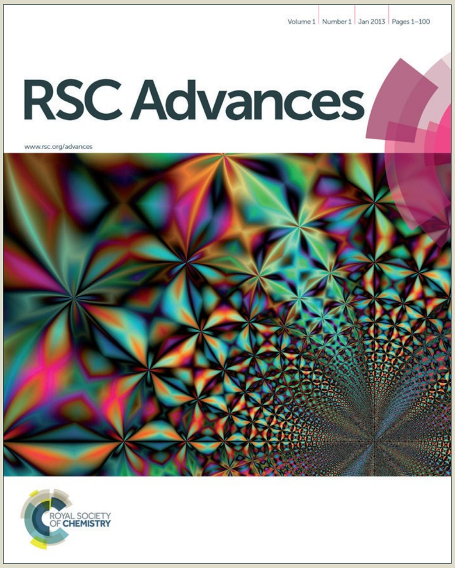

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SO_3H and NH_2^+ Functional Carbon-based Solid Acid Catalyzed Transesterification and Biodiesel Production

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The SO_3H and NH_2^+ functional carbon-based solid acid was used as a highly activity heterogeneous catalyst for the transesterification of various carboxylic methyl esters with alcohols under mild conditions. It also showed high catalytic performance for transesterification of triolein with methanol or isopropanol. Furthermore, it was able to catalyze simultaneous esterification and transesterification of rice oil and Butter respectively, the yields of biodiesel obtained were up to 94%, and the catalyst could be easily recovered and reused more than ten times without loss of activity, which indicated the carbon-based solid acid was a potential catalyst for the biodiesel industry.

Introduction

Esters are important organic compounds possessing various applications in the fine chemical industry, materials science and biodiesel industry.[1,2,3] Transesterification of esters also was regarded as an alternative method to synthesize diverse esters in case the carboxylic acids were poorly soluble or had very high viscosity and high adsorption, or simply if the actual feedstock consists of esters.[4,5,6] Especially in the process of biodiesel production, transesterification of triglycerides with low alcohols was a usable method to produce monoesters of fatty acids.

Biodiesel is a promising alternative to conventional petroleum based diesel fuel.[7,8] It was defined as the alkyl (Me, Et, *etc.*) monoesters of fatty acids from renewable resources,[9,10] such as vegetable oils, animal fats, and waste restaurant oils and greases.[11,12,13,14] Because different oils and fats contained a range of free fatty acids (FFA) and water concentrations in addition to triglycerides, the biodiesel was usually produced by acid-catalyzed esterification of free fatty acids, followed by base-catalyzed transesterification of triglycerides after removed water in order to avoid formation of soap and emulsions which make phase separation of the glycerol and the methyl esters difficult.[15,16] Traditionally, the strong Brønsted acids such as sulfuric acid, *p*-toluenesulfonic acid were used as catalysts for esterification,[17,18] and strong Brønsted bases such as sodium or potassium hydroxides were used for transesterification.[19] However, the separation and recovery of these homogeneous catalysts were the main problems. Neutralization of highly corrosive strong acids or bases resulted in the formation of salts, which must be washed away from the products to generate significant amount of wasters. Concerning the increasing environmental and economic concerts, recent researches had mostly focused on the application of heterogeneous catalysts as replacements of homogenous catalysts for esterification and transesterification, because they could be readily separated from the products and repeated reuse.[20]

Recently, we had successfully prepared a carbon-based solid acid (GDTCSA) through one-step of heating the mixture of D-glucose, diphenylammonium tosylate ($[Ph_2NH_2]^+[OTs]^-$) and TsOH. Its composition was determined by elemental analysis to be $CH_{0.89}O_{0.2}N_{0.03}S_{0.04}$, which indicates that sulfur not only existed in the forms of *p*-TsOH to form a salt with diphenylamine, but there is also about 1/4 sulfur attached to the polycyclic aromatic carbon sheets in the forms of SO_3H groups, the acid amount of SO_3H groups and $[Ph_2NH_2]^+[OTs]^-$ is 2.43 $mmol\cdot g^{-1}$. And $[Ph_2NH_2]^+[OTs]^-$ is the main active site. The catalyst showed high activity and selectivity in the catalytic ester condensation, and was recycled ten times without losing the catalytic activity.[21] In the next work, we found GDTCSA also exhibited the high activity for transesterification of different structural carboxylic methyl esters with alcohols, and it was an effective catalyst for the simultaneous esterification and transesterification of a variety of greases having 5 or 20wt% of FFA contents with methanol or isopropanol. In this report, we would describe in detail its catalytic performance for transesterification and biodiesel production.

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Results and discussion

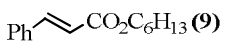
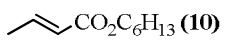
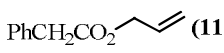
GDTCSA catalyzed transesterification of methyl carboxylates with alcohols

We initiated our studies of transesterification using methyl 4-phenylbutyrate and hexanol as model substrates to investigate the optimal reaction conditions including temperature, time, mass ratio of materials and catalyst loading. It was found that the conversion of methyl 4-phenylbutyrate transesterified with hexanol (mass ratio of 1 : 1.5) could reach 94% when the reaction was carried out at 80 °C for 6 hours with 5 mol% GDTCSA under solvent free conditions.

Under the optimized conditions, we investigated the scope with regard to carboxylic acid methyl esters and alcohols. The results were summarized in Table 1. The transesterification of methyl phenylacetate, methyl 4-phenylbutyrate, or line chain carboxylic acid methyl esters with straight-chain alcohols (Entries 1, 2, 3, 4, 5, 6) and allylic alcohol (Entry 11), were efficiently catalyzed by GDTCSA to afford the corresponding esters in high yields. Steric hindrance methyl pivalate (Entry 7), methyl benzoate (Entry 8) and α, ß-unsaturated carboxylic acid methyl esters (Entries 9, 10) were converted to the corresponding hexyl ester in good yields with higher temperature and longer time. Specially, secondary alcohols, for example, cyclododecanol, cyclohexanol and (-)-Menthol (Entries 12-16) also reacted with carboxylic acid methyl esters to give transesterification products effectively at 120 °C for 11-15 hours, which also showed GDTCSA had good selectivity.

Table 1 Transesterification reaction between methyl carboxylates and alcohols catalyzed by GDTCSA.[a]

$$\underset{(1.0\text{ eq.})}{R^1CO_2CH_3} + \underset{(1.5\text{ eq.})}{R^2OH} \xrightarrow{\text{GDTCSA (5 mol\%)}} R^1CO_2R^2 + CH_3OH$$

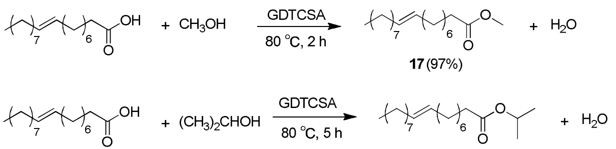
Entry	$R^1CO_2R^2$	t (h)/T (°C)	Yield (%)[b]	Entry	$R^1CO_2R^2$	t (h)/T (°C)	Yield (%)[b]
1	$PhCH_2CO_2C_{12}H_{25}$ **(1)**	9/80	95	9	 **(9)**	18/120	91
2	$PhCH_2CO_2Bn$ **(2)**	6/80	92	10	 **(10)**	16/120	90
3	$Ph(CH_2)_3CO_2C_6H_{13}$ **(3)**	6/80	94	11	 **(11)**	7/80	93
4	$Ph(CH_2)_3CO_2C_8H_{17}$ **(4)**	7/80	95	12	$PhCH_2CO_2C_{12}H_{23}$[d] **(12)**	13/120	92
5	$C_{11}H_{23}CO_2C_6H_{13}$ **(5)**	8/80	93	13	$Ph(CH_2)_3CO_2C_{12}H_{23}$[d] **(13)**	15/120	85
6	$C_{17}H_{33}CO_2C_6H_{13}$[c] **(6)**	9/80	91	14	$PhCH_2CO_2C_6H_{11}$[e] **(14)**	11/120	92
7	t-$BuCO_2C_6H_{13}$ **(7)**	13/100	91	15	$C_{11}H_{23}CO_2C_6H_{11}$[e] **(15)**	13120	94
8	$PhCO_2C_6H_{13}$ **(8)**	16/120	90	16	$Ph(CH_2)_3CO_2C_{10}H_{19}$[f] **(16)**	15/120	90[g]

[a] Unless otherwise noted, a solution of methyl carboxylate (2 mmol) and alcohol (3 mmol) was heated at a certain temperature in the presence of GDTCSA (2.43 mmol NH_2^+ and $SO_3H\cdot g^{-1}$; 40 mg, 0.1 mmol). [b] Isolated yields. [c] Oleic acid ($C_{18}H_{34}O_2$) was used. [d] Cyclododecanol ($C_{12}H_{23}OH$) was used. [e] Cyclohexanol ($C_6H_{11}OH$) was used. [f] (-)-Menthol ($C_{10}H_{19}OH$) was used. [g] $[\alpha]_D^{25}$ - 59.2 ° (c 1.38, CH_2Cl_2).

GDTCSA catalyzed biodiesel production

In our studies, the solid acid GDTCSA showed the high catalytic activity for both esterification and transesterification, so it was applicable to the synthesis of biodiesel. We firstly investigated the esterification of oleic acid with small molecule alcohols catalyzed by GDTCSA. As shown in Scheme 1, the GDTCSA exhibited the high catalytic activity for the esterification of oleic acid with methanol under the conditions of mass ratio of oleic acid to alcohol of 1 : 2, 2 mol% catalyst, 80 °C and atmospheric pressure. The methyl oleate (**17**) yield reached 97%.

We also investigated the reaction of oleic acid and isopropanol. Methyl or ethyl esters of vegetable oils or animal fats had considerable higher crystallization temperatures than diesel fuel, which affect biodiesel performance at temperatures below ~ 0 °C.[22] Branched fatty acid esters derived by replacing the methyl group in the ester moiety with branched groups such as isopropyl and isobutyl had been reported possessed lower melting points and their mixtures had lower cloud and pour points, it could reduce the tendency of biodiesel to crystallize at low temperatures.[23] In our experiments, GDTCSA also could catalyze the esterification of oleic acid and isopropanol efficiently, the isopropyl oleate (**18**) was smooth obtained with 96% yield (Scheme 1).



Scheme 1 Esterification between oleic acid and alcohols catalyzed by GDTCSA.

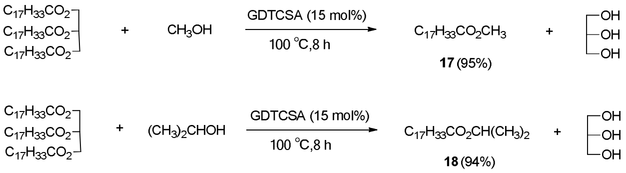
Next, we studied the transesterification of triolein with methanol catalyzed by GDTCSA (Table 2). It could be seen, the conversion of methyl oleate had reached 97% when the mass ratio of triolein and methanol was 1 : 0.6 (Entry 2). The effect of temperature and time on the conversion of methyl oleate was also evaluated, and the admirable temperature within 8 hours was 100 °C (Entries 2, 4, 5). Too higher temperature (Entry 5) and too longer time (Entry 9) were not necessary for the further increase of the conversion. Further, the influence of amount of catalyst on the conversion was checked from 10 mol% to 20 mol% (Entries 2, 6, 7), and the optimal amount of catalyst was 15 mol%. To sum up, the optimum conditions for transesterification of triolein with methanol were as follows: the mass ratio of triolein and methanol 1 : 0.6, the reaction temperature 100 °C, reaction time 8 hours and 15 mol% of GDTCSA in seal tube. Methyl oleate (**17**) was isolated in 95% under these reaction conditions (Scheme 2).

Table 2 Optimization of the transesterification reaction of triolein and methanol catalyzed by GDTCSA.[a]

Entry	W(Methanol) : W(Triolein)	Temp. (°C)	Catalyst (mol%)	Time (h)	Conv. (%)[b]
1	1.2	100	15	8	98
2	0.6	100	15	8	97
3	0.3	100	15	8	86
4	0.6	80	15	8	84
5	0.6	120	15	8	98
6	0.6	100	10	8	88
7	0.6	100	20	8	99
8	0.6	100	15	6	85
9	0.6	100	15	10	98

[a] The reactions were carry out in a 50 mL seal tube. [b] The conversion of methyl oleate based on triolein was evaluated by HPLC analysis.

The transesterification of triolein with isopropanol was tested with GDTCSA as catalyst. In generally, transesterification with the secondary alcohols was less smooth and gave lower yields compared with primary alcohols due to steric hindrance.[24] But in our experiments, triolein was converted to the isopropyl oleate (**18**) in excellent yield (94%) under the same conditions as shown in Scheme 2.



Scheme 2 Transesterification reaction between triolein and alcohols catalyzed by GDTCSA.

Furthermore, we checked the recycling of the GDTCSA catalyzed transesterification of triolein with methanol. After completion of the reaction, the catalyst was easily recovered from reaction mixture by centrifugation, washed with *n*-heptane and dried. The results of recycling experiments were summarized in Table 3. As shown in Table 3, the conversion of the desired product in all cases was found to be almost similar which confirmed that the GDTCSA catalyst can be reused efficiently without any significant loss in activity for ten runs.

Table 3 The cycle experiments of catalytic activity for transesterification of triolein and methanol.[a]

Run	1	2	3	4	5	6	7	8	9	10
Conv. (%)[b]	97	97	97	97	96	96	96	96	95	95

[a] Reagents and conditions: triolein (0.89 g, 1 mmol), methanol (0.54 g, 17 mmol) and GDTCSA (2.43 mmol NH_2^+ and $SO_3H{\cdot}g^{-1}$; 60 mg, 0.15 mmol) were reacted in a 50 mL seal tube under 100 °C for 8 hours. The recovered catalyst was reused for the next reaction with keeping same mole ratio. [b] The conversion of methyl oleate based on triolein over time was evaluated by HPLC analysis.

We then applied this catalytic system to the synthesis of biodiesel. Rice oil (20 wt% FFA, 1-2 wt% water) was smoothly converted with methanol (Table 4, Entry 1). It could be obviously seen from ^1H NMR spectra (Fig.1), methyl ester (CH_3OOC-) peak occurred at 3.6 ppm (Fig.1 b), methine (-CH-) and methylene (-CH_2-) peaks at 5.2 and 4.2 ppm of triglycerides in material (Fig.1 a) disappeared respectively in the ^1H NMR of product.[25] We also examined the reaction of rice oil with isopropanol (Table 4, Entry 2), the grease was converted into isopropyl esters using GDTCSA as catalyst. The methine (-CH-) of isopropyl ester at 5.0 ppm could be observed in the ^1H NMR of product (Fig.1 c).[26] Further, Butter (5 wt% FFA, 0.2-0.5 wt% water) was treated with methanol or isopropanol in same conditions (Table 4, Entries 3, 4), and it could be seen from ^1H NMR spectra (Fig.2), similar results were obtained.

Table 4 The reaction of greases and alcohols catalyzed by GDTCSA.[a]

Entry	Grease	Alcohol	Yield (%)[b]
1	Rice oil[c]	MeOH	96
2	Rice oil[c]	^{i}PrOH	99
3	Butter[d]	MeOH	95
4	Butter[d]	^{i}PrOH	98

[a] Reagents and conditions: grease (5.3 g), methanol or isopropanol (3.2 g) and GDTCSA (2.43 mmol NH_2^+ and $SO_3H{\cdot}g^{-1}$; 0.36 g, 0.9 mmol) were reacted in a 50 mL seal tube at 100 °C for 8 hours. [b] Isolated weight yields. [c] rice oil (20 wt% FFA, 1-2 wt% water). [d] Butter (5 wt% FFA, 0.2-0.5 wt% water).

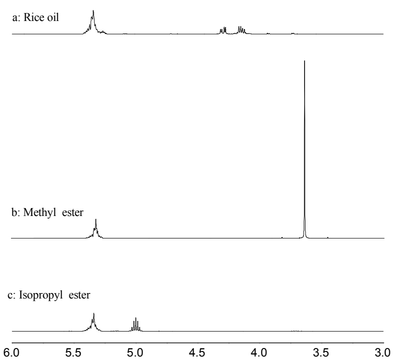


Fig. 1 ^1H NMR spectra of rice oil and esters.

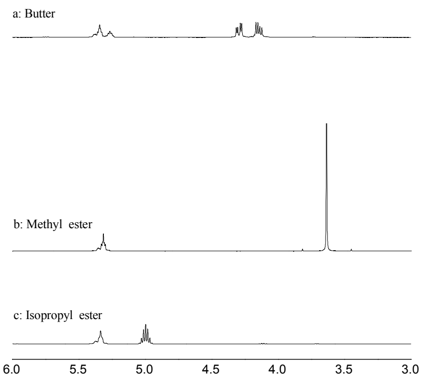


Fig. 2 ^1H NMR spectra of Butter and esters.

Furthermore, the recycling of the GDTCSA catalyzed reaction of rice oil and isopropanol was checked. And it also could be recovered and reused more than ten times without loss of activity (Table 5).

Table 5 The cycle experiments of catalytic activity for reaction of rice oil and isopropanol.[a]

Run	1	2	3	4	5	6	7	8	9	10
Conv. (%)[b]	98	98	98	97	97	97	97	96	96	96

[a] Reagents and conditions: rice oil (5.3 g), isopropanol (3.2 g) and GDTCSA (2.43 mmol NH_2^+ and $SO_3H{\cdot}g^{-1}$; 0.36 g, 0.9 mmol) were reacted in a 50 mL seal tube under 100 °C for 8 hours. The recovered catalyst was reused for the next reaction with keeping same mole ratio. [b] The conversion of isopropyl oleate based on rice oil over time was evaluated by HPLC analysis.

Through the above experiment results, it was found that GDTCSA had high catalytic activity for both esterification and transesterification, the free water and produced water in the greases did not affect the conversion of biodiesel since GDTCSA had a strong hydrophobicity.

Conclusions

In summary, the carbon-based solid acid Functionalized with NH_2^+ and SO_3H Groups was used as a highly activity catalyst for transesterification. The carbon material showed broad substrate scopes for transesterification under mild reaction conditions. What's more, the carbon-based solid acid could be used to catalyze vegetable oil and animal fat to prepare biodiesel by the simultaneous esterification and transesterification. And the catalyst could be recovered and recycled without any significant loss in activity during ten cycles.

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