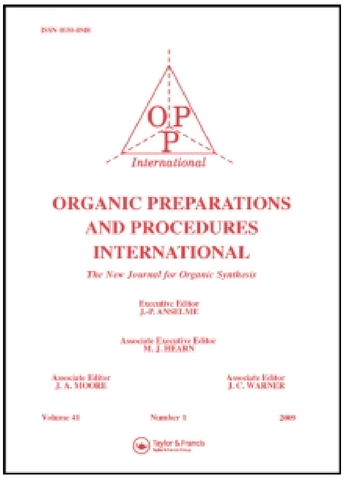

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EFFICIENT ESTERIFICATION OF ALIPHATIC CARBOXYLIC ACIDS CATALYZED BY COPPER METHANESULFONATE

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EFFICIENT ESTERIFICATION OF ALIPHATIC CARBOXYLIC ACIDS CATALYZED BY COPPER METHANESULFONATE

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Traditional catalysts for the esterification of carboxylic acids such as sulfuric acid and hydrochloric acid, are corrosive and often difficult to remove.[1] Several new types of catalysts and/or methods have been explored, and include hafnium salts,[2] zirconium salts,[3] scandium salts,[4] diphenylammonium triflate (DPAT),[5] aluminium salts,[6] tetraalkylammonium fluorides,[7] lanthanide salts,[8] ion exchange resins,[9] polyaniline salts,[10] zeolites,[11,12] heteropoly compounds,[13] solid superacids,[14] etc. The esterification of carboxylic acids with equimolar amounts of alcohols using eco-friendly catalysts, such as new solid reagents that are less toxic and facilitate recovery and recycling, is a most desirable goal. We now report copper methanesulfonate (CMS)[15] exhibits efficient catalytic activity and reusability in some esterifications of aliphatic carboxylic acids with alcohols.

The catalytic activity of various metal Lewis acids (1.0 mol%) were investigated in the esterification of lauric acid (0.05 mol) with *n*-butanol (0.055 mol) at reflux temperature with cyclohexane (5 mL) for 2.5 h. *Table 1* shows that both $Cu(CH_3SO_3)_2$ [CMS] and $Ce(SO_4)_2$ exhibit highly effective catalytic activity in this reaction (yield > 91%). Tin tetrachloride is known as a good esterification catalyst, but its catalytic activity is much lower than that of CMS or cerium (IV) sulfate. Under the same conditions, various other metal salts such as $KAl(SO_4)_2$, $FeCl_3$, $FeSO_4$, $CuCl_2$, $Cu(acac)_2$, $CuSO_4$ are either less active or inert, and $AlCl_3$, $CeCl_3$ and $Cu(OAc)_2$ even inhibit the reaction (the yield is lower than 22%). Although it is evident that the high catalytic activity of CMS is attributable to the $CH_3SO_3^-$ anion, its role is still not clear.

CMS is insoluble in esters and cyclohexane, and only slightly soluble in a mixture of lauric acid and *n*-butanol; however, CMS is soluble in water. At the initial stage of reaction, the system gradually changes from turbid to clear because the produced water is not removed quickly. As more and more water separated from the reaction mixture, CMS gradually precipitates. As a result, the system becomes turbid again, and CMS can be separated by a simple filtration after reaction. This phenomenon exhibits a solid-liquid-solid phase-transfer catalytic phenomenon,[16] which is controlled by the amount of water in the reaction. Therefore, it is necessary to remove the water from the reaction medium for the separation of CMS. In contrast, the catalytic activity of cerium sulfate would be lost for its hydrolysis in reuse.

Table 1. Catalytic Activity of Various Lewis Acids in the Esterification of Lauric Acid with *n*-Butanol

Catalyst	Yield of Ester (%)	Catalyst	Yield of Ester (%)
none	22	$AlCl_3•6H_2O$	3
$Cu(CH_3SO_3)_2•4H_2O$	94	$Ce(SO_4)_2•4H_2O$	92
$CuSO_4•5H_2O$	72	$CeCl_3•7H_2O$	7
$Cu(acac)_2$	33	$SnCl_4•5H_2O$	43
$CuCl_2•2H_2O$	23	$FeCl_3•6H_2O$	52
$Cu(OAc)_2•H_2O$	16	$FeSO_4•7H_2O$	8
$KAl(SO_4)_2•12H_2O$	46	----	----

Reaction conditions: lauric acid, 0.05 mol; *n*-butanol, 0.055 mol; cyclohexane, 5 mL; catalyst, 1.0 mol%; reaction temperature, 85~90°C; reaction time, 2.5 h.

The optimized reaction conditions are summarized in *Table 2*. Entries (1~5 in *Table 2*) show that the increase of ester yield is proportional to the molar ratio of alcohol to acid. High

Table 2. Effect of Various Reaction Conditions of the Esterification of Lauric Acid with *n*-Butanol using CMS as Catalyst

Entry	Alcohol/Acid (molar ratio)	Cyclohexane (mL)	CMS (mol%)	Time (h)	Yield (%)
1	1.0:1	5	1.0	2.5	88
2	1.1:1	5	1.0	2.5	94
3	1.2:1	5	1.0	2.5	95
4	1.3:1	5	1.0	2.5	96
5	1.5:1	5	1.0	2.5	97
6	1.1:1	0	1.0	2.5	82
7	1.1:1	2.5	1.0	2.5	96
8	1.1:1	10	1.0	2.5	79
9	1.1:1	20	1.0	2.5	56
10	1.1:1	5	0	2.5	30
11	1.1:1	2.5	0.25	2.5	96
12	1.1:1	2.5	0.5	2.5	97
13	1.1:1	2.5	1.5	2.5	96
14	1.1:1	2.5	0.5	1.5	94
15	1.1:1	2.5	0.5	2.0	96
16	1.1:1	2.5	0.5	3.0	97

Reaction conditions: lauric acid, 0.05 mol; reaction temperature, 85~90°C molar ratio of alcohol to acid moves equilibrium toward ester formation and acid converting; however, this will result in a waste of alcohol and further problems in product purification. In addition, the increased yield is no longer evident while the molar ratio of alcohol to acid exceeds 1.1:1.0. So the 1.1:1.0 is an appropriate molar ratio of *n*-butanol to lauric acid under the present conditions. Remarkably, using equimolar of alcohol and acid, the yield of ester is 88%.

The water produced has an inhibitive effect on the catalytic activity and handling of the catalyst, and will limit the maximum obtainable conversion. Removal of the water produced is favorable to the synthesized ester. Entries (2, 6~9 in *Table 2*) show that the yield is 82% in the absence of water-carrying agent, while the yield is 96% in the presence of 2.5 mL cyclohexane. Thereafter, the yield obviously decreases with the increase of cyclohexane. This decrease could be attributed to the fact that the addition of the cyclohexane to the reaction system causes a decrease of the reactant concentration. However, it is necessary to add an appropriate amount of water-carrying agent to enhance the yield of ester. For the situation mentioned above, 2.5 mL of cyclohexane is suitable (*ca.* 47 molar percent of lauric acid).

Entries (7, 10~13 in *Table 2*) show that the influence of various amount of CMS on the yield of *n*-butyl laurate. While the yield is 97% at the 0.5 mol% of CMS, it decreases slightly with the concentration of catalyst is increased from 0.5 to 1.5 mol%. So the 0.5 mol% of CMS is an ideal amount to obtain high yield under the present conditions.

Dependence of the yield of *n*-butyl laurate on reaction time is shown in Entries (12, 14~16 in *Table 2*). It is clear that the longer the reaction time, the higher yield. However, the reaction is nearly complete after 2.0 h, longer reaction time is not necessary to increase conversion of lauric acid.

The above shows that CMS is an effective catalyst in the esterification of lauric acid with *n*-butanol. However, one of the most important properties for catalyst is to be reusable. The experiment was repeated eight times with recovered catalyst without any further treatment. The reaction conditions are the same as *Table 1*. For comparison, the reusability of copper sulfate was also examined. CMS exhibits an excellent reusability because its activity in the 8th run is still over 98% compared to that of the first run in the reaction of lauric acid with *n*-butanol. In constrast, the activity of copper sulfate decreases rapidly with recycling.

The scope of the esterification of different aliphatic acids with different alcohols catalyzed by CMS was investigated (*Table 3*). The yield of laurate increases with increasing carbon number of the alcohol. The reasons may be that higher alcohols have higher boiling points and lower solubility in saturated sodium chloride water solution in water separator. For the same carbon number alcohols, the laurate yield of normal alcohol is higher than that of isomeric alcohol. Steric hindrance of isomeric alcohols may be a factor. It is found that the solubility of ethanol in saturated sodium chloride water solution in water separator is very high; therefore, the yield of the ethyl laurate is very low.

Table 3. Esterification of Carboxylic Acids with Alcohols using CMS as Catalyst

Entry	Conditions	Ester	Yield (%)		Bp /°C	
			First run	Final run	Meas.	*Lit.*[17, 18]
1	a	Ethyl laurate	8	----	272^{764}	273^{764}
2	a	Propyl laurate	79	----	204^{60}	205^{60}
3	a	Isopropyl laurate	67	----	197^{60}	196^{60}
4	a	*n*-Butyl laurate	94	93 (8th)	178^{18}	180^{18}
5	a	Isobutyl laurate	91	87 (8th)	173^{18}	----
6	a	Sec-butyl laurate	37	----	171^{18}	----
7	a	Cyclohexyl laurate	86	41 (4th)	174^{2}	----
8	a	Isoamyl laurate	96	----	169^{2}	170^{2}
9	a	Benzyl Laurate	96	72 (6th)	207^{12}	$209\text{-}211^{12}$
10	a	*n*-Octyl laurate	97	----	185^{2}	----
11	b	*n*-Butyl acetate	98	97 (6th)	124^{760}	$125\text{-}126.5^{760}$
12	b	Isobutyl acetate	95	87 (6th)	117^{760}	117.2^{760}
13	b	Isoamyl acetate	99	94 (5th)	140^{760}	142^{760}
14	b	Benzyl acetate	99	93(5th)	214^{760}	215.5^{760}
15	b	Isopropyl chloroacetate	92	87 (8th)	151^{760}	$150.4\text{-}151.6^{760}$
16	c	Isoamyl butyrate	96	96 (5th)	180^{760}	179^{765}
17*	a	*n*-Butyl laurate	72	61 (8th)	178^{18}	180^{18}
18*	b	Isoamyl acetate	83	----	140^{760}	142^{760}
19*	c	Isoamyl butyrate	80	----	180^{760}	179^{765}

*: $CuSO_4$ as catalyst.

Reaction conditions: a) lauric acid, 0.05 mol; alcohols, 0.055 mol; cyclohexane, 5 mL; CMS, 1.0 mol%; reaction temperature, 85-90°C; reaction time, 2.5 h; b) acetic acid and chloroacetic acid, 0.167 mol; alcohols, 0.20 mol; cyclohexane, 5 mL; CMS, 1.0 mol%; reaction temperature, 85-90°C; reaction time, 2.5 h; c) butyric acid, 0.167 mol; isoamyl alcohol, 0.20 mol; CMS, 0.5 mol%; reaction temperature, 130~135°C; reaction time, 2.5 h

Although CMS displays stable reusability without loss of catalytic activity in the many esterification reactions (entries 4, 5, 11~16 in *Table 3*), it gradually lost activity in synthesis of cyclohexyl laurate and benzyl laurate with four runs and six runs, respectively. It is to be noted that excellent yields can be obtained in the absence of cyclohexane in the esterification of butyric acid with isoamyl alcohol.

EXPERIMENTAL SECTION

All reagents are analytical pure. The thermal analysis of CMS was obtained using Pyris 1 TGA of Perkin Elmer. Infrared spectra of CMS and butyl laurate were recorded using Spectrum GX series Fourier Transform instrument of Perkin Elmer. Autosystem XL series Chromatography instrument of Perkin Elmer was use to analyze the product. A ^{1}HNMR spectrum of Butyl laurate was determined on a Varian 200 Gemini spectrometer in $CDCl_3$ with TMS as an internal standard. An EI-MS spectrum was recorded using an AMD 604 spectrometer (Cs^+, 10 keV).

General Procedure for Preparation of CMS.- Cupric oxide (8.0 g, 0.1 mol) was added in portions to a solution of methanesulfonic acid (19.2 g, 0.2 mol) in water (12 g), and the mixture was refluxed and stirred for 1 h. The solution obtained was filtered to remove the unreacted cupric oxide and the filtrate was allowed to crystallize at room temperature and dried in vacuum at 100°C for 3 h. CMS was characterized using TGA and FTIR. The results show its structural formula $[(Cu(CH_3SO_3)_2 \bullet 4H_2O)]$ to be the same as the literature.[19,20]

CMS, FTIR (KBr cm^{-1}), 3276, 2940, 1661, 1421, 1384, 1193, 1050, 779, 619, 534.

FTIR (Nujol Mull cm^{-1}), 3189, 1663, 1218, 1150, 1049, 778, 638, 529.

TG (N_2): loss of crystal water, 22.19% (temp. 140.9~219.0°C); decomposed temperature bound, 374.2~424.8°C; the residue of Cu_2O, measured value 21.21% (Temp. 800°C), (calculated value 21.97%).

Typical Procedure for Esterification.- The esterification reaction of lauric acid with *n*-butanol was carried out in a 100 mL flask equipped with water condenser and water separator. A mixture of lauric acid (10.0 g, 0.05 mol), *n*-butanol (4.16 g, 0.055 mol), CMS (0.163 g, 1.0 mol%) and cyclohexane (5 mL) in a RB flask was refluxed at 85~90°C in an oil bath and performed with vigorous stirring by using a magnetic stirrer for 2.5 h. GC, which showed that there are not side-reactions, was used to monitor reaction system. Toward the end of an esterification, the acid value of the reaction mixture was determined by titration against alcoholic KOH with phenolphalein as indicator. The yield of *n*-butyl laurate was calculated according to the acid value (94%). Finally, evaporation of cyclohexane under reduced pressure gave the crude material, which was purified by silica-gel column chromatography (hexane:ether = 10:1) to give the desired the *n*-butyl laurate (12.0 g, 94%), bp. 178[18] (*lit.* bp. 180[18]) as a colorless oil.

^{1}HNMR ($CDCl_3$): δ 0.88 (t, 3H), 0.93 (t, 3H), 1.26 (m, 14H), 1.32 (m, 2H), 1.42 (m, 2H), 1.51-1.61 (m, 4H), 2.28 (t, 2H, CH_2CO), 4.06 (t, 2H, CH_2O). IR (liquid film cm^{-1}): 2969, 2927, 2855, 1740, 1467, 1389, 1176, 722. EI-MS (m/z): 256 ($[M]^+$, 15%), 201 (53%), 183 (23%), 116 (22%), 73 (20%), 57 (41%), 56 (100%), 55 (20%).

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