Esterification of Long Chain Aliphatic Acids with Long Chain Alcohols Catalyzed by Multi-valent Metal Salts

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Some typical multi-valent metal salts, such as chloride, nitrate, sulfate, and acetate of Fe(III), Al(III), Ga(III), In(III), Zr(IV), Hf(IV), Zn(II), Co(II), Ni(II), Mn(III), Cr(III), and Cu(II) have catalytic acitivties for the esterification of saturated and unsaturated long chain aliphatic acids with long chain aliphatic alcohols. These catalysts were sponteneously separated from the reaction mixtures, and could be subjected to the recycle use for the further reactions.

Esters of long chain aliphatic acid and alcohols are used as emulsifiers or oiling agents for foods, personal care emollients; surfactants and base materials for perfumery; spin finishes and textiles; lubricants for plastics; paint and ink additives and for mechanical processing, etc.[1] They are also used as solvents or co-solvents, and oil carrier in agricultural industry. However, they have been produced conventionally by the esterification of acid and alcohols using mineral acid, such as concentrated sulfuric acid, as catalyst.[2,3] These catalysts, in general, suffer from the inherent problem of corrosiveness, high susceptibility to water, difficulty in catalyst recovery, environmental hazards, waste control, etc. It is important to replace these highly corrosive, hazardous, and polluting acids with environment conscious catalysts, which are active under mild conditions, and easily recovered, and reused for the new reactions.

Recent concerns are homogeneous and heterogeneous catalysts for the esterification of carboxylic acid with an equal amount of alcohols.[4–16] Very recently, Yamamoto and his co-workers reported the esterification of carboxylic acids with equimolar alcohols using zirconyl and hafnoyl chlorides.[11–14] Bartoli and his co-workers also described $Zn(ClO_4)_2{\cdot}6H_2O$ catalyzed condensation of nearly equimolar amount of acids and alcohols without solvent.[15] We described successful synthesis of the esters with the combination of "*long chain acids and long chain alcohols*," where carbon numbers are both equal to or higher than 10, using unsupported and supported $ZrOCl_2{\cdot}8H_2O$ as the catalysts.[16,17] These results encouraged us to investigate catalytic performances of some multi-valent metal salts. In this paper, we describe surprising catalytic performances of some metal salts of Fe(III), Al(III), Ga(III), In(III), Zr(IV), Hf(IV), Zn(II), Co(II), Ni(II), Mn(III), Cr(III), and Cu(II) in the esterification of saturated and unsaturated long chain acids with long chain alcohols.

The esterification was carried out in a single-necked, round-bottomed flask (100 mL) equipped with a Teflon-coated magnetic stirring bar and a Dean-Stark apparatus surmounted with a reflux condenser. Equimolar amounts of each of the substrates (6 mmol) and metal salts (0.12 mmol) in 40 mL of mesitylene were charged into the round-bottomed flask. The mixture was heated to reflux in boiling mesitylene (162 °C). After 24 h, the temperature of the reaction mixture was cooled down to ambient temperature, and the catalyst was separated from the reaction mixture by filtration. The aliquots were analyzed by GC to determine the conversion and product yield.

Table 1 summarizes the esterification of palmitic acid (hexadecanoic acid) with cetyl alcohol (1-hexadecanol) using metal chloride catalysts. Unexpectedly, catalytic activities for the esterification were observed on the wide range of metal salts. Particularly, Fe(III), Ga(III), In(III), and Zn(II) chlorides showed very high catalytic activities for the esterification (Table 1, Entries 1 and 3–5): their activities were in higher or comparable level of $ZrOCl_2{\cdot}8H_2O$ (Table 1, Entry 6).[16] Al(III), Co(II), Ni(II), Mn(III), Cr(III), and Cu(II) chlorides gave the good to moderate yield of cetyl palmitate (Table 1, Entries 2 and 8–12); however, Mg(II), Ca(II), and Na(I) chlorides had no catalytic activities for the esterification (Table 1, Entries 13–15).

Table 2 summarizes activities of metal salt catalysts in the esterification of palmitic acid with cetyl alcohol. Chlorides have higher activities among the salts, and nitrate, sulfate, and acetate have the high to moderate catalytic activities. The order of the activity was also very similar to that of the chlorides. These results suggest that cationic metal moieties play an important role on catalytically active species.

Table 3 shows the esterification of saturated, branched, and unsaturated aliphatic acids with primary and secondary alcohols using ferric and other chlorides. The catalytic activities in the esterification of palmitic acid using $FeCl_3{\cdot}6H_2O$ were decreased

Table 1. The esterification of palmitic acid with cetyl alcohol catalyzed by metal chloride[a]

Entry	Metal salt	Yield/%
1	$FeCl_3{\cdot}6H_2O$[b]	95.8
2	$AlCl_3{\cdot}6H_2O$	73.8
3	$GaCl_3$	97.5
4	$InCl_3$	98.6
5	$ZnCl_2$	81.5
6	$ZrOCl_2{\cdot}8H_2O$	86.2
7	$HfOCl_2{\cdot}8H_2O$	98.7
8	$CoCl_2{\cdot}6H_2O$	70.5
9	$CrCl_3{\cdot}6H_2O$	48.8
10	$MnCl_2{\cdot}4H_2O$	53.8
11	$NiCl_2{\cdot}6H_2O$	32.3
12	$CuCl_2{\cdot}2H_2O$	37.7
13	$MgCl_2{\cdot}6H_2O$	12.5
14	$CaCl_2{\cdot}2H_2O$	14.0
15	NaCl	13.0
16	—	12.8

[a]Reaction conditions: substrate: palmitic acid, 6 mmol, cetyl alcohol, 6 mmol; catalyst: 0.12 mmol; solvent, mesitylene 40 mL; reaction temperature, 162 °C; reaction time, 24 h. [b]Similar results were obtained by anhydrous $FeCl_3$ as catalyst.

Table 2. The esterification of palmitic acid with cetyl alcohol catalyzed by metal salts[a]

Metal salt	Yield/%			
	Chloride	Nitrate	Sulfate	Acetate
Fe(III)	95.8	93.5	88.2	
Al(III)	73.8	53.6	49.2	72.4[b]
Ga(III)	97.5	98.0		
In(III)	98.6	95.6	89.1	
Zr(IV)	86.2	92.5	84.3	88.0
Zn(II)	81.5	76.6	79.5	78.2
Co(II)	70.5	71.8	72.2	65.0

[a]Reaction conditions: substrate: palmitic acid, 6 mmol, cetyl alcohol, 6 mmol; catalyst: 0.12 mmol; solvent, mesitylene 40 mL; reaction temperature, 162 °C; reaction time, 24 h. [b]$Al_2O(OAc)_4 \cdot nH_2O$.

Table 3. The esterification of some acids and alcohols catalyzed by metal chloride[a]

Entry	Matal salt	Acid	Alcohol	Yield /%
1	Fe(III)	Palmitic acid	Lauryl alcohol[c]	>99
2	Fe(III)	Palmitic acid	Myristyl alcohol[d]	>99
3	Fe(III)	Palmitic acid	Cetyl Alcohol	95.8
4	Fe(III)	Palmitic acid	Stearyl alcohol[e]	84.5
5	Fe(III)	Palmitic acid	2-Decanol	83.6
6	Al(III)	Palmitic acid	2-Decanol	67.4
7	Ga(III)	Palmitic acid	2-Decanol	82.5
8	In(III)	Palmitic acid	2-Decanol	87.0
9	Zn(II)	Palmitic acid	2-Decanol	36.2
10	Fe(III)	Palmitic acid	2-Dodecanol	82.5
11	Fe(III)	Palmitic acid	2-Tetradecanol	78.8
12	Fe(III)	Palmitic acid	2-Hexadecanol	69.8
13	Fe(III)	Oleic acid[f]	Cetyl alcohol	91.6
14	Fe(III)	Oleic acid	2-Decanol	96.0
15	Fe(III)	Linoleic acid[g]	Cetyl alcohol	97.0
16	Fe(III)	Linoleic acid	2-Decanol	95.2
17	Fe(III)	Isostearic acid[h]	Cetyl alcohol	88.7
18	Fe(III)	Isostearic acid	2-Decanol	40.0[b]

[a]Reaction conditions: substrate: acid, 6 mmol; alcohol, 6 mmol; catalyst: 0.12 mmol; solvent, mesitylene 40 mL; reaction temperature, 162 °C; reaction time, 24 h. [b]Catalyst, 0.6 mmol. [c]1-Dodecanol. [d]1-Tetradecanol. [e]1-Octadecanol. [f](*Z*)-9-Octadecenoic acid. [g](*Z*,*Z*)-9,12-Octadecandienoic acid. [h]2-Heptylundecanoic acid.

with the increase in carbon number of alcohols: $C_{12} \approx C_{14} > C_{16} \gg C_{18}$ (Table 3, Entries 1–4). The similar decrease of the yield was observed in the case of $ZrOCl_2 \cdot 8H_2O$.[16] Interaction of acid and alcohols with catalyst should become difficult with increasing their carbon numbers, especially for stearyl alcohol.

The esterification of palmitic acid with 2-decanol is also summarized in Table 3. The metal chloride listed as active for the esterification of palmitic acid with cetyl alcohol had the catalytic activities for the esterification with 2-decanol, although $ZnCl_2$ was less active (Table 3, Entries 5–9). The activities of $FeCl_3 \cdot 6H_2O$ for the esterification of palmitic acid with secondary alcohols was decreased with carbon number in the order: $C_{10} > C_{12} > C_{14} > C_{16}$ (Table 3, Entries 5 and 10–12).

The esterification of oleic and linoleic acids with cetyl alcohol and 2-decanol using $FeCl_3 \cdot 6H_2O$ occurred to give corresponding esters in high yields (Table 3, Entries 13–16). In these cases, no isomerization of unsaturated acids to trans-isomers was observed during the esterification.

The esterification of isostearic acid (2-heptylundecanoic acid) with cetyl alcohol and 2-decanol using $FeCl_3 \cdot 6H_2O$ was less active than the case of palmitic acids (Table 3, Entries 17 and 18). Particularly, the reactivity with 2-decanol was low even in the presence of five fold amount of catalyst.

We could suggest that these activities appeared by hydrolyzed cationic species of multi-valent metal salts.[18] Particularly, there is a possibility of the participation of cationic metal clusters of Fe(III), Al(III), Ga(III), In(III), Zr(IV), Hf(IV), Zn(II), Co(II), and Ni(II), which are formed easily in their aqueous solutions.

In conclusion, some multi-valent metal salts of iron, aluminum, gallium, indium, and zinc were effective catalysts for the esterification of long chain carboxylic acids with long chain primary and secondary alcohols. Metal salts, such as chloride, nitrate, sulfate, and acetate, are highly active for the esterification, and gave almost the same yield of esters.

The investigation on further aspects of the catalysis, particularly, on catalytic active species and the recyclability of catalysts, is under progress, and will be published in near future.

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References

1 “Fatty Acids in Industry: Processes, Properties, Derivatives, Applications,” ed. by R. W. Johnson and E. Fritz, Marcel Dekker, New York (1988).
2 “The Chemistry of Carboxylic Acids and Esters,” ed. by S. Patai, John Wiley, New York (1969).
3 J. Otera, “Esterification: Methods, Reactions, and Applications,” Wiley-VCH, Weinheim (2003).
4 C. Lacaze-Dufaure and Z. Mouloungui, *Appl. Catal., A: General*, **204**, 223 (2000).
5 K. Wakasugi, T. Misaki, K. Yamada, and Y. Tanabe, *Tetrahedron Lett.*, **41**, 5249 (2000).
6 K. Wakasugi, A. Nakamura, A. Iida, Y. Nishii, N. Nakatani, S. Fukushima, and Y. Tanabe, *Tetrahedron*, **59**, 5337 (2003).
7 K. Wakasugi, A. Iida, T. Misaki, Y. Nishii, and Y. Tanabe, *Adv. Synth. Catal.*, **345**, 1209 (2003).
8 K. Manabe, S. Iimura, X.-M. Sun, and S. Kobayashi, *J. Am. Chem. Soc.*, **124**, 11971 (2002).
9 X. Hao, A. Yoshida, and J. Nishikido, *Tetrahedron Lett.*, **45**, 781 (2004).
10 Y. Oohashi, K. Fukumoto, and T. Mukaiyama, *Chem. Lett.*, **33**, 968 (2004).
11 K. Ishihara, S. Ohara, and H. Yamamoto, *Science*, **290**, 1140 (2000).
12 K. Ishihara, M. Nakayama, S. Ohara, and H. Yamamoto, *Synlett*, **2001**, 1117.
13 K. Ishihara, M. Nakayama, S. Ohara, and H. Yamamoto, *Tetrahedron*, **58**, 8179 (2002).
14 M. Nakayama, A. Sato, K. Ishihara, and H. Yamamoto, *Adv. Synth. Catal.*, **346**, 1275 (2004).
15 G. Bartoli, J. Boeglin, M. Bosco, M. Locatelli, M. Massaccesi, P. Melchiorre, and L. Sambri, *Adv. Synth. Catal.*, **347**, 33 (2005).
16 K. Mantri, K. Komura, and Y. Sugi, *Synthesis*, **2005**, 1939.
17 K. Mantri, K. Komura, and Y. Sugi, *Green Chem.*, **7**, 677 (2005).
18 C. F. Bases, Jr. and R. E. Mesner, “The Hydrolysis of Cations,” John Wiley & Sons, Inc., New York (1976).