Recent Developments on the Mechanism and Kinetics of Esterification Reaction Promoted by Various Catalysts

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1. Introduction

Esters have played a significant role in daily living and chemical industry, such as plasticizers, fragrance, adhesive and lubricants (Joseph et al., 2005; Mbaraka & Shanks, 2006; Krause et al., 2009; Martínez et al., 2011). The vast majority of esters can be prepared using esterification reaction in the chemical engineering industry. Esterification has acquired further improvement from the engineering side; this mainly depends on the research of esterification kinetics. On the other hand, the need to control chemical reactions at the molecular level, which depends critically on the catalytic mechanism, is rapidly increasing (Salciccioli et al., 2011).

In the recent years, various esterification mechanisms were proposed for homogeneous and heterogeneous systems. Base on the mechanism, numerous kinetic models have been developed to represent the kinetic behaviors of esterification, such as simple orders or the power-law model, the pseudo-homogeneous model, the L-H model, the E-R model, etc.

Herein, we review the mechanisms of esterification catalyzed by inorganic acid, Lewis acid, metallic compounds, solid acids, ion-exchange resin, respectively. Meanwhile, the kinetics for each esterification is also conducted in detail. The study on the mechanism of various catalysts is not only useful in the present applications but it is required to enhance the scope of their applications. Therefore, it is desired to research and develop more efficient catalysts for high yield ester production, under mild reaction conditions. The esterification kinetics is important for simulation and design of a reactor.

A literature survey more than 90 relevant references has been done in this chapter. The studies on esterification are mainly focused on the following aspects: (1) establishing the adequate reaction mechanism according to the research papers, and (2) evaluating the available esterification kinetics.

2. Esterification mechanism and kinetic model

2.1 Inorganic acids

Inorganic acids, such as H_2SO_4, HCl and HI, are still being widely applied in the chemical industry (Liu et al., 2006; Schmitt et al., 2008). Under this condition, they are used as

homogenous catalysts for cheap price, high activity and efficiency (greater density of acid sites per gram) (Sanz et al., 2002), stable performance. There is no doubt that mineral acid-catalyzed esterifications have been the subjects of extensive studies because of their long history (Liu et al., 2006; Vahteristo et al., 2008). For instance, it can be mentioned that Berthelot and Saint-Gilles studied the equilibrium of acetic acid with ethanol in 1862(Huiping & Xiaohua, 2006).

Many researchers have conducted a number of experiments to study the mechanism and kinetics of esterifications promoted by mineral acids (Cardoso et al., 2008). Summarizing recent research and development, esterification is an additive-eliminate course in the presence of mineral acid catalyst, generally complying with the following four typical and mature mechanisms.

2.1.1 Bimolecular reaction

In 1895, Emil Fischer discovered that esters are formed simply by heating a carboxylic acid in alcohol solution containing a small amount of strong acid catalyst (Zhang et al., 1995; Rönnback et al., 1997; Otera & Nishikido, 2009). The following mechanism, which includes five elementary reactions, was proposed:

1.   Ketonic oxygen is easy to capture hydrogen ion to form protonated carbonyl substrate.
2.   The substrate makes carbon atom of carboxyl possess higher electropositive, which is conducive to the attack of nucleophile (RCOH) to generate a tetrahedral intermediate.
3.   Transfer of a proton from one oxygen atom to another yields a second tetrahedral intermediate and converts the OH group into a good leaving group.
4.   The acyl-oxygen bond disconnects and one water molecule lost.
5.   Loss of a proton gives the ester product.
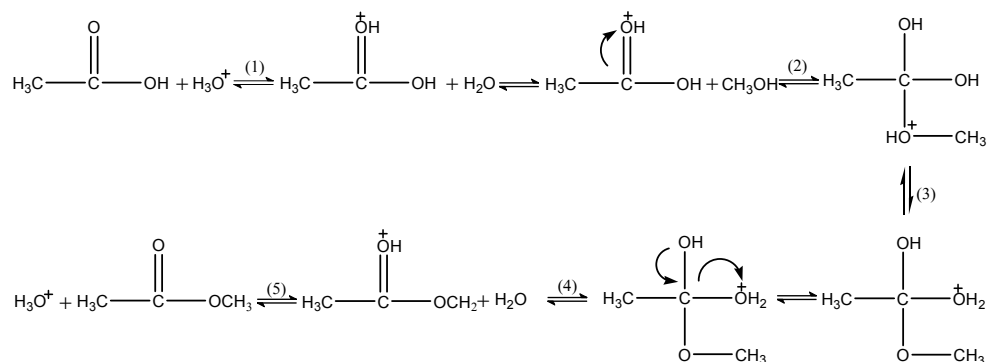
The chemical reaction can be expressed as Figure 1.

Fig. 1. Mechanism of bimolecular reaction

Streitwieser explained how the proton transfers specifically in 1985(Streitwieser et al., 1985; Liu et al., 2006; Fei & Zhao, 2009). The above chemical step (3) can be written as Figure 2:
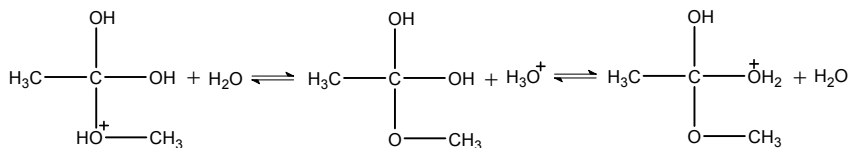
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Fig. 2. The proton transfers step

In addition, Streitweiser considered that step (2) is the rate-determining stage. The total reaction is:

$$CH_3COOH + CH_3OH \rightleftharpoons CH_3COOCH_3 + H_2O \tag{1}$$

The result of the reaction is that the rupture of carboxylic acid acyl-oxygen bond occurs, and the hydroxy of acid is replaced by alkoxy, which is a nucleophilic substitution process of carboxylic acids.

Esterifications of primary alcohols, secondary alcohols with carboxylic acids comply with this mechanism usually. According to this mechanism, the intermediate with a tetrahedral structure is more crowd than reactants, which makes the structure of carboxylic acid and alcohol have a significant effect on the easy of esterification.

The activity of different structures of the alcohol and carboxylic acid in esterification obeys the following order: Alcohol: $CH_3OH > RCH_2OH > R_2CHOH$; Acid: $CH_3COOH > RCH_2COOH > R_2CHCOOH > R_3CCOOH$ (Solomons, 1986; March, 1992; TianQuan 1992; Fei & Zhao, 2009).It shows that straight-chain structure is easier than branched- chain structure to esterification, and the more the branched-chain is, the lower the rate will be.

Based on the above mechanism proposed by Streitweiser, Rönnback, et al. developed a esterification kinetic model of carboxylic acid with methanol in the presence of hydrogen iodide though isothermal batch experiments at 30-60℃. The catalyst concentration varied from 0.05 to 10.0 wt%. Because the proton-donation step (1) as well as the subsequent steps (3)-(5) is assumed to be rapid, the simplified mechanism shown in Figure 3:
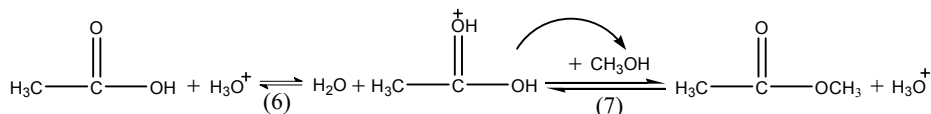

Fig. 3. The simplified mechanism

The reaction rate can therefore be expressed as:

$$r = r_2 = k_2 c_A c_{CH_3OH} - k_{-2} c_E c_{H_3O^+} \tag{2}$$

where r is the total rate, r_2 is the rate of step(2), A is $CH_3C(OH)_2^+$ and E is CH_3COOCH_3.

The concentration of the intermediate A is obtained after applying the quasi-equilibrium hypothesis on the rapid step(6):

$$K_6 = K_1 = c_A \cdot c_{H_2O} / c_{CH_3COOH} \cdot c_{H_3O^+} \tag{3}$$

The rate equation is rewritten as follows,

$$r = r_2 = K_1 k_2 \left(\frac{c_{H_3O^+}}{c_{H_2O}} \right) \left[c_{CH_3COOH} \cdot c_{CH_3OH} - \frac{c_E \cdot c_{H_2O}}{K_1 (k_2/k_{-2})} \right] \tag{4}$$

The product K_1 (k_2/k_{-2}) equals the equilibrium constant of the overall reaction K_{E2}. In addition, the product $K_1 k_2$ is denoted by a lumped constant $k_2{}'$. Thus, we obtain for r_2,

$$r = r_2 = k_2{}' \left(\frac{c_{H_3O^+}}{c_{H_2O}} \right) \left(c_{CH_3COOH} \cdot c_{CH_3OH} - \frac{c_E \cdot c_{H_2O}}{K_{E2}} \right) \tag{5}$$

The kinetic and equilibrium parameters included in Equation (5) are estimated from experimental data with regression analysis. Simulation of the model with the estimated parameters revealed that Equation (5) can predict the experimental trends in the acid-catalyzed esterification correctly.

2.1.2 Single-molecule reaction

The tertiary alcohol is prone to generate carbocation under acidic condition. Therefore, the mechanism of tert- esterification is different from that of the primary and secondary alcohol, it follows the single-molecule reaction process(shown in Figure 4):The tertiary alcohol combines with protons to generate protonated alcohol(1); The protonated alcohol is got rid of a molecule water to produce tert-carbocation(2), which is very stable; Then the electrophilic attacking is taken place between the tert-carbocation and oxygen atom of carboxylate, the protonated ester(3) is yielded; The loss of a proton from the protonated ester gives the product(4) (Bart et al., 1994).
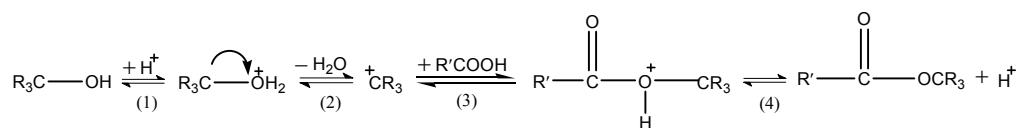

Fig. 4. Mechanism of tert-esterification

2.1.3 Large-steric reaction

Aromatic acid has serious steric hindrance. If there are both ortho-methyls, just as 2.4.6-trimethyl benzoic acid, the alcohol molecule is so difficult to access to carboxyl that the esterification cannot occur. However, if 2.4.6- trimethyl benzoic acid is dissolved in the 100% sulfuric-acid solution, acylilum ion will be formed as shown in Figure 5. Then the added alcohol with the acylilum ion produced ester. The reaction will conduct smoothly (Streitwieser et al., 1985).

This kind of esterification could occur for the reason that carbon atom of the acylilum ion is sp^2 hybridized and coplanar with the benzene ring, Then alcohol molecule can be virtually unhindered to attack the acylilum ion from above or below of the molecular plane. Esterifications conducts with this mechanism are merely few.
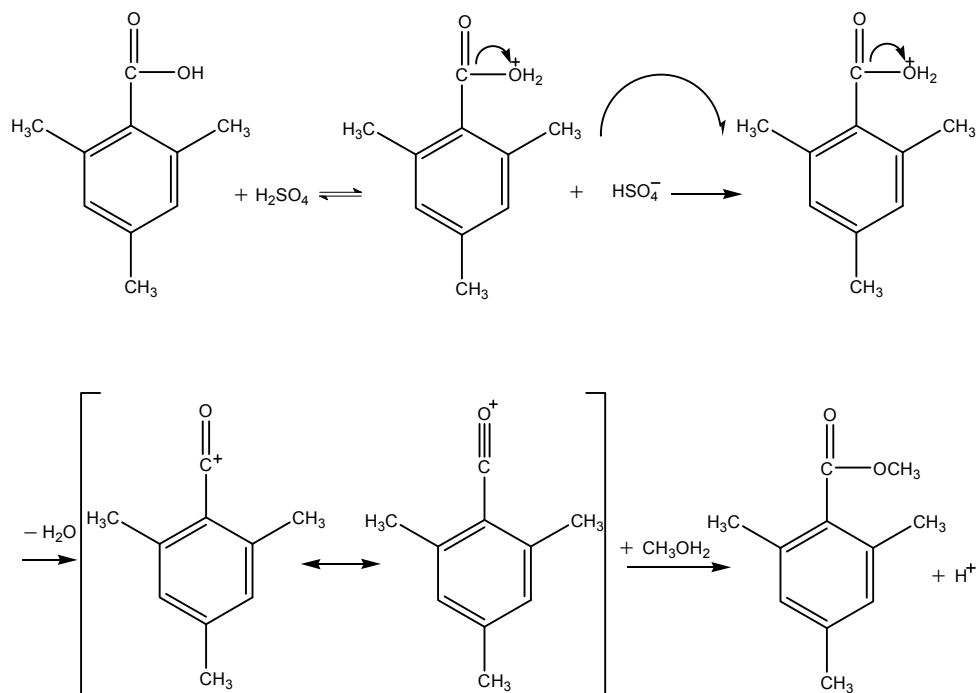
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Fig. 5. Mechanism of large-steric reaction

2.1.4 Sulfuric acid

Dhanuka showed that the mechanism of sulfuric acid-catalyzed esterification is the model of alkyl sulfuric intermediate. It's a two-step reaction. R´-O-SO₃H firstly is generated via sulfuric acid with alcohol, which is treated as a catalyst in the second step (Lide, 1994):

$$R'OH + H_2SO_4 \rightleftharpoons R'OSO_3 + H_2O \tag{6}$$

$$RCOOH + R'OH \xrightleftharpoons{R'OSO_3} RCOOR' + H_2O \tag{7}$$
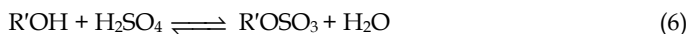
The alkylation reaction of sulfuric acid with alcohol is irreversible (Aranda et al., 2008).Therefore the reaction rate can be expressed as:

$$r = k(C_A C_B - C_W C_E / K) \tag{8}$$

where k is rate constant and K is equilibrium constant; C_A, C_B, C_W, C_E is the concentration of carboxylic acid, alcohol, water and ester, respectively.

In 2009, Fei, *et al.* studied on the esterification behaviors of neo-polyhydric alcohols with fatty acids catalyzed by sulfuric acid. It was found that the esterification follows the above mechanism.

2.2 Lewis acids

Lewis acid is a compound or ionic species that can accept an electron pair from a donor compound to form a Lewis adduct, such as $ZnCl_2$, $Mg(ClO_4)_2$, $Sn[N(SO_2-n-C_8F_{17})_2]_4$. It is potentially useful on the production of esters as a catalyst, the reason is that it can be easily separated from the reaction media (Sanchez et al., 1992; Cardoso et al., 2009); moreover, comparing with Bronsted acid, template effects are to be expected as Lewis acid sterically bulkier than a proton. In 1964, Anantakrishnan, et al. investigated the esterification reaction of Ac_2O with 50% MeOH, EtOH, PrOH, and iso-PrOH, in 50% Me_2CO or Dioxane as solvent, using Lewis acid ($ZnCl_2$) as catalyst.

Along with the scientific and technological progress and social development, more and more researchers have concerned about this issue, including the kinds of catalysts, the mechanism and kinetics of reaction. Thus, the contents containing the reaction mechanism and esterification kinetics have been significantly reviewed according to the type of catalysts as follows.

2.2.1 Metal chloride

Ethyl oleate was synthesized by the esterification of and ethanol catalyzed by $SnCl_2 \cdot 2H_2O$ (Cardoso et al., 2008). Under the circumstance of excess ethanol, the effects of the concentration of the catalyst and oleic acid, and temperature on the reaction rate were investigated. A related esterification mechanism was presented and described as follows: in presence of Sn^{2+}($SnCl_2 \cdot 2H_2O$) catalyst, the carbonyl of the fatty acid is polarized to activate of substrate, which makes the nucleophilic attack to the molecules by ethanol become more favorable. Cardoso et al. investigated the effect of different carbonic chain of alcohol (methyl alcohol, ethyl alcohol, n-propyl alcohol, n-butyl alcohol) on the conversion of oleic acid into respective ester. The results showed that the conversion rate was down with the increase of carbon chain of alcohol, which indicated that high bulk hindrance occurs on the hydroxyl of the alcohol, and the efficient attack of them to the polarized carbonyl of oleic acid is reduced. However, it is not clear how the carbonyl is polarized by Sn^{2+}.

Kinetic data of esterification of ethanol and oleic acid catalyzed by $SnCl_2$ ($n_{ethanol} : n_{oleic\ acid} : n_{SnCl2}$ = 120 : 1 : 0.01) were measured at the reflux temperature, and kinetic model was obtained as follows,

$$\ln C = -0.00278 \times t - 2.3155 \qquad (9)$$

where C is the concentration of oleic acid, t is the reaction time.

The effectiveness of the catalyst $SnCl_2 \bullet 2H_2O$ has been investigated in a broad range of concentrations, and the results are approximately concomitant with a first order dependence in relation to the catalyst concentration. The effect of the temperature on the initial rate of the esterification was determined, showing that an increase in the reaction temperature was caused a corresponding improvement on the reaction rate, especially at a range of 45-75°C. The value of activation energy for the reaction was determined from the data of the initial rate to be 46.69 kJ·mol^{-1}.

The kinetics of catalytic esterification of castor oil with lauric acid using $SnCl_2 \bullet 2H_2O$ was studied (Kulkarni & Sawant, 2003). Effects of the catalyst concentration and temperature on

the progress of the reaction were investigated. The reaction was assumed to be a first order with respect to each reactant. For the irreversible, bimolecular-type second order reaction,

$$A+B \xrightarrow{\quad Catalyst \quad} Product \tag{10}$$

The consumption rate of A ($-r_A$) is expressed by,

$$-r_A = kC_C C_A C_B \tag{11}$$

where C_A, C_B, C_C is the concentration of lauric acid, hydroxyl group and catalyst (mol/mL), respectively.

The catalyst concentration was constant throughout the reaction; therefore, Equation (11) can be rewritten as

$$-r_A = k'C_A C_B \ , \ k' = kC_C \tag{12}$$

The integrated form of Equation (12) using fractional conversion is,

$$\ln[(1-X_B)/(1-X_A)] = (C_{B0} - C_{A0})k't \tag{13}$$

where X_A, X_B is fractional conversion of the lauric acid and the -OH group, respectively; C_{A0}, C_{B0} is initial concentration of the lauric acid and hydroxyl group (mol/mL), respectively; and k is the second-order rate constant (mL^{2}mol^{-2}min^{-1}).

The esterification reaction of castor oil and lauric acid was carried out using $SnCl_2 \cdot 2H_2O$ as catalyst (0.25,0.5,1.0 and 2.0 % w/w catalyst loadings) at 185℃ and the kinetic data were measured. The results showed that there was a good linearity relationship between ln $[(1-X_B)/(1-X_A)]$ and t. The plot of k' versus C_C was close to a straight line. For the given values of C_{B0}, C_{A0} and C_C, the kinetic model of esterification of castor oil and lauric acid was obtained at 185°C,

$$\ln[(1-X_B)/(1-X_A)] = 1.62 \times 10^6 (C_{B0} - C_{A0})C_C t \tag{14}$$

It was investigated the esterification of octanoic acid and n-octyl alcohol utilizing metallic chlorides (KCl, $CoCl_2$, $MgCl_2$, $ZnCl_2$, $FeCl_3$ etc.) in a stirred tank reactor (Santos, 1996). The results showed that the best efficiency of the formatted ester (n-octyl octanoate) was obtained with ferric chloride, indicating that the higher electronegativity of the metallic ion and the existence of free d orbitals in the transition metals are responsible for the higher yield of ester. Thus, the existence of free d orbitals in Fe^{3+} (its configuration: 3d^3) gives the possibility of the formation of complexes with OH groups of the reactants, which explains the highest activity found for $FeCl_3 \cdot 6H_2O$ in this way. Generally, in the catalytic systems whose bases were constituted by a transition metal, such as Fe, Co, Mn, Zn, the mechanism of esterification can similarly be ascribed to the above mentioned.

The esterification reaction of octanoic acid and n-octyl alcohol was carried out using $CoCl_2 \cdot 2H_2O$ as catalyst (0, 0.0385, 0.077 mol/l) at 70℃ and the kinetic data were measured. The experimental curves suggest that the kinetics of esterification between octanoic acid and n-octyl alcohol can be described by an irreversible second order power model, considering the catalyst concentration as a constant in the kinetic model proposed. The activation energy is seen to have a value of 53 kcal/mol (Urteaga et al., 1994).

The reaction rate went on a power law model of second order, one for the alcohol and one for the acid,

$$r=kC_{alcohol}C_{acid} \tag{15}$$

where k is kinetic constant ($l \, mol^{-1}min^{-1}$)

$$r=9.30 \times 10^{-4}C_{alcohol}C_{acid} \tag{16}$$

Catalyst	k[l mol^{-1} min^{-1}]	R^2
KCl	0.95×10^{-4}	0.988
CaCl$_2$•6H$_2$O	0.83×10^{-4}	0.980
NiCl$_2$•6H$_2$O	1.86×10^{-4}	0.805
CoCl$_2$•6H$_2$O	1.69×10^{-4}	0.994
MgCl$_2$•6H$_2$O	5.87×10^{-4}	0.986
MnCl$_2$•6H$_2$O	1.20×10^{-4}	0.852
FeCl$_2$•6H$_2$O	1.62×10^{-4}	0.977
BaCl$_2$•2H$_2$O	0.96×10^{-4}	0.955
SnCl$_2$•2H$_2$O	10.00×10^{-4}	0.943
ZnCl$_2$•XH$_2$O	1.54×10^{-4}	0.876
AlCl$_3$•6H$_2$O	6.91×10^{-4}	0.876
SnCl$_4$	9.50×10^{-4}	0.896
FeCl$_3$•6H$_2$O	9.30×10^{-4}	0.845

Table 1. Kinetic constant for homogeneous reactions

It was also observed that the homogeneous reactions were fitted much better than the pseudo-homogeneous reactions to proposed kinetics model. The reason for it is that an important influence of the physical steps that could have place in the global mechanism of this reaction.

2.2.2 Perchlorate

Perchlorates are of great chemical interest and importance. The high electronegativity, together with the relatively low charge density, results in poor complexing ability of the perchlorate ion. Metal perchlorates can therefore act as powerful Lewis acids, with this character mainly being exploited to activate bidentate compounds (Bartoli et al., 2007). Magnesium perchlorate is one of the most active Lewis acids for esterification. By 2003, Gooβen & Döhring synthesized various esters through a decarboxylative esterification of alkyl and aryl carboxylic acids with dialkyl dicarbonates in the presence of 1 mol% of Mg(ClO$_4$)$_2$. However, more in-depth investigations on the mechanism of this reaction are underway.

Until 2006, Bartoli, et al. explored the efficiency of Perchlorates (such as Mg(ClO$_4$)$_2$, LiClO$_4$, Zn(ClO$_4$)$_2$) as catalyst to activate diethyl dicarbonate for preparing alkyl and aryl ethyl carbonates. The results showed that among the above catalysts, Mg(ClO$_4$)$_2$ is the most efficient one. The reactions between diethyl dicarbonate and various alcohols including aliphatic alcohols and aryl alcohols were studied, and the results obtained suggest that the reaction rate depends on the acidity of the starting hydroxy compound, and not on its

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nucleophilicity. Herein, the reaction mechanism was presented to explain the observed reaction characteristics. In fact, the more acidic and less nucleophilic phenols react faster than aliphatic alcohols. Thus, the release of the alcoholic proton should be involved in the rate-determining step. A reasonable mechanistic hypothesis is depicted as follows (Figure 6),
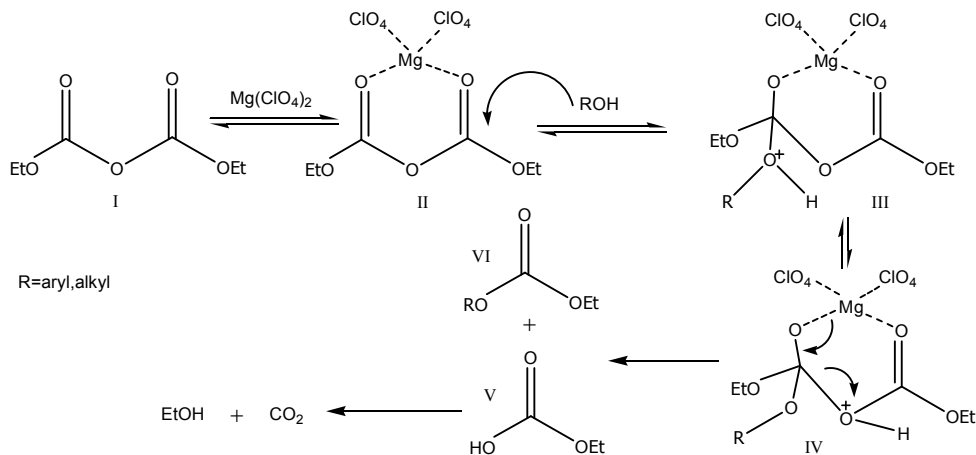

Fig. 6. Mechanism for preparing alkyl and aryl ethyl carbonates catalyzed by $Mg(ClO_4)_2$

Due to the ability of coordinating with 1,3-dicarbonyl compounds, $Mg(ClO_4)_2$ reacts with diethyl dicarbonate to form complex (II), which can undergo the addition of the alcohol to form intermediate (III). An internal proton shift in (III) can produce intermediate (IV), which can irreversibly decompose to the mixed carbonate (VI) and to the carbonic acid monoester (V). Owing to its high instability, (V) immediately produces EtOH and CO_2. The irreversibility of the last two steps drives the overall process towards (III). This explanation accounts for the formation of the mixed carbonate (VI) as the major product of the reaction (Jousseaume et al., 2003).

Nevertheless, this is a speculative hypothesis; more studies are in progress to find experimental evidence to elucidate the reaction mechanism.

2.3 Organometallic compound

Organometallic compounds containing bonds between carbons and metals provide a source of nucleophilic carbon atoms which can react with electrophilic carbon to form a new carbon-carbon bond (Banach et al., 2001; Finelli et al., 2004). Organometallics find practical uses in catalytic processes. For example, Titanium tetrabutoxide, Butylhydroxyoxo-stannane are well-known catalysts for the esterification between diacid and diol in polyester industry (Grzesik et al., 2000; Prabhakarn et al., 2011). The catalytic mechanism and kinetic model of related catalysts are reviewed in the following discussions.

2.3.1 Titanate

Titanium-based catalysts have been known for many years and actually are widely used for the production of poly (butylene terephthalate) (PBT), poly (trimethylene terephthalate)

(PTT), and so on. Recently, the developments of titanium-based catalysts make a marvelous progress (Liu et al., 2006), such as titanium dioxide based catalyst (C-94) mainly focusing on designing to be stable and having good activity and color.

The mechanism of the mono-esterification between terephthalic acid (TPA) and 1,4-butanediol (BDO) catalyzed by Ti(OBu)$_4$ was proposed (Tian et al., 2010). As shown in Figure 7, the reaction involves the formation of an adduct between a carbonyl group and Ti atom.
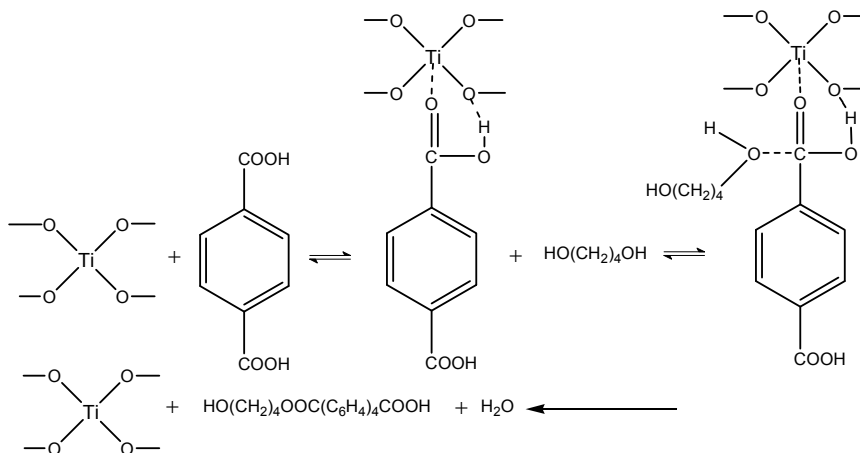

Fig. 7. Mechanism of the mono-esterification between BDO and TPA catalyzed by Ti(OBu)$_4$

Although the reaction system of TPA and BDO is heterogeneous, it can be assumed that the esterification occurs only in the liquid phase. The initial rate method is used to predict the reaction rate. The kinetic model of mono-esterification between TPA and BDO catalyzed by Ti(OBu)$_4$ in the temperature of 463-483K was investigated (Bhutada & Pangarkar, 1986). The reaction rate r can be described as,

$$r = kC_A^n C_B^m \qquad (17)$$

where C_A, C_B is the concentrations of TPA and BDO, respectively, k is the reaction rate constant, n and m is the reaction order with respect to A and B.

The reaction order can be obtained from experiments in which the initial rates are measured at a series of initial reactant concentrations. The results show that the reaction order for TPA and BDO is nearly a constant of 0.7 and 0.9, respectively. Therefore, the rate equation of the esterification is written as follows,

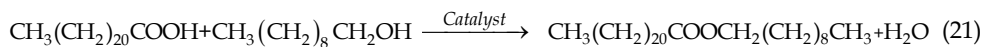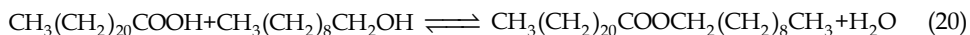$$r = k_{Ti} C_B^{0.9} C_A^{0.7} \qquad (18)$$

$$\ln k_{Ti} = 11.73 - 7.67 \times 10^3 / T (R^2 = 0.997) \qquad (19)$$

where k_{Ti} is the rate constant (L$^{0.6}$ · mol$^{-0.6}$ · min^{-1}), R^2 is the correlation coefficient.

The reaction of behenic acid with fatty alcohols (decanol, lauryl alcohol, myristyl alcohol and cetyl alcohol) was studied by Tiwari, et al. (Tiwari & Sawant, 2005) using TBT as

catalyst in the temperature range of 165-185℃.The reaction rate for the catalytic reaction is the sum of the rates of both the uncatalyzed (Equation (20)) and the catalyzed reactions (Equation (21)),

$$CH_3(CH_2)_{20}COOH+CH_3(CH_2)_8CH_2OH \rightleftharpoons CH_3(CH_2)_{20}COOCH_2(CH_2)_8CH_3+H_2O \quad (20)$$

$$CH_3(CH_2)_{20}COOH+CH_3(CH_2)_8CH_2OH \xrightarrow{Catalyst} CH_3(CH_2)_{20}COOCH_2(CH_2)_8CH_3+H_2O \quad (21)$$

Excess of the acids is used to get almost complete conversion of the alcohols, and the unreacted acid was easily removed from the ester as a sodium salt. Assuming that it is first order dependence of the reaction rate on each reactant and the catalyst, the overall rate expression in the integrated form becomes,

$$X_A / (1 - X_A) = C_{A0}kt \quad (22)$$

where X_A is fractional conversion of behenic acid; C_{A0} is initial concentration of behenic acid; $k = k_c C_c + k_{uc}$, k_c is catalyzed reaction rate constant, k_{uc} is uncatalyzed reaction rate constant; C_C is catalyst concentration.

The kinetic data show that there is a reasonably good agreement between experimental points and the ones calculated by Equation (22). The values of activation energy obtained for the uncatalyzed (ΔE_{uc}) and catalyzed (ΔE_c) reaction of behenic acid with decanol, lauryl alcohol, myristyl alcohol and cetyl alcohol are shown in Table 2.The model Equation (22) is also appropriate for the reaction of erucic acid with cetyl alcohol and oleyl alcohol using TBT as a catalyst (Tiwari & Sawant, 2005).

Alcohol	ΔE_{uc}(kJ mol⁻¹)	ΔE_c (kJ mol⁻¹)
decanol	68.1	86.2
lauryl alcohol	69.2	79.6
myristyl alcohol	64.5	78.6
cetyl alcohol	67.3	87.1

Table 2. Activation energy value for uncatalyzed and catalyzed reaction

2.3.2 Butylhydroxyoxo-stannane

Stannum-based catalysts such as butylhydroxyoxo-stannane (BuSnOOH) are commonly used for the synthesis of poly (ethylene terephthalate) (PET) (Patel et al., 2007), poly (butylene terephthalate) (PBT) and so on. Due to the similarity in coordination number and electronegativity between Ti and Sn, as shown in Figure 8, the mechanism of BuSnOOH catalyst is also proposed by TIAN, et al.

The initial rate method will also be used in this reacting system. The kinetic model of mono-esterification reaction between terephthalic acid (TPA) and 1,4-butanediol (BDO) is expressed as follow,

$$r = k_{Sn}C_B^{0.9}C_A^2 \quad (23)$$

$$\ln k_{Sn} = 9.58 - 6.42 \times 10^3 / (R^2 = 0.999) \tag{24}$$

where C_A and C_B is the concentrations of TPA and BDO, respectively; k_{Sn} is the rate constant $(L^{1.9} \cdot mol^{-1.9} \cdot min^{-1})$.
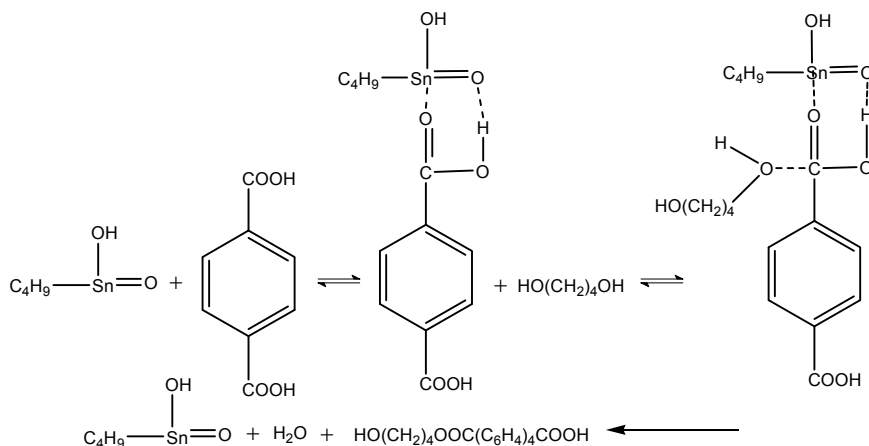
Fig. 8. Mechanism of the mono-esterification between BDO and TPA catalyzed by BuSnOOH

2.3.3 Fluorous metaloxide

In 2004, Otera investigated the transesterification and esterification of various acids and alcohols using 1, 3-disubstituted tetraalkyldistannoxanes as catalyst, and found that the catalytic mechanism different from that proposed for tetraalkyldistannoxanes. In the latter case, the initial step is substitution of the bridging X group to give an alkoxydistannoxane intermediate, $(YR_2SnOSnR_2OR)_2$, which works as an alkoxyl donor. In contrast, for 1, 3-disubstituted tetraalkyldistannoxanes, no substitution takes place at the bridging position by an alkoxy group. As described above, the bridging chlorine in 1, 3-disubstituted tetraalkyldistannoxanes is never substituted by isothiocyanate ion, but experiences strong association.

A related mechanism of the esterification is proposed that both alcohol and acid coordinate on the terminal tin atom (Yoshida et al., 2006), on which the interchange between the hydroxyl groups of carboxylic acids and the alkoxy groups of alcohols takes place. Meanwhile, since water, one of the products, is less fluorophilic, the esterification of carboxylic acids with alcohols should proceed efficiently.

Fluorous distannoxanes exhibit unusually high preference for fluorous solvents over common organic solvents thanks to coverage of the molecular surface with fluoroalkyl groups. While the fluorous biphase technology had been high-lighted mainly in terms of facile separation of products and fluorous catalysts, it has now been revealed that the equilibrium is also controllable under fluorous biphase conditions. Thus, the esterification has been completely driven in the desired direction by use of a 1:1 ratio of starting materials without recourse to any dehydration technique.

2.4 Solid acids

The research for solid acids has become active since the early 1970s. In 1971, Isao, et al. investigated the esterification of ethanol with acetic acid on silica-alumina, and a simple kinetic model based on a Langmuir-Hinshelwood mechanism was proposed. Since then, the esterification catalyzed by solid acids is widely studied and largely reported (Jiang et al., 2008; Jothiramalingam & Wang, 2009; Li et al., 2010). Herein, the esterification mechanisms and kinetic models according to the different types of solid acids are reviewed, such as sulfate-supported metal oxides (SO_4^{2-}/M_xO_y), TPA/SnO$_2$.

2.4.1 TPA/SnO$_2$

The esterification of palmitic acid with methanol using 12-Tungstophosphoric acid (TPA)/SnO$_2$ was investigated (Srilatha et al., 2011). The reaction is shown as follows:

$$C_{15}H_{31}COOH + CH_3OH \underset{}{\overset{k}{\rightleftharpoons}} C_{15}H_{31}COOCH_3 + H_2O \tag{25}$$

$$\quad\text{(A)} \qquad\qquad \text{(B)} \qquad\qquad \text{(C)} \qquad\qquad \text{(D)}$$
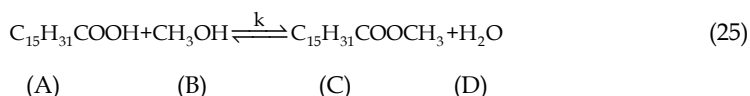
As shown in Figure 9, the mechanism of this esterification is proposed,
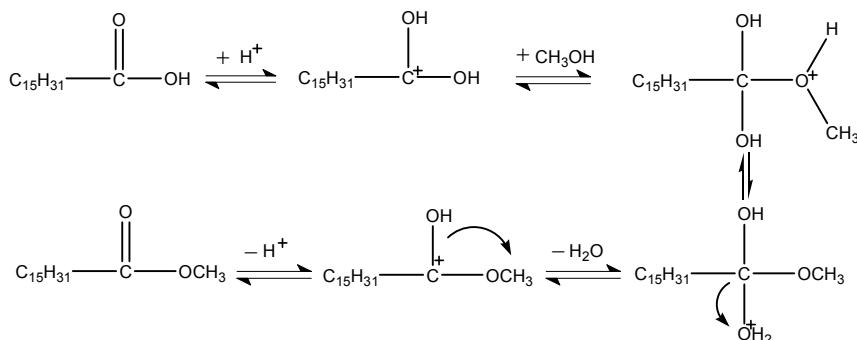
Fig. 9. Mechanism of acid catalyzed esterification of carboxylic acid

The catalyst initiates the esterification reaction by donating a proton to palmitic acid molecule. The palmitic acid is then subjected to nucleophilic attack by the hydroxyl group of methanol, and the reaction continues with water elimination.

As the large excess of methanol, it could be safely assumed to be a first-order pseudo-homogeneous reaction. The esterification reaction was carried out using 15 wt% TPA/SnO$_2$ as catalyst（w_A: w_{cat}=5:1）in the temperature range of 45-65℃ and the kinetic data were measured.

The reaction rate can be described as follows:

$$-ln(1-X_A) = kt \tag{26}$$

where X_A is the conversation of palmitic acid, t is the reaction time, k is the reaction rate constant.

The plots of $-\ln(1-X_A)$ versus t at different temperatures showed that there was a good linearity relationship. Linear fitting to $\ln k$ - $1/T$ curve was carried out and the reaction rate constant can be described as follows:

$$k = \exp(8.66 - 4369 / T) \tag{27}$$

The activation energy was obtained as 36.33 kJ mol^{-1}.

2.4.2 SO_4^{2-}/M_xO_y

The solid superacid (SO_4^{2-}/M_xO_y) is a new type of catalyst used in esterification (Jiang et al., 2004). M_xO_y are usually some transition metal oxides such as ZrO_2 and TiO_2.

In 2010, Rattanaphra, et al. investigated the esterification of myristic acid with methanol catalyzed by sulfated zirconia. The mechanism of esterification is probably following Langmuir-Hinshelwood model (Arata, 2009; Reddy & Patil, 2009). It is possible that methanol and myristic acid are preferentially adsorbed on the Bronsted acid sites of sulfated zirconia during esterification. The hydroxyl group of methanol is protonated by Bronsted acid on the catalyst surface while the protonation of myristic acid on an adjacent site leads to the carbocation. Deprotonation of methanol oxygen produces the nucleophile, which attacks the carbocation to generate a tetrahedral intermediate. As shown in Figure 10, the tetrahedral intermediate eliminates water to form ester.
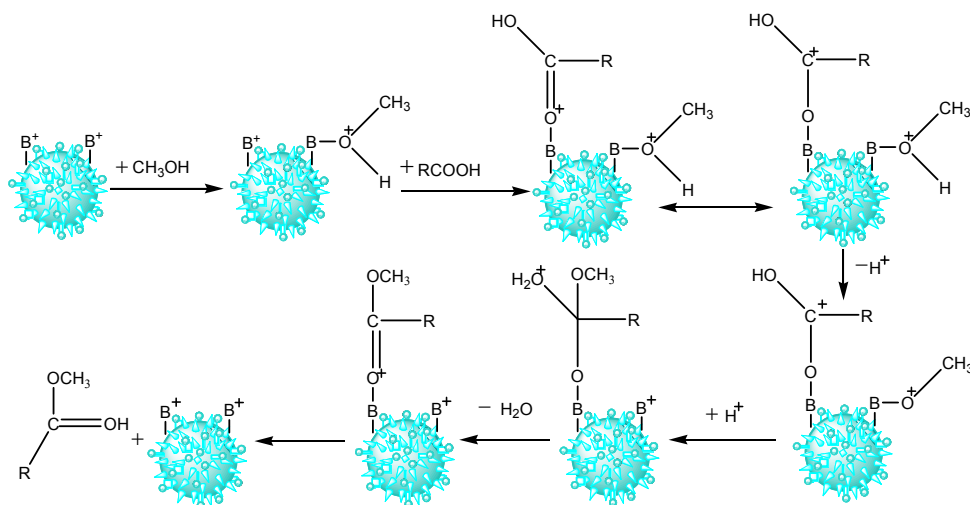
Fig. 10. Mechanism of esterification catalyzed by sulfated zirconia

In 2011, Rattanaphra, et al. also investigated the kinetic model of myristic acid esterification with methanol using sulfated zirconia as catalyst. The reaction is shown as follows:

$$CH_3(CH_2)_{12}COOH + CH_3OH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3(CH_2)_{12}COOCH_3 + H_2O \tag{28}$$

$$\text{(A)} \qquad\qquad \text{(B)} \qquad\qquad\qquad \text{(E)} \qquad\qquad \text{(W)}$$
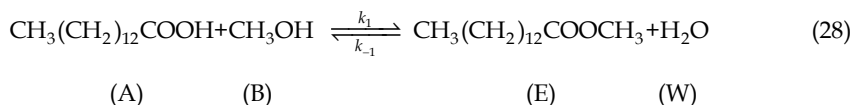
The stirring rate is sufficient to overcome the diffusion limitation of reactive species. Therefore, the performance of pseudo-homogeneous model can be considered as satisfactory to correlate the kinetic data for the esterification. The rate equation can be written as follows:

$$-r_A = -\frac{dC_A}{dt} = k_1 C_A C_B - k_{-1} C_E C_W \tag{29}$$

where C_A, C_B, C_E and C_W is the concentration of myristic acid, methanol, myristic acid methyl ester and water respectively, k_1 is the forward rate constant and k_{-1} is the backward rate constant.

The equation can be rearranged to be:

$$\frac{dX_A}{dt} = k_1 C_{A0}[(1-X_A)(M-X_A) - \frac{1}{K_e}X_A^2] \tag{30}$$

where X_A is the conversion of myristic acid，C_{A0} is the initial concentration of myristic acid, K_e is the equilibrium constant, M is the concentration ratio of methanol to myristic acid ($M=C_{B0}/C_{A0}$).

$$K_e = \frac{k_1}{k_{-1}} = \frac{X_{Ae}^2}{(1-X_{Ae})(M-X_{Ae})} \tag{31}$$

The relationship between temperature and the forward rate constant in the temperature range of 393-443K is given as following equations,

$$k_1 = \exp(2.88 - 2707/T) \tag{32}$$

The linear coefficient is 0.996, and the activation energy is 22.51 kJ / mol.

In 2004, Jiang, et al. studied the esterification of n-pentanol with benzoic acid using Al-pillared clay (PILC) supported SO_4^{2-} /TiO_2 superacid catalyst (Fang et al., 2010), and find that it is known that the generation of super acid sites in the system of SO_4^{2-} /M_xO_y solid superacid is necessarily promoted by the sulfur of the metal oxides, the more acid sites formed, the higher catalytic activity exhibited. Therefore, Al-PILC carrier can effectively enhance the catalytic activity.

In 2010, Zubir, et al. investigated the kinetic behavior of the heterogeneous catalyzed esterification of oleic acid with ethanol using tungstated zirconia as a catalyst in the temperature range of 303.15- 323.15K (Otera, 1993).

$$CH_3(CH_2)_7 CH=CH(CH_2)_7 COOH+CH_3CH_2OH \rightleftharpoons CH_3(CH_2)_7 CH=CH(CH_2)_7 COOCH_2CH_3+H_2O \tag{33}$$
$$\text{(A)} \qquad\qquad \text{(B)} \qquad\qquad \text{(C)} \qquad\qquad \text{(D)}$$
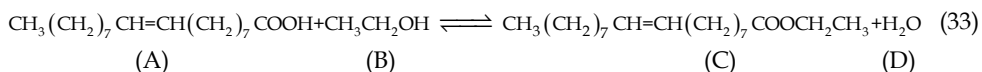
The kinetics of esterification reaction can be expressed using a pseudo-homogeneous second-order equilibrium model in the absence of any intraparticle diffusional limitation as follows:

$$-r_A = k(C_A C_B - C_C C_D / K_e) \tag{34}$$

where C_A, C_B, C_C, C_D is the concentration of oleic acid, ethanol, ethyl oleate and water, respectively, k is the kinetic constants for the forward reaction, K_e is the equilibrium constant.

$$K_e = \exp(29.42 - 10536/T) \tag{35}$$

$$k = \exp(23.43 - 6242/T). \tag{36}$$

The value of activation energy is 51.9 kJ·mol⁻¹. The goodness-of-fit of the experimental data to the proposed model is assessed by comparing the experimental reaction rate with the theoretical prediction, and the experimental data are reproduced with errors not greater than 10%.

2.5 Ion-exchange resin

Ion-exchange resins, especially the cation-exchange resins such as Dowex, Amberlyst series are manufactured mainly by sulfonation of ethylbenzene first, followed by a cross-link with divinylbenzene (Liu & Tan, 2001; Alexandratos, 2008; Tesser et al., 2010). Because of their selective adsorption of reactants, surface acid site features, and swelling nature, these resins not only catalyze the esterification reaction but also affect the equilibrium conversion. They also show excellent performance such as reusable, mechanical separation, continuous operation as a heterogeneous catalyst in esterification (Yang et al., 2007; JagadeeshBabu et al., 2011; Ju et al., 2011; Toor et al., 2011).

By 1965, Bochner, et al. evaluated the performance of Dowex 50WX-8 as a catalyst for the esterification of salicylic acid with methanol. Through analyzing the experimental results, the Langmuir-isotherm applied to this system to describe the reaction rate. Since then, various mechanisms and kinetics of esterification between acids and alcohols catalyzed by cation- exchange resins were proposed. Here is an overview of the reaction mechanisms and kinetic models according to the type of cation-exchange resins.

2.5.1 Dowex

Dowex, a common cation-exchange resin, is widely used as catalysts in esterification (Vahteristo et al., 2009). In 2005, Kulawska, et al. investigated the esterification of maleic anhydride with octyl, decyl or dodecyl alcohol over Dowex 50Wx8-100, and the kinetic data were measured in the temperature range of 403-433 K (C_{0ALC}/C_{0MA} =5:1). Based on the data, a first order reaction was found- first order with respect to acid and zero order with respect to alcohol. The reaction rate can be described as follows,

$$r = -\frac{dc_M}{dt} = kc_M \tag{37}$$

where c_M is the concentration of maleic monoester, t is reaction time.

The values of activation energy are 66.0 (±0.65) kJ/mol, 58.6 (±0.4) kJ/mol, and 66.1(±0.4) kJ/mol for dioctyl, didencyl, and didodecyl maleate formation, respectively. However, the effects of the catalyst (the particle size and the concentration) and the mass transfer resistance on the reaction rate were not taken into account.

The esterification kinetics of acetic acid with iso-butanol catalyzed by Dowex 50 Wx2 was studied (Izci & Bodur, 2007). It is considered to be reversible reactions and can be described by pseudo-homogeneous (PH) model. The general reaction rate expression can be written as follows,

$$-r_A = k_1 \left(C_A \times C_B - C_E \times C_W / K \right) \tag{38}$$

where subscripts A, B, E and W is acid, alcohol, ester and water, respectively, k_1 is forward reaction rate constant (L mol^{-1} min^{-1}), K is the equilibrium constant of the reaction.

It is found that this bimolecular type is second order reaction. The values of k_1 for different temperatures are 0.24x10^3 (318K), 1.00x10^3 (333K), 3.07x10^3 (348K). The activation energy was found to be 1.745 kJ·mol^{-1} in the presence of Dowex 50 Wx2. However, the PH model does not take into account the resin swelling ratio, adsorption of the components and the non-ideal thermodynamic behavior of reactants and products (Ali &Merchant, 2006; Patel & Saha, 2007; Jeřábek et al., 2010; Erdem & Kara, 2011).

The kinetics of Dowex 50 Wx8-catalyzed esterification was studied between acetic acid and benzyl alcohol (Ali & Merchant, 2009). The swelling ratio of Dowex 50 Wx8 in different solvent was measured, and the results show that it decreases in the order of water, benzyl alcohol, acetic acid, benzyl acetate. Water appears to be preferentially adsorbed by the catalyst from a binary solution of acetic acid and water, and hinders the approach of butanol to the protonated acid. Therefore, the water exerts an adverse effect on the esterification rate.

The initial reaction rates of esterification between acetic acid and benzyl alcohol were measured at various conditions, and the Eley-Rideal (ER) model was used to correlate the data and showed a high degree of fit, indicating that the surface reaction between adsorbed alcohol and acid in the bulk is the rate-limiting step during the initial stage of the reaction. The ER model of this esterification can be described as follow,

$$ri = \frac{\left[M_{cat} k_f K_{alc} \left(a_{acid} a_{alc} - \left(a_{ester} a_{water} / K_a \right) \right) \right]}{\left[1 + K_{alc} a_{alc} + K_{water} a_{water} \right]} \tag{39}$$

$$k_f = 55770 \times \exp \left(-6661.4 / T \right) \tag{40}$$

$$\ln \left(K_a \right) = \left(-1279 / T \right) + 6.810 \tag{41}$$

where M_{cat} is the mass of the catalyst, g; a_{acid}, a_{alc}, a_{ester}, a_{water} is the activity of acid, alcohol, ester, water in the liquid phase, respectively; k_f is forward reaction rate constant for the esterification, mol g^{-1} s^{-1}. K_a is activity reaction equilibrium constant. K_{acid}, K_{alc}, K_{water} is adsorption equilibrium constant for the alcohol present in the system, respectively.

The activation energy form the above relationship was found to be 55.4kJ/mol.

However, as the reaction proceeds, the acid adsorption term might have to be introduced and in such an event the reaction kinetics would be represented by a dual site mechanistic, such as Langmuir-Hinshelwood (LH) model.

In 2011, Ju, et al. measured the kinetic data for the esterification of butyric acid with n-butanol over Dowex 50Wx8-400, and correlated with various types of kinetic models. Strong resin water affinity was taken into account, and the non-ideality of the system was considered by applying the no-random two liquid (NRTL) model. The comparisons of the conversion of butyric acid with reaction time between experimental data and ones predicted by these kinetic models reveal that the ER model and LH model are the most reasonable fit for describing the mechanism, with the total average error 12.52%. Surface reaction is the rate determining step, and the affinity between resin and water is found to be not strong. Therefore, the most possible esterification reaction mechanisms can be proposed as following lists:

1. Single site mechanism: the adsorbed butyric acid onto the catalysts reacts with non-adsorbed n-butanol in the bulk.
2. Single site mechanism: the adsorbed n-butanol onto the catalyst reacts with non-adsorbed butyric acid in the bulk.
3. Dual site mechanism: both the reactants adsorbed on the catalyst surface and react there.

In 2007, Ali, et al. studied the esterification of 1-propanol with propionic acid catalyzed by Dowex 50Wx8-400. The experiments were carried out over a temperature range of 303.15-333.15K, and the reaction mechanism for the esterification was proposed (Lilja et al., 2002). The reaction is initiated by the transfer of a proton from the catalyst to the carboxylic acid，and the carbonium ion is formed during the reaction. The ion is accessible for a nucleophilic attack by the hydroxyl group from the alcohol. After that, a molecule of water is lost from the ion. Finally, the catalyst is recovered by the transfer of proton from the ion to the catalyst surface. This mechanism is represented by the following scheme (Figure 11):
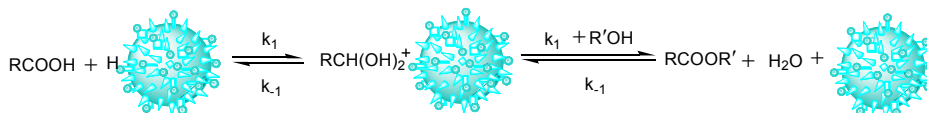
Fig. 11. Mechanism for the esterification catalyzed by Dowex 50Wx8-400

The donation of a proton is commonly assumed to be a fast step, and the nucleophilic substitution is usually assumed to be the rate determined step.

Based on the above reaction mechanism, external and internal diffusion can be negligible, and the E-R model (Equation (39)) is applied. The activity coefficients of components can be predicted using UNIFAC model. Meanwhile, by taking into account the strong water affinity for Dowex 50Wx8-400, a correction term (a) was added to the activity term for water in rate expression. The experimental results for the esterification between 1-propanol and propionic acid were modeled according to the above kinetic model. The total average error between the predicted and experimental mole fractions of acid is 1.65%. The activation energy for the forward reaction was estimated to be 67.3 kJ /mol.

The effect of different alcohols on the conversion of propionic acid was investigated using methanol, ethanol, 1-propanol and 1-butanol. The results reveal that the conversion of

propionic acid at the same time intervals decreases with increasing the chain length of the alcohol, indicating that the chain length of alcohol has a retarding effect on the reaction rate. It is ascribing to the steric hindrance. Meanwhile, the LH model is used to correlate the above experimental data, and the total average error between the predicted and experimental mole fractions of acid is 5.71%.

Interestingly, the kinetic study of esterifications between the same acid (acetic acid) and different alcohol (benzyl alcohol, 2-propanol) in the presence of Dowex 50x8 reveal that the ER model and the LH model is the most suitable predictive model, respectively. These observations seem to indicate that the 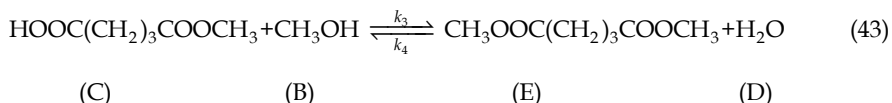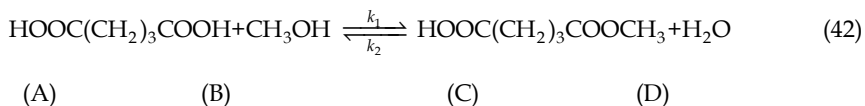type of acid and alcohol play an important role in determining the number of sites involved in this heterogeneously catalyzed reaction.

2.5.2 Amberlyst

Amberlyst, acidic cation-exchange resin bead, was widely used as excellent heterogeneous acid catalysts for a wide variety of organic reactions owing to its macroreticular and continuous open pore structure (Pöpken et al., 2000; Kolah et al., 2007; Pereira et al., 2008; Tsai et al., 2011).

In 2011, Tsai, et al. investigated the kinetic behavior of heterogeneous esterification of dibasic acids such as glutaric acid with methanol over Amberlyst 35. As shown in Equation (42) and Equation (43), the esterification includes two reversible reactions in series accompanying with an intermediate of monomethyl glutarate (MMG):

$$HOOC(CH_2)_3COOH + CH_3OH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} HOOC(CH_2)_3COOCH_3 + H_2O \qquad (42)$$

$$\text{(A)} \qquad\qquad \text{(B)} \qquad\qquad \text{(C)} \qquad\qquad \text{(D)}$$

$$HOOC(CH_2)_3COOCH_3 + CH_3OH \underset{k_4}{\overset{k_3}{\rightleftharpoons}} CH_3OOC(CH_2)_3COOCH_3 + H_2O \qquad (43)$$

$$\text{(C)} \qquad\qquad \text{(B)} \qquad\qquad \text{(E)} \qquad\qquad \text{(D)}$$

where A, B, C, D, E is glutaric acid, methanol, monomethyl glutarate, water, dimethyl glutarate, respectively, k_1, k_3 is forward reaction rate constants, and k_2, k_4 is backward reaction rate constants, respectively, (cm^{6}g^{-1}min^{-1}mol^{-1}).

The large excess of methanol was taken in this study due to the low solubility of glutaric acid in methanol. The kinetic data which had been determined experimentally for the esterification were correlated with quasi-homogeneous (*QH*) model (Schmitt & Hasse, 2006). Comparing with the experimental values, the QH model represents well the conversions of glutaric acid and the mole fractions of each constituent component varying with the contact time. The values of the rate constants were determined by fitting the kinetic data to the reaction rate expressions simultaneously. The temperature dependent k_1, k_2, k_3, k_4 were listed in Table 3,
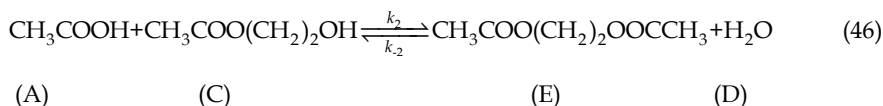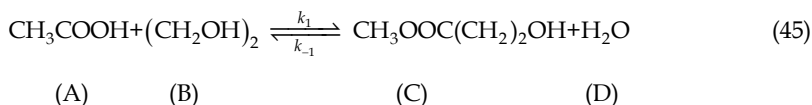
$$k_i = k_{i0} \exp(-\Delta E / RT) \; (i = 1,2,3,4) \qquad (44)$$

It should be noted that the kinetic constants reported above include the swelling effects of Amberlyst 35 beads and just for this two-stage esterification system. However, the non-ideal thermodynamic behavior of reactants and products was not taken into account.

	k_1	k_2	k_3	k_4
k_0	3.346x10⁷±1.01	6.416x10³±1.00	3.487x10⁵±1.01	1.958x10⁹±1.01
$\Delta E / R$	4417.4±1.7	84.5±0.001	2042.2±1.7	5974.6±4.0

Table 3. Each of reaction rate constant for the esterification

In 2008, Schmid, et al. investigated the reaction kinetics of the consecutive, reversible liquid-phase esterification of ethylene glycol with acetic acid to ethylene glycol monoacetate and ethylene glycol diacetate using Amberlyst 36 as catalyst in the temperature range from 333.15K to 363.15K. As shown in Equation (45) and Equation (46), the reaction contains two parts: the formation of the mono-acetylated ethyleneglycol and its hydrolysis as backward reaction; the consecutive esterification of the mono-acetylated ethylene glycol to ethylene glycol diacetate and its hydrosis:

$$CH_3COOH + (CH_2OH)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3OOC(CH_2)_2OH + H_2O \qquad (45)$$

$$\quad\quad (A) \quad\quad\quad (B) \quad\quad\quad\quad\quad (C) \quad\quad\quad\quad\quad (D)$$

$$CH_3COOH + CH_3COO(CH_2)_2OH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CH_3COO(CH_2)_2OOCCH_3 + H_2O \qquad (46)$$

$$\quad (A) \quad\quad\quad\quad (C) \quad\quad\quad\quad\quad\quad (E) \quad\quad\quad\quad (D)$$

The acetic acid initiates swelling of the resin, which results in easy accessible acid groups for the reaction and free mobility of all the components. Therefore, a pseudo-homogeneous (PH) kinetic model is applicable. For the reaction, there is,

$$r_m = \frac{1}{m_{cat}} \frac{1}{v_i} \frac{dn_i}{dt} = k_1 a_A a_B - k_{-1} a_C a_D + k_2 a_C a_A - k_{-2} a_E a_D \qquad (47)$$

where k_1, k_2, k_{-1}, k_{-2} is the forward and backward rate constants, respectively, (mol g⁻¹ s⁻¹), a_i is the activity of each component, and it is calculated using the UNQUAC model, m_{cat} is the mass of catalyst.

The values of k_1, k_2, k_{-1}, k_{-2} is 539.14, 156.43, 114.41, 95.68, respectively, and the mean squared deviation between calculated and experimental mole fractions is 4.53×10⁻².

The kinetic behavior of esterification of lactic acid with isopropanol over Amberlyst 15 was investigated (Toor et al., 2011; Kirbaslar et al., 2001), at different temperatures from 323K to 353K. The ER model was used to describe the reaction mechanism that takes place between adsorbed molecules of isopropanol and the molecules of lactic acid in bulk. The adsorption of ester is reported to be negligible. Hence the rate equation can be described as follows,

$$\frac{dX_A}{dt} = k_1 C_{A0} (w / V) \left[(1 - X_A)(M - X_A) - \frac{X_A^2}{K_e} \right] \qquad (48)$$

where k_1 is Rate constant for esterification reaction, M is molar ratio of isopropanol to lactic acid, K_e is equilibrium rate constant.

The value of activation energy is found to be 22l J/mol, and at each different temperature, the rate constants is 1.058x10⁻⁵ (323.15 K), 1.235x10⁻⁵ (333.15 K), 1.588x10⁻⁵ (343.15 K),

2.117x10^{-5} (353.15 K), respectively. The predicted values of lactic acid fractional conversion are in close agreement with the experimental within the range of experimental error.

The heterogeneous esterification of propionic acid with n-butanol over Amberlyst 35 for the synthesis of n-butyl propionate was investigated (Lee et al., 2002). The esterification is shown as follows,

$$CH_3CH(OH)COOH + CH_3(CH_2)_3OH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3CH(OH)COO(CH_2)_3CH_3 + H_2O \qquad (49)$$

$$\quad (A) \qquad\qquad (B) \qquad\qquad\qquad (C) \qquad\qquad (D)$$

The kinetics data of the liquid-solid catalytic esterification are correlated with various kinetic models, over wide ranges of temperature and feed composition. The activity coefficients calculated using the NTRL model are utilized to represent the non-ideality behavior of the species in the liquid solutions. Meanwhile, the effects of film diffusion and pore diffusion appear to be negligible at the experimental conditions. The results reveal that the Langmuir-Hinshelwood (LH) model yielded the best representation for the kinetic behavior of the liquid-solid catalytic esterification:

$$-r_A = \frac{2.9782 \times 10^{10} \exp(-7664/T)[a_A a_B - 0.01847 \exp(819.06/T)a_C a_D]}{[1 + 3.70a_D]^2} \qquad (50)$$

The activation energy of reaction is about 6.81kJmol^{-1}. This model is capable of representing the kinetic behavior of the liquid-solid catalytic esterification at temperatures from 353.15 to 373.15 K over entire range of the experimental feed compositions.

The kinetics of esterification between acrylic acid and propylene glycol in the presence of Amberlyst 15 was investigated (Altıokka & Ödeş, 2009). Taking into account the general esterification reaction as well as polymerization of acrylic acid and products, the overall reaction mechanism is proposed to be:

$$CH_2CHCOOH + CH_3CHOHCH_2OH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CH_2CHCOOC_3H_6OH + H_2O \qquad (51)$$

$$\quad (A) \qquad\qquad (P) \qquad\qquad\qquad (T) \qquad\qquad (W)$$

$$2CH_2CHCOOH \overset{k_3}{\rightleftharpoons} CH_2CHCOOOCCHCH_2 + H_2O \qquad (52)$$

$$\quad (A) \qquad\qquad\qquad (T1) \qquad\qquad (W)$$

$$2CH_2CHCOOC_3H_6OH \overset{k_4}{\rightleftharpoons} C_{12}H_{18}O_5 + H_2O \qquad (53)$$

$$\quad (T) \qquad\qquad (T2) \qquad\qquad (W)$$

Some of the dimer molecules formed here may transform into polymer. Assuming that each reaction step is elementary, the corresponding rate expression can be written.

$$\frac{dC_A}{dt} = -k_1 C_A C_P + k_2 C_T C_W - k_3 C_A^2$$

$$\frac{dC_P}{dt} = -k_1 C_A C_P + k_2 C_T C_W$$

$$\frac{dC_T}{dt} = k_1 C_A C_P - k_2 C_T C_W - k_4 C_T^2 \qquad (54)$$

$$\frac{dC_W}{dt} = k_1 C_A C_P - k_2 C_T C_W$$

The reaction rate constants k_1, k_2, k_3 and k_4, in Equation (54) are determined, and shown in Table 4, where k_1, k_2 is forward and backward reaction rate constants in Equation(51), and k_3, k_4 is forward reaction rate constants in Equation(52) and Equation(53), respectively,(L min^{-1} mol^{-1}), T is absolute temperature in K.

Together with the experimental data, the concentration-time curves based on the model were obtained under given reaction conditions; there is a reasonably good agreement between calculated curves and experimental points.

	k_1	k_2	k_3	k_4
k_0	4.249×10^9	1.015×10^6	1.584×10^{27}	1.871×10^{13}
$\Delta E/R$	9667	7797	24710	12340

Table 4. Each of reaction rate constant for the esterification

3. Conclusions

This chapter discussed esterification mechanisms, and evaluated the kinetics objectively and quantitatively, which provided a most effective way to select catalyst and design reactor for different esterification systems. It is discovered that some new catalysts (such as lipases, room temperature ionic liquids) have being used in esterification; nevertheless, there are few research on the case. Herein, it is worthy to be investigated deeply.

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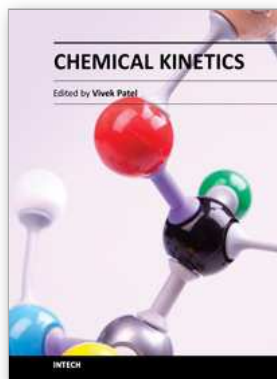
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Edited by Dr Vivek Patel

Chemical Kinetics relates to the rates of chemical reactions and factors such as concentration and temperature, which affects the rates of chemical reactions. Such studies are important in providing essential evidence as to the mechanisms of chemical processes. The book is designed to help the reader, particularly students and researchers of physical science, understand the chemical kinetics mechanics and chemical reactions. The selection of topics addressed and the examples, tables and graphs used to illustrate them are governed, to a large extent, by the fact that this book is aimed primarily at physical science (mainly chemistry) technologists. Undoubtedly, this book contains "must read" materials for students, engineers, and researchers working in the chemistry and chemical kinetics area. This book provides valuable insight into the mechanisms and chemical reactions. It is written in concise, self-explanatory and informative manner by a world class scientists in the field.

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