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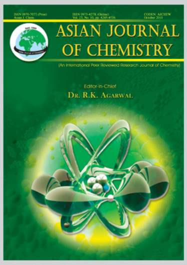

Kinetics on Synthesis of Propyl Acetate Catalyzed with Expansible Graphite

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The reaction for heterogeneous synthesis of propyl acetate catalyzed by expansible graphite was investigated in a stirred batch reactor. By the elimination of internal and external diffusion, the concentration change of acetic acid with reaction time was determined and the parameters of the kinetic model for the reversible second-order reaction were evaluated by the initial reaction rate method. The frequency factor was 5.46×10^7 L/(mol min) and the activation energy was 18.03 kJ/mol under the conditions of 353.2-383.2 K, 101.3 kPa, mass ratio of catalyst is 6-10 % of total mass of acetic arid and propanol. The accuracy of the reaction kinetic equation was testified and the result showed that the calculated values agreed well with the experimental value and the maximum deviation of the calculated value comparing with the experimental results was 10.8 %.

Key Words: Expandable graphite, Sulfuric acid intercalation, Propyl acetate, Kinetics.

INTRODUCTION

As a kind of flavour reagent with fruit taste, propyl acetate has been widely used in food machining, printing and it is called as all-purpose solvent for its excellent solubility for many organic reagents. In the synthesis of propyl acetate, H_2SO_4 is the traditionary catalyst and the use of H_2SO_4 often causes problems such as equipment corrosion and environment pollution.

Expandable graphite is a kind of new material, which is prepared through intercalation reaction of non-carbon substance such as H_2SO_4 under the condition of chemical or electric chemistry oxidation[1-3]. It is normally used as adsorbent of oil and other environmental pollutants after being expanded under high temperature[4,5]. At the same time, expandable graphite can be used as solid super acid catalyst in acylation reaction for its intercalation of sulfuric acid[6]. Li *et al.*[7] studied the catalysis activity of expandable graphite in the synthesis of acetic ether. Pang *et al.*[8] prepared isoamyl acetate with expandable graphite as catalysts and got a yield of 96 %. No research has been reported for the synthesis of propyl acetate under the catalysis of expandable graphite. In this research, expandable graphite was prepared through chemical oxidation of potassium permanganate and intercalation of sulfuric acid. Chemical reaction kinetics on propyl acetate was studied and the kinetics model and model parameter were calculated.

EXPERIMENTAL

Natural graphite (C, 5092) was provided by Action Carbon Co. Ltd., Baoding, China. Acetic acid, propanol, H_2SO_4 (98 %), $KMnO_4$, Na_2CO_3, $CaCl_2$, NaCl are all analytical reagents.

WAY refractor (Shanghai, China); GC-4000A (Beingjing, China); PHS-3C acid meter (Shanghai, China); FTS-40 Fourier transform infra-red spectrometer (America Biorad) were used in this experiment.

Preparation of expandable graphite: With the mass ratio of 1.0 : 0.12 : 5.0 of C : $KMnO_4$: H_2SO_4 (98 %), the definite amount of graphite C, $KMnO_4$ and H_2SO_4 (diluted to a mass concentration of 75 % with de-ionized water before mixed with graphite) are mixed under 30 ºC. Reaction lasts 0.5 h under stirring, the products are washed with de-ionized water until pH reaches to 6-7 and then it is diped in de-ionized water for 2 h. After filtration and dryness at 75-80 ºC for about 3 h, expandable graphite is formed.

Preparation of propyl acetate and kinetic experiments: At a definite mole ratio, acetic acid and propanol are added into the reactor appending stirrer and water segregator. Reaction lasts a certain time under the catalysis of expandable graphite. Then the products are filtrated under *vacuum*, washed with saturated solution of Na_2CO_3, $CaCl_2$ and NaCl, respectively. The upper layer solution is distilled under atmospheric pressure, the fraction corresponding to boiling point of 92-98 ºC is collected. Then distillate is analyzed with refractor and IR, respectively. Refractive index of the collected product is detected as 1.3835 at 25 ºC (reported value 1.383-1.385). In the IR spectrum analysis of the distillate, characteristic peak of C-H (2952 cm^{-1}), C-C (=O)-O (1178 cm^{-1}) are all observed.

Suitable esterification condition is: molar ratio of propanol to acetic acid keeps 2:1, mass of expandable graphite keeps 8 % of the total mass of reactants, reaction lasts 0.5- 1 h and temperature keeps at the boiling point.

In kinetic experiments, mole ratio of propanol and acetic acid are set as 2:1, reaction temperature is adjusted and controlled through adjustment of heating power and stirring rate can be regulated and controlled with velometer. Sample is drawn at an interval of 5 min by using a 2 mL injector and then diluted with distilled water, finally the concentration of acetic acid is analyzed with acid meter. Percent conversion of acetic acid can be calculated according to eqn. (1).

$$Y = \frac{C_{AO} - C_A}{C_{AO}} \times 100\% \qquad (1)$$

RESULTS AND DISCUSSION

Reaction between propanol and acetic acid is reversible as described in eqn. (2), propyl acetate and water are produced. GC analysis of reaction mixture give peaks of propanol, acetic acid and propyl acetate, no other substance is detected. The results testify by-products in this esterification can be neglected.

$$C_3H_7OH + CH_3COOH \rightleftharpoons CH_3COOC_3H_7 + H_2O \qquad (2)$$

Esterification of propanol and acetic acid under the catalysis of expandable graphite is a heterogeneous reaction. Reaction process on a porous catalyst generally involves three stages: (i) external diffusion; (ii) internal diffusion; (iii) adsorption and reaction. To eliminate the influence of external diffusion and internal diffusion, feasible stirring speed and expandable graphite granularity are tested. When the stirring speed is above 200 rpm, affection of external diffusion can be neglected. expandable graphites with granularity of 50 mesh and 80 mesh are tested, respectively and no difference is observed. So when the stirring speed is controlled above 200 r min^{-1}, 50 mesh expandable graphite is used as catalyst, external diffusion and internal diffusion can be ignored and esterification of propanol, acetic acid can be regarded as a homogeneous reaction. Mechanism of this reversible second-order reaction can be described as eqn. (3)[9-11] .

$$(-r_A) = f(w)\cdot k_O \cdot e^{-Ea/RT}(C_AC_B - C_EC_W/K)(mol/(L\cdot min)^{-1}) \qquad (3)$$

Kinetic experiment data: Under definite temperature and expandable graphite dosage, changes of acetic acid concentration along with reaction time are detected. Plots of acetic acid percent conversion Y *versus* t are drawn in order to get the initial reaction rate through finding slope of the curve at the initial time. Influence of expandable graphite dosage w_{EG} and temperature on initial reaction rate of acetic acid is listed in Table-1.

Influence of expandable graphite dosage on initial reaction rate of acetic acid: Based on results of experiment 1-5, plot of acetic acid initial reaction rate versus dosage of expandable graphite w_{EG} is showed in Fig. 1. The curve is fitted with origin program and eqn. (4) can be obtained.

$$f(w) = -0.0006416 + 0.0004437w, \ (r = 0.9918, N = 5) \qquad (4)$$

Determination of frequency factor and activation energy: Suppose: $ae^{b/T} = k_oC_{AO}C_{BO}e^{-Ea/RT}$, $b = -Ea/R$

TABLE-1
KINETIC DATA OF THE ESTERIFICATION

Number	w_{EG} (g)	T (ºC)	Reaction rate (mol/min)
1	2.1688	90	2.90×10^{-4}
2	2.5303	90	5.31×10^{-4}
3	2.8918	90	6.21×10^{-4}
4	3.2533	90	8.17×10^{-4}
5	3.6147	90	9.49×10^{-4}
6	2.8918	80	5.31×10^{-4}
7	2.8918	90	6.21×10^{-4}
8	2.8918	100	7.23×10^{-4}
9	2.8918	110	9.66×10^{-4}

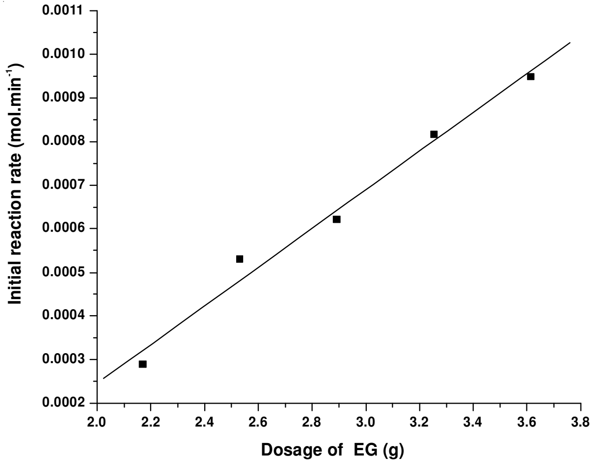

Fig. 1. Relationship between dosage of expandable graphite and acetic acid initial reaction rate

So:$(-r_{A,O}) = ae^{b/T}$ and $(-r_{A,O})$ corresponds to acetic acid initial reaction rate.

Based on $(-r_{A,O}) = ae^{b/T}$, it can be changed as: $\ln(-r_{A,O}) = \ln a + b/T$. Plot of $\ln(-r_{A,O})$ *versus* 1/T is showed in Fig. 2. The curve is fitted with origin program and values of a and b are obtained as following:

$a = 0.2553$, $b = -2167.0$ ($r = 0.9691$, $N = 5$)

For: $k_oC_{AO}C_{BO} = a$;

So: $k_0 = a/C_{AO}C_{BO} = 5.457 \times 10^7$ L/(mol min)$^{-1}$

$Ea = -bR = 2169{}^*8.314 = 1.803 \times 10^4$ J/mol

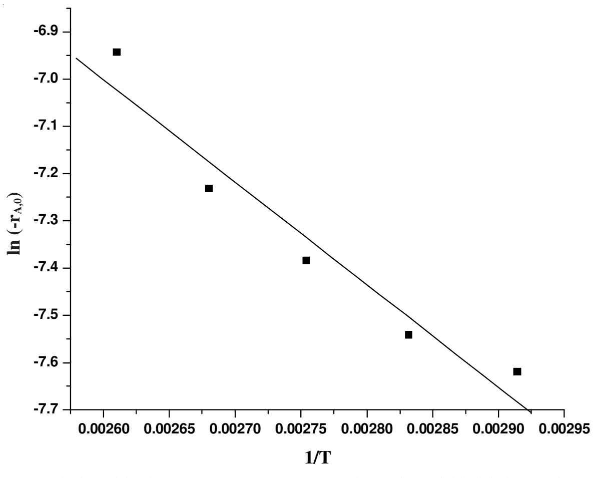

Fig. 2. Relationship between temperature and acetic acid initial reaction rate

Detection of equilibrium constant: Equilibrium constant K of the esterification can be written as eqn. (5).

$$K = \frac{C_{Ef}C_{Wf}}{C_{Af}C_{Bf}} \qquad (5)$$

where, C_{Ef}, C_{Wf}, C_{Af} and C_{Bf} are the equilibrium concentration of propyl acetate, water, acetic acid and propanol, respectively.

To get K, the reaction is carried out under the condition of molar ratio of propanol to acetic acid keeps 2:1, mass of expandable graphite keeps 8 % of the total mass of reactants and temperature keeps at 90 ºC. Sample is drawn at an interval of 5.0 min until the reaction reaches equilibrium state. Per cent conversion of acetic acid are calculated according to eqn. (1) and equilibrium concentration of propyl acetate, water, acetic acid, propanol can be obtained (Fig. 3). Then the K is calculated as 0.183. Influence of temperature on K can be ignored when the changes of temperature is not obvious. K = 0.183 can use to the calculation of kinetic parameter.

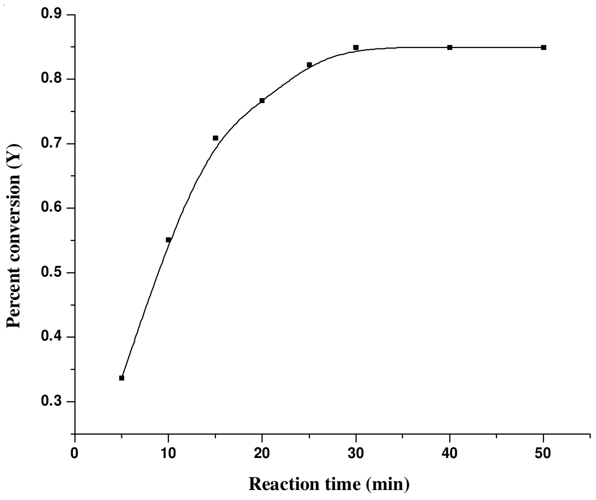

Fig. 3. Changes of acetic acid percent conversion with time

Foundation of kinetic model and its validation: According to the above results, kinetic model of the esterification can be described as eqn. (6):

$$(-r_A) = f(w).k_0.e^{-EA/RT}(C_AC_B\text{-}C_EC_W/K)\ \text{mol/(L·min)}$$
$$= (0.0006416 + 0.0004437w).54566530e^{-18030.6/RT}$$
$$(C_AC_B\text{-}C_EC_W/0.183 \qquad (6)$$

To validate the correctness of the kinetic model, the calculated reaction rate of $(-r_{A,The})$ according to eqn. (6) are compared with that of $(-r_{A,Exp})$ detected through experiments. Results showed in Table-2 illustrates values of $(-r_{A,The})$ are agreed well with that of $(-r_{A,Exp})$ and the maximum deviation of the calculated value comparing with the experimental results was 10.8 %.

Average of $(-r_{A,Exp})$- $(-r_{A,The})$ and unbiased variance are calculated according to eqns. (7) and (8) :

$$\overline{X} = \frac{\sum_{i=1}^{n}[(-rA,_{Exp})_i - (-rA,_{The})_i]}{n} = \frac{\sum_{i=1}^{n}X_i}{n} = 6.583\times10^{-6} \qquad (7)$$

$$s = \sqrt{\frac{\sum_{i=1}^{n}X_i^{\ 2}}{n-1}} = 9.13\times10^{-6} \qquad (8)$$

Data t-test is carried out with a confidence of 98 %. Results showed in eqn. (9) testified the calculated values are agreed well with experimental values. Kinetic model gotten form experiment data is coincident with the real reaction process.

TABLE-2
COMPARISON OF $(-r_{A,Exp})$ with $(-r_{A,The})$

No.	W_{EG} (g)	T (ºC)	t (min)	$(-r_{A,Exp})$ (mol/ min)	$(-r_{A,The})$ (mol/ min)	$(-r_{A,Exp})$- $(-r_{A,The})$ X
1	2.1688	90	5	0.000274	0.000266	0.000008
2	2.1688	90	10	0.000282	0.000273	0.000009
3	2.1688	90	15	0.000250	0.000240	0.000010
4	1.1688	90	20	0.000217	0.000205	0.000002
5	2.8918	90	10	0.000914	0.000912	0.000009
6	2.8918	90	15	0.000775	0.000766	0.000007
7	2.8918	90	20	0.000631	0.000624	0.000011
8	2.8918	90	25	0.000526	0.000515	0.000010
9	2.8918	70	5	0.000667	0.000657	0.000011
10	2.8918	70	10	0.000579	0.000568	-0.000004
11	2.8918	70	15	0.000545	0.000549	-0.000006
12	2.8918	70	20	0.000491	0.000497	

$$t_{\frac{a}{2}}(11) = \frac{\overline{X} - \mu_0}{\frac{s}{\sqrt{n}}} = 2.394 < t_{0.01}(11) = 3.11 \quad (\mu_0 = 0) \qquad (9)$$

Conclusion

Eliminating the disturbance of external diffusion and internal diffusion, kinetics of esterification reaction between acetic acid and propanol under the catalysis of expandable graphite can be described as eqn. (6) and the model is coincident with the real reaction process with high confidence.

Symbol illumination

C_A-concentration of acetic acid (mol/L); C_B-concentration of propanol (mol/L); C_E-concentration of propyl acetate (mol/ L); C_W-concentration of water (mol/L); w-mass of expandable graphite (g); E_a-activation energy (J/mol); Y-percent conversion of acetic acid; K-equilibrium constant; k_0-frequency factor (L/(mol min)), $(-r_A)$-reation rate of acetic acid [mol/(L min)]; R-gas constant [8314J/(mol K)]; t-reaction time (min); T-temperature (K); f(w)-function under the influence of catalyst.

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