REACTION CONDITIONS AND KINETICS FOR SYNTHESIZING n-BUTYL ACETATE

Cong Yufeng[a]

Effects of different reaction conditions on the synthetic method of n-butyl acetate have been reviewed in the present paper. Different catalysts consisting inorganic salt like ($Ce(S_2O_8)_2$/SBA-15, $NH_4Fe(SO_4)_2 \cdot 12H_2O$) and oxide ($MoO_3/SiO_2$) have also been introduced. Kinetics equations have also been applied on n-butyl acetate system. The results showed that kinetic equations may predict the distribution of product and the experimental data are in agreement with the quantitatively analytical conclusions drawn from the calculated data.

* Corresponding Author
    Fax: 86-24-56860869
    E-Mail: congyufeng2012@hotmail.com
[a]   Liaoning Shihua University, Fushun, Liaoning, P.R. China.

Introduction

n-Butyl acetate is one of the important fine chemical products. It is widely used in different areas such as solvent, plasticizer, resin, painting, perfume, cosmetics, medicine, surfactant and other organic syntheses[1] Acetic acid and n-butanol are used as feedstock to manufacture n-butyl acetate in the industry. Concentrated sulphuric acid is one of the main catalysts. Apart from several advantages, concentrated sulphuric acid has a lot of disadvantages also, such as tainted products due to strong oxidizing nature, it is very difficult to purify, even after several washings, due to complicated process lot of waste water is discharged which is also a environmental pollution problem and equipments are corroded.[2] Inorganic salt like ($Ce(S_2O_8)_2$/SBA-15, $FeNH_4(SO_4)_2 \cdot 12H_2O$) and oxide ($MoO_3/SiO_2$) are the best catalysts. They have high catalytic performance, selectivity and non-corrosive in nature. [3]

In the present paper, different catalysts such as inorganic salt ($Ce(S_2O_8)_2$, $NH_4Fe(SO_4)_2 \cdot 12H_2O$) and oxide ($MoO_3/SiO_2$) have been discussed. Effects of different reaction conditions on the synthetic method of n-butyl acetate have also been reviewed. Furthermore, kinetics equations have also been applied.

Discussion

Effects of the reaction time on the yields of n-butyl acetate by the addition of $Ce(S_2O_8)_2$ -SBA-15 as a catalyst

Yin Yanlei [4] has reported the preparation of n-butyl acetate and the effect of the reaction conditions on its yield. $Ce(S_2O_8)_2$ and SBA-15 catalysts were ground and roasted to generate n-butyl acetate. It was supposed that molar ratio (1.0:1.2) and amount (0.0375g) of acetic acid to n-butanol and the amount of catalyst kept constants. Effects of the reaction time on the yield of n-butyl acetate,

has also been discussed. Table 1 showed effects of the reaction time on the yields of n-butyl acetate. The yields of n-butyl acetate increased with an increase of the reaction time. The maximum yield of n-butyl acetate was 96.58%, when the reaction time was about three hours. The experimental results showed that $Ce(S_2O_8)_2$ and SBA-15 had good catalytic performance and were reused several times.

Table 1. effects of the reaction time on the yields of n-butyl acetate

Reaction time, h	0.5	1.0	1.5	2.0	2.5	3.0
Yield, %	30.00	69.98	83.21	95.13	96.01	96.58

Effect of the AcOH/n-BuOH ratio on the yield in the presence of $NH_4Fe(SO_4)_2 \cdot 12H_2O$ catalyst

Kong Xiangwen [5] explained why $NH_4Fe(SO_4)_2 \cdot 12H_2O$ as a catalyst replaced concentrated sulfuric acid to generate n-butyl acetate. It was found that the reaction time and the amount of catalyst kept at constants were 0.75 hours and 1.1g, respectively. Effects of the molar ratio of acetic acid to n-butanol on the yields of n-butyl acetate had been discussed. Results are recorded in Table 2. First the yields of n-butyl acetate increased and then decreased with an increase in the molar ratio of acetic acid to n-butanol. When the molar ratio of acetic acid to n-butanol was 1.0:1.2, the maximum yield of n-butyl acetate reached 98.1%. $NH_4Fe(SO_4)_2 \cdot 12H_2O$ one of the best catalysts was used to synthesise n-butyl acetate because it was very economic, stable and insoluble in organic acids and alcohol. After the reaction, $NH_4Fe(SO_4)_2 \cdot 12H_2O$ became insoluble material and was easily separated from the reaction system. It had high catalytic performance and selectivity and non-corrosive.

Table 2. effects of the molar ratio of acetic acid to n-butanol on the yields of n-butyl acetate

Molar ratio of AcOH to n-BuOH	1.0:1.0	1.0:1.1	1.0:1.2	1.0:1.3	1.0:1.4
Yield (%)	90.7	93.6	98.1	94.3	90.4

Effects of the amount of MoO$_3$/SiO$_2$ catalyst catalyst on the yields of n-BuOAc

Li Shuchang[6] described the preparation of MoO$_3$/SiO$_2$ and the effect of the reaction conditions such as the reaction time, the molar ratio of acetic acid to n-butanol, the amount of catalyst and number of reuse of catalyst on the yield of n-butyl acetate. It was found that the reaction time and the molar ratio of acetic acid to n-butanol kept at constants were 3 hours and 1.0:4.0, respectively. Effects of the amount of catalyst on the yields of n-butyl acetate had been discussed. Table 3 presented effects of the amount of catalyst on the yields of n-butyl acetate. The yields of n-butyl acetate firstly increased and then decreased with an increase in the amount of catalyst. When the amount of catalyst was 1.0, the maximum yield of n-butyl acetate arrived at 95.6%.

Table 3. effects of the amount of catalyst on the yields of n-butyl acetate

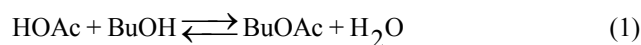| Catalyst amount, g	0.6	0.8	1.0	1.2	1.4
Yield, %	62.3	78.6	95.6	91.7	84.5

Kinetics equations of n-butyl acetate

Qiu Ting [7] used cation exchange resin as a feedstock and described effects of the reaction conditions such as the stirring speed, the catalyst particle size (cation exchange resin), the reaction temperature, the molar ratio of acetic acid to n-butanol and the amount of catalyst on the yield of n-butyl acetate. The kinetic model LHHW was used to calculate the experimental data. The experimental results showed that the surface reaction was the main control step of acetic acid and n-butanol. Its reaction enthalpy was -1.838×10^4 J/mol. The activation energies of the forward and reverse reaction were 5.238×10^4 J/mol and 3.929×10^4 J/mol, respectively. The pre-exponential factors were 1.015×10^4 mol/(g·s) and 3.148 mol/(g·s), respectively.
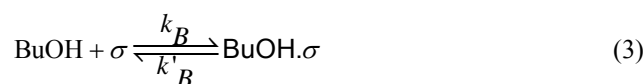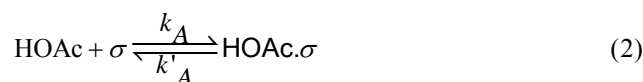
The reaction of acetic acid and n-butanol was the heterogeneous catalytic liquid-solid reaction. It consisted of several steps such as the reactant was diffused from the liquid phase to the external surface area of the catalyst, and then spread from the external surface area of the catalyst to the internal surface area. The reactant was absorbed and the reaction took place at the same time. The product was desorbed and diffused to the external surface area of the catalyst, and then spread from the external surface area of the catalyst to the liquid phase. The real reaction process was absorption, the surface reaction and desorption in advance of ignoring the internal and external diffusion. Based on the principle of LHHW model, it was supposed that (1) catalytic and active centres were their acid parts. (2) The reactant competed to be absorbed on catalytic and active centres with the product whose absorptions totally were single layer. (3) Acetic acid absorbed on one catalytic and active centre reacted with n-butanol absorbed on another catalytic and active centre. n-Butyl acetate was obtained from the internal surface area of the catalyst. (4) The surface reaction was the main control step.
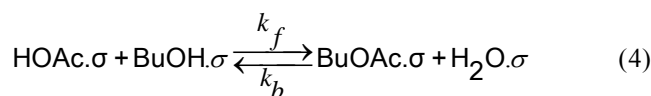
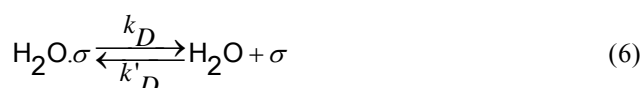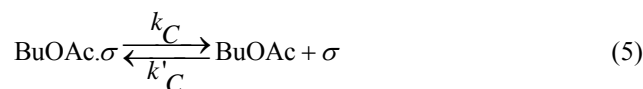The reaction of acetic acid and n-butanol was listed as follows:

$$HOAc + BuOH \rightleftarrows BuOAc + H_2O \tag{1}$$

Absorptions:

$$HOAc + \sigma \underset{k'_A}{\overset{k_A}{\rightleftarrows}} HOAc.\sigma \tag{2}$$

$$BuOH + \sigma \underset{k'_B}{\overset{k_B}{\rightleftarrows}} BuOH.\sigma \tag{3}$$

The surface reactions:

$$HOAc.\sigma + BuOH.\sigma \underset{k_b}{\overset{k_f}{\rightleftarrows}} BuOAc.\sigma + H_2O.\sigma \tag{4}$$

Desorptions:

$$BuOAc.\sigma \underset{k'_C}{\overset{k_C}{\rightleftarrows}} BuOAc + \sigma \tag{5}$$

$$H_2O.\sigma \underset{k'_D}{\overset{k_D}{\rightleftarrows}} H_2O + \sigma \tag{6}$$

where σ means the adsorption site. HOAc.σ, BuOH.σ, BuOAc.σ and H$_2$O.σ are the adsorption state of acetic acid, n- butanol, n-butyl acetate and water, respectively.

It is supposed that

$$K_{sHOAc} = k_A / k'_A,$$

$$K_{sBuOH} = k_B / k'_B,$$

$$K_{sBuOAc} = k'_C / k_C \text{ and}$$

$$K_{sH2O} = k'_D / k_D.$$

Furthermore, K_{sHOAc}, K_{sBuOH}, K_{sBuOAc} and K_{sH2O} are adsorption equilibrium constants of acetic acid, n-butanol, n-butyl acetate and water, respectively. The total reaction rate, *r* is written as follows:

$$r = \frac{-ndx_{BuOH}}{dt} = \frac{M_{cat}(K_f K_{sHOAc} x_{HOAc} K_{sBuOH} x_{BuOH} - K_b K_{sBuOAc} x_{BuOAc} K_{sH_2O} x_{H_2O})}{(1 + K_{HOAc} x_{HOAc} + K_{sBuOH} x_{BuOH} + K_{sBuOAc} x_{BuOAc} + K_{sH_2O} x_{H_2O})^2} \quad (7)$$

where

r - the reaction rate, mol s^{-1}

M_{cat} - the amount of catalyst, g

K_f - the positive reaction rate, mol g^{-1}·s^{-1}

K_b - the negative reaction rate, mol g^{-1}·s^{-1}

x_i - the molar fraction of substance

n – the amount of substance, mol.

When the reaction equilibrium constant K_s is equal to $K_f K_{sHoAc} K_{sBuOH}/K_b K_{sBuoAc} K_{sH2O}$, Eqn. (7) can be simplified to Eqn. (8)

$$r = \frac{M_{cat} K_f K_{HOAc} K_{sBuOH} \left[x_{HOAc} x_{BuOH} - \dfrac{x_{BuOAc} K_{sH_2O} x_{H_2O}}{K_s} \right]}{(1 + K_{sHOAc} x_{HOAc} + K_{sBuOH} x_{BuOH} + K_{sBuOAc} x_{BuOAc} K_{sH_2O} x_{H_2O})^2} \quad (8)$$

The experimental data are calculated by using the particle swarm optimization algorithm. The above model parameters are shown in Table 4. The reaction equilibrium constants (Ks) decrease with an increase in the reaction temperature, however, the positive and negative reaction rate gradually increase with the increase in the reaction temperature. This proves that this particular reaction is an exothermic in nature. The higher the reaction temperature shorter is the time to reach reaction equilibrium.

Table 4. parameters of kinetic model

T (°C)	K_{sHAc}	K_{sBuOH}	K_{sBuAc}	K_{sH2O}	$K_f \times 10^4$ (mol/(g·s))	$K_b \times 10^6$ (mol/(g·s))	K_s
75	4.2051	5.8754	14.9870	8.6886	1.2530	4.0149	5.9215
80	4.1115	4.3115	12.8400	7.8040	1.4862	4.8346	5.4383
85	4.0884	2.9421	11.0160	7.2986	1.9465	5.8273	4.9973
90	3.9753	1.8702	9.5009	6.4785	2.6502	7.0350	4.5502

Based on the above the experimental data, the regression Eqn. (9), (10), (11) and (12) are written as follows:

$K_{sHOAc} = 1.188 \times \exp(3.658 \times 10^3 /RT)$ (9)

$K_{sBuOH} = 5.80 \times 10^{-12} \times \exp(8.014 \times 10^4 /RT)$ (10)

$K_{sBuOAc} = 2.40 \times 10^{-4} \times \exp(3.197 \times 10^4 /RT)$ (11)

$K_{sH2O} = 8.941 \times 10^{-3} \times \exp(1.991 \times 10^4 /RT)$ (12)

The maximum yield of n-butyl acetate reached 96.58% in three hours by the addition of Ce(S$_2$O$_8$)$_2$/SBA-15.

The maximum yield of n-butyl acetate arrived at 98.1% under the condition of acetic acid/n-butanol ratio (1.0:1.2).

The maximum yield of n-butyl acetate was 95.6% when the amount of catalyst was 1.0.

The reaction speed rate Eqn. was obtained and predicted the distribution of product.

Conclusion

Using acetic acid and n-butanol as feed stocks and (Ce(S$_2$O$_8$)$_2$/SBA-15, FeNH$_4$(SO$_4$)$_2$·12H$_2$O) and oxide (MoO$_3$/SiO$_2$) as catalysts, effects of the reaction time, acetic acid/ n-butanol ratio and the amount of catalyst have been discussed. The experimental results obtained are as follows:

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