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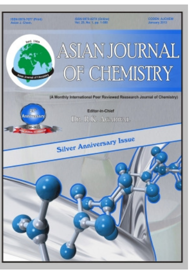

Ultrasound Assisted Heteropoly Acid Catalyst SiW_{12}/SiO_2 for Synthesis of Benzyl Acetate

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Under ultrasonic radiation, benzyl acetate is synthesized from benzyl alcohol and glacial acetic acid in presence of catalyst SiW_{12}/SiO_2. The catalyst was prepared and characterized by IR, X-ray diffraction and SEM in the experiment. The XRD result indicates that heteropoly acid retains the Keggin-type structure. The kinetic parameters of reaction were, respectively measured at 90, 100 and 110 ºC and the kinetic equation was built. Then, the effects of reaction temperature, the amount of catalyst, molar ratio of benzyl alcohol to glacial acetic acid and ultrasonic intensity on the esterification yield were discussed. The results showed that the optimum operating parameters for the present work when 10 kHz ultrasonic frequency and 1.0 W/cm^2 ultrasonic intensity are as follows: reaction temperature: 110 ºC, use amount of catalyst: 1.5 g, molar ratio of benzyl alcohol to glacial acetic acid: 1.5; reaction time: 75 min. Under such conditions, the esterification yield of the reaction reached above 95.3 %.

Key Words: Benzyl Acetate, Ultrasound, Benzyl alcohol, Glacial acetic acid, Esterification.

INTRODUCTION

Benzyl acetate, a kind of edible spice that can be used according to the relevant regulations of the state, is widely used in preparation of apple, banana, papaya and other types of fragrance[1]. It is also widely used in textile and dye industry as solvent. At present, benzyl acetate is synthesized by homogeneous catalysis of acetic acid and benzyl butanol in industrial production, but the oxidizability and dehydration property of concentrated sulfuric acid leads to so many disadvantages such as many side reactions, complex post-treatment, large amount of wastewater, serious corrosion to equipment and great pressure on the environment[2,3].

Heteropoly acid has been widely recognized and applied as a kind of environmental friendly catalyst. It has many advantages: for example, it has the structure characteristics of complexes and metal oxides and it also has strong acidity, redox property, stable structure, high regeneration speed, high activity[4], low pollution, unique acidic property, pseudo liquid phase, multi-function (strong acidity, strong oxidizability, polymerization retardation and photoelectrocatalysis), no corrosion to equipment and it can be well modified[5]. Therefore, the application of heteropoly acid in chemical reaction has a good prospect. The problem in traditional bio-reaction processes, such as complicated separation process and difficult recycles of catalyst, could be solved well by using supported heteropoly acid catalysts. In general, the carriers can be chosen in high surface area materials (SiO_2[6], SBA- 5[7] and MCM-41[8]).

Now, more and more researchers are paying attention to ultrasound[9,10]. It provides the chemical researchers with an unusual way of making energy introduced into molecule, optimizing the chemical reaction conditions, avoiding high temperature and high pressure, shortening reaction time, changing surface features and improving reaction yield and selectivity[11,12].

To meet the requirements for green chemistry synthesis routes, The optimum conditions for the preparation of benzyl acetate with SiW_{12}/SiO_2 catalyst and the kinetics are discussed in the paper. The kinetic parameters of reaction were measured and the kinetic equation was built. The results provided a reliable theoretical and experimental basis for the further development of the synthesis process of benzyl acetate.

EXPERIMENTAL

CH_3COOH, $C_8H_{20}O_4Si$, HCl, C_7H_8O, SiW_{12}, $C_2H_6O_2$, C_2H_6O, $C_2H_4O_2$ and NaOH were procured by Shanghai Experiment Reagent Co. Ltd. All these reagents were reagent grade chemicals.

The FT/IR spectra are recorded on a Nicolet Impact 380 infrared spectrophotometer placing the materials in KBr pellets. The wide angle XRD were recorded by using a Bruker D8 diffractometer and small angle using a Bruker D8 Advance

XRD diffractometer equipped with a gobel mirror using CuK$_\alpha$ radiation (λ = 1.5418 × 10^{-10} m), tube voltage 40 kV, tube current 30 mA, scan scope 5-60°, scan step 0.05° and scan rate 0.2 s/step. DGC-1200 ultrasonic processor (10 kHz, 0-250 V), hydrophone (CS-3) and oscillograph (SR8) were also used in the experiments. CS-3 hydrophone (made by Institute of Acoustics, Chinese Academy of Sciences) was used to measure and estimate the ultrasonic intensity in the solution.

Preparation of catalyst SiW_{12}/SiO_2[13]: 34.65 g of TEOS, 20.65 g of ethylene glycol and 20 g of ethanol dissolved in a 250 mL beaker; then make the solutions mixed and heated to 80 ºC, followed by the addition of SiW_{12}. After stirring for 0.5 h, run the ultrasound and add 60 g ethanol, 15 g distilled water into the solution. The slurry was further heated at 80 ºC for 8 h so as to obtain a clear jelly. Finally, the product was left for 24 h at room temperature. The final solid was identified as the catalyst SiW_{12}/SiO_2.

Synthesis of benzyl acetate: The sonochemical reactor produced by Wuxi Dejia Electronics Co. Ltd., is used for the experimental setup for the preparation of benzyl acetate. Ultrasonic horn, the device used for the generation of cavitation, operates at the frequency of 10 kHz (voltage output 0-250 V). The diameter of ultrasonic horn with the frequency of 10 kHz is 2.1 cm. The reactions were carried out in a four necked bottle of 250 mL capacity where the reaction volume (*ca.* 100 mL) was kept constant for all the reactions. The thermometer and water separator were installed on the necks. In a typical procedure, the right amount of catalyst was added to toluene, which was dissolved in the mixed solvent of the proper amount of acetic acid and benzyl alcohol. Then the mixture was heated for 2 h. The magnetic stirrer was provided to stir the mixtures. The reaction mixture samples were taken out at each 15 min interval and titrated with 0.4 mol/L NaOH solution to determine the amount of unconverted acetic acid in terms of acid value.

Determination of the esterification yield R was carried out by following GB 1668-81 acid determination, it was obtained by the following equation[14]:

$$R = \left(1 - \frac{V_t}{V_0}\right) \times 100\ \%$$

where V_0 (mL) is the volume of sodium hydroxide solution consumed for titration before reaction while V_t (mL) is the volume of sodium hydroxide solution consumed for titration at time t.

Infrared spectrum results of benzyl acetate are as follows: 1745 cm^{-1} is C=O stretching band. The correlation peak of CH_3 is C-H asymmetric stretching vibration absorption band (2965 cm^{-1}), C-H symmetric stretching vibration absorption band (2894 cm^{-1}) and C-H in-plane bending vibration absorption peak (1462 and 1367 cm^{-1}). The characteristic peak of C-O-C is 1240 and 1067 cm^{-1}. 1607, 1498 and 1460 cm^{-1} are the C=C stretching vibration band of benzene ring. The results implied that the product is benzyl acetate.

RESULTS AND DISCUSSION

Characterization of catalyst

IR: Fig. 1 is the infrared spectrums about active component SiW_{12}, catalyst SiW_{12}/SiO_2 and carrier SiO_2. It was analyzed by infra-red spectrum with KBr squash method. The spectrum are as follows: In 1000-700 cm^{-1} fingerprint region, the synthetic product shows obvious four characteristic absorption peaks of keggin structure heteropolyanion: 979, 926, 879 and 783 cm^{-1}, which, respectively belong to the absorption vibration peak of ν(W=O), ν(Si-O), ν(W-Ob-W) and ν(W-Oc-W)[15]. The results imply that the product is intact keggin structure polyoxometallate.

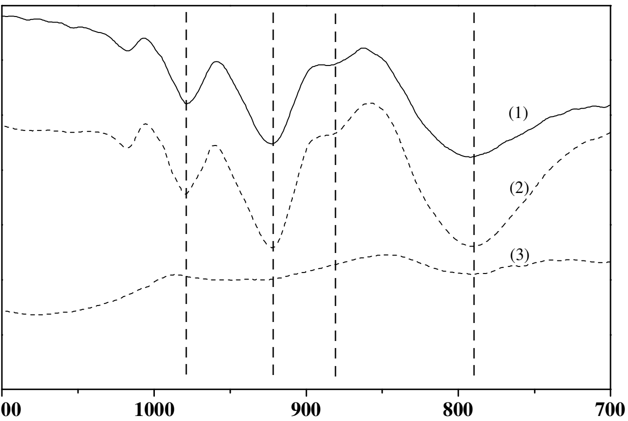


Fig. 1. IR of SiW_{12}/SiO_2 catalyst [(1) SiW_{12} (2) 40 % SiW_{12}/SiO_2; (3) SiO_2]

XRD: Fig. 2 is the X-ray diffraction about active component the SiW_{12}, catalyst SiW_{12}/SiO_2 and carrier SiO_2. It showed that the XRD of carrier SiO_2 didn't show the characteristic peak. The characteristic peak of active component SiW_{12} appears at 8°. From the Fig. 2, it implied that characteristic peak of catalyst SiW_{12}/SiO_2 was the same with the peak of active component SiW_{12}. It demonstrated that SiW_{12} was dispersed on the carrier SiO_2 surface and that part of SiW_{12} crystals gathered into large on the carrier SiO_2 surface. From the XRD of catalyst, the intact keggin structure of SiW_{12}/ SiO_2 can be seen at four angles: 10-11, 17-19, 22-30 and 35-38°[16].

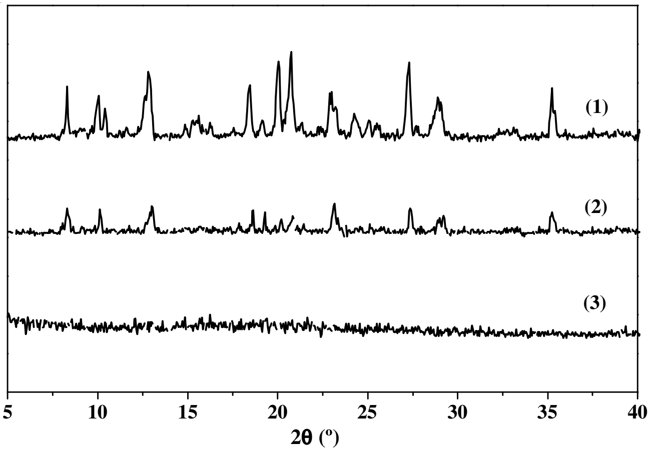


Fig. 2. XRD of SiW_{12}/SiO_2 catalyst [(1) SiW_{12}; (2) SiW_{12}/SiO_2; (3) SiO_2]

Effect of reaction temperature: The effect of reaction temperature (90, 100, 110 and 120 ºC) on the esterification of benzyl acetate was examined. In Fig. 3, it was found that the esterification yields at the reaction temperature 90 ºC was the lowest (75 %). Remarkably, the esterification yield increased with the increase of reaction temperature. A comparison was made for the reaction at 110 and 120 ºC; the two curves almost coincide and the esterification yields could all up to 95 % in 75 min. The optimal reaction temperature was 110 ºC. These data implied that esterification was closely related to the reaction temperature.

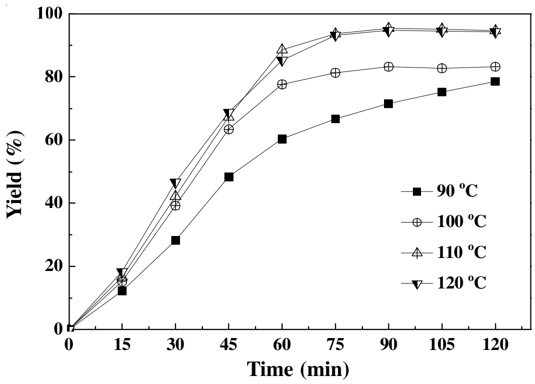


Fig. 3. Relationship between esterification yield and reaction temperature. (*n*(acid)/*n*(benzyl alcohol) = 1:1.5, amount of catalyst 1.5 g, ultrasonic frequency: 10 kHz, ultrasonic intensity: 1.0 W/cm^2)

Effect of amount of catalyst: The effect of catalyst amount (0.5, 1.0, 1.5 and 2.0 g) on the esterification of benzyl acetate was examined. As shown in Fig. 6, the effect of catalyst of 0.5 and 1.0 g were significantly poor. The yields were 80 and 85 %, respectively. A comparison was made for the catalyst amount of 1.5 and 2.0 g, the esterification of 2.0 g was higher before 45 min. After 45 min, the esterification at the amount of catalyst of 1.5 and 2.0 g were almost the same. It is worth noting that the esterification could up to 95.0 % in 75 min with the amount of catalyst of 1.5 and 2.0 g. The result implied us that esterification was closely related to the amount of catalyst. The esterification reaction takes place between acetic acid adsorbed on the SiO_2 surface, forming electrophile and benzyl alcohol in the liquid phase (**Scheme-I**). The optimal amount of catalyst was 1.5 g.

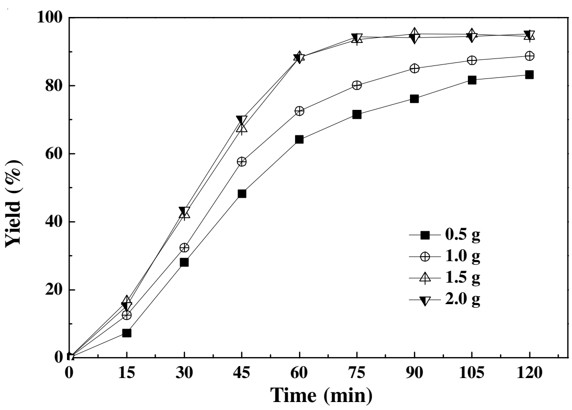
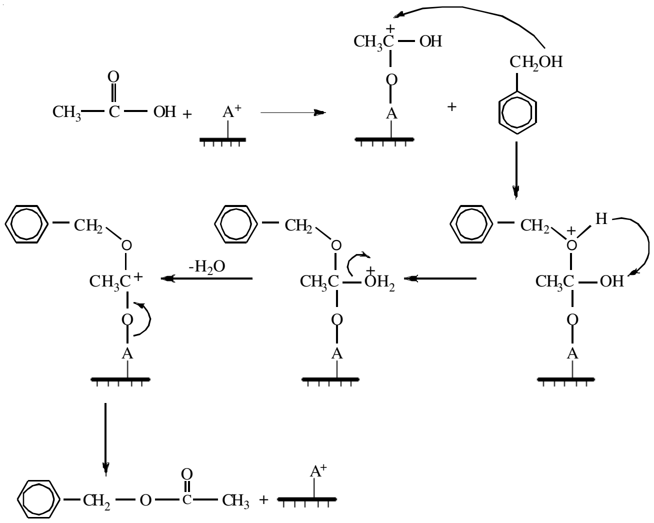


Fig. 4. Relationship between esterification yield and amount of catalyst. (Temperature 110 ºC, *n*(acid)/*n*(benzyl alcohol) = 1:1.5, ultrasonic frequency: 10 kHz ,ultrasonic intensity: 1.0 W/cm^2)



A^+ = acid site on SiO_2

Scheme-I: Possible reaction mechanism for the esterification of benzyl alcohol with acetic acid by SiW_{12}/SiO_2

Effect of molar ratio: The effect of molar ratio on the rate of reaction was investigated at four different molar ratios of benzyl alcohol to acetic acid *viz*., 1:1, 1.5:1, 2:1 and 2.5:1 under constant reaction temperature (110 ºC) and the ultrasounic frequency of 10 kHz. The results have been shown in Fig. 5. We can easily observe from the figure that an initial increase in the molar ratio from 1:1 to 1.5:1 significantly increases the extent of equilibrium conversion, but beyond this optimum molar ratio of 1.5:1, only marginal improvement in the rate of reaction and equilibrium conversion is observed. It should be noted here that dependency of the rate of the reaction on the molar ratio is less significant in the present case as compared to higher ratio of benzyl alcohol to acetic acid (2:1). If molar ratio continues to increase to 2.5, the esterification yield decreased sharply. It implied that the yield may decrease because the relative concentration of acid and catalyst was reduced by using the excessive benzyl alcohol.

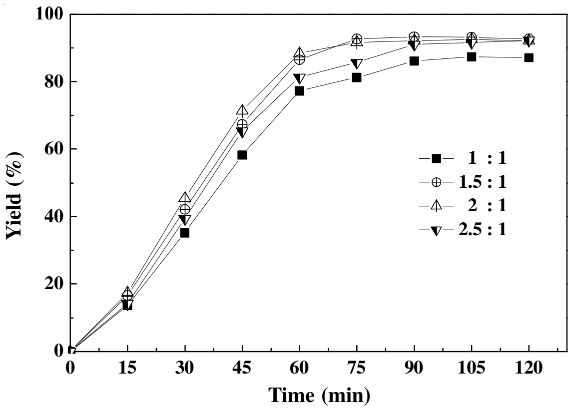


Fig. 5. Relationship between esterification yield and molar ratio (temperature 110 ºC, amount of catalyst 1.5 g, ultrasonic frequency: 10 kHz, ultrasonic intensity: 1.0 W/cm^2)

Study on kinetics: Since there is no kinetic data on ultrasound assisted synthesis of benzyl acetate, a kinetic model for the esterification reaction was developed. The esterification reaction between acetic acid and benzyl is a reversible reaction with SiW_{12}/SiO_2 as catalyst. For the reaction equilibrium can be moved to the right by removing the water produced in the esterification process, it can be assumed as a second order and nonreversible. The related model can be expressed as follows[17]:

$$r = -\frac{d_{C_A}}{d_t} = kC_A C_B \quad (1)$$

where (C_A) is the concentration of acetic acid, (C_B) is concentration of benzyl acetate, k is the second order rate constants in the reaction.

If $Y = C_{B_0} - C_{A_0}$, then $C_B - C_A = Y$, $C_B = Y + C_A$, the model can be rewritten as:

$$-\frac{d_{C_A}}{d_t} = kC_A (Y + C_A) \quad (2)$$

The differential eqn. 2 can be solved by Matlab as follows:

$$kt = \frac{1}{Y} \ln\left(\frac{Y}{C_A} + 1\right) + C \quad (3)$$

Simplifying the eqn. 4 as:

$$\frac{1}{Y} \ln\left(\frac{Y}{C_A} + 1\right) = kt - C \quad (4)$$

The kinetic parameters of this reaction under different reaction temperatures have been estimated by using Origin. The equilibrium constants at different temperatures have been all given in Table-1.

According to Arrhenius eqn. 5, activation energy and frequency factor were all showed in Table-2.

$$\ln k = -\frac{E_q}{RT} + \ln A \quad (5)$$

The kinetics equation of benzyl acetate with SiW_{12}/SiO_2 by ultrasound was calculated as:

$$-\frac{dC_A}{dt} = 3.863 \times 10^4 \exp\left(-\frac{5.912 \times 10^4}{RT}\right) C_A C_B$$

Conclusion

The results of present work have showed us that SiW_{12}/SiO_2 catalyst can be effectively used for the esterification process for synthesis of benzyl acetate. Two conclusions have been given as follows: The optimum parameters of the esterification process at ultrasonic frequency of 10 kHz and ultrasound intensity of 1.0 W/cm^2 have been found to be reaction

TABLE-1
REACTION RATE CONSTANTS UNDER DIFFERENT TEMPERATURES (90-110 ºC)

Temperature (ºC)	Time (min)	C_A (mol/L)	$\frac{1}{Y}\ln\left(\frac{Y}{C_A}+1\right)$	k [L (mol s^{-1})]	R^2
90	0	3.773600	0.16263	1.2021 × 10^{-4}	0.9812
	15	3.313221	0.23159		
	30	2.709445	0.33821		
	45	1.950951	0.51228		
	60	1.309439	0.7236		
	75	1.067929	0.83165		
	90	0.924532	0.90807		
	105	0.784909	0.99484		
	120	0.732078	1.03177		
100	0	3.773600	0.16263	1.9714 × 10^{-4}	0.9593
	15	3.200013	0.25001		
	30	2.294349	0.42635		
	45	1.381138	0.69534		
	60	0.845286	0.95557		
	75	0.705663	1.05125		
	90	0.633965	1.10804		
	105	0.652833	1.09249		
	120	0.633965	1.10804		
110	0	3.773600	0.16263	3.3491 × 10^{-4}	0.9559
	15	3.147182	0.25884		
	30	2.184914	0.45225		
	45	1.233967	0.75506		
	60	0.433964	1.30892		
	75	0.241510	1.61953		
	90	0.177359	1.78316		
	105	0.184906	1.76107		
	120	0.203774	1.70957		

TABLE-2
APPARENT ACTIVATION ENERGY (90-110 ºC)

T (K)	$\frac{1}{T}\times10^{-3}$	ln k	E (kJ mol^{-1})	lnA	A [L (mol h)$^{-1}$]
363	2.755	-9.02627	59.12	10.5551	3.863*10^4
373	2.681	-8.5316			
383	2.611	-8.00165			

temperature 110 ºC, amount of catalyst 1.5 g and molar ratios of benzyl alcohol to acetic acid 1.5:1.0. Under these conditions, the esterification yield of the reaction reached above 95.3 %. The kinetics equation of benzyl acetate with SiW_{12}/SiO_2 by ultrasound was calculated as:

$$-\frac{dC_A}{dt} = 3.863\times10^4 \exp\left(-\frac{5.912\times10^4}{RT}\right)C_A C_B$$

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