



# AN OVERVIEW ON SYNTHETIC METHODS OF ALKYL CINNAMATES

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Three synthetic methods of alkyl cinnamates using different catalysts such as heteropolyacids ( $\text{H}_8\text{SiW}_{12}\text{O}_{42}\cdot\text{XH}_2\text{O}$ ) and solid superacids ( $\text{SO}_4^{2-}/\text{La}_2\text{O}_3\text{-ZrO}_2\text{-HZSM-5}$  and  $\text{SO}_4^{2-}/\text{TiO}_2$ ) have been reviewed in the present paper. Effects of the reaction conditions such as the microwave heating power and times, the amount of the catalyst, the molar ratio of cinnamic acid to alcohols and the reaction time on the yields of alkyl cinnamates have also been discussed. The yields of alkyl cinnamates are improved by the addition of the abovementioned catalysts. Due to low investment costs and simple process these methods are having the advantages on other processes.

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## Introduction

Alkyl cinnamates are not only important organic intermediates but also widely used in different areas such as perfume essence, soap and flavouring essence due to pronouncing fruit or flower aromas.<sup>1</sup> Cinnamic acid under the condition of a catalyst reacts with alcohols to produce alkyl cinnamates. Alkyl cinnamates reviewed here consist of methyl cinnamate, ethyl cinnamate, n-propyl cinnamate, n-butyl cinnamate, isobutyl cinnamate, n-pentyl cinnamate and isopentyl cinnamate, etc.<sup>2</sup> There are two types of methods (the classical method and the microwave heating method) for manufacturing of alkyl cinnamates in industrial scale. The classical method means that cinnamic acid reacts with methanol or ethanol in the presence a catalyst to produce methyl cinnamate or ethyl cinnamate, respectively. This method has a lot of disadvantages such as consuming long time to finish the reaction, using benzene or toluene as a dehydrating agent, requiring a lot of catalysts and getting low yield of alkyl cinnamates, etc. Another method is the microwave heating method. Although the microwave heating method can decrease the reaction time and increase the yield of alkyl cinnamates, the unit is very complicated and it is very difficult to increase the output of alkyl cinnamates.<sup>3</sup>

In the present paper, three types of catalysts such as heteropoly acids ( $\text{H}_8\text{SiW}_{12}\text{O}_{42}\cdot\text{XH}_2\text{O}$ ) and solid super acids ( $\text{SO}_4^{2-}/\text{La}_2\text{O}_3\text{-ZrO}_2\text{-HZSM-5}$  and  $\text{SO}_4^{2-}/\text{TiO}_2$ ) have been discussed. Effects of the reaction conditions such as the microwave heating power, the microwave heating times, the amount of the catalyst, the molar ratio of cinnamic acid to alcohols and the reaction time on the yields of alkyl cinnamates have also been discussed. Furthermore, the optimal reaction conditions have also been pointed out.

## DISCUSSION

### $\text{H}_8\text{SiW}_{12}\text{O}_{42}\cdot\text{XH}_2\text{O}$ as a catalyst to produce ethyl cinnamate

Li Jing<sup>4</sup> introduced and described a synthetic method of ethyl cinnamate and studied the effect of the reaction conditions (the microwave heating power and heating times) on the yield of ethyl cinnamate. Using  $\text{H}_8\text{SiW}_{12}\text{O}_{42}\cdot\text{XH}_2\text{O}$  as a catalyst and cinnamic acid and ethanol as feedstocks produced ethyl cinnamate. The optimal microwave heating power and microwave heating times were 340 W and 20 minutes, respectively. It was observed that the microwave heating time, the amount of the catalyst, the molar ratio of cinnamic acid to ethanol were 20 minutes, 2.93% of cinnamic acid weight (g) and 1.0:7.0, respectively. Table 1 showed the relationship between the microwave heating power and the yields of ethyl cinnamate.

The yield of ethyl cinnamate increased with an increase in microwave electricity and heating power. When the microwave electricity and the heating power were 130 mA and 410 W, respectively, the maximum yield of ethyl cinnamate reached 94 %. However the product's colour was dark black, it proved that ethyl cinnamate was deeply oxidized. Therefore the best reaction condition was the microwave electricity (110 mA) and the microwave heating power (340 W). It was supposed that the microwave heating power, the amount of the catalyst, the molar ratio of cinnamic acid to ethanol were 340 W, 3.75 g and 1.0:7.0, respectively. Table 2 presented effect of the different microwave heating time on the yields of ethyl cinnamate. The yields of ethyl cinnamate increased with an increase of the microwave heating time. The optimal condition was the microwave heating time (30 minutes).

**Table 1.** The relationship between the microwave heating power and the yield of ethyl cinnamate

Microwave electricity (mA)	50	70	90	110	130
Microwave heating power(W)	150	200	285	340	410
Yield of ethyl cinnamate (%)	39	88	90	93	94

**Table 2.** The effect of the different microwave heating time on the yield of ethyl cinnamate.

Microwave heating time(min)	10	15	20	25	30
Yield of ethyl cinnamate (%)	77	89	93	94	95

**SO<sub>4</sub><sup>2-</sup>/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-HZSM-5 as a catalyst to generate n-butyl cinnamate**

Chen Shufen<sup>5</sup> described the synthetic method of SO<sub>4</sub><sup>2-</sup>/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-HZSM-5 and discussed about the effect of the reaction conditions such as the amount of SO<sub>4</sub><sup>2-</sup>/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-HZSM-5 and the molar ratio of cinnamic acid to n-butyl alcohol on the yields of n-butyl cinnamate. It was observed that the molar ratio of cinnamic acid to n-butyl alcohol and the reaction time were 1.0:5.0 and 2 hours, respectively. Table 3 showed the relationship between the amount of SO<sub>4</sub><sup>2-</sup>/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-HZSM-5 and the yields of n-butyl cinnamate. The yields of n-butyl cinnamate increased with an increase in amount of SO<sub>4</sub><sup>2-</sup>/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-HZSM-5. It was observed that the amount of SO<sub>4</sub><sup>2-</sup>/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-HZSM-5 and the reaction time were 1.8% of total reactant weight (g) and 2 hours, respectively. Table 4 presented effect of the molar ratio of cinnamic acid to n-butyl alcohol on the yields of n-butyl cinnamate. The yields of n-butyl cinnamate firstly increased and then decreased with an increase in the molar ratio of cinnamic acid to n-butyl alcohol. Based on the experimental results, the best amount of SO<sub>4</sub><sup>2-</sup>/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-HZSM-5 and the molar ratio of cinnamic acid to n-butyl alcohol were 1.8% of total reactant weight (g) and 1.0:5.0, respectively. The maximum yield of n-butyl cinnamate was 92.7%.

**Table 3.** the relationship between the amount of SO<sub>4</sub><sup>2-</sup>/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-HZSM-5 and the yields of n-butyl cinnamate

Catalyst, %	1.0	1.2	1.5	1.8	2.0
Yield of product (%)	85.7	88.4	90.3	92.7	92.8

**Table 4.** The effect of the molar ratio of cinnamic acid to n-butyl alcohol on the yields of n-butyl cinnamate

Molar ratio	1.0:2.0	1.0:3.0	1.0:4.0	1.0:5.0	1.0:6.0
Yield (%)	65.3	78.4	86.3	92.7	90.2

**SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub> as a catalyst to produce n-butyl cinnamate**

Xia Jinhong<sup>6</sup> introduced the preparation of SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub> and also studied the effect of the reaction time on the yield of butyl cinnamate. It is observed that the optimal molar of cinnamic acid to n-butyl alcohol and the amount of SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub> were 0.015 mol, 0.045 mol and 17.09% of total reactant weight (g), respectively. Table 5 showed the relationship between the reaction time and the yields of n-butyl cinnamate. The yields of n-butyl cinnamate firstly increased and then decreased with an increase in the reaction time. The best reaction time was 3.0 hours. The maximum yield of n-butyl cinnamate was 92.8%.

**Table 5.** The relationship between the reaction time and the yields of n-butyl cinnamate

Reaction time, h	1.5	2.0	2.5	3.0	4.0
Yield (%)	85.0	91.8	92.5	92.8	88.2

**CONCLUSION**

Based on the above discussion and review, using cinnamic acid and ethanol or n-butyl alcohol as feedstocks and heteropoly acids (H<sub>8</sub>SiW<sub>12</sub>O<sub>42</sub>·XH<sub>2</sub>O) and solid super acids (SO<sub>4</sub><sup>2-</sup>/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-HZSM-5 and SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub>) as catalysts, effect of the microwave heating power, the microwave heating times, the amount of the catalyst, the molar ratio of cinnamic acid to n-butyl alcohol and the reaction time on the yields of alkyl cinnamates have been discussed. The experimental results obtained are as follows:

- (1) When the microwave electricity, the microwave heating power and the microwave heating times were 130 mA, 410 W and 30 minutes, respectively, the maximum yield of ethyl cinnamate reached 94 % by the addition of H<sub>8</sub>SiW<sub>12</sub>O<sub>42</sub>·XH<sub>2</sub>O.
- (2) The best amount of SO<sub>4</sub><sup>2-</sup>/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-HZSM-5 and the molar ratio of cinnamic acid to n-butyl alcohol were 1.8% of total reactant weight (g) and 1.0:5.0, respectively.
- (3) The maximum yield of n-butyl cinnamate was 92.8% when the reaction time was 3.0 hours by the addition of SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub>.

**REFERENCES**

- <sup>1</sup> Guan, S. B., Wen, R. M., Yu, S. X. and Zhang, L. X. *Guangzhou Chemistry*, **2004**, 29(3), 24.
- <sup>2</sup> Xu, T. T. *Jiangsu Province Salt Science & Technology*, **2003**, 2, 11.
- <sup>3</sup> Wang, M. and Xu, F. *Guangdong Chemical Industry*, **2009**, 36(4), 37.
- <sup>4</sup> Li, J. and Wang, S. M. *Journal of Henan Normal University*, **2003**, 31(3), 111.
- <sup>5</sup> Chen, S. F., Gan, L. M., Shi, W. Q., Ma, L. H., Suo, L. N. and Yang, X. K. *Journal of Lanzhou Petrochemical College of Technology*, **2010**, 10(3), 9.
- <sup>6</sup> Xia, J. H. *Applied Chemical Industry*, **2004**, 33(3), 34.

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