



An overview on synthetic methods of ethyl acetate

Zhang Yongmei

Library Department, Liaoning Shihua University, Fushun, (CHINA)

E-mail: zh6688551@163.com

ABSTRACT

Synthetic methods of ethyl acetate (EA) such as an esterification method with acetic acid, a method of condensation with acetaldehyde, the catalytic dehydrogenation of ethanol and the direct addition of acetic acid to ethylene have been reviewed. Synthetic methods of ethyl acetate (EA) using different catalysts such as sulfonic acid (p - toluenesulfonic acid), inorganic acids (the weight ratio of carbon to H_2SO_4 (0.51 %) and H_2SO_4 with the microwave heating method), inorganic salts ($\text{Al}_2(\text{SO}_4)_3$, CuCl_2 and NaHSO_4), heteropolyacids (silicotungstic acid), carbon nanotube, styrene-acrylic acid copolymer, ionic liquids (1 - hexyl - pyridinium tetrafluoroborate and N - methyl imidazole hydrosulfate), strong acid cation exchange resins, heteropoly acid (phosphorus- molybdenum-vanadium heteropoly acid), $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ and solid super acid ($\text{SO}_4^{2-}/\text{TiO}_2$ and $\text{S}_2\text{O}_8^{2-}/\text{Fe}_2\text{O}_3\text{-TiO}_2\text{-Nd}_2\text{O}_3$) have also been discussed. © 2013 Trade Science Inc. - INDIA

KEYWORDS

Overview;
Synthetic methods;
Ethyl acetate.

INTRODUCTION

Ethyl acetate (EA) is a colourless liquid with a pleasantly fruity odour. Its molecular formula, melting point, boiling point, and flash point are $\text{C}_4\text{H}_8\text{O}_2$, -83.6°C , 77.2°C and -4°C , respectively. Ethyl acetate is hard to dissolve in water, but dissolves in organic solvents^[1]. Due to floral fragrance, it is widely used in different areas such as coating, fibre, artificial leather and synthetic rubber, etc^[2]. Synthetic methods of ethyl acetate consists of four types of methods such as the es-

terification method with acetic acids, the method of condensation with acetaldehyde, the catalytic dehydrogenation of ethanol and the direct addition of acetic acid to ethylene. The esterification method with acetic acid has not been used around the world. The catalytic dehydrogenation of ethanol and the direct addition of acetic acid to ethylene are used in the new unit. However, the esterification method with acetic acid is generally used in *China*^[3]. TABLE 1 show different synthetic methods of ethyl acetate^[4].

In the present paper, synthetic methods of ethyl

TABLE 1 : Different synthetic methods of ethyl acetate

Name	Eqn.	Catalyst	Country
The esterification method with acetic acids	$\text{C}_2\text{H}_5\text{OH} + \text{CH}_3\text{COOH} = \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$	H_2SO_4	China
The method of condensation with acetaldehyde	$2\text{CH}_3\text{CHO} = \text{CH}_3\text{COOC}_2\text{H}_5$	Al	Japan and Germany
the catalytic dehydrogenation of ethanol	$2\text{C}_2\text{H}_5\text{OH} = \text{CH}_3\text{COOC}_2\text{H}_5 + 2\text{H}_2$	Cu-Zn-Al	Japan and South Africa
the direct addition of acetic acid to ethylene	$\text{C}_2\text{H}_4 + \text{CH}_3\text{COOH} = \text{CH}_3\text{COOC}_2\text{H}_5$	Heteropolyacids	Japan

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acetate (EA) such as an esterification method with acetic acid, a method of condensation with acetaldehyde, the catalytic dehydrogenation of ethanol and the direct addition of acetic acid to ethylene are discussed. Different catalysts such as sulfonic acid (*p*-toluenesulfonic acid), inorganic acids (the weight ratio of carbon to H_2SO_4 (0.51 %) and H_2SO_4 with the microwave heating method), inorganic salts ($\text{Al}_2(\text{SO}_4)_3$, CuCl_2 and NaHSO_4), heteropolyacids (silicotungstic acid), carbon nanotube, styrene-acrylic acid copolymer, ionic liquids (1-hexyl-pyridinium tetrafluoroborate and *N*-methylimidazole hydrosulfate), strong acid cation exchange resins, heteropoly acid (phosphorus-molybdenum-vanadium heteropoly acid), $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ and solid super acid ($\text{SO}_4^{2-}/\text{TiO}_2$ and $\text{S}_2\text{O}_8^{2-}/\text{Fe}_2\text{O}_3\text{-TiO}_2\text{-Nd}_2\text{O}_3$) are also explained.

RESULTS AND DISCUSSION

An esterification method with acetic acid

The esterification method with acetic acid means that acetic acid reacts with alcohol under the condition of the catalyst. The advantage of this method is being very mature, easily getting feedstocks (acetic acid and alcohol), and requiring less investment. On the other hand, this method has a lot of disadvantages such as requiring high temperature to finish the reaction, having low utilization of acetic acid, more secondary reaction taking place, difficultly treating the production, easily damaging equipment, getting low yield of ethyl acetate and requiring high operating cost. Effects of different catalysts on the yield of ethyl acetate are introduced as follows.

p-Toluenesulfonic acid as a catalyst

Wu Yanhua^[2] used *p*-toluenesulfonic acid as the catalyst to synthesize ethyl acetate from acetic acid and alcohol. The optimal conditions were the molar ratio of acetic acid to alcohol (1.0 : 2.5), the reaction time (1 hr), the reaction temperature (80 °C) and the weight ratio of *p*-toluenesulfonic acid to acetic acid (7.94 %) respectively. The maximum yield of ethyl acetate was 91.5 %.

Carbon/ H_2SO_4 as a catalyst

Ma Peihua^[5] described a synthesis using the weight

ratio of carbon to H_2SO_4 (0.51 %) as the catalyst. The optimal conditions were the reaction time (2.0 hr), the molar ratio of acetic acid to alcohol (2.5 : 3.7) and the weight ratio of carbon/ H_2SO_4 to acetic acid (20.0 %) respectively. The maximum yield of ethyl acetate was 64.0 %.

H_2SO_4 as a catalyst with the microwave heating method

Zhang Xinwei^[6] used the microwave heating method to study on the synthesis of ethyl acetate. The optimal reaction conditions were: the microwave heating time (0.083 hr), the microwave heating power (400 W), the reaction temperature (110 °C), the molar ratio of acetic acid to alcohol (2.5 : 3.7), the weight ratio of H_2SO_4 to alcohol (120 %) respectively. The maximum yield of ethyl acetate was 92.0 %.

$\text{Al}_2(\text{SO}_4)_3$ as a catalyst

Sun Jingxia^[7] described the synthesis of ethyl acetate and used $\text{Al}_2(\text{SO}_4)_3$ as the catalyst. The optimal conditions were: the reaction temperature (70 °C), the molar ratio of acetic acid to alcohol (1.0 : 6.0) and the weight ratio of $\text{Al}_2(\text{SO}_4)_3$ to total reactant (0.5 %) respectively. The maximum yield of ethyl acetate was 97.8 %.

CuCl_2 as a catalyst with the microwave heating method

Chen Weiping^[8] used CuCl_2 as the catalyst with the microwave heating method to synthesize ethyl acetate. The optimal microwave heating time (0.2 hr), the microwave heating power (400 W), the molar ratio of acetic acid to alcohol (5.0 : 1.0) and the weight ratio of CuCl_2 to acetic acid (2.0 %) were introduced. The maximum yield of ethyl acetate was 68.0 %.

NaHSO_4 as a catalyst

Meng Xiangfu^[3] used NaHSO_4 as the catalyst and explained the reasons for its use. The optimal reaction conditions were: the reaction time (2.5 hr), the molar ratio of acetic acid to alcohol (3.3 : 4.95) and the weight ratio of carbon/ H_2SO_4 to acetic acid (3.33 %) respectively. The maximum yield of ethyl acetate was 87.5 %.

Silicotungstic acid as a catalyst

Gao Liquan^[9] used orthogonal experimental design

method to study on the synthesis of ethyl acetate. The optimal reaction conditions were: the reaction time (1.0 hr), the molar ratio of acetic acid to alcohol (1.0 : 2.0) and the weight ratio of silicotungstic acid to acetic acid (4.17 %) respectively. The maximum yield of ethyl acetate was 92.2 %.

Carbon nanotube as a catalyst

Yi Huiyang^[10] described the synthesis of carbon nanotube and ethyl acetate. The optimal conditions were: reaction time (2.5 hr), the molar ratio of acetic acid to alcohol (1.0 : 2.5) and the weight ratio of carbon nanotube to acetic acid (12.5 %) respectively. The maximum yield of ethyl acetate was 80.4 %.

Styrene - acrylic acid copolymer as a catalyst

LiuShenghuan^[11] described the synthesis of ethyl acetate by using styrene - acrylic acid copolymer as the catalyst. The optimal reaction conditions were: reaction time (0.83 hr), the molar ratio of acetic acid to alcohol (1.0 : 1.0) and the weight ratio of styrene - acrylic acid copolymer to acetic acid (25.42 %) respectively. The maximum yield of ethyl acetate was 90.0 %. The performance of the catalyst was very good when it was reused. For example, the yield of ethyl acetate was about 90.0 % even after it had been used 9 times.

1 - hexyl - pyridiniumtetrafluoroborate as a catalyst

Wei Zhiping^[12] described the use of 1 - hexyl - pyridiniumtetrafluoroborate as the catalyst. The optimal molar ratio of acetic acid to alcohol (1.1 : 1.0) and the molar ratio of 1 - hexyl - pyridiniumtetrafluoroborate to acetic acid (1.0 : 8.0) on the yield of ethyl acetate were mentioned. The maximum yield of ethyl acetate was 66.0 %.

N - methyl imidazole hydrosulfate as a catalyst

Tang Xiaoli^[13] described the use of N - methyl imidazole hydrosulfate as the catalyst. The optimal reaction conditions were: the reaction time (4.0 hr), the reaction temperature (60 °C), the molar ratio of acetic acid to alcohol to N - methyl imidazole hydrosulfate (1.0 : 1.5 : 0.2) respectively. The maximum yield of ethyl acetate was 84.2 %. The performance of N - methyl imidazole hydrosulfate as the catalyst was very bad when it was

reused. For example, the yield of ethyl acetate was only 74.6 % even after it had been used 3 times.

Strong acid cation exchange resins as a catalyst

Li Xu^[14] described the use of strong acid cation exchange resin as the catalyst. The optimal reaction conditions such as the reaction time (0.92 hr), the reaction temperature (70 °C), the molar ratio of acetic acid to alcohol (1.0 : 1.5), the weight ratio of strong acid cation exchange resin to alcohol (23.83 %) were introduced. The maximum yield of ethyl acetate was 62.5 %.

Phosphorus- molybdenum-vanadium heteropoly acid as a catalyst

Li Jinlei^[15] used phosphorus- molybdenum-vanadium heteropoly acid as the catalyst. The optimal reaction conditions were: the reaction time (0.5 hr), the reaction temperature (120 °C), the molar ratio of acetic acid to alcohol (1.0 : 2.5), the weight ratio of phosphorus- molybdenum-vanadium heteropoly acid to alcohol (5.0 %) respectively. The maximum yield of ethyl acetate was 84.7 %.

CuO/ZnO/Al₂O₃ as a catalyst

XiaoYonghong^[16] described how to prepare CuO/ZnO/Al₂O₃ and introduced the synthesis of ethyl acetate by using CuO/ZnO/Al₂O₃ as the catalyst. The optimal reaction temperature (120 °C), the reaction pressure (1.05 MPa), the calcination temperature (400 °C) and the molar ratio of Cu to Zn (1.0 : 1.0) were mentioned. The maximum yield and selectivity of ethyl acetate were 82.35 % and 89.62%, respectively.

SO₄²⁻/TiO₂ as a catalyst

HouWeiyan^[17] described the synthesis of SO₄²⁻/TiO₂ and ethyl acetate. The optimal reaction conditions were: Ti loading time (12.0 hr), the calcination temperature (400 °C), the calcination time (2.0 hr), the reaction temperature (80 °C), the reaction time (3.0 hr), the molar ratio of acetic acid to alcohol (1.0 : 1.8) and the weight ratio of SO₄²⁻/TiO₂ to acetic acid (33.33 %) respectively. The maximum yield of ethyl acetate was 97.0 %.

S₂O₈²⁻/Fe₂O₃-TiO₂-Nd₂O₃ as a catalyst

Yang Chunhua^[18] described the use of S₂O₈²⁻/Fe₂O₃

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- TiO_2 - Nd_2O_3 as the catalyst to synthesize ethyl acetate. The optimal reaction time (1.5 hr), the molar ratio of acetic acid to alcohol (3.0 : 1.0) and the weight ratio of $\text{S}_2\text{O}_8^{2-}/\text{Fe}_2\text{O}_3$ - TiO_2 - Nd_2O_3 to acetic acid (19.98 %) were introduced. The maximum yield of ethyl acetate was 92.0 %.

CONCLUSION

Based on the above discussion and review, p-toluenesulfonic acid is one of the best catalysts for the highest yield of ethyl acetate (91.5 %). On the other hand, strong acid cation exchange resin is the worst of the catalysts since the maximum yield of ethyl acetate was only 62.5 %.

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