AN OVERVIEW ON SYNTHETIC METHODS OF BENZYL ACETATE

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Synthetic methods of benzyl acetate using different catalysts such as strong acid cation exchange resins, inorganic salts (the weight ratio of $FeCl_3$ to carbon (46 %) and $Fe_2(SO_4)_3$), inorganic acids (H_2SO_4) heteropoly compounds ($(NH_4)_6[MnMo_9O_{32}]\cdot 8H_2O$), heteropolyacids (phosphotungstic acid), solid superacids ($S_2O_8^{2-}$ - Fe_2O_3 - ZnO, $S_2O_8^{2-}$ - Fe_2O_3 - CoO, $S_2O_8^{2-}$ - ZrO_2 - Al_2O_3, SO_4^{2-} - Al_2O_3, SO_4^{2-} - ZrO_2 - Nd_2O_3 and SO_4^{2-}- MoO_3 - TiO_2), organic salts (tris(trimethylsilylmethylene)tin chloride) and ionic liquids (N-methylpyrrolidone hydrosulfate and 1-methyl-3-(3-sulfopropyl)imidazolium tungstophosphate) have been reviewed. The above mentioned catalysts improved the yield of benzyl acetate. These methods have the advantage of simple process and low investment costs.

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Introduction

Benzyl acetate is a naturally occurring colourless oily liquid found in many flowers such as jasmine, ylang-ylang and tobira. Its molecular formula, melting point, boiling point, relative density (16 °C), refractive index n_D^{20} and flash point are $C_9H_{10}O_2$, 50 °C, 213 °C, 1.057, 1.5232 and 102 °C, respectively. Benzyl acetate is hard to dissolve in water, but dissolves in organic solvents. [1] Due to floral fragrance and low price, it is widely used in different areas such as soaps, essences and other industrial essences, etc. [2] Benzyl alcohol, with concentrated sulphuric acid as a catalyst, reacts with acetic acid to synthesise benzyl acetate. Concentrated sulphuric acid has a lot of disadvantages such as long reaction time, low yield and purity of benzyl acetate. Large amount of waste water is discharged to cause the problem of environmental pollution and equipments are seriously corroded at the same time. [3]

In the present paper, different catalysts such as strong acid cation exchange resins, inorganic salts (the weight ratio of $FeCl_3$ to carbon (46 %) and $Fe_2(SO_4)_3$), inorganic acids (H_2SO_4) heteropoly compounds ($(NH_4)_6[MnMo_9O_{32}]\cdot 8H_2O$), heteropolyacids (phosphotungstic acid), solid superacids ($S_2O_8^{2-}$ - Fe_2O_3 - ZnO, $S_2O_8^{2-}$ - Fe_2O_3 - CoO, $S_2O_8^{2-}$ - ZrO_2 - Al_2O_3, SO_4^{2-} - Al_2O_3, SO_4^{2-} - ZrO_2 - Nd_2O_3 and SO_4^{2-}- MoO_3 - TiO_2), organic salts (tris(trimethylsilylmethyl)tin chloride) and ionic liquids (N-methylpyrrolidone hydrosulfate) and 1-methyl-3-(3-sulfopropyl)imidazolium tungstophosphate) are discussed.

DISCUSSION

Strong acid cation exchange resin as a catalyst

Lan Ping[4] used strong acid cation exchange resin as a catalyst to synthesise benzyl acetate from acetic acid and benzyl alcohol. The optimal conditions were the molar ratio of acetic acid and benzyl alcohol (4.0 : 5.0), the reaction time (10 hours), the reaction temperature (100 °C) and the weight ratio of strong acid cation exchange resin to acetic acid (25 %) respectively. The maximum yield of benzyl acetate was 84.23 %. The performance of the catalyst was very good when it was reused. For example, the yield of benzyl acetate was 83.88 % even after it had been used 10 times.

Inorganic salts as catalysts

Yu Junfeng[5] described a similar synthesis using the weight ratio of $FeCl_3$ to carbon (46 %) as a catalyst. The optimal conditions were the reaction time (2.0 hours), the molar ratio of acetic acid to benzyl alcohol (1.0 :1.8) and the weight ratio of $FeCl_3$/carbon to acetic acid 33.33 %. The maximum yield was 89.10 %. $FeCl_3$/carbon had good catalytic performance.

Li Xiaoli[2] used $Fe_2(SO_4)_3$ as a catalyst. The optimal reaction time (2 hr), the molar ratio of acetic acid to benzyl alcohol (1.0 : 2.5) and the weight ratio of $Fe_2(SO_4)_3$ to acetic acid , 33.33 % were described. The maximum yield of benzyl acetate was 67.1 %.

H_2SO_4 as a catalyst

Chen Xi [6] used H_2SO_4 as the catalyst and explained the reasons for its use. The reaction conditions were: ultrasonic frequency (10 k Hz), ultrasonic intensity (1.0 W cm^{-2}) and the air velocity (0.3 L min^{-1}). The maximum yield of benzyl acetate was 65.8 %.

$(NH_4)_6[MnMo_9O_{32}]\cdot 8H_2O$ as a catalyst

Liu Shuheng[7] described the synthesis of $(NH_4)_6[MnMo_9O_{32}]\cdot 8H_2O$ and benzyl acetate. The optimal conditions were: reaction time (1.5 hr), the molar ratio of acetic acid to benzyl alcohol (2.0:1.0) and the weight ratio of $(NH_4)_6[MnMo_9O_{32}]\cdot 8H_2O$ to acetic acid (15 %). The maximum yield of benzyl acetate was 80.4 %.

The maximum yield of benzyl acetate was 69.3 % after the catalyst had been used 5 times

Phosphotungstic acid as a catalyst

Huang Haiyan[8] described the synthesis of benzyl acetate by using phosphotungstic acid as the catalyst. The optimal reaction conditions were: reaction time (2 hr), the molar ratio of acetic acid to benzyl alcohol (2.5:1.0) and the weight ratio of phosphotungstic acid to total reactant (2.54 %). The maximum yield of benzyl acetate was 90.0 %.

Solid superacids as catalysts

Table 3 showed that different solid superacids with different load had an effect on the yield of benzyl acetate. It is to be noted that Fe_2O_3 - CoO was the best loads because acid was evenly distributed on its surface, so the yield of benzyl acetate was very high.

Tri(trimethylsilyl - methylene) tin chloride as a catalyst

Chen Fushan[15] described the use of tris(trimethylsilyl methyl)tin chloride as the catalyst. The optimal reaction time (3.5 hr), the molar ratio of acetic acid to benzyl alcohol (3.5 : 1.0) and the weight ratio of tris(trimethylsilylmethyl)tin chloride to acetic acid (0.015 : 1.0) on yields of benzyl acetate were mentioned. The maximum yield of benzyl acetate was 91.5 %.

Ionic liquids as catalysts to generate benzyl acetate

Zhou Beilei[16] described the use of N-methylpyrrolidone hydrosulfate as the catalyst. The reaction conditions such as the reaction time (1 hr), the reaction temperature (110 °C), the molar ratio of acetic acid to benzyl alcohol (1.4:1.0), the weight ratio of N-methylpyrrolidone hydrosulfate to benzyl alcohol (1 %). The maximum yield of benzyl acetate was 98.6 %. The yield of benzyl acetate still reached 97.6 % on the use of the catalyst after it had been used 6 times.

Yang Min[17] used 1-methyl-3-(3-sulfopropyl)imidazolium tungstophosphate as a catalyst in place of concentrated sulfuric acid. The optimal reaction time (5 hr), the reaction temperature (110 °C), the molar ratio of acetic acid to benzyl alcohol (2.0 : 1.0), the molar ratio of 1-methyl-3-(3-sulfopropyl)imidazolium tungstophosphate to benzyl alcohol (0.2 %) were described. The maximum yield of benzyl acetate was 95.52 %, and it was 84.15 % after the catalyst had been used 5 times.

Table 1. effect of different t solid superacids on yields of benzyl acetate

Catalyst	Acetic acid to benzyl alcohol ratio	Weight ratio of the catalyst to total reactant (%)	Reaction time, h	Yield of benzyl acetate, %	Reference
$S_2O_8^{2-}$ - Fe_2O_3 - CoO	1.0:1.3	1.49	2.5	98.2	9
$S_2O_8^{2-}$ - ZrO_2 - Al_2O_3	1.0:1.3	1.98	2.5	98.0	10
$S_2O_8^{2-}$ - Fe_2O_3 - ZnO	1.7:1.0	0.83	2.5	85.2	11
SO_4^{2-} - ZrO_2 - Nd_2O_3	2.0:1.0	2.83	5.0	92.0	12
SO_4^{2-}- MoO_3 - TiO_2	1.3:1.0	0.41	2.0	87.2	13
SO_4^{2-} - Al_2O_3	2.0:1.0	3.5	6.0	76.0	14

CONCLUSION

Based on the above discussion and review, N-methyl pyrrolidone hydrosulfate is one of the best catalysts for the highest yield of benzyl acetate (98.6 %). However, due to high cost, N-methyl pyrrolidone hydrosulfate is not considered as the good choice for catalyst. $S_2O_8^{2-}$ - Fe_2O_3 - CoO is equally a good catalyst considering the yield of benzyl acetate (98.2 %) which is almost similar to that of N-methyl pyrrolidone hydrosulfate. H_2SO_4 is the worst of the catalysts since the maximum yield of benzyl acetate was only 65.8 %.

REFERENCES

[1]Wang, G. X., *Appl. Sci. Technol*., **2000**, *11*, 22.

[2]Li, X. L. and Zhang, K., *J. Changchun Normal Univer.*, **2008**, *27*(5), 22.

[3]Sun, D. G. and Wei, M., *Shandong Chem. Ind.*, **2006**, *35*(6), 24-25.

[4]Lan, P., Lan, L. H., Yan, R. Y., Wu, R. C., Li, M. and Liao, A. P., *Sci. Technol. Food Ind.*, **2005**, *26*(5), 128-132.

[5]Yu, J. F. and Zhu, L., *Sci. Technol. Food Ind.*, **2005**, *26*(1), 162-163.

[6]Chen, X., Wang, J., Lu, X. P. and Han, P. F., *J. Nanjing Univer. Technol.*, **2011**, *33*(3), 49-52.

[7]Liu, S. H., Wang, L. X., Yuan, H. and Yang, F. Z., *J. Cangzhou Normal Univer.*, **2012**, *28*(1), 9-11,27.

[8]Huang, H. Y., Xie, F. H. and Tang, P. W., *Appl. Chem. Ind.*, **2007**, *36*(3), 279-282.

[9]Zhang, Y. J., Li, H. P., Cheng, H. J. and Zhang, C. X., *J. Henan Normal Univer.*, **2006**, *34*(2), 89-93.

[10]Jin, H. F. and Li, W. G., *Chemistry World*, **2008**, *3*, 133-138.

[11]Zhang, Y. J., Wang, J. L. and Yang, H., *J. Zhengzhou Univer. Light Ind.* **2005**, *20*(3), 26-28.

[12]Yang, Y. W., Li, L. and Chen, H. Z., *Chem. Agents*, **2006**, *28*(11), 665-667.

[13]Sun, T., *Zhengjiang Chem. Ind.*, **2005**, *36*(7), 15-16.

[14]Wang, M. Y. and Qiu, L. G., *Chemistry and Adhesion*, **2007**, *29*(1), 27-29.

[15]Chen, F. S., Xu, J. P., Gao, E. L., Zhang, L. M. and Lin, S., *Speciality Petrochemicals*, **2011**, *28*(6), 37-39.

[16]Zhou, B. L., Fang, Y. X., Zhai, Z. C., Deng, Y. Q., Huang, B. H. and Lao, X. L., *ACTA Scientiarum Naturalium Universities Sunyatseni*, **2009**, *48*(4), 66-69.

[17]Yang, M., Xiong, Y., Peng, Q. R., Hu, J. P., Shi, X. Y. and Liu, Z. X., *China Food Additives*, **2010**, *5*, 149-153.

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