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Esterification of *tert*-Butanol and Acetic Acid by Silicotungestic Acid Catalyst Supported on Bentonite

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A series of solid acid catalysts were synthesized by incipient wetness impregnation method by varying the wt % of silicotungstic acid on bentonite. Silicotungestic acid supported on bentonite was used to catalytic synthesis of *tert*-butyl acetate with acetic acid and *tert*-butyl alcohol. The main reaction parameters such as silicotungstic acid loading on bentonite, the amount of catalyst, molar ratio of reactants, reaction temperature and reaction time have been investigated. The optimum conditions were determined as follows: silicotungstic acid loading on bentonite 25 wt %, catalyst 0.7 g, mole ratio of *tert*-butanol to acetic acid 1:1.1, reaction temperature 110 ºC and reaction time 2 h. The esterification yield of *tert*-butyl acetate was about 87.2 %. The catalyst could be used repeatedly for many times without distinct loss in activity.

Key Words: *tert*-Butyl acetate, Silicotungstic acid, Bentonite, Esterification.

INTRODUCTION

Esterification of alcohols, particularly normal alcohols, by carboxylic acids using homogeneous acid catalysts(*viz.* mineral acids) is well known[1]. However, it is extremely difficult to prepare *tert*-butyl ester by the esterification of *tert*-butanol using an acid catalyst. This is because of the high reactivity of *tert*-butanol in the presence of an acid, causing a rapid dehydration of the alcohol to *iso*-butylene, even at the room temperature[2]. Hence, there is a need to develop an environmentally benign method for the esterification of *tert*-butanol using a highly acitive, selective and reusable solid catalyst having a little or no acitivity for the dehydration of *tert*-butanol.

At present, the esterification reaction could be catalyzed by heterogeneous catalysts instead of homogeneous ones. Some heterogeneous catalysts reported include ion exchange resin, H-ZSM-5, zeolites-Y, niobic acid, sulfated oxides and SBA-15 supported heteropolyacids (HPA)[3-6]. They have many advantages, for example, they can be more easily separated and have higher catalytic activity.

In this work the silicotungestic acid catalyst supported on bentonite was employed in the synthesis of *tert*-butyl acetate. The main reaction parameters are silicotungestic acid loading on bentonite, the amounts of catalyst, molar ratio of reactants, reaction temperature and reaction time. Accurate control of these parameters is required in order to improve the yield of ester, hence, it is necessary to investigate systematically the effect of these reaction parameters. The optimum conditions were determined as follows: silicotungestic acid loading on bentonite 25 wt %, catalyst 0.7 g, mole ratio of *tert*-butanol to acetic acid 1:1.1, reaction temperature 110 ºC and reaction time 2 h. The esterification yield of *tert*-butyl acetate was about 87.2 %. The catalyst could be used repeatedly for many times without distinct loss in activity.

EXPERIMENTAL

Bentonite was obtained from Zhejiang Sanding Group Co. Ltd. and other reagents were of chemical grade and used without further purification.

The catalysts were prepared by wet impregnation method. A series of catalysts having different loading ranging from 10-30 wt % were synthesized by impregnating 5 g of bentonite with an aqueous solution of silicotungestic acid (STA) (30 mL of conductivity water) under constant stirring 6 h followed by heating till complete evaporation of water. It was dried in an oven at 110 ºC for 4 h, then in miffle at 250 ºC for 5 h.

Esterification reaction: The esterification reaction was carried out under batch reaction conditions using a 250 mL flask fitted with a water divider, a stirrer and a thermometer. The outlet of the water divider was connected to a reflux condenser. The temperature of the oilbath was fixed at the certain reaction temperature until reaction time was reached. A typical reaction mixture in the reactor contained acetic acid (0.165

mol), *tert*-butanol (0.15 mol), 10 mL toluene and the catalyst. In all cases, the reaction conversion ratio was determined by neutralization titration and calculated as follows:

$$\text{Conversion}\,(\%) = \frac{A_1 - A_2}{A_1} \times 100\,\% \quad (1)$$

where A_1 and A_2 were the acid values of the reactant mixture before and after the reaction, respectively.

RESULTS AND DISCUSSION

Influence of silicotungestic acid loading on bentonite: The influence of silicotungestic acid loading on bentonite on the acetic acid conversion was given in Fig. 1 under other identical reaction conditions. The silicotungestic acid loading on bentonite was varied from 10-30 wt % while keeping the molar ratio of alcohol: acid at 1:1.1, catalyst 0.7 g and reaction temperature at 110 ºC. The reaction was carried out for 2 h and the products were analyzed. The conversion of acetic acid increases with silicotungestic acid loading on bentonite, reaching a maximum at 25 wt % silicotungestic acid and almost no changing thereafter.

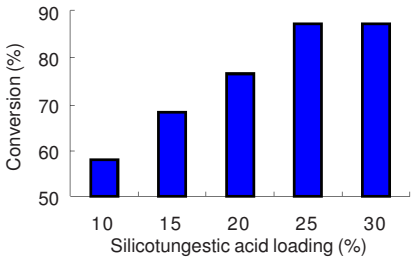

Fig. 1. Effect of silicotungestic acid loading on esterification of *tert*-butyanol and acetic acid carried out at reaction temperature = 110 ºC, *n*-butanol:acetic acid = 1:1.1, time = 2 h

Influence of catalyst amount: The amount of catalyst was varied from 0.3-0.8 g using 25 wt % silicotungestic acid while keeping the molar ratio of alcohol:acid at 1:1.1 and reaction temperature at 110 ºC. The reaction was carried out for 2 h and the products were analyzed. The results are represented in Fig. 2. With the increase in catalyst amount from 0.4-0.7 g, the conversion of acetic acid increases from 73.6-87.2 % and almost no changing thereafter.

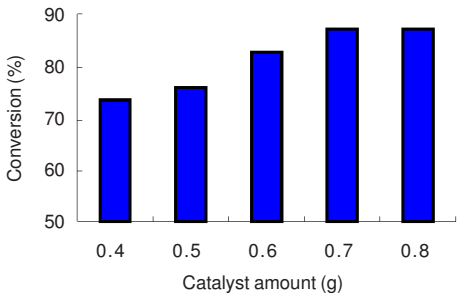

Fig. 2. Effect of catalyst amount on esterification of *tert*-butyanol and acetic acid carried out at reaction temperature = 110 ºC, *tert*-butanol:acetic acid = 1:1.1, time = 2 h

Influence of reaction temperature: Fig. 3 illustrates the effect of reaction temperature on the esterification of acetic acid with *n*-butanol. The reaction was carried out in the temperature region 80-120 ºC taking 25 wt % silicotungestic acid as catalyst without altering other reaction parameters. The conversion increased from 67.5-87.2 % with a change in reaction temperature from 80-110 ºC. With further increase in reaction temperature, an increased conversion was observed.

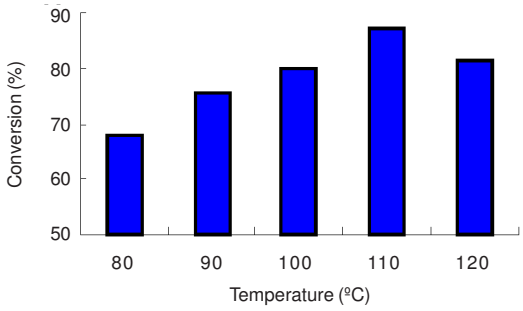

Fig. 3. Effect of reaction temperature on esterification of *tert*-butyanol and acetic acid using 25 wt % of silicotungestic acid as catalyst; catalyst amount = 0.7 g, *tert*-butanol:acetic acid = 1:1.1, time = 2 h

Influence of molar ratio of reactants: Mole ratios of *tert*-butanol to acetic acid were varied from 1:0.9-1:1.3 and the result was shown in Fig. 4. In all cases and in all mole ratios of the reactants, *tert*-butyl acetate was observed as the main product. The conversion increased from 60.5-87.2 % with a change in mole ratio of *n*-butanol to acetic acid from 1:0.9-1:1.1. With further increase in mole ratio of *n*-butanol to acetic acid, a slightly decrease in conversion was observed.

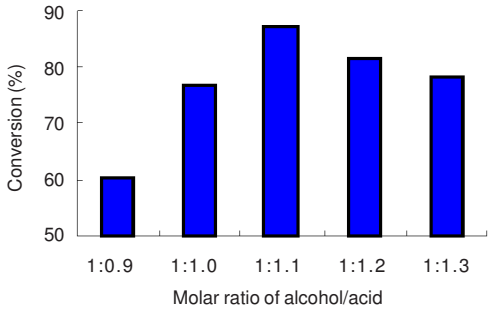

Fig. 4. Effect of molar ratio of alcohol/acid on esterification of *tert*-butyanol and acetic acid using 25 wt % silicotungestic acid as catalyst, catalyst amount 0.7 g, reaction temperature 110 ºC, time = 2 h

Influence of reaction time: The influence of reaction time on the acetic acid conversion was given in Fig. 5 using 25 wt % silicotungestic acid as catalyst (0.7 g) under other identical reaction conditions. A gradual rise in the conversion was seen with increase in duration of the reaction period. As seen from Fig. 5, in 2 h of reaction time, 87.2 % of conversion is obtained, where as at the end of 2.5 h only 98.4 % of the reaction is complete. This suggests that 2 h is sufficient to optimize the reaction parameters.

Reusability of the catalyst: The catalyst with 25 wt % loading was used for recycling experiments. In order to regenerate the catalyst after 2 h reaction, it was separated by filtration, washed with conductivity water several times, dried and calcined at 120 ºC and used in the esterification reaction with a fresh reaction mixture. In the regenerated sample after five cycles, the yield decreases by 5 %.

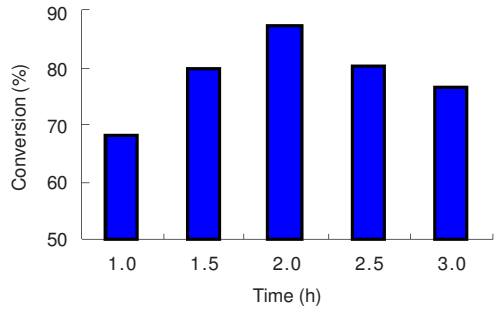

Fig. 5. Effect of reaction time on esterification of *tert*-butyanol and acetic acid using 25 wt % silicotungestic acid as catalyst, catalyst amount = 0.7 g, *n*-butanol: acetic acid = 1:1.1

Conclusion

Silicotungestic acid (25 wt %) supported on bentonite acts as an efficient and stable solid acid catalyst for esterification of *tert*-butyanol and acetic acid. The catalyst can be regenerated easily and reused at least five times.

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