ISSN 2278-7763

Catalytic Synthesis of Sec-butyl Acetate on Sulfoacid Resin

NIE Xin[1], LI Jian[1], YANG Li-na[1], WANG Lu-xun[2] , XU Long[1]

[1] Department of Petrochemistry, Liaoning Shihua University, Fushun, China; [2] Jinxi Petrochemical Company, Petrochina, Huludao, China.

Email: niexin0317@163.com

ABSTRACT

In this experiment, acetic acid and sec-butanol are used as raw materials for the synthesis of sec-butyl acetate with the sulfoacid resin D005 as the catalyst, the influences of operating parameters including reaction temperature, reaction time, mole ratio and the amount of catalyst were investigated to determine the proper process conditions. It is shown that the proper process conditions are: temperature 120℃, time4h, mole ratio of sec-butanol to acetic acid is 1.2:1, the amount of catalyst 15%（weight）, then acetic acid conversion rate is 64%. In optimal conditions, the catalyst was reused five times; the acetic acid conversion rate is still more than 63%, so the catalyst has good stability.

Key words： Esterification;Sec-butyl acetate; Sulfoacid resin

1. INTRODUCTION

Sec-butyl acetate which is slightly yellow transparent oily liquid and possess unique aroma of ester material belong to low carbon fatty acid. Sec-butyl acetate is insoluble in water, but it can dissolve with alcohol, ether and other organic solvents. Sec-butyl acetate is acetic esters organic solvent. With the unceasing enhancement worldwide environmental consciousness, people tend to use sec-butyl acetate such oxygenated solvent gradually, thus sec-butyl acetate gradually replace toxic aromatic and ketone solvents in coatings. The performance of sec-butyl acetate is similar to n-butyl acetate, and the price is lower than n-butyl acetate. So sec-butyl acetate has good development potential.Sec-butyl acetate is widely existing in the fruit such as apples, bananas, grapes, pears. Sec-butyl acetate is a kind of widely used organic chemical products and mainly used for paint solvent, diluent, all kinds of vegetable oil and resin solvent. It also used for medical and pharmaceutical [1]. The synthesis of sec-butyl acetate is not so easy due to the side reaction for the dehydration of sec-butyl alcohol and the high steric hindrance when the reaction occurs, therefore the selectivity of the catalyst is very crucial, and the catalyst with high dehydration activity will decrease the objective product's yield. The traditional synthesis method is with acetic acid and sec-butyl alcohol as the feeds, with sulfuric acid or proton acid for example benzene sulfonic acid as catalyst. Due to poor selectivity of concentrated sulfuric acid, there are many effects, for example side effect occurring and the difficulty of separation and purification of products, and severe environmental pollution and equipment corrosion which is disadvantageous for industrial production. So people are actively looking for new environmentally friendly catalyst [2], [3], [4].

Although the sulfonic acid resin is a kind of the commonly industrialized catalyst in some reactions, it is seldom used in the esterification. As the heterogeneous catalyst, it not only can overcome the disadvantages of concentrated sulfuric acid as the catalyst, but also simplify the process of separation and purification of product, and reduce the energy consumption and the generation of acid waste water [5].

2. EXPERIMENTAL

2.1 Experiment reagent and instrument

ISSN 2278-7763

Acetic acid(AR), 5% Phenolphthalein indicator were purchased from Baishi Co., Ltd Tianji, China;sec-butanol(CP)was purchased from China National Medicines Co.,Ltd; NaOH(AR), 37% HCL were purchased from chemical reagent factory, Shenyang; sulfoacid resin D005(AR)was purchased from Mingzhu special resin co., Ltd Dandong, China.

2.2 The pretreatment of the catalyst

The sulfonic acid resin was treated with 4% HCl, deionized water, 4% NaOH and deionized water in turn until the water is neutral, and then the resin was dried at 100℃ for more than 12h.

2.3 Esterification

A certain amount of sulfonic acid resin D005, acetic acid and sec-butyl alcohol are put into the round bottom flask which is in DF - 101s collector-type constant temperature heating magnetic stirrer at some temperature with stirring. Under a certain temperature, then the raw material is heated with reflux for certain hours, then the acetic acid conversion rate is calculated.

the acid values before and after reaction were determined with a solution of 0.05mol sodium hydroxide, and the acetic acid conversion rate is calculated as followings:

$$\text{Acetic acid conversion rate} = \left(1-\frac{V_1}{V_0}\right) \times 100\%$$

V1—the volume that consumption of 1.5mol·L-1NaOH before reaction

V0—the volume that consumption of 1.5mol·L-1NaOH after reaction

3. RESULTS AND DISCUSSION

3.1 Catalytic Activity Contrast

At the reaction condition: temperature 120℃, time2h, mole ratio of sec-butanol to acetic acid is 1.1:1, the amount of catalyst 10%（weight），Hβ zeolite、$FeCl_3$ and sulfoacid resin were used as the catalysts to compare the catalytic activity. The results are shown in table 1. The data from table 1 shows that without catalyst the acetic acid conversion rate is only 38.0%. Using Hβ zeolite as the catalyst, the acetic acid conversion rate is 46.0%. However, this result is too low to sec-butyl acetate catalytic Synthesis. The catalytic activity of $FeCl_3$ is the best, and the acetic acid conversion rate is 66.0%, However, $FeCl_3$ dissolved in reaction liquid making product with deeper color, catalyst recycling is difficult and not reused[6], [7]. So sulfoacid resin is the appropriate catalyst.

Table 1 Catalytic activity contrast

serial number	Catalyst	Acetic acid conversion rate%
1	None	38.0
2	Hβ zeolite	46.0
3	$FeCl_3$	66.0
4	sulfoacid resin	64.0

ISSN 2278-7763

3.2 Reaction Time Effect on Acetic Acid Conversion Rate

At the reaction condition: temperature 120℃, mole ratioof sec-butanol to acetic acid is 1.1:1, the amount of sulfoacid resin 10%（weight），influence of reaction time was studied, and the results are shown in figure 1. With the increasing of reaction time, the acetic acid conversion rate increases. When the time is 4h, the acetic acid conversion rate is larger than other time. When prolong the reaction time, the acetic acid conversion rate declined. The reasons for this phenomenon are that the esterification reaction is reversible reaction and may due to the adsorption effect of catalyst. Because in the longer reaction time, raw material be adsorbed more on the surface of the catalyst. So the appropriate time is 4h.

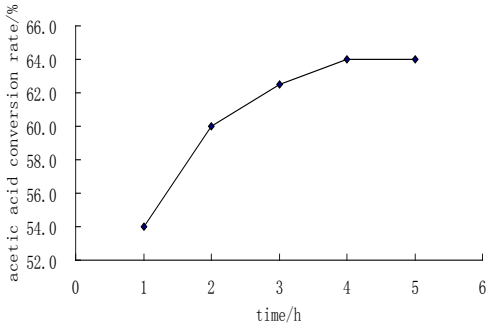

Figure1 reaction time effect on acetic acid conversion rate

3.3 Reaction Temperature Effect on Acetic Acid Conversion Rate

At the reaction condition: time 2h, mole ratio of sec-butanol to acetic acid is 1.1:1, the amount of sulfoacid resin 10%（weight），the influences of reaction temperature were studied. The results are shown in figure 2, it can be seen that at low temperature, the esterification are incomplete, the acetic acid conversion rate increases with the increasing of reaction temperature. When the temperature is 120℃, theacetic acid conversion rates no longer increase. Because the temperature is too high, the reaction can make more by-products. So the appropriate temperature is 120℃

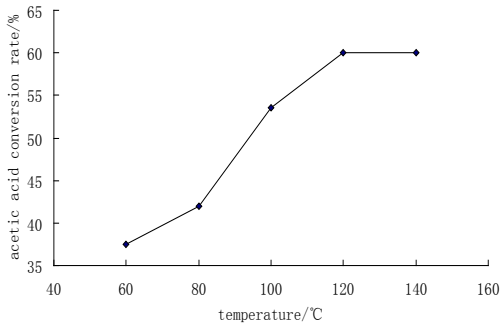

Figure 2 reaction temperature effects on acetic acid conversion rate

ISSN 2278-7763

3.4 The Amount of Catalyst Effect on Acetic Acid Conversion rate

At the reaction condition: time 2h, mole ratio of sec-butanol to acetic acid is 1.1:1, temperature 120℃, the influences of the amount of sulfoacid resin were studied. The results are shown in figure 3. It can be seen that the acetic acid conversion rate increases with the increasing of the amount of catalyst for the increasing catalyst activity centers. But when the catalyst is more than 15%（weight）, acetic acid conversion rate fall slightly. This is because the adsorption of feeds and products on the catalyst which reduces the mass transfer rate, so the appropriate the amount of catalyst is 15%（weight）.

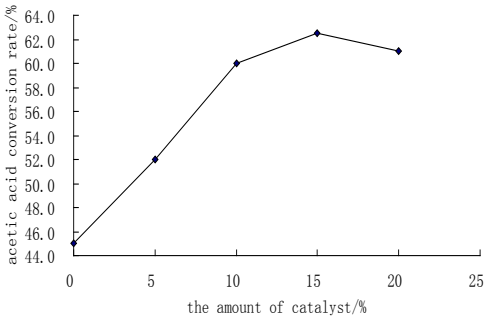

Figure 3 the amount of catalyst effect on acetic acid conversion rate

3.5 mole ratio of sec-butanol to acetic acid is effect on acetic acid conversion rate

At the reaction condition: time 2h, temperature 120℃, the amount of sulfoacid resin 10%（weight）, the influences of mole ratio of the feed(sec-butanol: acetic acid) were studied. The results are shown in figure 4, It can be seen that appropriately increase of the amount of the sec-butanol, can help balance move to generate sec-butyl acetate direction. But when the mole ratio of sec-butanol to acetic acid is more than 1.2 :1, acetic acid concentration declines, which results in the decrease of the acetic acid conversion rate, so the appropriate mole ratio of sec-butanol to acetic acid is 1.2:1.

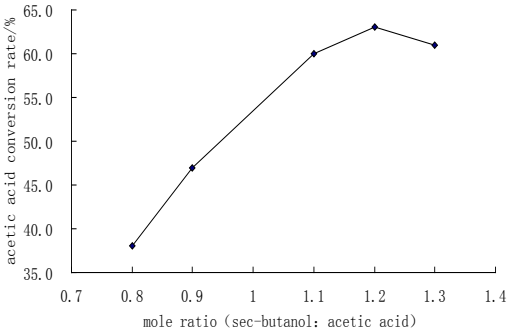

Figure 4 mole ratio of sec-butanol to acetic acid is effect on acetic acid conversion rate

3.6 The performance of reused catalysts

At the reaction condition: time 2h, temperature 120℃, the amount of sulfoacid resin15%（weight）, mole ratio of sec-butanol to acetic acid is 1.1:1 . The catalysts were used for several times in the reaction, and the reaction results with the used catalyst are shown in figure 5. It can be seen that the sulfoacid resin

ISSN 2278-7763

has good stability. The acetic acid conversion rate is still as high as 63% after 4 times of reactions.

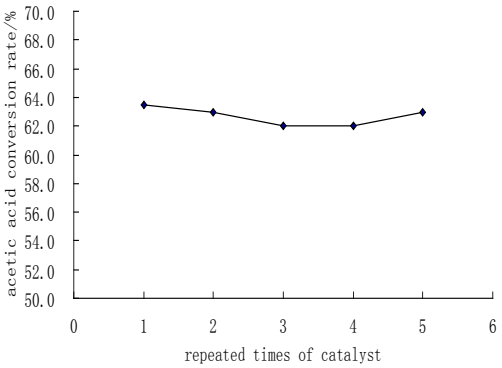

Figure 5 the performance of reused catalyst effect on acetic acid conversion rate

4. CONCLUSIONS

With sulfoacid resin as the catalyst the appropriate reaction parameters are: temperature 120℃, time 4h, mole ratio of sec-butanol to acetic acid is 1.2:1, the amount of catalyst 15%（weight）, then acetic acid conversion rate is 64%. The acetic acid conversion rate when the reaction has repeated 5 times is still as high as 63%, and the catalyst which is not dissolved in the reactants can easily separate from the reaction completely.

5. REFERENCES

[1] Amornchai A. , Kittipong K., Worapon K., Piyasan P., Suttichai A., Production of n-butyl acetate from dilute acetic acid and n-butanol using different reactive distillation systems: Economic analysis, Journal of the Taiwan Institute of Chemical Engineers, 2009.40: 21~28

[2] Ramesh C.，Mahender G., Ravindranath N., Biswanath D., A simple，mild and efficient procedure for selective cleavage of prenyl esters using silica — supported sodium hydrogen sulphate as a heterogenous catalyst [J]，Tetrahedron letters , 2003, 44(7):1465~1467

[3] Pascale D., Jacques C. V., Eric P., Gthrd H., Frederic L., Heteropolyacids supported on activated carbonas catalysts for the esterification of acrylic acid by butanol, Applied Catalysis A: General 129(1995): 217~227

[4] D.L. Trimm, The regeneration or disposal of deactivated heterogeneous catalysts, Applied Catalysis A, 2001, 212:153~160

[5] Sergej B., Sandra P., Oliver B., Peter M., David L., Rudolf We. ,Hans H., Influence of ion-exchange resin catalysts on side reactions of the esterification of n-Butanol with acetic acid, Chemical Engineering Science 2006, 2(61):753~765

[6] Adharvana Chari M，Syamasundar K．Polymer(PVP) supported ferric chloride: an efficient and recyclable heterogeneous catalyst for high yield synthesis of 1，5 — benzodiazepine derivatives under solvent free conditions and microwave irradiation［J］．Catalysis communications，2005，6(1) :67—70．

[7] Ramesh C，Mahender G，Ravindranath N，Biswanath D．A simple，mild and efficient procedure for selective cleavage of prenyl esters using silica-supported sodium hydrogen sulphate as a heterogenous catalyst［J］．Tetrahedron letters，2003，44(7) :1465 — 1467.

