The Synthesis of Multi-heteropoly Acid Containing Titanium and Its Application on Esterification Reaction

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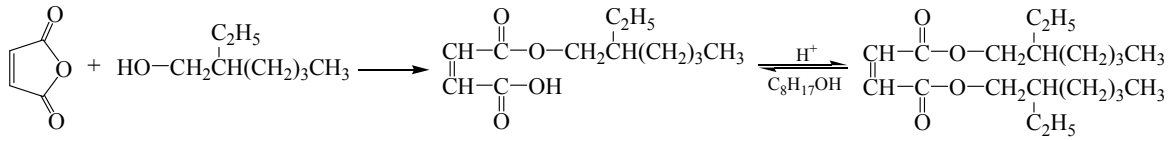
Abstract. The novel ternary undecatungstotitanotitanic heteropoly acid (H_4Ti (H_2O) $TiW_{11}O_{39}$) was synthesized successfully by the method of ion exchanging-concentration. It was used as the catalyst for the esterification of maleic anhydride with 2-ethylhexyl alcohol in liquid phase. The effects of reaction time, ratio of anhydride to alcohol and the amount of water-carrying agent toluene on synthesizing di-2-ethylhexyl maleate were investigated. The suitable condition for synthesizing the ester was obtained. The catalyst has outstanding advantages such as high esterification rate, less catalyst consumption.

1. Introduction

Heteropoly acid is a kind of solid super acid, which has been widely used as a new type of catalyst in organic synthesis reactions. It has many advantages such as high catalytic activity, low equipment corrosion, and small pollution. It has many reports on its catalytic esterification reaction [1-2].

Maleic acid di-2-ethylhexyl maleate, also known as two ethylhexyl maleate, is abbreviated as DOM. It is an important internal plasticizer. It is widely used in paint, coatings, adhesives, fiber treatment agents and so on. The products have the advantages of good gloss, aging resistance, acid alkali resistance and so on. In addition, it is also widely used in the fields of petroleum and paper making, is also an important chemical intermediates [3].



At present, the catalyst used in the industrial production of diethylhexyl maleate is still sulfuric acid. Although sulfuric acid is used as a catalyst, it is inexpensive and easy to obtain, but it requires high corrosion resistance of equipment, large amount of waste water, and long process flow. Operation is troublesome, due to long reaction period, high temperature, many side reactions, and poor product quality. Therefore, the current research on the synthesis of DOM is mainly focused on the research of catalysts, Wu uses a composite solid superacid SO_4^{2-}/ZrO_2-TiO_2 as a catalyst [4], Luo used solid acid catalyst SO_4^{2-}/TiO_2 as catalyst [5], Zou Changjun and others used macroporous strong acidic styrene cation exchange resin catalyst [6]. However, these methods generally have the

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disadvantages of low catalyst activity, large amount, or pressure operation, and high equipment and operation requirements.

At present, the catalyst used in the industry is still concentrated sulfuric acid, and the development of a catalyst that can achieve the catalytic effect of concentrated sulfuric acid and overcome its shortcomings is an urgent problem to be solved. The novel multi-heteropoly acid undecatungstotitanotitanic acid composite [H_4Ti (H_2O) $TiW_{11}O_{39}$] was used for the catalytic synthesis of DOM. The catalytic performance was more excellent. It had the outstanding advantages of less catalyst and higher esterification rate.

2. Experimental section

2.1. Instruments and Reagents

Experimental instruments include the Beijing Rayleigh WQF-510A FTIR infrared spectrometer and the Beijing General Analysis TU-1901 double beam UV-Vis spectrophotometer. All reagents used were of analytical grade.

2.2. Preparation of heteropoly acids

Heteropoly acid catalyst H_4Ti (H_2O) $TiW_{11}O_{39}$ was synthesized according to the literature.

Take 18.15g Na_2WO_4 $2H_2O$ and add 100mL deionized water to dissolve it. The pH value of the ice acetic acid solution is 6.3, heated to the micro tenging, and the side stirring edge slowly drops the Ti^{4+} solution of 0.33 mol/L ($TiCl_4$ dissolved in the 0.1 mol/L hydrochloric acid) 15mL, and the pH value is 5.5. After half an hour of reaction, 0.33mol /L Ti^{4+} solution was added to 15mL, and the pH value was adjusted to 5 with glacial acetic acid. After continuing to react to 1.5h, filtering, adding a proper amount of ethanol into the filtrate and precipitating a colorless oil, after placing the refrigerator in the refrigerator, separating the oil, adding some deionized water and adding a proper amount of ethanol to precipitate the oil, after repeated operation and purification for 3 times, dissolved in 40mL water, and added a proper amount of hydrogen cation exchange resin. The pH value of the stirring solution is less than 1, and undecatungstotitanotitanic acid can be prepared.

2.3. Esterification

The maleic anhydride 5.0g, undecatungstotitanotitanic acid catalyst 0.1g, a proper amount of 2-ethylhexyl alcohol, toluene and zeolite are added to the three bottles of 100mL, and the oil water separator is added to the oil-water separator. The saturated sodium chloride solution is added to the oil-water separator and heated to the reflux. The reaction has been reacted for a certain time, and the toluene is steamed out and cooled to room temperature 15 minutes before the end of the reaction. After that, an appropriate amount of solution was taken and the acid value was determined by 0.05mol/L sodium hydroxide standard solution.

The acid value was determined according to the national standard method, and the esterification rate was calculated according to the following formula.

$$\text{esterification rate} = \frac{\text{Acidity value before reaction} - \text{acid value after reaction}}{\text{Acidity value before reaction}} \times 100\%$$

The ester decompressed distillation is refined, and the catalyst is stored in the reactor. The esterification catalysis of the catalyst under the next same condition is not treated directly. The catalytic activity is repeated for five times. The catalytic activity has no obvious difference, the catalyst can be reused many times.

3. Results and discussion

3.1. Infrared and UV spectra of heteropoly acids

Figure 1 and Figure 2 show there are 5 characteristic peaks in the infrared spectrum of the synthetic products, which conform to the characteristic vibration of Keggin heteropoly acids, respectively: V Od 966 cm^{-1} as terminal oxygen atoms, V Ob 889cm^{-1} as co top oxygen atoms, V Oc 804cm^{-1}, 742cm^{-1} as the oxygen atoms shared by the common side, and V Oa 436 cm^{-1} as the oxygen atom connected with the titanium atom. In the UV spectrum, there are two absorption bands, which are Od → W 195 nm and Ob/Oc → W 262 nm, which conform to the characteristic absorption of Keggin heteropoly acids and be the transition of tungsten oxygen bonds.

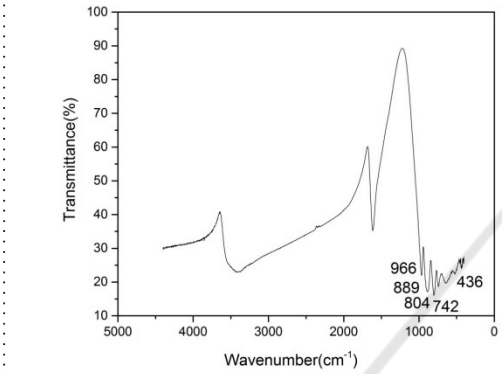

Figure 1. infrared spectrum of heteropoly acid $H_4Ti(H_2O)TiW_{11}O_{39}$

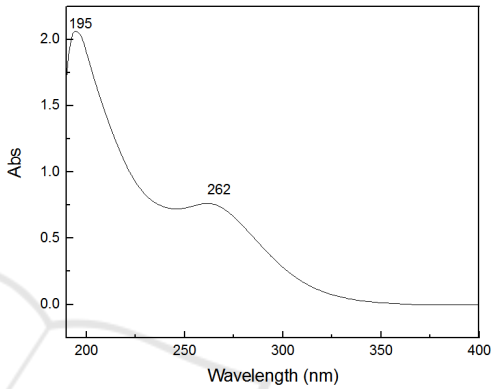

Figure 2. UV spectra of heteropoly acid $H_4Ti(H_2O)TiW_{11}O_{39}$

3.2. Selection of esterification conditions

For the molar ratio of maleic anhydride to 2- ethylhexanol, the reaction time and the amount of three conditions for toluene, see Table 1, the optimum reaction conditions are the molar ratio of maleic anhydride to 2- ethyl hexanol, the reaction time 4 hours, the dosage of toluene with water agent 10ml, and the esterification rate of two ethyl hexyl maleate to 99.5%.

Table 1. Data of esterification reaction

NO.	reaction time (h)	anhydride alcohol ratio (mol)	Toluene (mL)	esterification rate (%)
1	3	3	15	84.3
2	4	3	15	93.8
3	5	3	15	95.7
4	4	2.5	15	86.8
5	4	3.5	15	96.3
6	4	3	5	94.7
7	4	3	10	99.5
8	4	3	20	88.6

Maleic anhydride (maleic anhydride) is a highly active acylate, which reacts with 2- ethyl hexanol to produce monoester quickly. One carboxyl group is retained in the mono ester molecule, which can continue to react with 2- ethylhexyl alcohol to produce diester, but the acylation activity of carboxylic acid is weak and needs to be carried out in the presence of acid catalyst. Heteropoly acid

as catalyst has mild reaction conditions, high esterification rate, and can be reused. [10] This is determined by the characteristics of heteropoly acid catalyst. The esterification reaction of carboxylic acid is reversible. In order to improve the conversion of reversible reaction, the amount of 2- ethyl hexanol in reactant can be increased, but excessive excess makes the cost increase. The better method is to reduce the concentration of the product and add the toluene with water agent, which can make the reaction water leave the reaction system and get a higher conversion rate.

4. Conclusions

The synthesis of two ethyl hexyl maleate with undecatungstotitanotitanic acid as catalyst was used as a catalyst for the synthesis of two ethyl hexyl maleate. It was easy to operate, and a good esterification rate was obtained. The catalytic activity was high and the amount of catalyst was less. It could be reused continuously. No waste acid was discharged and there was no environmental pollution. It was of positive significance to the solution of the existing sulfuric acid catalytic process.

Acknowledgments

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