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A Study of Heteropoly Complexes of Rare Earths as Catalyst Promoter in the Synthesis of Ethyl Acetate

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Abstract: The capability of the synthesized heteropoly complexes of rare earths $\{K_{10}[(O_{39}W_{11}Si)Ln(Gly)_3Ln(SiW_{11}O_{39})]\cdot 9H_2O$ (Ln=La, Pr, Nd, Sm, Eu, Gd, Tb, Dy)$\}$ as the catalyst promoter in the synthesis of the ethyl acetate was studied. The results showed that the quantity of H_2SO_4 used for synthesizing the ethyl acetate can be reduced by 75% and the yield reached 98% at the optional condition.

Keywords: Heteropoly complexes of rare earths, catalyst promoter, ethyl acetate.

Ethyl acetate(EA) is a kind of important materials in chemistry industry. The synthesis of EA is catalyzed by the oil of vitriol (H_2SO_4) in the industry. The preparation method of EA from acetic acid and alcohol using the large quantity of H_2SO_4 has many shortages of environment pollution, equipment erosion and low yield [1]. Recently heteropoly acids were used as catalysts [1,2]. Because most of the heteropoly acids are in liquid state and need to have the solid supporting materials [3]. So we synthesized the solid target complexes $\{K_{10}[(O_{39}W_{11}Si)Ln(Gly)_3Ln(SiW_{11}O_{39})]\cdot 9H_2O$ (Ln=La, Pr, Nd, Sm, Eu, Gd, Tb, Dy)$\}$ [4] as the catalyst promoter in the synthesis of EA. In the presence of these complexes, the quantity of H_2SO_4 can be reduced by 75% [5] and the yield can be heightened from about 73% up to 98%.

For exploring the effect of different kinds of rare earths, the quantities of the catalyst promoter and H_2SO_4, the reation time and the volume ratio(V_1/V_2) of acetic acid-alcohol on the yield of EA were investigated. Firstly, the effect of different complexes on the yield of EA under the same conditions of V_1/V_2=10 mL/8.5 mL and 1.2×10^{-6} mol H_2SO_4 was tested. The results obtained were shown in **Figure 1**, indicating that the compex of La(III) is the best catalyst promoter in these complexes. So most discussion was done to the complex of La(III) thereinafter. Then the relation of the yield with the quantity of the catalyst promoter was studied when the quantities of H_2SO_4 were 0.6×10^{-6} mol and 1.2×10^{-6} mol respectively. The results showed that the best quantity of the catalyst promoter was between 0.035~0.040 g, and the yield was much higher when the quantity of H_2SO_4 is 1.2×10^{-6} mol than 0.6×10^{-6} mol. **Figure 2** showed that the yield was enhanced

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Figure 1 The effect of different complexes on the yield of EA

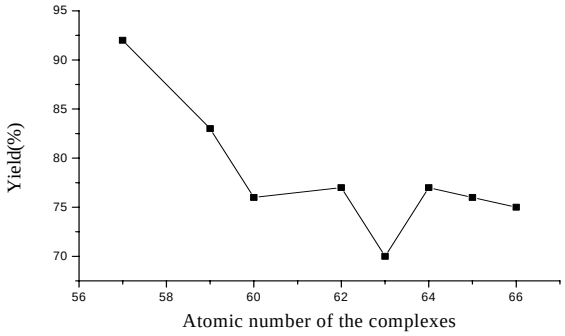


Figure 2 Relation of the yield with the quantity of H_2SO_4

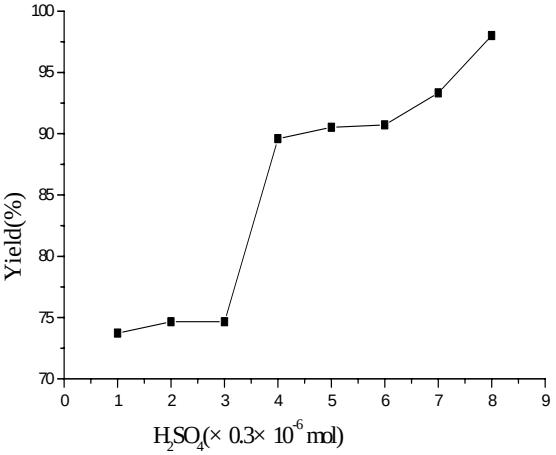
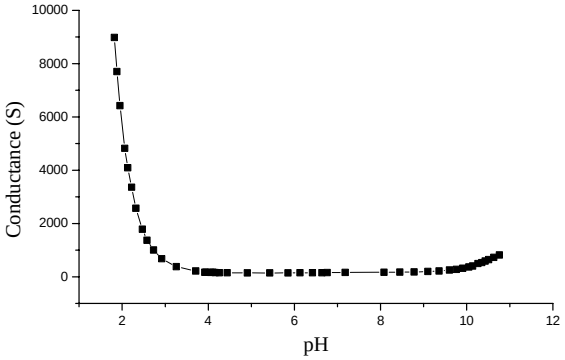


Figure 3 The conductance *vs* pH relation for the complex of La



with the increase of the quantity of H_2SO_4 and the relation looked like the staircase. **Figure 3** showed the conductance of the complex *vs* pH relation at the room temperature, indicating that when the pH is between 3~10 the target complexes are stable. When the quantity of H_2SO_4 reached 2.8×10^{-6} mol, the target complexes decomposed and affected the process for the synthesis of EA and the yield became very low. So the quantity of H_2SO_4 should be strictly controlled when the target complex is used as catalyst promoter.

The process for the synthesis of EA was inspected by HP-6890 gaschromatograph apparatus, took 1 mL of samples every 5 minutes. The results revealed that the reaction was in equilibrium after 25 minutes, and then the reaction rate slowed down, showing that the best reaction time is about 25 minutes.

Finally the relation of the acetic acid-alcohol volume ratio with the yield was studied. As shown in **Table 1**, the yield of EA was 98%, when the acetic acid-alcohol volume ratio was 2:1. In order to assure the purity of EA, temperatures of the distillation were strictly controlled under 76°C.

Table 1 Relation of the yield of EA with the acetic acid-alcohol volume ratio

V_1/V_2	1.2	1.5	2.0	2.5	3.0
Yield/%	93	96	98	92	85

V_1: the volume of acetic acid; V_2: the volume of alcohol

Experimental

The target complexes were synthesized according to the reference 4. The synthesis of ethyl acetate was based on reference 2. All the chemicals were of A.R grade. The volume of alcohol was 8.5 mL and the acetic acid was excess.

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