Esterification catalytic over Imidazolium Ionic Liquid Modified salt of phosphotungstic Acid catalyst

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Abstract: A solid acid was prepared by the reaction of phosphotungstic acid (HPW)with 1-methylimidazolium sulfobutyrolactone (MIMSB) and characterized by the methods of X-ray powder diffraction, FT-IR, potentiometric titration and SEM. Then the solid acid was employed for esterification to evaluate its acid-catalytic activity. Various reaction parameters, including catalyst dosage, reaction time, n-butanel/butyric acid molar ratio and reaction temperature were systematically examined. These results indicated that the prepared catalyst maintained the Keggin structure of the raw HPW, and had high acidity. The catalyst exhibited excellent catalytic activity in esterification of n-butyric acid and n-butanol.93. 4% conversion of n-butyric acid was obtained under the optimized reaction conditions. The catalyst also had good stability.

Keywords: heteropoly acid, ionic liquid, catalysis, esterification

1. Introduction

Heopolylic acids are widely used in acid catalytic reaction, REDOX reaction and photoelectric catalytic reaction, such as acid catalyst, can be used in esterification reaction, alkylation reaction, acetal (ketone) synthesis and other reactions[1,2]. However, due to the good solubility of polyamino acids in polar solvents, it is difficult to recover after reaction, and it is not suitable for direct use in heterogeneous reactions. Therefore, a large number of literature has reported loaded heteropolylate or heteropolylate catalysts to facilitate the recovery and reuse of heteropolylate catalysts[3-5].

Heterpolyacid loading is used by impregnation method or sol-gel method to realize the load of polypolyacids with small surface area, such as phosphoric molybdic acid, phosphotungstic acid, on the carrier with high surface area (generally silica, molecular sieve, etc.). The loaded polyphenic acid has a high specific surface area and is easy to recover, but it loses the active phase seriously during use[3,4].exploitation Cstwenty、NH、Kten、AgtenIsocation can replace the anticharged proton in the structure of heteropolyacid, which can be obtained, which can be easily realized by reaction with cesium carbonate, cesium chloride and heteropolenic acid in water or water-alcohol solution Cstwentytake part in Hten Exchange, but the acids are generally less acidic than the parent acid[5-7]. In addition, solid acid catalysts can also be synthesized by modifying organic compounds, such as ammonium salt and polyacid, ionic liquid or organic-polyacid, which can also be better used in the acid catalytic reaction[8,9]·

A solid acid catalyst was prepared and applied to the esterification reaction of butyric acid and butanol.

2. Experimental part

2.1. Primary reagents and instruments

Phosphotungic acid (HPW), phosphorolybdic acid (HPM), Shanghai Maclin Biochemical Technology Co., Ltd.; Silicon Tungic Acid (HSiW), Anji Chemical; 1-sulfonate butyl-3-methyl imidazole internal salt (MIMSB), Shanghai Chengjie Chemical Co., Ltd.; n-butyl alcohol, Shanghai Jingchun Industrial Co., Ltd.; n-butyric acid, Tianjin chemical reagent #3 factory. XD -3Type X-ray powder diffractometer (Beijing Spectrum Analysis General Co., LTD.);FT 6700Type Fourier Transform Infrared Spectrometer (American Thermoelectric Company);HP 6890/5976Type GC-MS (HP);ZD -2AModel (Shanghai Dapu Instrument Co., Ltd.);JSM -6380Electron Microscopy (Japan Electronics Corporation).

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2.2. Catalyst preparation

Said to take HPW (0.0005mol,1.440g) Solved in 30mL In deionized water, and sonication5minPromote its complete dissolution; weigh MIMSB (0.0015mol,0.327g) Solved in 5mL In deionized water, then under stirring, slowly added to HPW In aqueous solution; after dripping, continue stirring at room temperature 24h. Mix the solution 80 °C Dry, to give a transparent gelatinous solid, denoted as [MIMSB]$_3$PW$_{12}$O$_{40}$. Using the same method, the polyacids were replaced with HPM And HSiW, Other solid acid catalysts can be prepared, respectively designated as [MIMSB]$_3$PMo$_{12}$O$_{40}$And [MIMSB]$_4$SiW$_{12}$O$_{40}$, among HSiW take part in MIMSB The molar ratio is1:4.

2.3. Characterization of catalysts

The catalyst phase was determined in the X Performed on a ray ray diffractometer, CU target, Nifiltering, KαRay, with a wavelength of 1.542 Regiment, pipe flow20mA, Tube pressure36kV. Ired spectroscopy was tested in the FT 6700Performed on a Fourier-transform infrared spectrometer, KBrPress, with a wave number range of 400-4000cm-1. Analysis of the catalyst acidity using the potential titration method,0.05g The catalyst is added to 15mL carbinol. Stir at room temperature 0.5h After, with0.05 NN-butylamine acetonitrile solution was titrated. Exploitation ZD -2AThe type automatic potential titrator detects the potential change of the solution.

2.4. Evaluation of the catalyst performance

The esterification reaction of n-butyric acid and n-butanol was performed in a round bottom flask equipped with a reflux condensation device, with the oil temperature controlling the reaction bath. In25mLIn the round bottom flask, add n-butyric acid (0.015mol,1.322And g), n-butanol (0.03mol,2.224G), adding catalyst (n-butyrate mass12%,0.159And g), heated up to100°C, Stir in the reflux reaction4h. After the reaction, the products were analyzed by GC-MS and the catalyst was filtered back and directly used to catalyze the esterification reaction again.

3. Results and discussion

3.1. Characterization of catalysts

3.1.1. Catalyst XRD analysis

graph1As shown HPW、MIMSB As well as synthesis [MIMSB]$_3$PW$_{12}$O$_{40}$and so on XRD spectrogram. HPW take part in MIMSB showed strongly sharp diffraction peaks, indicating that both exist in a better crystalline state. but [MIMSB]$_3$PW$_{12}$O$_{40}$ take part in HPW reach MIMSB The diffraction spectrum is completely different, almost no obvious diffraction peak appears, indicating that it exists in an amorphous state. XRD bear The fruit indicates that [MIMSB]$_3$PW$_{12}$O$_{40}$ fault HPW reach MIMSB Simple mixing, but rather the reaction to produce an amorphous new matter.

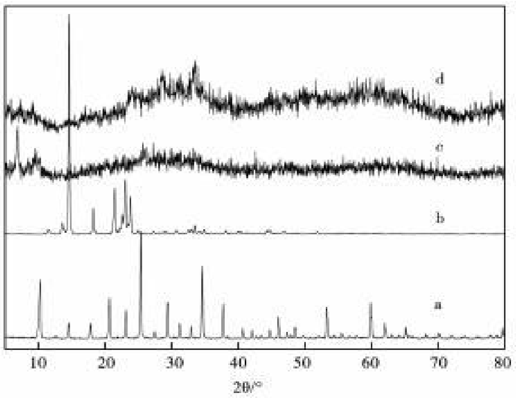

Figure 1. Catalyst XRD graph

pour:a:HPW;b:MIMSB;c:[MIMSB]$_3$PW$_{12}$O$_{40}$.;d:retrieve [MIMSB]$_3$PW$_{12}$O$_{40}$.

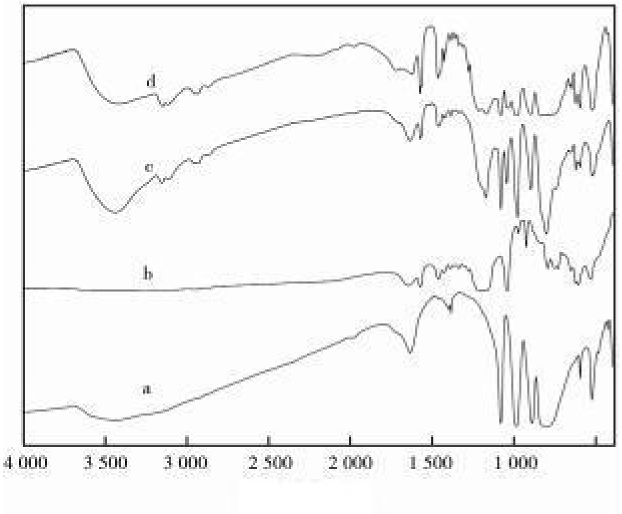

Figure 2. Catalyst IRgraph

pour:a:HPW;b:MIMSB;c:[MIMSB]$_3$PW$_{12}$O$_{40}$.;d: retrieve [MIMSB]$_3$PW$_{12}$O$_{40}$.

3.1.2. *Catalyst IR analyse*

Graph 2 As shown HPW 、MIMS Breach [MIMSB]3PW$_{12}$O$_{40}$and so on Rspectrogram. Phosphotungstate in 700-100cm^{-1}Four appeared in the place Keggin The characteristic absorption peak of the Iin structure:1080cm^{-1}、985cm^{-1}、888cm^{-1}、807cm^{-1}, This is in accordance with the literature Which was reported in the [7] keggin The nic phosphotungstate acid of the in structure. MIMSB in1577cm^{-1}The absorption peak is on the imidazole ring C=N The expansion of vibration,1041cm-1reach1170cm^{-1}For the symmetric and asymmetric extension of the sulfonic acid group[10]. The synthesized catalyst in the800cm^{-1}、896cm^{-1}、978cm^{-1}、1070cm^{-1}The place appeared kegging The characteristic absorption peak of the structure, which indicates that the catalyst retains the original HPW and so on keggin Structure; meanwhile, in the1040cm-1as well as1070cm^{-1}The occurrence of absorption peaks indicates the presence of ionic liquids in the catalyst, which is well illustrated [MIMSB]$_3$PW$_{12}$O$_{40}$yesHPWtake part in MIMSB is combined to generate a new catalyst, which interacts with XRD The results match that of.

3.1.3. *Acid degree analysis of the catalyst*

The acid strength of solid acid catalysts can be analyzed by using potential titration methods, Fig3As shown HPW And [MIMSB]$_3$PW$_{12}$O$_{40}$The potential titration plot of the Fig. Pecchi et al[11]Consider the starting titration potential Ei>100mvForvery strong acid,0<Ei<100mThe v is strong acid, and the amount of n-butyl amine-acetonitrile solution at titrating the inflection point can indicate the total amount of acidic point. By the figure3 As you can see, HPW and so on Ei For385mv, This is acidic with it Strong match; and HPW compare with,[MIMSB]$_3$PW$_{12}$O$_{40}$acidThe intensity has decreased slightly, though Ei Still reach377mv, And upon reaching the titration inflection point, [MIMSB]$_3$PW$_{12}$O$_{40}$ More n-butylamine was consumed, indicating it than the same quality HPW With multiple acid quantity points, which may be associated with [MIMSB]$_3$PW$_{12}$O$_{40}$There are sulfonic acid groups involved.

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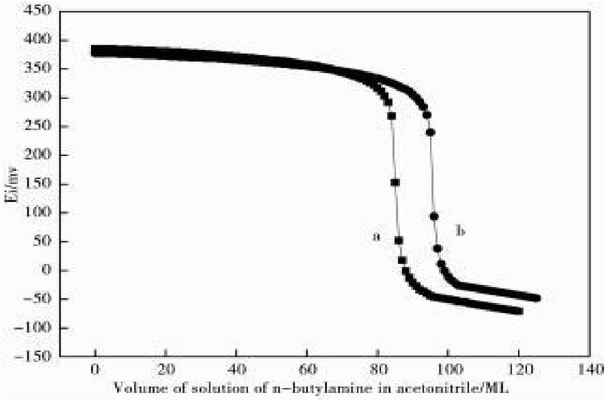

Figure 3. The potential titration curve of the catalyst

pour: a: HPW; B:$[MZMSB\ ]_3PW_{12}O_{40}$.

3.1.4. Electron microscope (SEM) analysis of the catalyst

Grap h4Shown are the HPW And $[MIMSB]_3PW_{12}O_{40}$ and so on SEM graph. HPW Group Gather into about 100μmSize and irregularly shaped particles, with MIMSB still appears as irregular particles, but the particles are smaller, about20μm, The surface is wrinkled and relatively smooth.

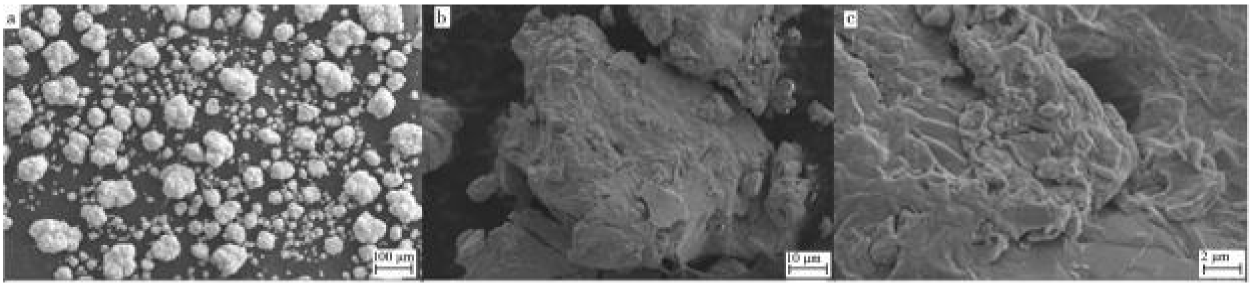

Figure 4 Catalyst SEM

pour:a.HPW (100μm);b.$[MIMSB\ ]_3PW_{12}O_{40}$(20μm);c.$[MIMSB\ ]_3PW_{12}O_{40}$(2μm).

3.2. Catalyst activity evaluation

Respectively, by the synthesis of $[MIMSB]_3PW_{12}O_{40}$ $[MIMSB]_3SiW_{12}O_{40}$And $[MIMSB\ ]3PMo_{12}O_{40}$As the catalyst, catalytic n-butyric acid and positive buty Esterification of alcohol, in which the catalyst amount is butyrate mass12%The alcohol-acid ratio is2:1, In 80 °C reaction3h. All three catalysts are difficult to dissolve in the reaction system, and the analytical reactants show that butyl butyrate is the only product, under the same conditions, [MIMSB]3PW12O40Showed the best catalytic performance, and the yield was reached62.8%. This may be associated with $[MIMSB]3PW_{12}O_{40}$.With a higher acid strength and more acidic points are associated.

3.2.1. Effect of the amount of catalyst on the yield of catalytic esterification

Graph 5 As shown in $[MIMSB\ ]_3PW_{12}O_{40}$ As a catalyst, it catalyzes the results of the esterification reaction of butyrate with butanol at different amounts. When no catalyst is used, the reaction 4h The yield of 21.2%, After the addition of butyrate mass4After% catalyst, a higher ester yield can be obtained (75.2%), And with the increase of the catalyst amount, the yield of the ester is further and significantly increased, in the catalyst amount of 12At%, the esterification yield was93.4%; However, in the catalyst dosage of14%, Little change in yield, which could be that the excess catalyst would limit the reactant contact and thus hinder the reaction. So under the conditions used in the experiment, the optimal catalyst amount is Bullic acid mass12.0%

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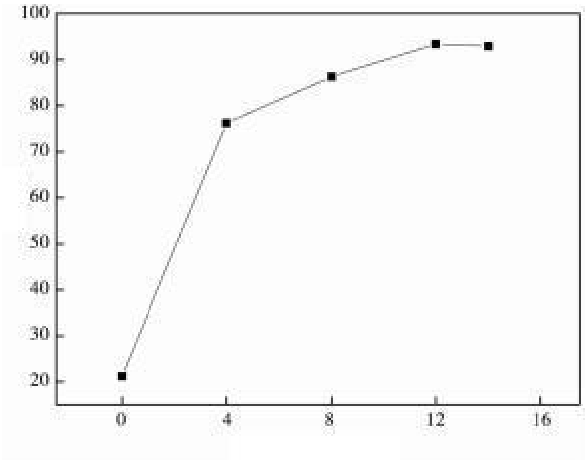

Figure 5. Effect of the amount of catalyst on the yield of catalytic esterification

Note: Reaction conditions: the molar ratio of n-butyric acid to n-butanol is1:6,The reaction temperature is100 ℃ , reaction time4h.

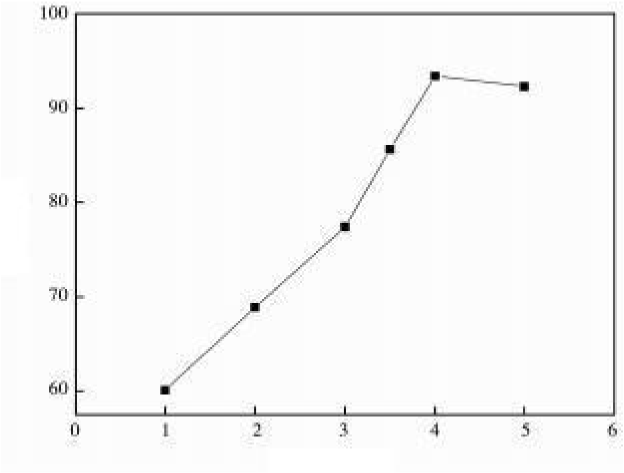

Figure 6. Effect of the reaction time on the yield of the catalytic esterification reaction

Note: Reaction conditions: the molar ratio of n-butyric acid to n-butanol is1:6The reaction temperature is100℃,The amount of catalyst is of n-butyric acid12.0% time.

3.2.2. Effect of the reaction time on the yield of the catalytic esterification reaction

Graph 6 Shown are the altered reaction times, and the [MIMSB]$_3$PW$_{12}$O$_{40}$Results of the catalytic esterification of butyric acid with butanol. Reaction 1h The esterification yield has been reached60%, Note again that the [MIMSB]$_3$PW$_{12}$O$_{40}$ It shows good catalytic performance; with the reaction time, the esterification yield continues to increase when the reaction4After h, the yield is at the maximum, though when the reaction time is5hTime, with little change in yield. This may be because the esterification into a reversible reaction and, under the experimental conditions,4To reach equilibrium around h, so the optimal time to select the reaction is 4h.

3.2.3. Effect of the reaction temperature on the catalytic esterification reaction

Graph 7 Shown, at different reaction temperatures, [MIMSB]$_3$PW$_{12}$O$_{40}$Catalytic butyrate and buty The result of the alcohol esterification reaction, the reaction temperature, respectively60℃、70℃、80℃、90℃、100℃ and110℃. As the reaction temperature was given by60℃ increase to100℃, The esterification yield was determined by 42.3% increase to 93.4%This indicates that increasing the reaction temperature is favorable for esterification, which needs to be performed at higher temperatures; however, when the

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reaction temperature is increased110 ℃, The yield has decreased, which may be caused by the high temperature prompting the reverse reaction.

3.2.4. Effect of different molar ratios of reactants on the catalytic esterification reaction

To move the reaction in the direction of ester formation, the general esterification reaction alcohol is in excess, Fig8 Shown is to change the molar ratio of n-butanol to n-butyric acid, in [MIMSB]$_3$PW$_{12}$O$_{40}$ Result of the esterification reaction under catalysis. At equimolar amounts of alcohololate, the esterification yield at 65% Above, when the amount of alcohol is increased to 2:1 Time, the yield increased significantly; continue to increase the alcohol dosage respectively3:1.4、1.5:1 And 6:1, The yield increases further, but the rate increases slowly, and when the acid mol ratio is reached 7:1 Time, the yield was slightly reduced. The excessive alcohol will cause the dilution of the catalyst, thus causes the reduction of esterification yield. In order to ensure the maximum esterification conversion of butyric acid in a short time, the ratio of butyric acid and butyric acid was selected under the experimental conditions6:1.

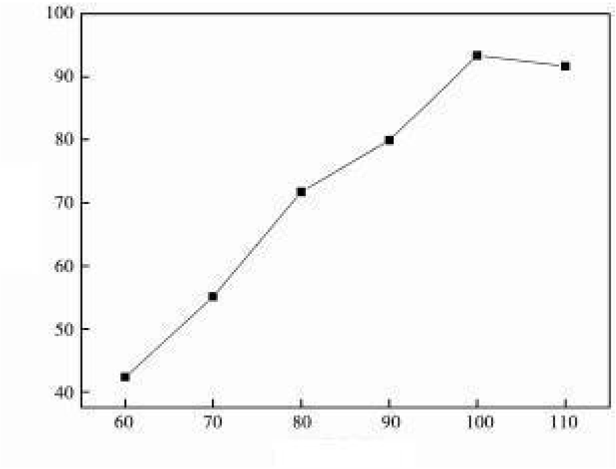

Figure 7. Effect of the reaction temperature on the catalytic esterification reaction

Note: Reaction conditions: the molar ratio of n-butyric acid to n-butanol is1:6The reaction time is 4h, The amount of the catalyst is of the mass of n-butyric acid12%.

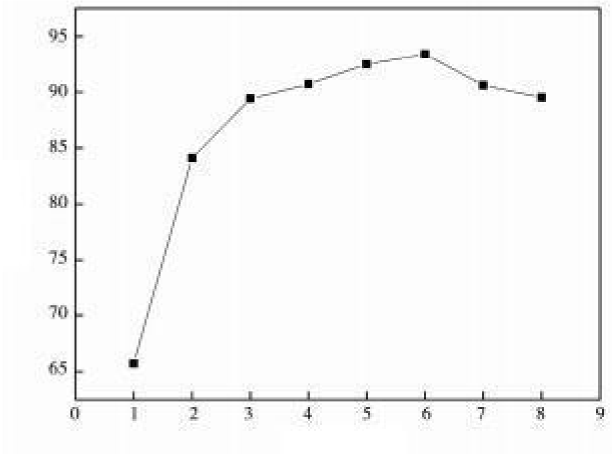

Figure 8. Effect of alkolate molar ratio on catalytic esterification

Note: Reaction conditions: the reaction time4hThe reaction temperature is100 ℃ ,The amount of catalyst is of n-butyric acid12%.The suitability of the catalyst

Use [MIMSB]$_3$Pw$_{12}$O$_{40}$To urge Chemical agent, catalyzes the esterification of n-butyric acid with different alcohols, and the results are listed in the table1. It can be seen that when catalyzing the reaction of straight chain alcohol and butyric acid, [MI MSB] 3Pw12O40 all showed excellent catalytic performance and achieved high esterification yield. However, the esterification yield of iso butanol and secondary butyl alcohol and butyrate is low, which may be related to the increased resistance of alkyl carbon chain in alcohol.

After the esterification reaction, the catalyst was recovered for XRD and IR analysis. The results are listed in Figure 1 and Figure 2 respectively. It can be seen that the catalyst is still amorphous after the reaction, especially the infrared spectrum is similar to that before use, which indicates that the keggin structure of the catalyst was not significantly affected in the reaction process, and the catalyst showed good stability.

Table 1 $[MIMSB]_3PW_{12}O_{40}$Catalyzes the reaction of n-butyric acid with different alcohols

acid	mellow wine	mole ratio	productivity /%
ethacetic acid	carbinol	1:8	94.6
ethacetic acid	alcohol	1:8	99.8
ethacetic acid	propanol ethyl carbinol	1:8	92.1
ethacetic acid	butanol	1:6	93.4
ethacetic acid	isobutanol	1:6	71.9
ethacetic acid	sec.-butyl alcohol	1:6	26.0

Note: Reaction conditions: the amount of catalyst is n-butyric acid mass12%, The reaction temperature was 100℃, reaction4h.

4. Conclusion

(1) The internal salt concentration of 1-butyl sulfonate-3-methylimidazole was achieved by mixing the aqueous solutionkegg The combination of in-structured phosphotungstic acid, for the synthesis of a novel solid acid catalyst, still has keggin structure and higher acid strength and more acid quantity points.

(2) In the esterification reaction of n-butyric acid and n-butanol, the synthesis of [MIMSB]3Pw12O40The catalyst showed good catalytic performance, and the yield of butyl butyrate was reached under more optimized conditions93.4%.

(3) The catalyst can be recovered by simple filtration, and the phase of the catalystkegg The in structure was not significantly altered and showed better stability.

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