H-ZSM-5 Catalyst in Synthesis of Diethylene Glycol Methyl Ether Acetate

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Abstract—optimizing Si/Al is 25, 38, 50, 80 four kinds of models of Na type molecular sieve, 1 mol/L concentration of ammonium nitrate by immersion, mixing, filtering, by means of the modified roasting, prepared a variety of models of H-ZSM-5 catalyst for synthesis of diethylene glycol methyl ether acetate(DGMEA). Carrier system research H-ZSM-5 zeolite catalyst in diethylene glycol dimethyl ether and direct esterification of acetic acid catalytic activity and preparation method of catalyst, the synthesis of DGMEA optimum conditions and catalyst, improve the raw material conversion rate, using XRD, TEM, FTIR and N2 adsorption-stripping way of catalyst, such as the characterization of the system. Experimental results show that in addition to the reaction temperature, time, alcohol acid mole ratio, catalyst mass, H-ZSM-5 zeolite catalyst, acid strength, stripping rate and competitive system will influence the final reaction of ester yield and selectivity. Under 85~92 ℃ temperature, using cyclohexane as dehydrant, alkyd ratio of 1:1.1, catalyst mass was 2 %, bear the load of acid amount was 15 %, 60 minutes, DGMEA yield up to 96.94 %, 100 % acetic acid conversion rate. This is mainly because acid combined with molecular sieve much channel structure play a role in the reaction.

Keywords-H-ZSM-5; DGMEA; esterification; more porous

I. INTRODUCTION

DGMEA is a non public hazards with multifunctional solvents, widely used in car paint, television sets, refrigerators, aircraft coat of high-grade paint; As the coalescing aid of emulsioni paint, largely due to the product has excellent solubility and slow evaporation rate, thus in the production of slow drying nitrocellulose lacquer, natural paint or spray paint process, is the ideal solvent. In the research work of this paper, mainly for the following work: system research new catalyst in the diethylene glycol methyl ether and esterification of acetic acid in the catalytic activity, selectivity and stability, and get the best preparation conditions, the synthesis of DGMEA best reaction process conditions of preparation of a new catalyst instead of concentrated sulfuric acid catalytic synthesis of DGMEA, study to choose the optimal alcohol acid ratio, reaction time and ratio of active component quality process conditions and choice of dehydrant, further improve the yield of the product. Domestic only one manufacturer and two foreign manufacturers, in the small-scale production and research and development stage, so DGMEA has a great potential for mining[1-10].

II. EXPERIMENT

A. Reagents and raw materials

This experiment used reagents are analytically pure. ZSM-5 powder for commercial, relative crystallinity of more than 85 %, 700 ^{o}C, hydrothermal stability of aperture 5A, specific surface area is larger than 340.

B. Characterization instruments and methods

Characterization instruments: Nicolet company 740 type Fourier transform infrared spectrometer; Quantachrome company CHEMBET-3000 type chemical adsorption instrument. Low temperature N2 adsorption characterization in AUTUSORB-1 Quantachrome company on the physical adsorption instrument, static adsorption method with N2 determination of specific surface area and pore volume of the catalyst

C. Catalytic synthesis reaction mechanism

Diethylene glycol dimethyl ether and acetic acid in the presence of acidic catalyst in esterification reaction, H+ and C=O double oxygen, decrease the electron cloud density of carbon atoms of carboxyl and, in turn, diethylene glycol methyl ether molecules attack after electron cloud density low carbon atoms, the formation of diethylene glycol methyl ether and intermediates of acetic acid, then the intermediate lose a molecule of water, lose a H+, the resulting DGMEA.

III. RESULTS AND DISCUSSION

1) *Catalyst characterization*

a) *XRD characterization*

From Fig .1 can see clearly the sample in the vicinity of 8o and 24o has obvious two characteristic peak cluster, there is no other obvious peak, and the two peak clusters with pure molecular sieve ZSM-5 spectrum peak, presumably catalyst load form for ion exchange, the design idea of consistent with the experiment, and did not destroy the molecular structure, and no other impurities are introduced. In addition to all this figure to within 5o and smooth curve, shows that synthesis of mesoporous catalysts are random irregular distribution, satisfy the test requirement, so this is our goal to H-ZSM-5 solid acid catalyst.

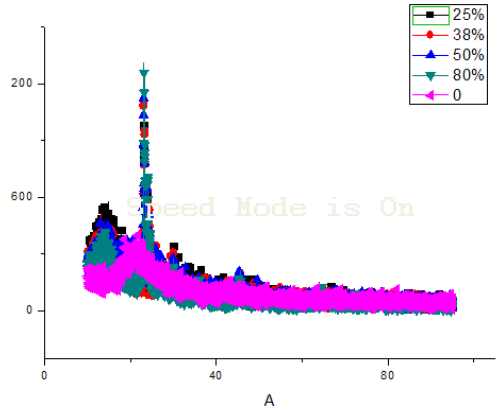

Figure 1. H-ZSM-5 solid acid catalyst for the XRD spectra

b) *FTIR characterization*

550 cm-1 secondary peak five yuan for molecular sieve double ring features vibration peak, the peak of 450 cm-1 is internal tetrahedron vibration peak, especially in the more than 1220, 1150~1050, 795 cm-1 a strong peak, the characteristic peaks of ZSM-5, this clearly indicates that the sample has the characteristics of typical structure of ZSM-5 frame vibration peak, proves that the synthesis catalyst is H-ZSM-5 solid acid catalyst.

c) *TEM characterization*

For the synthesis of the TEM images of the sample. Can be seen from the first picture of synthesis of particle size distribution of solid acid catalyst between 300~400 nm, and small small irregular edges of convex concave spherical, speculated that it may be a smaller molecular sieve nanorods aggregate. Due to not to join other organic matter, nanorods by self-assembly to form the final nearly spherical morphology, at the same time can obviously see small nanorods self-assembly into a large multi-level structure of sub-micron ball. Finally a drawings can be seen that the synthesis of H-ZSM-5 solid acid catalyst has relatively perfect multilevel channel structure, most of the nanorods beam shaped state of aggregation line throughout the grid work of the molecular sieve, the synthesis of molecular sieves has good crystallinity.

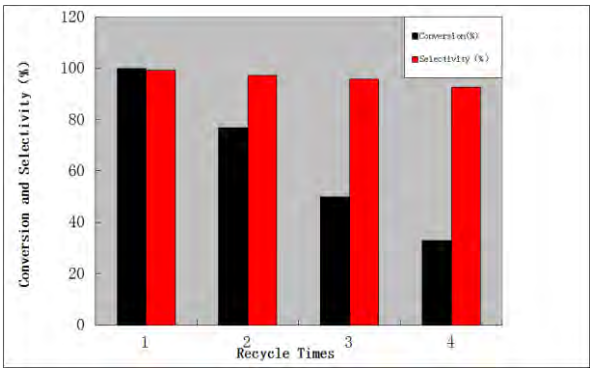

Figure 2. Reusability of H2SO4/H-ZSM-5 catalyst

2) *Catalyst service life*

By Fig .2 can be seen that the catalyst used only for the first time, close to 100% of the conversion after each use a drop about 20%, but still can keep after 4 times reuse satisfactory selectivity, so from the Angle of the engineering process, consider using bed reactor, the catalyst cycle repeated many times fully reaction will significantly increase production. Analysis of conversion rate dropped significantly with the increase of use four reasons: first, the catalyst in the esterification reaction for the first time, the carrier adsorption reaction raw material dilute the active component, lower the active components, at the same time of active component combined with alcohol ether by further reduce the number of active component, so the strength of the catalyst and the quantity will be increased with the increase of frequency is reduced, ultimately affect the conversion rate. Second, the solid acid catalyst synthesis process is difficult to guarantee

is completely absolute form of ion exchange, there may be part of the active component by physical or chemical adsorption load on the molecular sieve, this part of the active component in the reaction kettle is likely to free in raw materials, can no longer be recycled into the catalyst activity for next time use. Third, the core of the esterification catalyst is activated by Brφnsted acid acetic acid of carbonyl, good catalytic activity for catalyst, acetic acid strength must be greater than it's inevitable to form catalyst and alcohol ether competition reaction and has the advantages of other by-products generated ester, thus greatly reduces the amount of actual catalyst, is the most direct evidence of reaction end recycling of catalyst could be far less than the inputs. Fourth, the reaction temperature under mild reaction conditions is in commonly 85~85 ℃, and won't reach the catalytic cracking reaction of above 550 ℃, resulting in heterogeneous catalysts play a leading catalysis can be load in molecular sieve H+ free carrier of the active component in molecular sieve contains a large number of hydroxyl hydrogen can only have weak and extremely gentle slow catalytic effect, this can be from H molecular sieve and Na type molecular sieve esterification rate and reaction time on the comparison of proven.

a) catalyst activity evaluation

TABLEI. Summary of the catalytic activity evaluation[a]

Catalyst	Catalyst loading(wt%)	Alcohol : Acid	DGMEA Yield(%)	Selectivity (%)[b]
HZSM-5/H_2SO_4	1.1	1:1.1	99.25	100
HZSM-5/Ti_2SO_4	1.0	1:1.2	82.41	100
HZSM-5/H_3PO_4	1.1	1:1.1	62.54	90.78
HZSM-5/H_3PO_4-12MoO_3	1.0	1:1.2	46.28	82.61
HZSM-5/$H_4[Si(W_3O_{10})_4]\cdot 8H_2O$	1.0	1:1.2	35.59	65.91
HZSM-5/$H_3[P(W_3O_{10})_4]\cdot 8H_2O$	1.2	1:1.1	25.82	42.36

[a] Reaction conditions: temperature 100 ^{0}C, reaction time: 120 minutes.
[b] Selectivity to DGMEA.

As can be seen from table 1 with H2SO4 active component compared to other active component has the obvious advantage of yield and selectivity of 100%. Effect of the second Ti2SO4 is used as the active component, the yield reached 82.41 %.But Ti2SO4 need to experience the Lewis acid to Brφnsted acid transformation can play a catalytic role, the process has a lot of uncertainty, so use Ti2SO4 as active component often get yield is not stable. Test also adopted H3PO, H3PO4-12MoO3, H4[Si(W3O10)4]·8H2O and H3[P(W3O10)4]·8H2O as active component through the contrast test. Experimental data show that phosphoric acid can have high selectivity but not ideal production rate of only 62.54 %. The rest of the hetero-poly acid on the yield and selectivity were too low. So H2SO4 as active component is the most appropriate.

IV. CONCLUSION

In this paper a new type of solid acid catalyst instead of H2SO4 catalyst in synthesis of DGMEA, overcome the disadvantages of traditional industry bring a series of H2SO4. We will review the active components of H2SO4, different Si/Al ratio of ZSM-5 as catalyst carrier, the preparation of a new catalyst instead of H2SO4 catalyst in synthesis of DGMEA. H-ZSM-5 solid acid catalysts for catalytic synthesis of diethylene glycol methyl ether acetate esterification reaction time for 60 minutes and a single H2SO4 as a catalyst for catalytic synthesis of DGMEA esterification reaction time, in the chemical production in the future for product can be used in the fixed bed catalytic synthesis, recycling, has reliable security. As a result, the new H-ZSM-5 solid acid catalyst has green, environmental protection, the chemical model of circular economy. This topic preparation of a new type of H-ZSM-5 acid solid acid catalyst for B acid center, intensity of H0=-11.9, acid amount of 0.014 mmol/m2. And experiments for synthesis of DGMEA for preliminary process parameters: alkyd mole ratio of 1:1,1, dosage of catalyst was 2.59 %, the reaction time of 60 minutes or so, the reaction temperature is 85~92 ℃, using cyclohexane as dehydrant, in this process parameters under the condition of the esterification rate was 96.94 %.

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