Inserting Ethoxyl into Ethyl Acetate Catalyzed by Inorganic Al-Mg Composite Oxides

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A one-step technique is provided for producing olig-ethylene glycol ethyl ether acetate (olig-EGEEA) by inserting ethylene oxide (EO) into the linkage between carbonyl carbon and the ester oxygen of ethyl acetate (EA). Ethoxylation of ethyl acetate with Al-Mg composite oxide catalysts containing both acidic and basic active sites was studied. The catalysts for ethoxylation of ethyl acetate was screened out based on the ratio of acidic/basic active sites on the catalyst surface aiming at high product selectivity of mono- ethylene glycol ethyl ether acetate (MEGEEA). In this work, the best selectivity of MEGEEA (51.5%, w/w) was obtained at following conditions: amount of catalyst, 1.1 g/100g ethyl acetate; initial pressure, 0.1 MPa; reaction temperature, 145-150 ^{o}C; molar ratio of EA to EO, 5:1; feeding rate of EO, 0.25 $g\cdot min^{-1}$. The product selectivity of MEGEEA was not decreased dramatically after the catalyst had been used ten times.

1. Introduction

Olig-ethylene glycol ethyl ether acetate (olig-EGEEA), especially mono or di-EGEEA are excellent solvents for dye, paint, pigment. Olig-EGEEA with higher molecular weight has been used in formulation of antifreeze. So far the production of olig-EGEEA has been using two-step technique, which is, using ethylene oxide, alcohol and carbonic acid or ester, synthesizes through etherealization followed by esterification or transesterification. Comparing to the one-step approach reported in this paper, the two-step techniques are complicated in process, has to use strong acid (as the reactant or catalyst) or strong base (as catalyst or initiator), produce much more by-products and are difficult in purification since the product and the by-products would form several azeotropes.

The one-step technique provided in this paper (as showed in scheme 1), using carbonic ester as starting material to react with ethylene oxide, produces olig-EGEEA without the formation of many by-products such as water, alcohol; and there is no need to use strong acid or base during the reaction. Therefore

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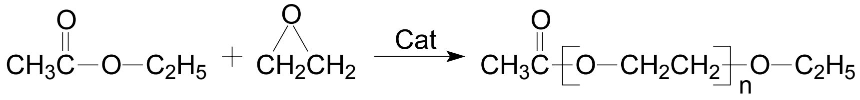
the production of olig-EGEEA becomes much simple and economic. Hoechst Co. used zirconium chloride and/or aluminium chloride as main catalyst, together with triethyl amine to catalyze the one-step synthesis of olig-EGEEA[1]. Hama *et al*.[2-4] also reported a similar approach through a reaction between a fatty acid alkyl ester with an alkylene oxide in the presence of a composite metal-oxide catalyst whose surface is modified with a metal hydroxide or a metal alkoxide. However, the catalyst they studied was mainly used for manufacturing fatty acid ester of polyoxyalkylene alkyl ether, using a fatty acid alkyl ester to react with the metal alkoxide to form a mediator before the ethoxylation. Besides, inserting ethoxyl to short chain ester is more difficult than that to long chain like fatty acid ester due to their low boiling point and vaporization.



Scheme 1. One-step approach of synthesis of olig-EGEEA (desired n=1,2)

In this paper, we developed a one-step technique to insert ethoxyl into ethyl acetate catalyzed by inorganic Al-Mg composite oxides. The catalyst was prepared from Al-Mg composite oxide calcined with slight amount of Fe, Ni or some other metal (all were group VIII metals) oxides and sodium carbonate[5,6], which has both acidic and basic active sites on the surface. To achieve high selectivity of mono- EGEEA, reaction factors such as ratio of acidic/basic active sites (acidic to basic) of the catalyst, reactant molar ratio (*n*(EA) : *n*(EO), ethyl acetate to ethylene oxide), feeding rate of EO and initial reaction pressure were studied to set the appropriate operation parameters.

2. Experimental Section

2.1. Apparatus and Reagents

Ethyl acetate, reagent grade; ethylene oxide, Yangzi Petrochemical; Al-Mg composite oxide catalyst, perpared and characterised as described in reference 5,6, with different ratio of acidic/basic active sites as 0.28, 0.38, 0.45, 0.53, 0.63, 0.70, respectively; WHF-0.5L high pressure reactor, Shandong Weihai Autmatic Control Reaction Kettle Co.; GC, FULI 9697, FULI Analytical Instrument, Zhejiang,China; ESI-MS, ZMD MS,Waters; IR , MB 104, ABB Bomem.

2.2. Synthesis of olig-ethylene glycol ethyl ether acetate

100 g ethyl acetate and 1.1 g catalyst were added into a 500 mL reactor, closed the lip and then completely blow out the reactor with nitrogen for 3 times. After heating the reactant mixture to the desired temperature, ethylene oxide was added with desired amount in a constant feeding rate into the reactor. Upon finishing the addition of EO, remained the reaction under stirring 15 min at the desired reaction temperature.

2.3. Analytical Methods

2.3.1. Electro-Spray Ionization Mass Spectrometry (ESI-MS) Analysis of olig-EGEEA

ESI-MS (ES^+) was applied to identify the compositions of crude product.

2.3.2. Gas chromatography (GC), GC-MS analysis of olig-EGEEA

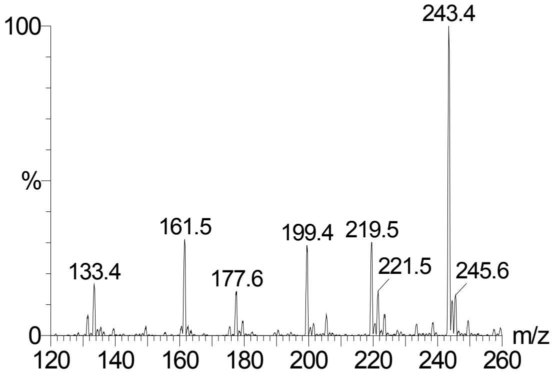
Further product separation and structure characterizing was performed by GC-MS measurement. A computer-controlled Trace gas chromatograph equipped with a PEG-30 column, and Trace MS detector was served. The gas chromatograph column temperature was held at 50 °C for 2 min then increased to 200 °C at 10 °C/min, and then held at 200 °C for 15 min.

Quantitative analysis of the product composition was performed with GC measurement. Ethyl heptanoate was added as an internal standard. FULI 9697 gas chromatograph equipped with a SE-54 column separated the sample constituents. The gas chromatograph column temperature was held at 200 °C. SrAdv chromatograph station was used for the signals produced by the flame ionization detector to produce chromatograms and perform the quantitative analysis.

3. Results and Discussion

3.1. The inserted ethoxylation of ethyl acetate

As described in section 2.3, a slight yellow liquid was obtained after the reaction. The ESI-MS spectrum of the crude product is as Figure1.



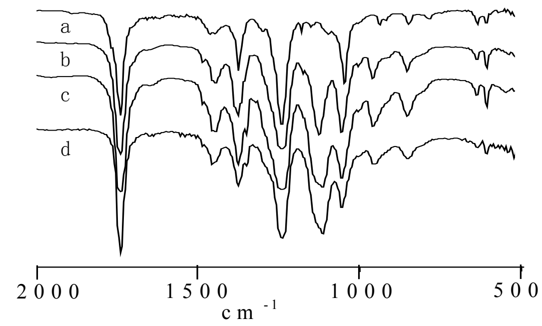
m/z＝199.4,243.4 indicate $(M+Na)^+$ peak of DEGEEA and TEGEEA(tri-ethylene glycol ethyl ether acetate) , respectively；

m/z＝133.4, 177.6, 221.5 indicate $(M+H)^+$ peak of MEGEEA, DEGEEA and TEGEEA, respectively.

Figure 1. ESI-MS spectrum of pre- product before fractionating

（reaction conditions:initial pressure, 0.1 MPa; reaction temperature, 155-160^{o}C; n(EA) : n(EO)＝2:1; feeding rate of EO, 0.25 g•min^{-1}）

Removing ethyl acetate from the crude product by vacuum distillation at 400Pa and then collecting distillation fractions of 36 ^{o}C; to 38 ^{o}C, 86 ^{o}C to 88 ^{o}C, and 134 ^{o}C to 136 ^{o}C. GC measurement shows that the mass fractions for olig-EGEEA in each distillation fraction was: w(MEGEEA)＝99.7%, w(DEGEEA)＝98.0%, w(TEGEEA)＝95.9%, respectively.



a：ethyl acetate b：fraction between 36 ^{o}C to 38 ^{o}C c： fraction between 86 ^{o}C to 88 ^{o}C d：fraction between 134 ^{o}C to 136 ^{o}C

Figure 2. FT-IR spectrum of product distillation fractions

（reaction conditions: initial pressure, 0.1 MPa; reaction temperature, 155-160 ^{o}C; n(EA) : n(EO)＝2:1; feeding rate of EO, 0.25 g•min^{-1}）

The measurement of FT-IR and ESI-MS characterized that the desired ethoxylation of ethyl acetate was accomplished.

3.2. Influence of ratio of acidic/basic active sites on product selectivity

The formed mono-EGEEA can react with the coming EO to form a series of product with an EO adduct distribution. Our previous studies[5] indicates that the most important impact factor on the adduct distribution of the products is the ratio of acidic/basic active sites on the catalyst surface, in a certain range, high ratio induces narrow adduct distribution, i.e., high selectivity. So in order to obtain high selectivity of mono-EGEEA (w(MEGEEA), defined as its mass fraction in the product), catalyst has to be screened out from those with different ratio of acidic/basic active sites. Thus we chose a serious catalyst with ratios of acidic/basic active sites of 0.28 - 0. 7, which provided high conversion of the ester[5]. Figure 3 shows that the optimum ratio of acidic/basic active sites for the highest selectivity (42.5%) of mono-EGEEA was 0.63, where the total amount of mono- and di-EGEEA reached the highest (70.9%) also. This result confirmed again that high product selectivity requires a suitable ratio of acidic/basic active sites. More acidic sites favours the formation of mono-EGEEA, but extra acidic sites would help the self-polymerization of EO and therefore induced less formation of olig-EGEEA. The later was confirmed by more PEG detected in the product mixture (data not shown).

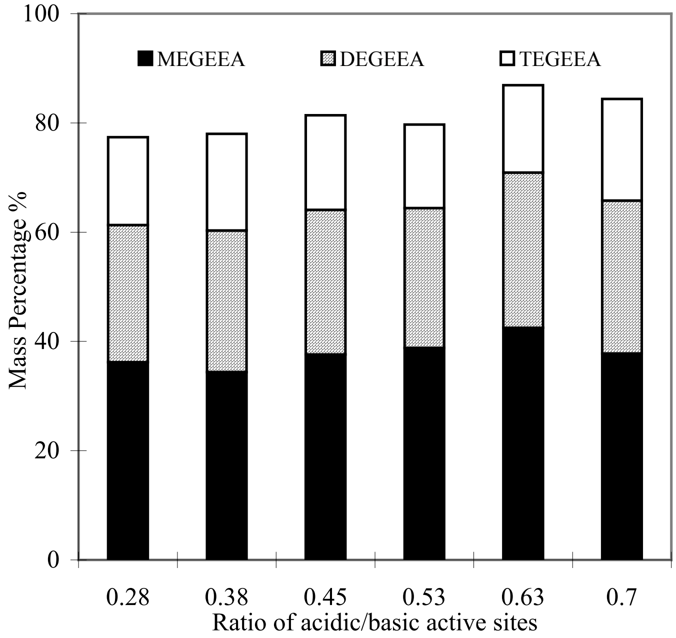


Figure 3. Influence of ratio of acidic/basic active sites on product selectivity （initial pressure, 0.1 MPa; reaction temperature, 155-160 ^{o}C; *n*(EA) : *n*(EO)＝2:1; feeding rate of EO, 0.25 g•min^{-1}）

The used catalyst, say, the one with a ratio of acidic/basic active sites of 0.63 can be reused after filter, washing and drying. The selectivity of MEGEEA was 42.6%, 41.6% and 40.5%, after used twice, three times and 10 times, respectively.

The catalyst with a ratio of acidic/basic active sites of 0.63 was used over all following sections.

3.3. Influence of reaction conditions on product selectivity

3.3.1. Influence of molar ratio of ethyl acetate to ethoxyl oxide

Figure 4 illustrates that the selectivity of mono-EGEEA increased with increasing molar ratio of ethyl acetate to ethoxyl oxide, i.e, n(EA):n(EO) until the ratio reached 5:1, where the mass percentage of mono-EGEEA was 51.5% and the total amount of olig-EGEEA reached the highest (74.5%). While increasing n(EA) : n(EO) to 8:1, although the mass percentage of mono-EGEEA increased to 57.3% but the total amount of olig-EGEEA (74.4%) almost remained the same as that of n(EA) : n(EO) of 5:1, therefore, for the sake of economics, the suitable n(EA) : n(EO) is 5:1.

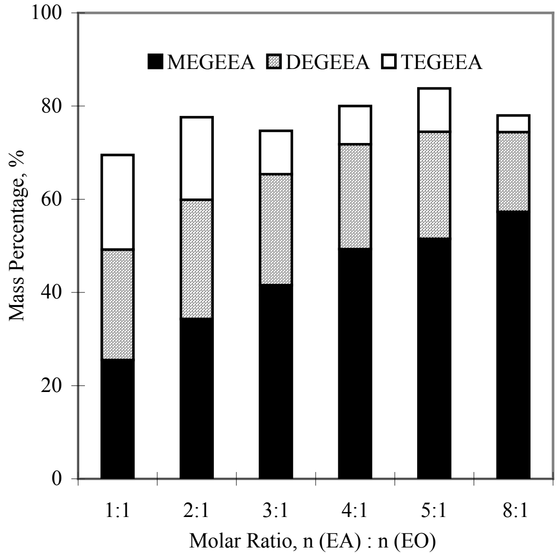


Figure 4. Influence of *n*(EA) : *n*(EO) on product selectivity (initial pressure, 0.1 MPa; reaction temperature, 155-160 °C; feeding rate of EO, 0.4 g•min^{-1})

3.3.2. Influence of initial reaction pressure

The initial reaction pressure here defined as the pressure in the reactor before heating the reactor. Inserting ethoxyl into ethyl acetate is a reaction of volume reducing, so the initial system pressure affects the reaction by influencing the partial pressure of ethylene oxide. As shown in Table 1, increasing the initial pressure decreased the selectivity of MEGEEA and olig-EGEEA. At the meantime, the reaction rate slowed down dramatically under higher initial pressure (data not shown).

Table 1. Influence of initial pressure on product selectivity*

Initial pressure (Mpa)	*w*(MEGEEA) (%)	*w*(DEGEEA) (%)	*w*(TEGEEA) (%)
0.1	42.5	28.4	16.0
0.2	39.2	26.4	16.7

* feeding rate of EO, 0.25 g•min^{-1}; initial pressure, 0.1 Mpa; reaction temperature, 155-160 °C; *n*(EA) : *n*(EO)＝2:1

3.3.3. Influence of reaction temperature

Table 2 shows that lower reaction temperature yielded higher selectivity of

MEGEEA. Reactions conducted below 130 °C were very slow or even not happened. So the suitable temperature is 145-150 °C.

Table 2. Influence of reaction temperature on product selectivity

Reaction temperature (°C)	*w*(MEGEEA) (%)	*w*(DEGEEA) (%)	*w*(TEGEEA) (%)
135-140	42.0	19.7	9.8
145-150	41.1	20.5	10.9
155-160	38.8	25.6	15.3
165-170	38.1	27.1	16.9

[*] initial pressure, 0.1 Mpa; feeding rate of EO, 0.25 g•min^{-1}; *n*(EA) : *n*(EO)＝2:1

3.3.4. Influence of EO feeding rate

High feeding speed can speed up the reaction but lower down the selectivity. We finally chose 0.25g•min^{-1} as the applied feeding rate of EO.

Table 3. Influence of feed rate of EO on product selectivity[*]

EO feeding rate (g•min^{-1})	*w*(MEGEEA) (%)	*w*(DEGEEA) (%)	*w*(TEGEEA) (%)
0.80	28.1	25.0	18.1
0.40	34.3	25.6	17.7
0.30	37.2	26.0	16.2
0.25	42.5	28.4	16.0

[*] initial pressure, 0.1 MPa; reaction temperature, 155-160 °C; *n*(EA) : *n*(EO)＝2:1

3.4. The ethoxylation conducted under optimum conditions

In a conclusion, the suitable reaction parameters for this technique are: catalyst with a ratio of acidic/basic activity sites of 0.63; initial pressure, 0.1 Mpa; reaction temperature, 145-150 °C; molar ratio of the reactants, *n*(EA):*n*(EO)＝5:1; EO feeding rate, 0.25 g•min^{-1}. We further screened the catalysts with different ratio of acidic/basic activity sites under the above conditions, the optimum activity sites ratio still remains the same as the above(0.63), while the product selectivity was: *w*(EGEEA)＝51.5%, *w*(DEGEEA)＝22.3% and *w*(TEGEEA)＝8.5%.

4. Conclusions

This study shows the production of olig-EGEEA by one-step inserting ethylene oxide into ethyl acetate can be achieved through Al-Mg composite oxide catalysts containing both acidic and basic active sites. Adjusting the ratio of acidic/basic active sites on the catalyst surface and other operation parameters can improve product selectivity of olig-EGEEA. In this work, the best selectivity of MEGEEA (51.5%, w/w) was obtained at following conditions: amount of catalyst, 1.1 g/100g ethyl acetate; initial pressure, 0.1 MPa; reaction temperature, 145-150 ^{o}C; molar ratio of EA to EO, 5:1; feeding rate of EO, 0.25 g•min^{-1}. The product selectivity of MEGEEA was not decreased dramatically after the catalyst had been used ten times. Operating at these conditions permits a complete experimental run to be accomplished in 2-3 h (starting from feeding EO).

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