

Preparation, Characterization and Catalytic Activity of Alkyl Benzene Sulfonic Acid Carbon-Based Acid Catalyst

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Abstract

Based on starch and series of alkyl benzene sulfonic acid as the materials, a novel carbon-based solid acid catalyst is synthesized using hydrothermal method. This catalyst exhibits much higher catalytic activity in the reaction of esterification of Mono-fatty alcohol polyoxyethylene maleate esters with 1,4-butanediol. The structure of carbon-based solid acid catalyst was characterized by IR and XRD, characterizations showed that this catalyst exhibited high $-SO_3H$ loading. Reusability of the carbon-based solid acid catalyst for esterification showed that after recycling five times the activity remained unchanged.

Keywords

Alkyl Benzene Sulfonic Acid, Carbon-Based Solid Acid Catalyst, Esterification

1. Introduction

The principles of green chemistry and increasing concerns about environmental issues have stimulated the research for recyclable strong solid acids to replace of conventional toxic and corrosive acid catalysts, such as sulfuric acid [1]. Integration of acidic functional groups (e.g., $-SO_3H$) into solid surface, e.g. carbonaceous [2]-[5] or silica-based materials [6]-[9], has been explored to produce promising solid acids. Among them, the sulfonated carbon materials have received much attention due to their low costs, high stability, and high activities. Sulfonated carbonaceous materials were usually synthesized through the oxidation of carbon materials by sulfur acid [10] [12] or oleum [13] [14] to generate sulfonic acid groups on the surface. For example, Hara *et al.*

[10] [11] obtained a series of carbon-based catalysts with acid densities ranging from 0.37 to 1.34 mmol H⁺/g by the sulfonation of incompletely carbonized sugars. Similarly, Budarin *et al.* [12] synthesized a mesoporous sulfonated Starbon-400 with 0.5 mmol/g SO₃H loading. An ordered mesoporous phenol-formaldehyde resin [14] was also functionalized with sulfonate groups by putting the material in the vapor of fuming sulfuric acid inside an autoclave. Ryoo *et al.* [15] synthesized an ordered mesoporous carbons (OMCs) through the nanocasting technique using OMCS as templates or via self-assembly of phenolic resins and block copolymers [16] [17]. These materials exhibit high surface area, narrow pore size distribution, and large pore volume. Recently, a new class of sulfonated carbons (C-SO₃H) derived from the incomplete carbonization of simple sugars and starch were reported to show excellent catalytic performance for the synthesis of biodiesel [18]-[20].

2. Experiment Procedures

Alkyl benzene sulfonic acid was synthesized according to the literature; fatty alcohol polyoxyethylene ether (AEO-3) was from Liao Yang Oak polyether Co., Ltd. (Liaoyang, Liaoning Province, China). The catalyst was synthesized according to the literature. Maleic anhydride (MAH) was obtained from Kemiou (Tianjin, China). Nitrogen was of high grade purity from Xue Long (99.99% purity, Daqing, China). The IR spectra was obtained on a 4300 Shimadzu spectrophotometer as KBr disks. XRD (Rigaku, Tokyo, Japan).

2.1. Synthesis of Alkyl Benzene Sulfonic Acid

The synthesis procedure of alkyl benzene sulfonic acid is as shown in the References [21]-[24], and the molecular structure of alkyl aryl benzene sulfonic acid as following in **Scheme 1**.

2.2. Synthesis of the Carbon-Based Solid Acid Catalyst

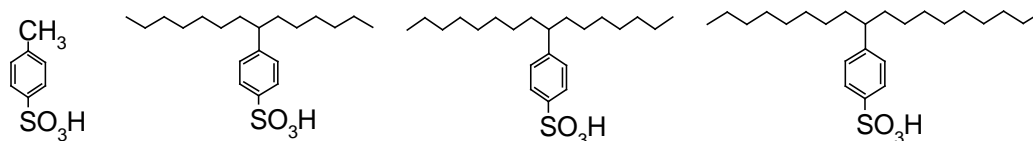
In typical procedure: 15 g starch and 15 g sulfonic acid were mixed together and transferred to the quartz furnace. The mixture was heated to 200°C from room temperature with the heating rate of 1°C/min and remained at 200°C for 12 h under nitrogen atmosphere. After cooling to room temperature, obtained black solid was washed with deionized water until no acidity detected in the filtrate. The novel solid acid was obtained after drying at 120°C overnight in an oven and grinding it into fine flour. P-toluene sulphonic acid carbon-based solid acid catalyst, tetradecyl benzene sulphonic acid carbon-based solid acid catalyst, hexadecyl benzene sulphonic acid carbon-based solid acid catalyst and octadecyle benzene sulphonic acid carbon-based solid acid catalyst are abbreviated in what follows as cat 1, cat 2, cat 3, cat 4 respectively.

2.3. Synthesis of Mono-Fatty Alcohol Polyoxyethylene Maleate Esters

Mono-fatty alcohol polyoxyethylene maleate esters were synthesized by 0.1 mol (9.806 g) of maleic anhydride (MAH) reacted to 0.1 mol (31.695 g, M = 317.695 g/mol) of fatty alcohol polyoxyethylene (AEO-3) and 0.1% (wt) p-toluene sulphonic acid served as a catalyst for 8 h with heating at 80°C. Standard titration solution of NaOH was used to determine the system acid value, and when the variation of acid value was less than 1 mg/h, it was regarded as near the end point of esterification. The crude product was recrystallized from ethanol and water (V/V = 1:1) to three times. Compound 1a was obtained in 95.66%.

2.4. Synthesis of Bis(Mono-Fatty Alcohol Polyoxyethylene Maleate)1,4-Butanediol Ester

0.05 mol (20.515 g) of compound 1 reacted with 0.025 mol (2.253 g) of 1,4-butanediol and 1% (wt) of carbon-based solid acid served as catalyst under vacuum degree of -0.09 mpa at 150°C reacting 10 h. and real-time detection of acid value. The esterification rate was calculated using the following formula [25]-[27]: (Er) = (1-



Scheme 1. The molecular structure of alkyl aryl benzene sulfonic acid.

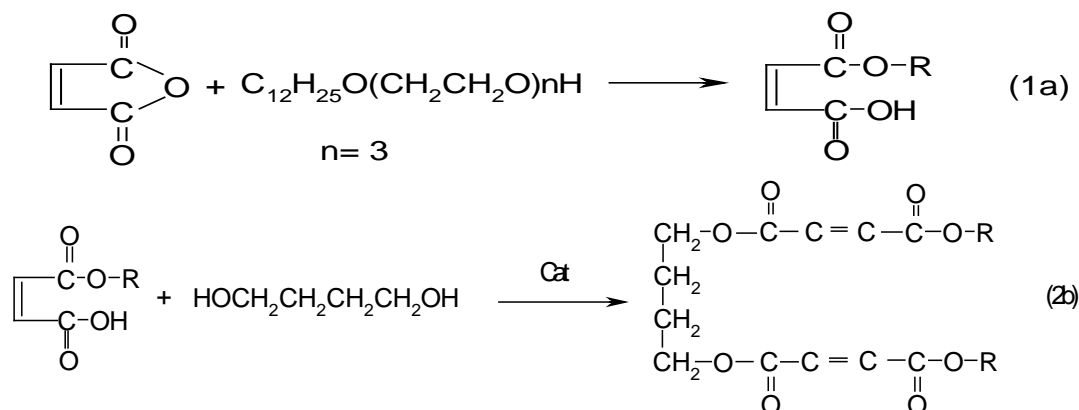
$AV_a/AV_b \times 100\%$, where Er is esterification rate, AV_a is Final acid value, AV_b is Initial acid value. The typical procedure (Scheme 2).

3. Results and Discussion

The reaction mechanism is most probably like this: Firstly, the starch was dehydrated into small organic molecules, mainly 5-(hydroxymethyl)-2-furaldehyde (HMF) [28]-[30], and the generated HMF could be hydrothermally carbonized into a carbon-rich resin as well as react with alkyl benzene sulfonic acid to “embed” sulfonic acid groups as is shown in Scheme 3.

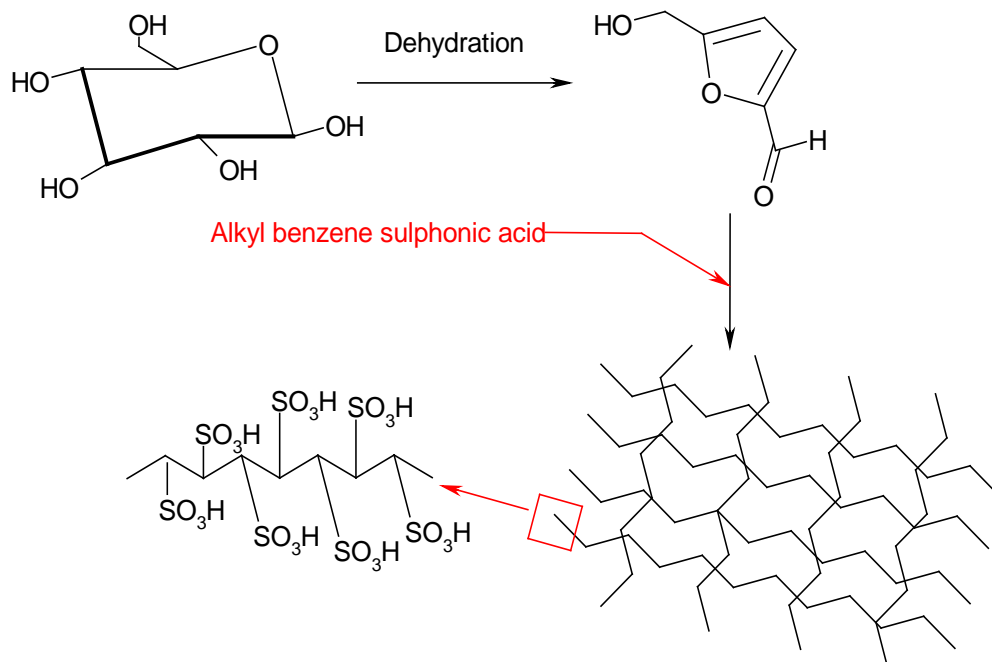
3.1. Characterization of Carbon-Based Solid Acid Catalyst

The FT-IR spectrum Figure 1 showed that the carbon-based solid acid contain resident functionalities including,



Cat 1: p-toluene sulphonic acid catalyst, Cat 2: tetradecyl benzene sulphonic acid catalyst
Cat 3: hexadecyl benzene sulphonic acid catalyst, Cat 4: octadecyle benzene sulphonic acid catalyst

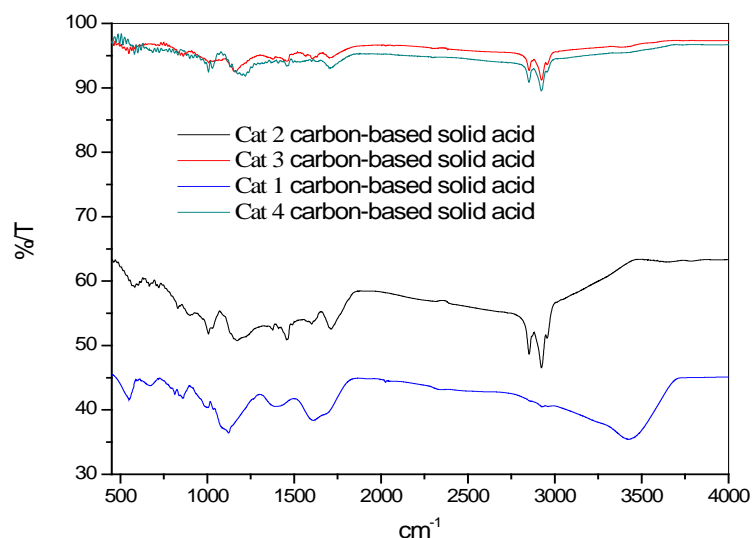
Scheme 2. Synthesis route of the reaction.



Scheme 3. Hydrothermal method to synthesis of carbon-based solid acid.

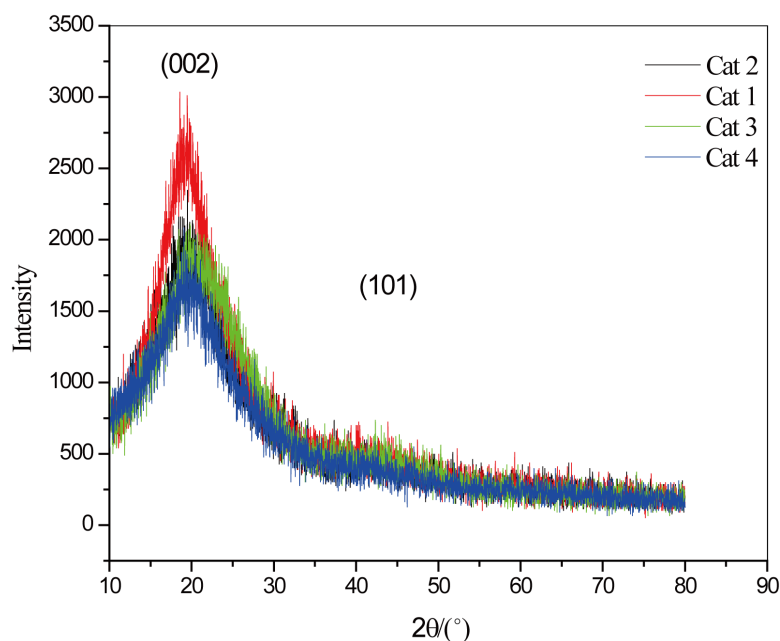
1007 cm^{-1} , 1032 cm^{-1} (S=O str). 1118 cm^{-1} (SO_3H str), 1710 cm^{-1} (C=O bend), 3450 cm^{-1} (OH str) On the other hand, the bands due to -OH stretching at 3420 cm^{-1} , and C=C bonds stretching at 1620 cm^{-1} were observed for both samples independent of the sulfonation. It is shown that the carbon-based solid acid have the group of $-\text{SO}_3\text{H}$.

The XRD pattern (Figure 2) contains two broad and weak diffraction peaks C (002) diffraction peak ($2\theta = 10^\circ - 35^\circ$) attributable to amorphous carbon composed of aromatic carbon sheets oriented in a considerably ran



Cat 1: p-toluene sulphonic acid catalyst, Cat 2: tetradecyl benzene sulphonic acid catalyst
Cat 3: hexadecyl benzene sulphonic acid catalyst, Cat 4: octadecyle benzene sulphonc acid catalyst
The IR spectra was obtained on a 4300 Shimadzu spectrophotometer as KBr disks.

Figure 1. FT-IR spectrum of carbon-based solid acid.



Cat 1: p-toluene sulphonic acid catalyst, Cat 2: tetradecyl benzene sulphonic acid catalyst
Cat 3: hexadecyl benzene sulphonic acid catalyst, Cat 4: octadecyle benzene sulphonc acid catalyst

Figure 2. XRD of carbon-based solid acid XRD (Rigaku, Tokyo, Japan).

dom fashion. A definitive C (101) diffraction peak ($2\theta = 35^\circ - 45^\circ$) due to the a axis of the graphite structure can be seen. The X-ray diffractogram is similar to that of char because the sulfonic acid groups were attached to edges of isotropic carbon sheets and the solid acid exhibits broad diffraction peaks of amorphous carbon [31]-[33].

3.2. Qrthogonal Experiment of Cat 1 Carbon-Based Solid Acid

The optimum reaction conditions from **Table 1** was obtained as follows: $m_{\text{starch}}:m_{\text{cat 1}} = 1:1$, reaction temperature: 220°C , reaction time: 10 h, All results were repeated for three times: Esterification rate were 91.85%, 90.63% and 90.71% respectively, average value was 91.06%.

3.3. Qrthogonal Experiment of Cat 2 Carbon-Based Solid Acid

The optimum reaction conditions from **Table 2** was obtained as follows: reaction temperature: 180°C ; reaction

Table 1. Qrthogonal experiment of Cat 1 carbon-based solid acid.

Factor	Temperature/ $^\circ\text{C}$	Hour/h	$m_{\text{starch}}:m_{\text{cat1}}^*$	Esterification rate/%
Experiment 1	180	8	1:1	91.57
Experiment 2	200	10	1:1	90.49
Experiment 3	220	12	1:	85.88
Experiment 4	180	10	2:1	87.13
Experiment 5	200	12	2:1	88.65
Experiment 6	220	8	2:1	90.12
Experiment 7	180	12	3:1	87.12
Experiment 8	200	8	3:1	85.89
Experiment 9	220	10	3:1	91.72
Average 1	88.607	89.193	89.313	
Average 2	88.343	89.780	88.633	
Average 3	89.240	87.217	88.243	
Standard deviation	0.897	2.563	1.070	

* Average 1 is experiments 1, 4, 7; Average 2 is 2, 5, 8; Average 3 is 3, 6, 9.

Table 2. Qrthogonal experiment of Cat 2 carbon-based solid acid.

Factor	Temperature/ $^\circ\text{C}$	Hour/h	$m_{\text{starch}}:m_{\text{cat2}}$	Esterification rate/%
Experiment 1	180	8	1:1	93.92
Experiment 2	180	10	2:1	90.82
Experiment 3	180	12	3:1	88.52
Experiment 4	200	8	2:1	90.27
Experiment 5	200	10	3:1	89.99
Experiment 6	200	12	1:1	89.35
Experiment 7	220	8	3:1	71.17
Experiment 8	220	10	1:1	88.15
Experiment 9	220	12	2:1	85.98
Average 1	91.087	85.120	90.473	
Average 2	89.870	89.653	89.023	
Average 3	81.767	87.950	83.227	
Standard deviation	9.320	4.533	7.246	

* Average 1 is experiments 1, 4, 7; Average 2 is 2, 5, 8; Average 3 is 3, 6, 9.

time: 10 h; $m_{\text{starch}}:m_{\text{cat2}} = 1:1$, All results were repeated for three times: Esterification rate were 88.04%, 86.98% and 90.82%, average value was 88.61%.

3.4. Qrthogonal Experiment of Cat 3 Carbon-Based Solid Acid

The optimum reaction conditions from **Table 3** was obtained as follows: reaction temperature: 220°C, reaction time: 10 h, $m_{\text{starch}}:m_{\text{cat3}} = 1:3$, All results were repeated for three times: Esterification rate were 91.08%, 89.42% and 89.92%, average value was 90.14%.

3.5. Qrthogonal Experiment of Cat 4 Carbon-Based Solid Acid

The optimum reaction conditions from **Table 4** was obtained as follows: reaction temperature: 180°C; reaction time: 12 h; $m_{\text{starch}}:m_{\text{cat4}} = 1:1$, All results were repeated for three times: Esterification rate were 90.07%, 91.98% and 93.06%, average value was 91.70%.

Table 3. Qrthogonal experiment of Cat 3 carbon-based solid acid.

Factor	Temperature/°C	Hour/h	$m_{\text{starch}}:m_{\text{cat3}}$	Esterification rate/%
Experiment 1	180	8	1:1	80.02
Experiment 2	180	10	2:1	81.18
Experiment 3	180	12	3:1	84.11
Experiment 4	200	8	2:1	80.38
Experiment 5	200	10	3:1	80.94
Experiment 6	200	12	1:1	77.39
Experiment 7	220	8	3:1	90.23
Experiment 8	220	10	1:1	90.67
Experiment 9	220	12	2:1	91.29
Average 1	81.770	83.543	82.693	
Average 2	79.570	84.263	84.283	
Average 3	90.730	84.263	85.093	
Standard deviation	11.160	0.720	2.400	

*Average 1 is experiments 1, 4, 7; Average 2 is 2, 5, 8; Average 3 is 3, 6, 9.

Table 4. Qrthogonal experiment of Cat 4 carbon-based solid acid.

Factor	Temperature/°C	Hour/h	$m_{\text{starch}}:m_{\text{cat4}}$	Esterification rate/%
Experiment 1	180	8	1:1	89.11
Experiment 2	180	10	2:1	89.68
Experiment 3	180	12	3:1	91.26
Experiment 4	200	8	2:1	90.1
Experiment 5	200	10	3:1	83.84
Experiment 6	200	12	1:1	90.53
Experiment 7	220	8	3:1	86.9
Experiment 8	220	10	1:1	91.93
Experiment 9	220	12	2:1	87.81
Average 1	90.017	88.703	90.523	
Average 2	88.157	88.483	89.197	
Average 3	88.880	89.867	87.333	
Standard deviation	1.860	1.384	3.190	

*Average 1 is experiments 1, 4, 7; Average 2 is 2, 5, 8; Average 3 is 3, 6, 9.

3.6. Comparison of Catalytic Activities

The esterification at 0.05 mol (20.515 g) of compound 1a reacted to 0.025 mol (2.253g) of 1,4-butanediol and 1% (wt) of carbon-based solid acid was used as catalyst under vacuum degree of -0.09 mpa at 150°C reacting 10 h. From **Figure 3** we can see that alkyl benzene sulfonic acid carbon-based solid acid catalyst (cat2, cat3, cat4) has the same catalytic activity with p-toluene sulphonic acid carbon-based solid acid catalyst (cat1) in the reaction of esterification of Mono-fatty alcohol polyoxyethylene maleate esters with 1,4-butanediol.

The reusability of the alkyl benzene sulfonic acid carbon-based solid acid catalyst was investigated for the reaction of esterification. After the reaction had reached equilibrium, the novel carbon-based acid was simply recovered by filtration and recycled for further reaction. It was confirmed that the activity remained unchanged, even after the catalyst had been recycled five times (**Figure 4**).

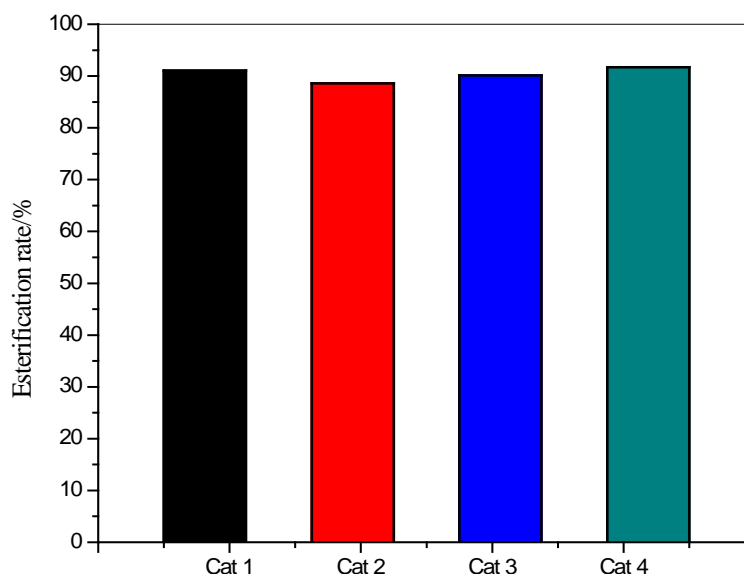


Figure 3. Catalytic activity.

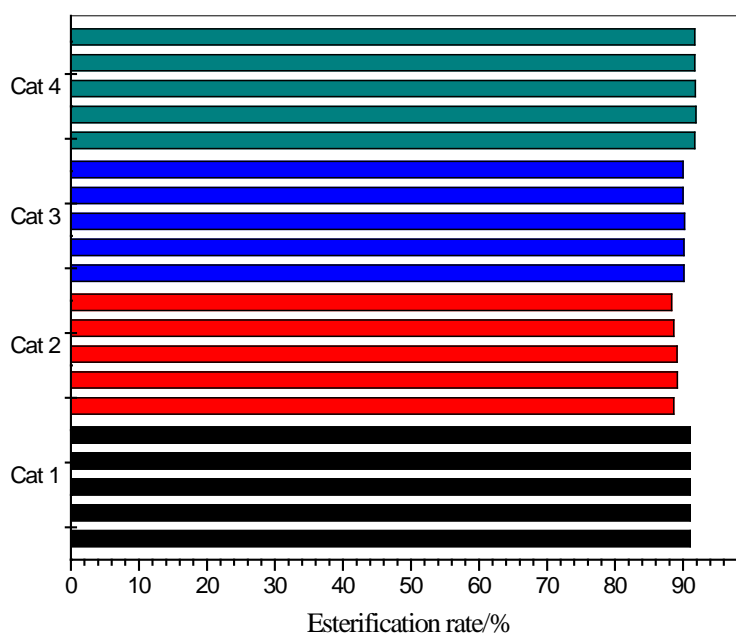


Figure 4. Reusability of carbon-based solid acid catalyst for esterification.

4. Conclusion

A novel and facile method for preparing highly active carbon-based solid-acid catalyst functionalized with sulfonic acid groups was reported. In this method, alkyl benzene sulfonic acid was used in the synthesis instead of concentrated/fuming sulfur acid and the preparation was made safer by avoiding usage of dangerous chemicals. The so-prepared catalyst exhibits much higher catalytic activity in the reaction of esterification of Mono-fatty alcohol polyoxyethylene maleate esters with 1,4-butanediol. The cycle usage test indicated that the catalyst prepared by this method was relative stable.

Acknowledgements

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