Hierarchical ZSM-12 Nanolayers for Esterification of Ethanol and Levulinic Acid to Ethyl Levulinate

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Abstract: Hierarchical ZSM-12 nanolayers have been successfully synthesized by hydrothermal process with dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride (TPOAC) as a second structure-directing agent (SDA). XRD and SEM results confirm the characteristic peaks of ZSM-12 and stacking nanolayers morphology, respectively. Moreover, the catalyst obviously exhibits high surface area and mesoporosity. To illustrate its benefit, esterification of bulky molecule such as levulinic acid and ethanol to ethyl levulinate has been studied. Preliminary results show that hierarchical ZSM-12 exhibits high ethanol conversion within 24 hr because of its large straight channels. It opens up perspectives for the design of hierarchically straight large-pore zeolites for bulky-molecule reactions.

Keywords: ZSM-12, Nanolayers, Ethyl levulinate.

1. Introduction

Ethyl Levulinate is one of the most important chemicals for many industries such as flavoring and fragrance industries. Moreover, it is an excellent additive as a diesel miscible biofuel (DMB) in regular diesel car engines[1]. In bio-oil upgrading, there are many approaches to improve the quality of bio-oil including hydrodeoxygenation (HDO), ketonisation, aldol condensation, and esterification. The most important alternative way is an esterification, which can upgrade bio-oils from alcohol and acid, resulting in reducing oxygen and acidity[2]. Zeolites are heterogeneous catalysts, facilitating esterification reactions by their acid properties. In addition, ZSM-12 containing MTW zeolite structure has one dimensional 12-membered rings channel, which appropriate for bulky molecules as ethyl levulinate[3]. However, the conventional ZSM-12 composes of only pure microporous structure causing to the diffusion limitation. In the present study, it opens up the new design of hierarchical ZSM-12 with stacking nanolayers structures to achieve the good efficiency for the reaction involving bulky molecules.

2. Experimental (or Theoretical)

Cyclic diammonium (CDM) was synthesized from α,α′-dichloro-p-xylene and N,N,N',N'-tetramethyl-1,6-hexanediamine to be used as a structure-directing agent (SDA) of large porous zeolite. Hierarchical ZSM-12 nanolayers was synthesized by the molar ratio of $30Na_2O$: $100SiO_2$: $1.25Al_2O_3$: 10CDM : $15H_2SO_4$: $6000H_2O$[4] with adding TPOAC as a second SDA. After the preparation of well mixing solution, the gel composition was transferred to Teflon-liner stainless steel autoclave reactor and then crystallized by a simple hydrothermal method. The catalyst was calcined at 650°C for 8 hr to remove templates. After that, it was treated in an aqueous solution of NH_3Cl at 80°C for 2 hr and then calcined at 550°C for 6 hr to produce the proton-formed catalyst. All catalysts were characterized by XRD, XRF, SEM, N_2 physisorption technique, and NH_3-TPD. Finally, they were tested in esterification reaction of ethanol and levulinic acid to obtain ethyl levulinate as a main product.

3. Results and discussion

Firstly, hierarchical ZSM-12 nanolayers have been successfully synthesized by varying TPOAC content to optimize the synthesized condition to obtain well-defined structures. According to XRD results, almost all samples show characteristic patterns of ZSM-12 with high crystallinity except the one synthesized by using TPOAC with the molar concentration of 0.14 M, containing the broad peak of amorphous phase. Interestingly,

SEM images demonstrate the evolution of crystal morphology as a function of TPOAC content. For example, the hierarchical ZSM-12 obtained using TPOAC with the molar concentration of 0.03 M results in forming very homogeneous particles with cubic structure on the surface, whereas the one synthesized using the appropriate TPOAC content contributes the beautiful stacking nanolayers. However, the morphology changes to amorphous topology when increasing the TPOAC content (the TPOAC molar concentration of 0.14 M). In addition, the hierarchical ZSM-12 exhibits high ethanol conversion of esterification with levulinic acid within 24 hr with almost 100 % selectivity of ethyl levulinate (not including water).

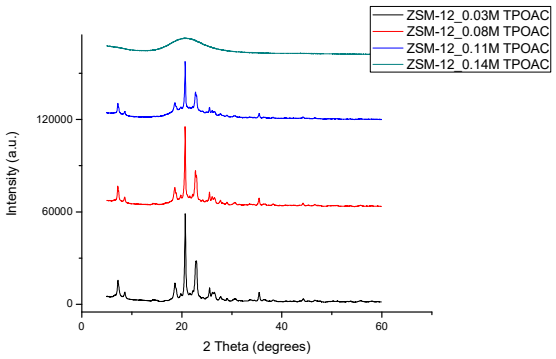

Figure 1. XRD patterns of synthesized ZSM-12 using various TPOAC contents (0.03, 0.08, 0.11 and 0.14 M)

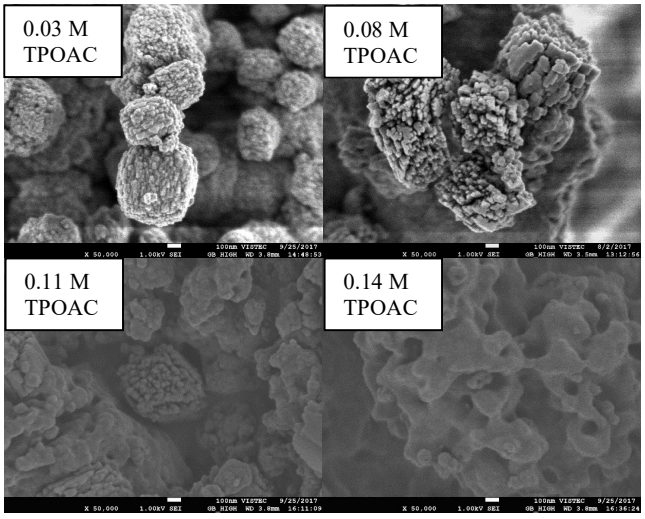

Figure 2. SEM images of synthesized ZSM-12 using various TPOAC contents (0.03, 0.08, 0.11 and 0.14 M)

4. Conclusions

Hierarchical ZSM-12 nanolayers have been successfully prepared with the aid of TPOAC in the molar concentration rage of 0.03 to 0.14 M. The most appropriate TPOAC content is 0.08 M. The preliminary results show that the hierarchical ZSM-12 exhibits high ethanol conversion to ethyl levulinate within 24 hr.

References

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