

Synthesis, characterization and catalytic activity of acetalization over Al-SBA-1 molecular sieve

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Al-SBA-1 분자체에서 acetalization 반응의 합성, 촉매활성화 및 특성

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Abstract

Al-SBA-1(Si/Al = 40, 80 and 120) and Al,Mg-SBA-1 (Si/(Al+Mg) = 40 and 80) molecular sieves were synthesized and characterized. Acetalization of n-heptanal with methanol was studied under autogenous pressure between 80 and 150°C. Since protonation of n-heptanal was fast, addition of methanol to the same to formed hemiacetal slowly whereas conversion of hemiacetal to acetal was fast. The catalysts exhibited nearly similar conversion irrespective of their difference in acidity, and all of them showed more than 80 % conversion either at 80 or 100°C. Hence it is evident that the difference in acidity is not so important in differentiating the activity of the catalysts. The large pore size and hydrophilic and hydrophobic properties are suggested to be the main factors that control acetalization.

1. Introduction

Mesoporous solid acid catalysts are advantageous as they are non-hazardous and free from mass transport limitations, possess high surface area and provide easy catalyst recovery. Based on the advantages of mesoporous materials, acetalization of n-heptanal with methanol was attempted for the first time over SBA-1 molecular sieves. The product, acetal, is used as a flavouring agent for beverages, chewing gum and condiments. Acetalization of n-heptanal has not been reported so far over solid acid catalysts in general and SBA-1 in particular.

2. Experimental

2.1. Preparation of the catalysts

Al-SBA-1 was synthesized as follows: solution

'A' was prepared by adding CTEABr (2.46 g) to dil. HCl (4.5N), cooled to 0°C and homogenized for 30 min. The pre-cooled (0°C) TEOS and aluminium hydroxide was then added to solution A under vigorous stirring which continued for 5 h at 0°C. The mixture was then heated at 100°C for 1 hr. The solid product was recovered by filtration and dried in an oven overnight at 100°C. The gel composition was: 1 TEOS: 0.0025-0.025 Al(OH)₃: 0.2 CTEABr: 10-56 HCl: 125-700 H₂O. The as-synthesized material was calcined in air at 550°C for 6 h. Al,Mg-SBA-1 (Si/(Al+Mg) = 40 and 80) molecular sieves were synthesized by adopting the same procedure. Magnesium acetate was used as the precursor for magnesium

2.2. Catalyst characterisation

2.2.1. XRD

The XRD patterns of Al-SBA-1(Si/Al = 40, 80

and 120), Al,Mg-SBA-1 ($\text{Si}/(\text{Al}+\text{Mg}) = 40$ and 80) are shown in Fig. 1. Al-SBA-1 molecular sieves showed characteristic patterns corresponding to (200), (210) and (211) of a three dimensional cubic structure (space group $\text{Pm}\bar{3}\text{n}$). These patterns matched well with the previous reports [1,2]. However, the intensity of patterns decreased with increase in the Si/Al ratio. Hence isomorphous substitution of silicon by aluminium is suggested to decrease the orderly arrangement of pores. The same observation was also noted in Al,Mg-SBA-1 catalysts. The intensity of the patterns of Al,Mg-SBA-1($\text{Si}/(\text{Al}+\text{Mg}) = 40$) was less than Al,Mg-SBA-1 ($\text{Si}/(\text{Al}+\text{Mg}) = 80$). In addition, the position of the patterns in both Al-SBA-1 and Al,Mg-SBA-1 are shifted to lower 2θ with the decrease in aluminium content. Hence the interplanar spacing of the planes might increase with decrease in the aluminium content.

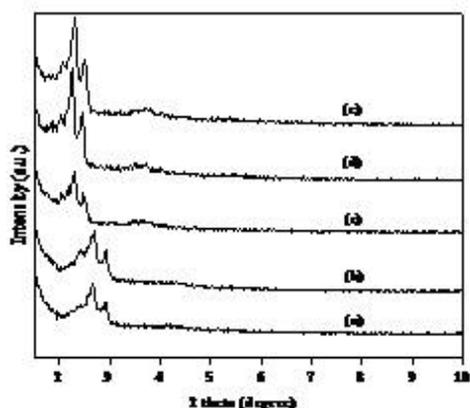


Fig.1. The XRD patterns of (a) Al-SBA-1(40), (b) Al-SBA-1(80), (c) Al-SBA-1(120), (d) Al,Mg-SBA-1(40) and (e) Al,Mg-SBA-1(80)

2.2.2. SEM

The SEM image of Al-SBA-1(40) is shown in Fig. 2. Most of the particles revealed spherical morphology with different size, but larger particles dominated over smaller particles. These larger particles have size in the range of 250–400 nm. Similar features were also shown by the images of other molecular sieves (Figure not shown). But the size of the particles is slightly smaller than that of Fig. 2. The morphology of the particles

is nearly same as that reported earlier [3].

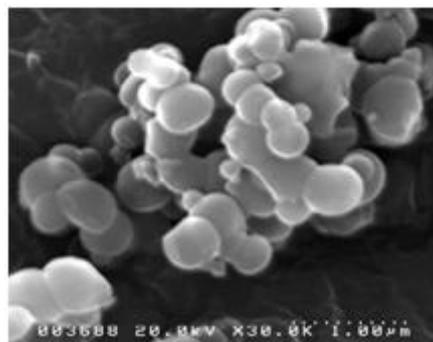


Fig. 2. SEM image of Al-SBA-1(40)

3. Result and discussion

Effect of temperature on acetalization over Al-SBA-1($\text{Si}/\text{Al} = 40, 80$ and 120) and Al,Mg-SBA-1($\text{Si}/(\text{Al}+\text{Mg}) = 40, 80$) are studied. The major products were hemiacetal, acetal and vinyl ether. The n-heptanal conversion over Al,Mg-SBA-1 also exhibited similar trend as that of Al-SBA-1 catalysts. The n-heptanal conversion decreased with increase in temperature, and both the catalysts showed nearly similar conversion. Hence, a slight increase in the acidity of Al-SBA-1(40) may be compensated by a slight increase in hydrophobicity of Al-SBA-1(80) in order to exhibit nearly similar conversion. The selectivity of hemiacetal increased with increase in temperature. Hence adsorption of hemiacetal on the acid sites may be hindered at high temperatures. At higher temperatures the selectivity of hemiacetal increased with increase in the hydrophobicity of the catalysts. This observation supports our view that increase in hydrophobicity of the catalysts partly suppressed the effect of temperature on adsorption. Effect of reaction time the n-heptanal conversion increased with increase in reaction time. The increase was significant upto 8 h. As the selectivity to hemiacetal is less, its formation must be a slow process. In other words protonation of n-heptanal is a slow process. The optimum feed ratio is 1:3. The slight increase in n-heptanal conversion at 1:5 and a subsequent decrease at 1:7 and 1:10 are

due to n-heptanal dilution by excess methanol. The effect of catalyst loading on n-heptanal conversion and products selectivity was studied. The optimum catalyst loading was found to be 0.05 g. Since the feed ratio was 1:3, methanol content around the active site need not be same with increase in the catalyst amount and hence conversion decreased at higher loading. The selectivity of hemiacetal clearly demonstrates the existence of unequal distribution of methanol close to acid sites. The selectivity of acetal increased from 0.03 to 0.05 g of the catalyst but decreased at higher loading.

4. Conclusions

This study concluded that SBA-1 catalysts exhibited similar n-heptanal conversion irrespective of Si/Al and Si/(Al+Mg) ratios. This conclusion elucidated that the reaction is mainly controlled by their hydrophilic-hydrophobic property and free diffusion of reactants and products rather the acidity of the catalysts. This study also revealed that mesoporous materials are better than microporous materials for acetalization of long chain aldehydes due to free diffusion in the mesoporous materials. This is a clean one-pot synthesis route for acetal compared to mineral acid catalyzed route.

5. Acknowledgements

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