

담지된 CTAB/MCM-41 and CTAB-Nafion/MCM-41 메조다공성 분자체의 제조 및 브롬화 반응에 사용

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(접수 2011. 4. 3; 수정 2011. 5. 19; 게재확정 2011. 6. 6)

Preparation of Supported CTAB/MCM-41 and CTAB-Nafion/MCM-41 Mesoporous Molecular Sieve and Their Use in the Brominating Reaction

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(Received April 3, 2011; Revised May 19, 2011; Accepted June 6, 2011)

요 약. CTAB 혹은 CTAB-나피온 촉매를 속빈 실리콘 튜브형 MCM-41에 담지시켰다. 이들 촉매들을 XRD, SEM, BET 등으로 분석하였다. 이들을 1,7-heptanediol 의 브롬화 반응 촉매로 사용하였고 다른 촉매들과 비교하였다. 이들 촉매들은 CTAB 보다 효과가 좋았으며 CTAB-Nafion/MCM-41 이 성능이 가장 우수하였다.

주제어: 메조다공성 분자체 MCM-41, 상전달 촉매, 산성 촉매, 담지

ABSTRACT. CTAB or CTAB-Nafion catalyst were successfully supported on siliceous hollow tubular MCM-41 which synthesized by hydrothermal method using CTAB as a single template or CTAB and Nafion-Na as mixed templates. The properties of two kinds of catalysts were characterized with XRD, SEM and adsorption and desorption isotherms of nitrogen and pore diameter distribution, respectively. Then they were applied to catalyze brominating reaction of 1,7-heptanediol, moreover the rate of brominating reaction with different catalysts was compared. The results showed that catalytic activities of CTAB/MCM-41 and CTAB-Nafion/MCM-41 are better than CTAB, and that of CTAB-Nafion/MCM-41 is the best because of its phase-transfer and strong acidity function. The two kinds of catalysts can be separated from the reactive products and recycled.

Keywords: Mesoporous molecular sieve MCM-41, Phase-transfer catalyst, Acidity catalyst, Supported, Brominating reaction

INTRODUCTION

1,7-dibromoheptane, an important fine intermediate, is usually prepared using 1,7-heptanediol and HBr, as raw materials and the concentrated sulfuric acid or CTAB as catalyst. Although the concentrated sulfuric acid and CTAB have high catalytic activities, they are difficult to be separated and recycled, and lead to environmental pollution, thus, the supported catalysts can help in developing healthy environment and have become the focus of the study.

In the field of phase transfer catalysts, Regen *et al.*¹⁻³ developed some methods to prepare three-phase transfer catalysts. Such as, quaternary ammonium salt can be bond with strongly alkaline anion exchange resin; or the supported PEG catalyst is prepared when the hydroxyl base of PEG is activated and bond to organic carrier; or acrylic

polymers containing benzylchlorine can be further quaternized to obtain three-phase phase transfer catalysts. The advantages of these catalysts are that they are insoluble in water and organic solvents, being recovered just by a simple filtration, easily separated and recycled, but the preparation of these catalysts are too complicated, and the reagents are so expensive, also the organic carriers have low mechanical strength and low thermal stability. In the field of acid-supported catalysts, the solid acid catalysts, such as zeolite molecular sieve, solid super acid, strong acidic cationic exchange resin and various supported solid acids, have become the focus of the study and application. But, zeolite molecular sieve is lower in acidity, solid super acid has low hydrothermal stability and strong acidic cationic exchange resin has low thermal stability, therefore, all of them are difficult in application in the hydrothermal system by using hydrobromic acid as brominating agent.

So, the supported catalysts have been a focus of various catalytic reactions due to its high activity and selectivity of the carrier. Mesoporous molecular sieve materials M41S,^{4,5} synthesized by Mobil company, with uniform size, higher specific surface area, pore volume and better thermal stability, has been widely used as a good catalyst carrier in chemical reaction. There are two kinds of studies on solid acids that using MCM-41 as carriers, one is solid super acid loaded on MCM-41;⁶⁻¹⁰ the other is that the silanol group of MCM-41 is activated firstly, then further treatment by grafted modification technology.^{11,12} When solid super acid is supported on MCM-41, the surface area of solid acid is increased greatly while acid strength has little change, but, this type of acid is not suitable for hydrothermal system yet, because acid strength will be tremendously decreased in the presence of water. Sulphonic group can be grafted to silanol groups on MCM-41 by surface graft modifications, which have advantages of stronger acidity, larger specific surface area and hydrothermal stability. However, the grafted modification technology is very complicated, the cost is high and the grafted chemical bonds are easy to hydrolyze in the acidic solution.

In this paper, CTAB or CTAB-Nafion can be successfully supported on MCM-41, when MCM-41 had been synthesized in a hydrothermal system using CTAB as a single template or CTAB and Nafion-Na as mixed templates, respectively. By using this method, two kinds of catalysts, i.e. MCM-41-supported phase transfer catalysts, MCM-41-supported acid catalysts and phase transfer catalyst, can be prepared easily. The prepared catalysts were characterized with XRD, SEM, adsorption and desorption isotherms of nitrogen and pore diameter distribution. Taking 1,7-heptanediol bromination as a probe reaction, the rates of brominating reaction of 1,7-heptanediol by using different catalysts were measured and compared, and the good catalytic activity and hydrothermal stability is verified.

EXPERIMENTAL

Reagents and Apparatus

CTAB, Na₂SiO₃·9H₂O, Sulfuric acid, Hydrochloric acid, Heptanediol, HBr are all AR reagents, and are obtained from Shanghai Reagent Co., Ltd., Nafion-Na solution is prepared by us in the laboratory and the concentration is 0.045 g/mL. Secondary deionized water is used.

Dmax-2000 type X-Ray Diffractometer, Japanese Rigaku Co., GC9800 gas chromatograph (Shanghai KeChuang Chromatography Instruments Co., Ltd.), NOVA4200e type

pore distribution analyzer by gas adsorption method (American Quantachrome Co.), Quonxe-2000 scanning electron microscope (SEM) (Holland FEI Co.) were used for this work.

Preparation of CTAB/MCM-41

The preparation process of CTAB/MCM-41 was reported in reference.⁵ Quantitative secondary deionized water and CTAB are put into a three-neck flask, and was stirred and dissolved at 40 °C, then sodium silicate solution of certain concentration is added through the dropping funnel at a suitable stirred rate, moreover, 10 % sulfuric acid is added to adjust pH to 10 and aged for 3 h at room temperature, colloidal solution are put into a high-pressure reactor, crystallized at 110 °C for 5 days. Then, the crystal grain is filtered and washed by deionized water until no sulfate ion, then dried at 80 °C for 24 h. Finally, the obtained powder is calcined at 560 °C for 5 h. The ratio of CTAB/MCM-41 is 1SiO₂:1Na₂O: xCTAB: yH₂O:zH₂SO₄, where x = 0.1- 0.6, y = 100-200, z is pH 8-11. The CTAB weight of sample was 2.71-3.18%.

Preparation of CTAB-Nafion/MCM-41

Quantitative Nafion-Na and CTAB solution of certain concentration was added into three-neck flask with a stirrer, the following procedures are the same as the above-described previously. CTAB-Nafion/MCM-41 can be obtained from the final solid powder by repeated ion exchange process with 3 mol/L HCl solution at 60 °C. The supported amount of Nafion can be adjusted by changing the quantity of Nafion-Na. The CTAB-Nafion weight of sample was 2.91-3.36 %.

Catalytic Characterization of CTAB/MCM-41 and CTAB-Nafion/MCM-41

The synthesis of 1,7 - dibromoheptane using 1,7-heptanediol and HBr as raw material was ever studied, the optimum conditions was obtained as follows: reaction time is 4 h, reaction temperature is 388.15 K, the mole ratio of 1,7-heptanediol and HBr is 3:1, yield is 99.2%.¹³ In this paper, the catalytic characterization of supported zeolite catalysts was investigated. The rates of brominating reaction under different catalysts are determined by taking 1,7-heptanediol bromination as the probe reaction. The relation between time and concentration of 1,7-heptanediol has been studied and is listed in *Table 1*. The experimental method is as follows: a mixture of 1.65 g 1,7-heptanediol and 5.5 mL hydrobromic acid, is put into a 50 mL three-neck flask, then quantitative catalyst is

Table 1. The relationship between concentration of 1,7-heptanediol (mol/L) and reaction time for different catalyst

| t, min | 30 | 60 | 90 | 120 | 150 |
|--------------------|--------|--------|--------|--------|--------|
| no cat | 1.7223 | 1.4002 | 1.1621 | 0.9680 | 0.8304 |
| CTAB | 1.6884 | 1.3532 | 1.1123 | 0.9180 | 0.7802 |
| CTAB/MCM-41 | 1.5702 | 1.1704 | 0.9032 | 0.6664 | 0.4802 |
| CTAB-Nafion/MCM-41 | 1.3930 | 0.9632 | 0.6921 | 0.5103 | 0.3830 |

added. The reaction is performed in an oil bath with a suitable temperature. After reaction, solid catalyst is filtered and washed with ethyl acetate. Moreover, the organic phase was separated and washed with water, neutralized and dried, and then the product is obtained to remove ethyl acetate using a rotary evaporator and is weighed. The product composition is determined by gas chromatograph.

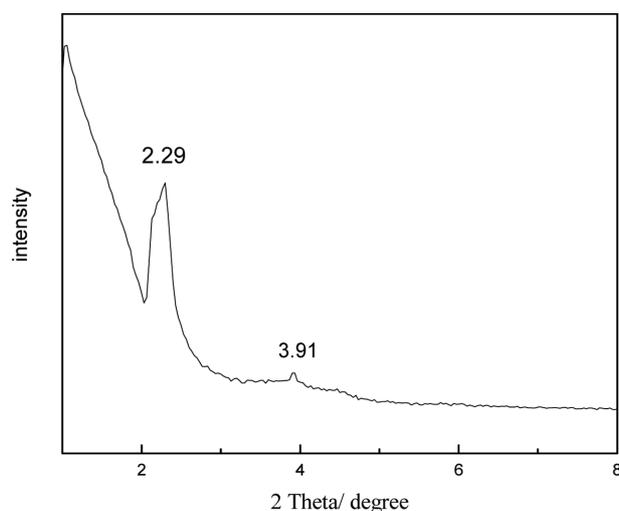
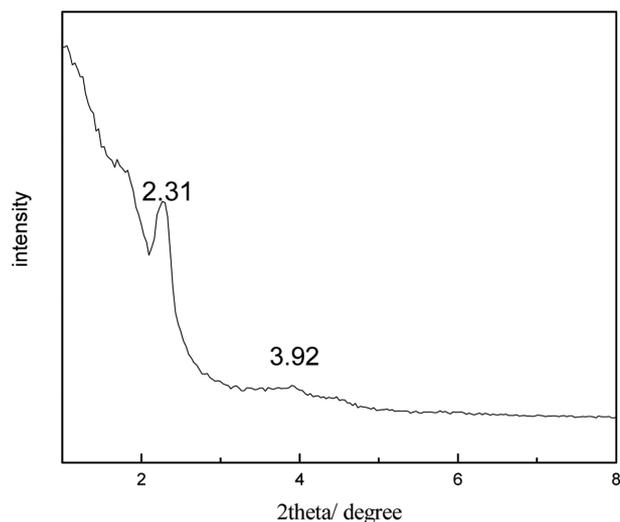
Recycling of CTAB/MCM-41 and CTAB-Nafion/MCM-41

The separated solid catalyst was washed with water, and then is dried at 80 °C in a vacuum oven. The recovered catalyst is put into reaction repeatedly. The concentration of 1,7-heptanediol is determined every 150 min to estimate the reusability of catalyst.

RESULTS AND DISCUSSION

Confirmation of MCM-41 Structure

The prepared catalysts were characterized with XRD and the results are shown in *Fig. 1* and *Fig. 2*. It can be seen from *Fig. 1* and *Fig. 2* that there is a strong diffraction peak for the reflection labeled (100) at $2\theta = 2.3^\circ$, and at 3.9° to 5° , the smaller peaks are for the reflection labeled (110), (200) and (210) respectively. The XRD spectra of


Fig. 1. XRD pattern of CTAB/MCM-41.

Fig. 2. XRD pattern of CTAB-Nafion/MCM-41.

MCM-41 is agreed with that of the literature,⁵ it shows that the obtained product is hexagonal mesophase MCM-41 molecular sieve. That is to say, although MCM-41 is supported by CTAB or CTAB-Nafion, it still maintains the typical characteristics of MCM-41 diffraction, namely, the pore structure remains unchanged after MCM-41 is supported by CTAB or CTAB-Nafion, and the pore distribution is still regularly arranged periodic hexagonal structure.

N_2 adsorption-desorption isotherms and pore size distribution curves of synthetic sample CTAB/MCM-41 and CTAB-Nafion/MCM-41 under the optimized conditions are shown in *Fig. 3* and *Fig. 4*. It has been found that the isotherms absorption curves are typical IV-type isothermal adsorption curve, this is absorption characteristics of mesoporous materials. There was a good linear relationship between the adsorption capacity and the partial pressure under low relative pressure ($P/P_0 < 0.25$), which is caused by the monolayer adsorption. The adsorption capacity increased with increasing relative pressure, there is an evident transition on curve due to N_2 capillary action. This point of inflexion is critical point, the pore size and distributions is judged according to the value of critical point and steepness of abrupt change of the curve. The specific surface area and the average pore volume of CTAB/

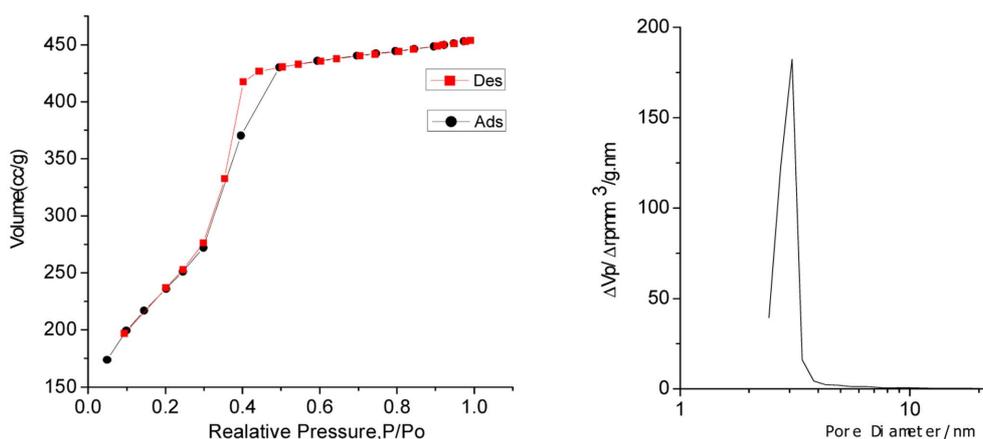


Fig. 3. N₂ adsorption-desorption isotherms and pore size distribution curves of sample CTAB/MCM-41.

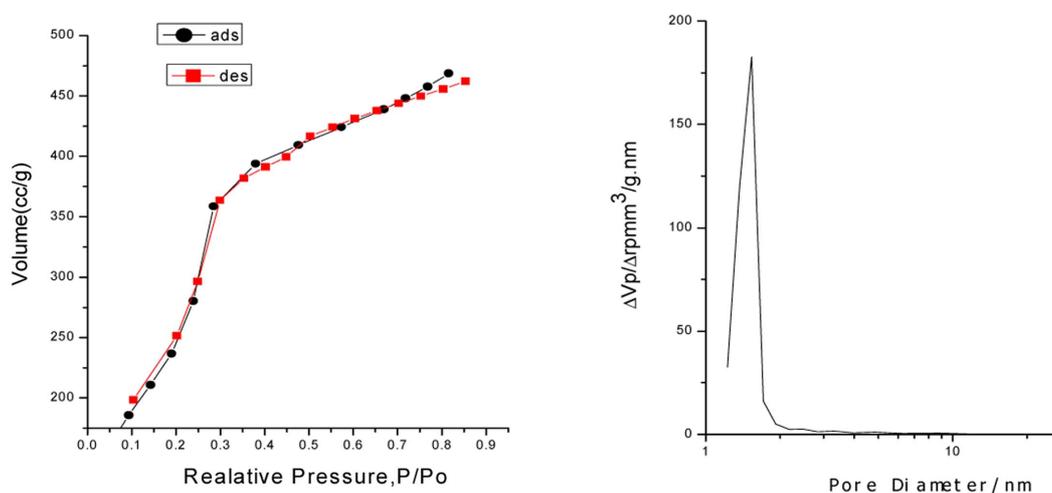


Fig. 4. N₂ adsorption-desorption isotherms and pore size distribution curves of sample CTAB-Nafion/MCM-41.

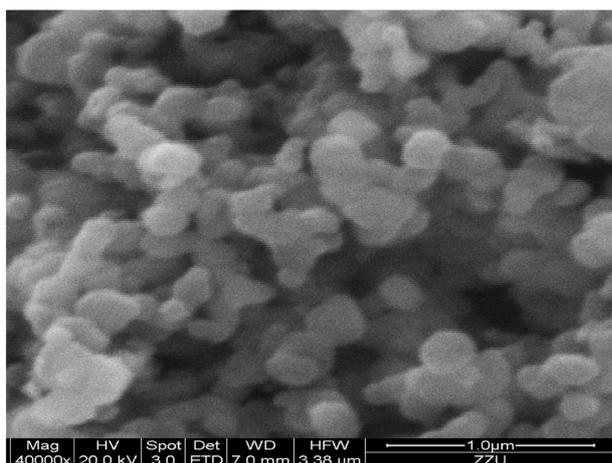


Fig. 5. SEM pattern of CTAB/MCM-41.

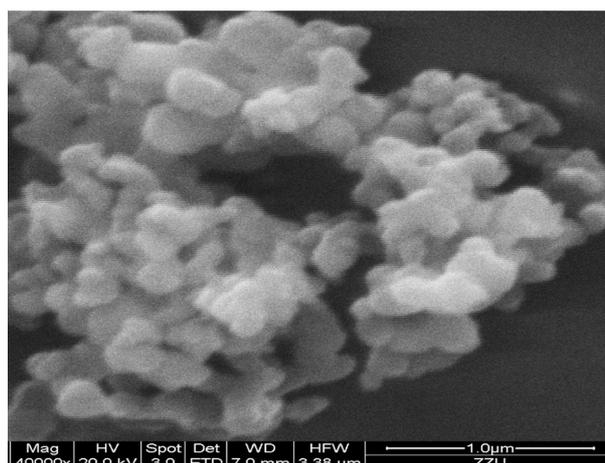


Fig. 6. SEM pattern of CTAB-Nafion/MCM-41.

MCM-41 is $546 \text{ m}^2 \cdot \text{g}^{-1}$ and $2.68 \text{ cm}^3 \cdot \text{g}^{-1}$ respectively. The specific surface area and the average pore volume of CTAB-Nafion/MCM-41 is $537 \text{ m}^2 \cdot \text{g}^{-1}$ and $2.28 \text{ cm}^3 \cdot \text{g}^{-1}$ respectively.

The microstructures of the samples were observed via scanning electron microscopy (SEM). SEM pattern of CTAB/MCM-41 and CTAB-Nafion/MCM-41 are listed

Table 2. The relationship between concentration of 1,7-heptanediol (mol/L) and reaction time for different dosage of CTAB

| t, min | 30 | 60 | 90 | 120 | 150 |
|----------|--------|--------|--------|--------|--------|
| 0.0000 g | 1.7223 | 1.4002 | 1.1621 | 0.9680 | 0.8304 |
| 0.0010 g | 1.7020 | 1.3801 | 1.1402 | 0.9611 | 0.7890 |
| 0.0015 g | 1.6964 | 1.3721 | 1.1332 | 0.9420 | 0.7860 |
| 0.0020 g | 1.6884 | 1.3532 | 1.1123 | 0.9180 | 0.7802 |
| 0.0025 g | 1.6902 | 1.3504 | 1.1104 | 0.9201 | 0.7811 |

in Fig. 5 and Fig. 6. The pattern was magnified 40000 times by SEM. The SEM pattern images that the crystal structure of CTAB/MCM-41 and CTAB-Nafion/MCM-41 is even and regular in appearance, and the particle size distribution is uniform.

Catalytic Activity

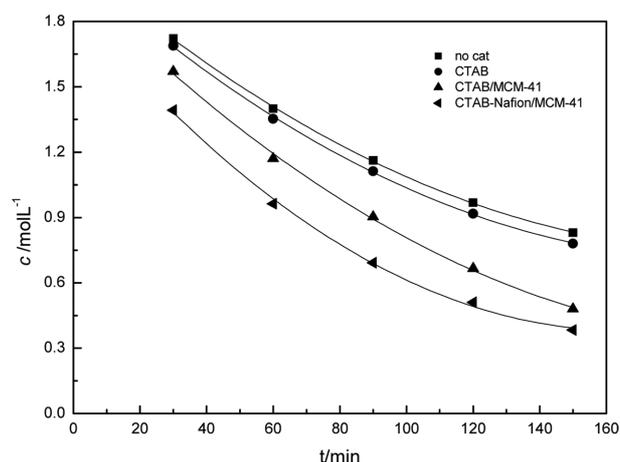
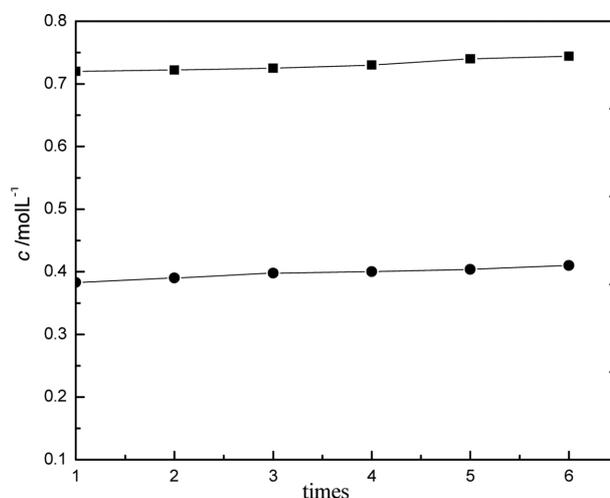
The optimum quantity of catalyst is determined to compare the catalytic activity. The relationship between concentration of 1,7-heptanediol (mol/L) and reaction time for different dosage of CTAB is listed in Table 2, it can be seen from Table 2 that the reaction rate will not increase any longer when dosage of CTAB is up to 0.0020 g. The calculated corresponding concentration of CTAB in the reaction system is 9.16×10^{-4} mol/L, which is in agreement with critical micelle concentration (cmc) 9.00×10^{-4} mol/L reported in literature.¹⁴ The optimum quantity of CTAB/MCM-41 and CTAB-Nafion/MCM-41 can be determined in the same way.

When the amounts of CTAB, CTAB/MCM-41 and CTAB-Nafion/MCM-41 are fixed to 0.002 g, 0.1 g and 0.1 g respectively, the relationship between the concentration of 1,7-heptanediol and reaction time by using different catalyst is shown in Table 1.

The mechanism of brominating reaction of 1,7-heptanediol and the kinetic model had been proposed and established,¹³ which shows that the brominating reaction of 1,7-heptanediol is a two-step reaction, and the 1,7-heptanediol bromination of the first step was a slow step and therefore the whole process is controlled by the first step. The established apparent kinetic equation was as follows:

$$c_A = \frac{F/2}{\exp\left(FA \exp\left(\frac{34.01m - 96.64}{8.3145T}\right)t - \ln\left(\frac{2c_{A,0}}{F + 2c_{A,0}}\right)\right) - 1}$$

Where $c_A/\text{mol}\cdot\text{L}^{-1}$ represents the concentration of 1,7-heptanediol; T/K is temperature of reaction; t/min represents reaction time; A is a pre-exponential factor, 3.28×10^9 ; m is the mass fraction of sulfuric acid; $F = c_{B,0} - 2c_{A,0}$, $c_{A,0}/\text{mol}\cdot\text{L}^{-1}$ and $c_{B,0}/\text{mol}\cdot\text{L}^{-1}$ represents the initial concentration of 1,7-heptanediol and hydrobromic acid, respectively.


Fig. 7. Effect of reaction rate by kinds of catalyst. —: regression curves calculated by rate equation.

Fig. 8. The recycled times of catalyst. ■: CTAB/MCM-41; ●: CTAB-Nafion/MCM-41.

The experimental data in Table 1 is correlated with the proposed rate eq. 1,¹³ the result shows that the calculated value is in good agreement with the experimental result. The correlated result is shown in Fig. 7. It can be seen from Fig. 7 that CTAB-Nafion/MCM-41 and CTAB/MCM-41 have obvious catalytic activity, especially CTAB-Nafion/MCM-41, has both the phase transfer catalytic action and acid catalytic function, it can accelerate greatly the rate of

brominating reaction of 1,7-heptanediol.

Recycling of the catalysts

Under the optimum conditions, the recycling of catalyst was researched, and the result was shown in Fig. 8. From Fig. 8, we can find that the concentration of 1,7-heptanediol is almost the same after the catalyst was recycled six times, which indicates that catalysts still maintain good selectivity and activity after recycling. There are two possible reasons for this: one is that the template is coated stably by the molecular sieves, and MCM-41 mesoporous molecular sieve itself has good thermal stability and hydrothermal stability, therefore the basic pore structure of molecular sieves have not been changed after chemical reaction; The other is that CTAB and Nafion has little solubility in water,^{15,16} and is also not dissolved in weak polar solvents, the active component has not been desorbed after the catalyst was recycled six times, therefore, the catalysts can still maintain fairly good selectivity and activity.

CONCLUSIONS

CTAB can be successfully supported on MCM-41, when mesoporous molecular sieve MCM-41 had been synthesized in a hydrothermal system using CTAB as a single template and had been calcined at 560 °C.

CTAB-Nafion can be successfully supported on MCM-41, when mesoporous molecular sieve MCM-41 had been synthesized in a hydrothermal system using CTAB and Nafion-Na as mixed templates and had been calcined at 560 °C and ion exchange process.

Supported molecular sieves CTAB/MCM-41 and CTAB-Nafion/MCM-41, have both the phase transfer and acid catalytic functions, which have high catalytic activities in the brominating reaction of 1,7-heptanediol. Because most of the chemical reaction need phase transfer catalyst or acid catalyst, therefore it can be foreseen that the supported catalysts will have broad application prospect in the fields of chemical reaction.

The experimental result shows that the supported molec-

ular sieves CTAB/MCM-41 and CTAB-Nafion/MCM-41 catalysts can be recovered only by a simple solid-liquid separation after reaction. And CTAB is supported, the emulsification of CTAB can be effectively prevented and the post-process can be simplified.

The experimental result shows that the supported catalysts can maintain fairly high catalytic activity and stability after the catalysts are recycled six times, they are the stable and environmentally friendly catalysts.

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