Synthesis and Catalytic Performance of Al-MCM-48 and Ti-MCM-48

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Abstract: Mesoporous sieves MCM-48 with hetero atom were synthesized by adding aluminum and titanium sources through hydrothermal method. The results showed that MCM-48 could be synthesized respectively by adjusting exactly the alkalinity of synthesis gel. The conversion rate of DIPB on Al-MCM-48 increased to 80% after 9 h and the selectivity of IPB was 97%. The conversion rate of styrene on Ti-MCM-48 increased to 9% after 8 h and the selectivity of benzaldehyde was 85%. The available active sites, which were introduced by aluminum and titanium atoms, were effectively utilized for catalyst reaction due to the presence of mesopores in Al-MCM-48 and Ti-MCM-48.

Keywords: Al-MCM-48, phase transition, styrene oxidation, Ti-MCM-48, transalkylation.

1. INTRODUCTION

The mesoporous materials have extensive application due to their excellent structural ordering, tunable pore size and high surface area and pore volume [1-3]. MCM-41, MCM-48 and MCM-50 are members of M41S family which have one-dimensional pore, three-dimensional pore and no pore structure respectively [4]. Due to the active sites' being accessible to the reactants pore, MCM-48 structure has more advantages of catalytic applications than the other materials [5].

In order to make the materials catalytically active, other elements have to be incorporated into the siliceous framework. Al-MCM-48 can be used as heterogeneous acid catalysts, especially for reactions involving bulky molecules which require moderate acid strength [6]. In post-synthesized MCM-48 containing hetero atoms, significant destruction of mesopore structure and short life of active sites are the great drawbacks [7]. Incorporation of hetero atoms by direct syntheses is needed urgently. It is well known that the pH value of the micelle solution plays a significant role in the formation of high quality mesoporous molecular sieves [4]. Most of the pH-dependencies have been outlined concerning hydrolysis and polycondensation of inorganic framework builder [8]. However, the effect of base concentration in the micellar solution on the formation of MCM-48 with aluminum and titanium atoms incorporation is rare in previous research. We conducted systematic study for finding the influence of the alkalinity of synthesis gel on the structure of mesoporous materials. Then we chose transalkylation of diisopropylbenzene (DIPB) with benzene and oxidation of styrene with H_2O_2 to assess the catalytic performance of the obtained Al-MCM-48 and Ti-MCM-48 respectively.

2. MATERIALS AND METHODS

Synthesis mixture of Al-MCM-48 was prepared as follows: Al source and Si source were added to the solution of cetyltrimethyl-ammonium bromide (CTAB, First Chemical Co., Beijing), NaOH (First Chemical Co., Shanghai) and deionized water. The molar composition of the above mixture was n (SiO_2): n (CTAB) : n (Na_2O) : n (H_2O) : n (Al_2O_3) = 1.00 : 0.156 : x : 55.6 : 0.025. The Al source was aluminum sulfate ($Al_2(SO_4)_3$, First Chemical Co., Beijing). The Si source was tetraethyl orthosilicate (TEOS, First Chemical Co., Beijing). This solution was stirred at 30 °C for 1 h. After that, the mixture was placed in a autoclave at 100 °C for 3 days. The solid product was recovered and calcined at 550 °C in air (5 °C /min) for 6 h. The synthesis mixture of Ti-MCM-48 was prepared similarly by adding Ti source and Si source into the mixture solution of CTAB, NaOH and H_2O. The molar composition of the above mixture was n (SiO_2): n (CTAB) : n (Na_2O) : n (H_2O) : n (TiO_2) = 1.00 : 0.156 : x : 55.6 : 0.02. The Ti source (w ($TiCl_4$) = 63.3%) was obtained by dissolving titanium tetrachloride ($TiCl_4$, First Chemical Co., Beijing) in isopropanol (First Chemical Co., Shanghai). The Si source was the same as TEOS that was applied in the synthesis of Al-MCM-48. This solution experienced the same treatment process like Al-MCM-48 to produce calcined Ti-MCM-48.

The prepared Al-MCM-48 was tested for transalkylation of DIPB with benzene in a fixed bed reactor at 523 K under 20 atmospheric pressures. The weight hourly space velocity (WHSVN) was 3.0 h^{-1}. The benzene to DIPB molar ratio was 2.33:1. The reaction mixture of benzene and DIPB was injected using a syringe pump. Reaction products were collected and analyzed with an Agilent 6820 gas chromatograph. The oxidation of styrene with H_2O_2 was examined as following reaction conditions. Catalyst (1 g), styrene (10 mL), H_2O_2 (30% aqueous solution, 9.7 g) and acetonitrile (30 mL) were placed into a reaction vessel. The resulting mixture was stirred at 65 ºC for 8 h. Reaction

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products were collected and analyzed with GC 7890F (Techcomp Scientific Instrument Co., Ltd., China).

3. RESULTS AND DISCUSSION

Fig. (**1**) shows the variety of XRD patterns of samples prepared in aluminum sulfate source in a series of Si/Na_2O ratio (x=0.238-0.350). At the lowest Si/Na_2O ratio (x=0.238), indexed peaks of synthesized samples were associated with the lamellar symmetry, mixed with a weak peak associated with the cubic symmetry. Then at x=0.301, synthesized samples showed the majority of peaks associated with the cubic symmetry, with a weak peak of the lamellar symmetry remained. Added Si/Na_2O ratio further to x=0.325, synthesized samples showed identical peaks associated with the cubic symmetry without any other peaks of impure phase existed. When Si/Na_2O ratio was added to x=0.350, the peaks associated with the hexagonal symmetry showed the production of MCM-41 under the Si/Na_2O ratio.

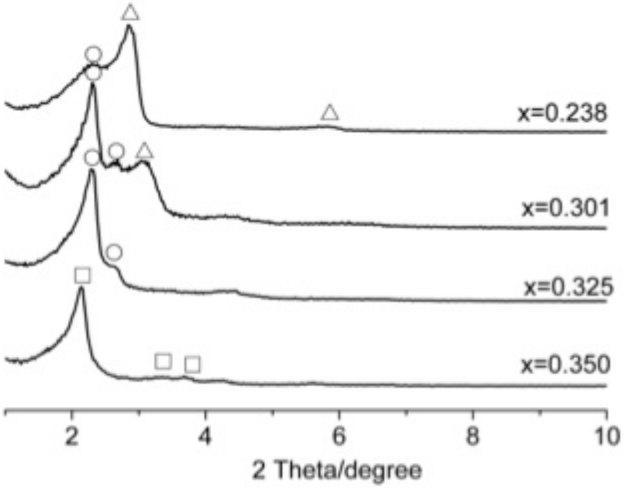

Fig. (1). XRD patterns of samples synthesized with aluminum sulfate (n (SiO_2) : n (CTAB) : n (Na_2O) : n (H_2O) : n (Al_2O_3) = 1.00 : 0.156 : x : 55.6 : 0.025). Square, circle and triangle indicate MCM-41, MCM-48 and MCM-50 respectively.

Fig. (**2**) shows the variety of XRD patterns of samples prepared in titanium tetrachloride source in a series of Si/Na_2O ratio (x=0.225-0.244) at Si/Ti=50. Compared with the XRD patterns of samples prepared at Si/Ti=50, the range of the ratio of Si/Na_2O in which phase transition happened becomes much narrower, although the sequence of phase transition is in the same way. Moreover, the weaker peaks associated with the cubic symmetry also suggest the poor quality of synthesized Ti-MCM-48 at lower Si/Ti ratio.

At different Si/Al ratios, catalytic performances of Al-MCM-48 were evaluated for transalkylation of DIPB with benzene. The conversion rates of DIPB and selectivity of IPB are shown in Figs. (**3**, **4**) respectively. It could be seen that the conversion rate of DIPB decreased from 90% to 80% after a reaction time of 9 h over the Al-MCM-48 with Si/Al = 60. However, for Al-MCM-48 with Si/Al = 40 and 20, the conversion rates of DIPB increased from 66% to 80% after 9 h under the same reaction conditions. The selectivity of IPB on Al-MCM-48 were very high at Si/Al = 20 and 40, which were about 97% in whole 9 h reaction time. These results indicated that Al-MCM-48 had good activity and stability for the transalkylation of DIPB with benzene and its activity and stability increased at high Si/Al ratios.

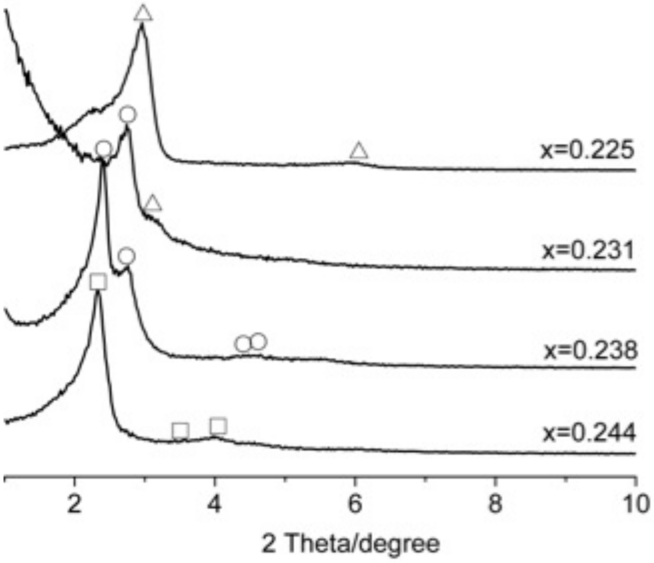

Fig. (2). XRD patterns of samples synthesized with titanium tetrachloride (n (SiO_2) : n (CTAB) : n (Na_2O) : n (H_2O) : n (TiO_2) = 1.00 : 0.156 : x : 55.6 : 0.02). Square, circle and triangle indicate MCM-41, MCM-48 and MCM-50 respectively.

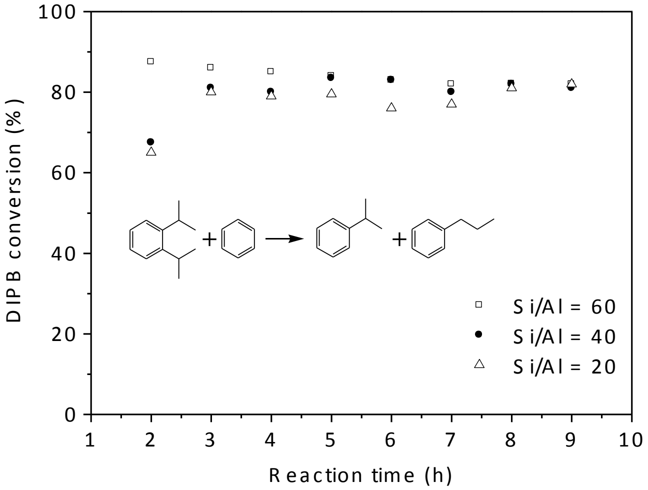

Fig. (3). DIPB conversions in transalkylation with benzene on Al-MCM-48 at different Si/Al ratios in a fixed bed reactor at 523 K under 20 atmospheric pressures. The weight hourly space velocity (WHSVN) was 3.0 h-1. The benzene to DIPB molar ratio was 2.33:1.

It is widely accepted that the accessibility of catalytic active sites plays a critical role in some diffusion-controlled reactions [10]. As has been reported and confirmed in previous studies, the available active sites in the mesoporous materials are effectively utilized. Hence the high conversion of DIPB could be attributed to the enhanced accessibility of catalytically active sites to reactant molecules on Al-MCM-48. The acid properties of catalyst (acid type, acid amount, acid strength and distribution, *etc.*), the nature of the hole, (channel structure and size, pore size distribution, specific surface area, *etc.*) and the nature of the crystal (crystal type, structure, Si/Al ratio, grain size, *etc.*) determined the catalytic activity of Al-MCM-48 for transalkylation [9]. The conversion rate of DIPB transalkylation reaction was directly related to the amount of B acid catalyst. Only when the amount of B acid reached to a certain concentration, the catalyst was not active.

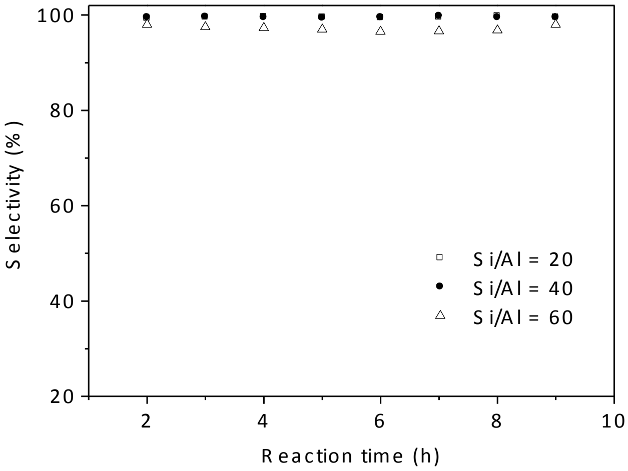

Fig. (4). IPB selectivity in DIPB transalkylation with benzene on Al-MCM-48 at different Si/Al ratios in a fixed bed reactor at 523 K under 20 atmospheric pressures. The weight hourly space velocity (WHSVN) was 3.0 h-1. The benzene to DIPB molar ratio was 2.33:1.

The catalytic performances of Ti-MCM-48 with different Si/Ti ratios were evaluated for oxidation of styrene with H_2O_2. The conversion rates of styrene and selectivity of the products are shown in Figs. (**5**, **6**). It could be seen that styrene conversion increased from 1% to 7% after a reaction time of 8 h over the Ti-MCM-48 with Si/Ti=100. However, for Ti-MCM-48 with Si/Ti = 50, the conversion of styrene increased from 1.1% to 9% after 8 h under the same reaction conditions. These results indicated that Ti-MCM-48 had good catalytic activity for the oxidation of styrene with H_2O_2 at two Si/Ti ratios and catalytic activity was increased with the content of Ti in Ti-MCM-48. For Ti-MCM-48 with Si/Ti=50, the selectivity of benzaldehyde and phenyloxirane increased from 75% and 0.1% to 85% and 5% respectively during a reaction time of 8 h. The selectivity of phyenylacetaldehyde decreased from 25% to 10% at the same time. This suggested that benzaldehyde was the main product for oxidation of styrene with H_2O_2 on Ti-MCM-48. The available active sites, which were introduced by titanium atoms, were effectively utilized for oxidation of styrene to produce benzaldehyde on Ti-MCM-48.

CONCLUSION

Under the influence of CTAB, TEOS, sodium hydroxide and different aluminum or titanium sources, the mesoporous sieves MCM-48 with hetero atoms were synthesized by adjusting the alkalinity of the synthesis gel exactly. Al-MCM-48 and Ti-MCM-48 showed promising catalytic performance in transalkylation of DIPB with benzene and oxidation of styrene with H_2O_2 respectively. The conversion rates of DIPB increases to 80% after 9 h on Al-MCM-48. The selectivities of IPB were very high at Si/Al = 20 and 40, which were about 97%. For Ti-MCM-48 with Si/Ti = 50, the conversion rate of styrene increased to 9% after 8 h and the selectivity of benzaldehyde was 85%.

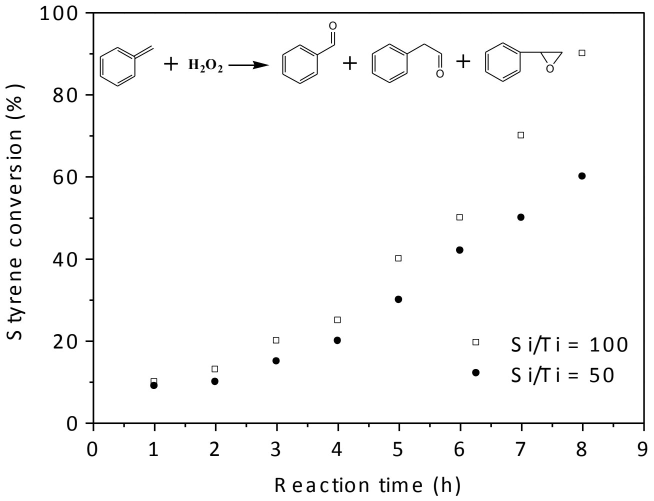

Fig. (5). Styrene conversions in oxidation on Ti-MCM-48 at different Si/Ti ratios with 1.0 g catalyst, 10 mL styrene, 9.7 g H_2O_2 (30% aqueous solution) and 30 mL acetonitrile.

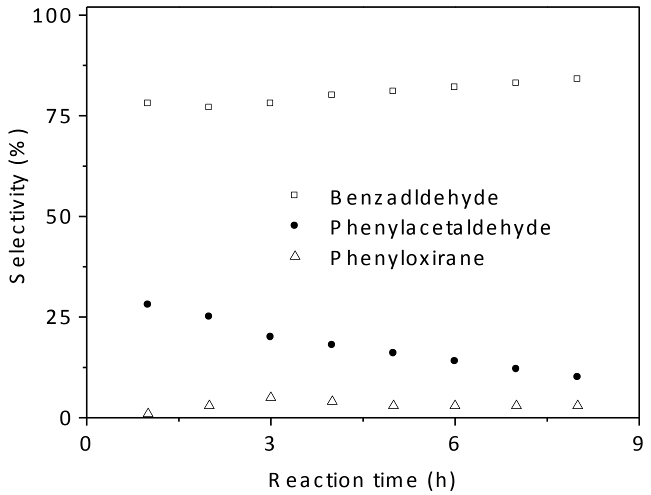

Fig. (6). Benzaldehyde, phyenylacetaldehyde, phenyloxirane selectivity in styrene oxidation on Ti-MCM-48 at different Si/Ti ratios with 1.0 g catalyst, 10 mL styrene, 9.7 g H_2O_2 (30% aqueous solution) and 30 mL acetonitrile.

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CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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