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Study on methane aromatization over MoO_3/HMCM-49 catalyst

D.Y. Wang, Q.B. Kan*, N. Xu, P. Wu, T.H. Wu[1]

Department of chemistry, Jilin University, Changchun, China

Abstract

Nanosize MCM-49 zeolite was synthesized by the hydrothermal method, and it was used as the support of MoO_3/zeolite catalysts for methane aromatization in the absence of oxidant under various reaction conditions. After the preparation method of catalysts and reaction conditions were optimized, high benzene selectivity of around 90% were obtained with a yield of more than 10% at 973 K over the 6 wt.% Mo/HMCM-49 catalyst and the catalyst can keep the activity for more than 150 h through several simple calcination in air to remove carbon deposition for reactivation. Compared to Mo/HZSM-5 catalysts, Mo/HMCM-49 is easier to prepare and more effective. We considered that the excellent catalytic performance of Mo/HMCM-49 catalyst for methane aromatization profits from the especial MWW type pore structure of MCM-49 zeolite in part.

Keywords: MCM-49; Methane aromatization; MoO_3; Zeolite

1. Introduction

Since the first non-oxidative aromatization catalyst Mo/HZSM-5 was found in 1993 [1], methane aromatization in the absence of oxidant has become a valuable and challengeable research in both academic and applied significance on methane conversion [1–8]. Investigators have obtained remarkable advancement in this domain, not only in theory of aromatization but also the practicability of catalysts. NMR, FT-IR, TPD, XPS, XRD and other physical or chemical techniques have revealed more messages about zeolite acid property, channel structure and active species that were relatived to oxygen-free methane aromatization [4–12]. Xu and his group investigated the necessity of Brünsted acid sites density for C–H bond activation [3]. Silica–aluminia zeolites with two-dimensional structure and aperture of about the dynamic diameter of benzene (0.6 nm) were suggested as fine supports [5]. The Mo_xC_y species were commonly regarded as the aromatization center, the interaction of which with Brünsted acid sites influenced the performance of catalysts for dehydro-aromatization of methane [7,8].

Mo/HZSM-5 is the most important catalyst that has been under intensive scrutiny. To improve the activity and stability of this catalytic system, various second component metal, such as Cu, Co, Ru, Fe, Pt, Ir, La, V, Zr were added [10–14]. It was reported that CO and CO_2 were beneficial to improve the catalytic performance of Mo/HZSM-5 [15,16]. The catalytic membrane reactor was used to remove hydrogen and then change the equilibrium limitation to react under low temperatures [17–19]. GaZSM-5 and BZSM-5 were studied as effective zeolite supports [20,21]. About 9–11% of methane conversion, 50–70% of benzene selectivity was obtained over Mo/HZSM-5 and the derived catalysts. In addition, W/HZSM-5 offered higher methane conversion at 1073 K or more [22]. Re/HZSM-5 was also reported as a low coke catalyst of oxygen-free aromatization [23]. Although much attention has been paid to the metal supported HZSM-5 catalysts, further improvement of the catalytic performance was imperatively desirable. Recently, as a new aromatization catalyst, Mo/HMCM-22 was much accounted of the researchers due to high stability [23].

MCM-49 has conformable structure of MWW type but different aluminum content and distribution with MCM-22. In this paper, Mo/HMCM-49 catalysts with various Mo contents were prepared and tested as the catalyst of methane aromatization in a fixed bed reactor under systematic reaction conditions.

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* Corresponding author. Tel.: +86 4318 499140; fax: +86 4318 949334.

E-mail address: wth@mail.jlu.edu.cn (T.H. Wu and Q.B. Kan).

[1] Co-corresponding author.

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2. Experimental

2.1. Preparation of MoO_3/HMCM-49 catalysts

The nanosize MCM-49 zeolite support with $Si/Al_2O_3 = 12.5$ was synthesized by a hydro-thermal procedure using hexamethyleneimine (HMI) as the template and silica gel as the silica source [24,25]. The original slurry was obtained by stirring the mixture of certain amounts of sodium aluminate, sodium hydroxide, HMI, silica gel and water. After being crystallized at 443 K with rotating rate of 60 rpm for 3 days, the resulting solids were filtrated, washed and dried. The occluded organic was removed by heating at 811 K for 3 h under a continuous flow of nitrogen before a flow of air was passed through for 6 h to obtain the calcined samples.

HMCM-49 was prepared by three times repeated ion-exchange of the calcined MCM-49 with an aqueous solution of 1 mol/L ammonium nitrate and the calcination in air at 773 K for 3 h.

The Mo/HMCM-49 catalysts with different Mo loadings were prepared by mechanical mixing of MoO_3 and HMCM-49 and calcination in air at 773 K for 3 h. At last, the powder samples were pressed, crushed, and sieved to granules with enough degree of hardness in the size range of 40–60 mesh for subsequent use in aromatization reactions.

The used catalyst is calcined for 3 h at 813 K in air to remove carbon deposition for reactivation. After calcination 1–2 wt.% MoO_3 powder and the calcined catalyst were mixed together for 30 min and then the mixture was roasted at 773 K for 2 h in a copple with a cover to complement the Mo component lost during the reaction.

2.2. Catalytic tests

Zeolite samples were examined by using XRD for phase identification and determination of the relative crystallinity. XRD measurements were carried out using Cu Kα radiation on the SHIMADZU XRD-6000 diffractometer in the range of 5–40° (2θ). The morphology and size of the zeolite crystals were determined using a HITACHI H-8100 transmission electron microscope.

Thermal analyses (TG and DTA) were performed using a Shimadzu DTG-60. The samples were run from 323 to 1073 K at a rate of 10 K/min under a flow of dry air.

FT-IR measurements were analyzed by Nicolet Impact 410 IR. Samples were prepared as KBr self-supporting wafers. The IR spectra were collected from 400 to $4000\ cm^{-1}$ at a resolution of $2\ cm^{-1}$.

The temperature-programmed desorption of NH_3 (NH_3-TPD) was carried out from room temperature to 873 K at a heating rate of 10 K/min. A thermal conductivity detector was employed to measure the amount of NH_3 in the effluent.

Catalytic tests were carried out under atmospheric pressure in a continuous flow fixed bed quartz reactor of 1 cm ID, which was charged with 0.5 g of catalyst pelleted and sized to 40–60 mesh. The feed gas mixture of 92.5% CH_4 and 7.5% N_2 was introduced into the reactor at 1500 mL/g h through a mass flow controller and the temperature was raised to 973 K within 45 min and kept at the temperature during reaction. An on-line gas chromatograph (GC-17A) was used, equipped with a 6 m × 3 mm HayeSep D 80/100 column to analyze H_2, N_2, CO, CO_2, CH_4, C_2H_4, C_2H_6 by on-line TCD and a CBP1-M50-025 (Shimadzu) quartz capillary to analyze condensable aromatics such as benzene, toluene, naphthalene by on-line FID. The methane conversion and the product selectivity were calculated on a carbon number base by inner standardization method.

3. Results and discussion

3.1. TEM and XRD pattern

The MCM-49 zeolite synthesized here has highly crystallinity and purity. On transmission electron micrographs, the crystals are uniform, thin regular hexagonal sheets, about 300–500 nm in diameter and 20–50 nm in thickness. The XRD pattern of MCM-49 sample shown in Fig. 1 accords well with those reported in the literature and patent [24,25]. After calcination, the MoO_3 diffuses well on/in the MCM-49 zeolite and no characteristic diffractive peaks of MoO_3 were found until its amount is up to 10 wt.% in the Mo/HMCM-49 catalyst. Moreover, the structure of zeolite is not destroyed by a long time reaction (over 200 h) under 973 K.

3.2. Effect of Mo contents on the catalytic performance of Mo/HMCM-49 catalysts

The reaction of methane aromatization under non-oxidative condition over Mo/HMCM-49 catalyst has some features as follows: the yield of methane descends slowly and smoothly with the proceeding of the reaction. The yield of benzene has an induction period in which there is no

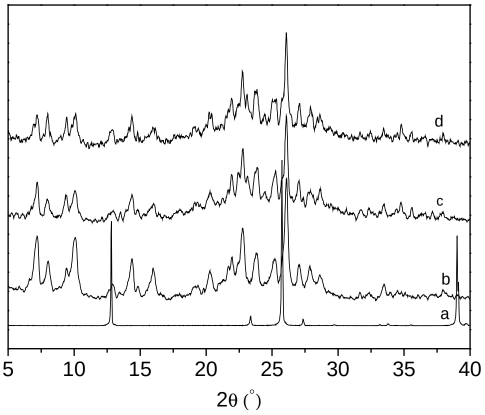

Fig. 1. X-ray diffraction pattern of HMCM-49 MoO_3 and Mo/HMCM-49: (a) HMCM-49; (b) MoO_3; (c) 6 wt.% Mo/HMCM-49; (d) 6 wt.% Mo/HMCM-49 (200 h reacted).

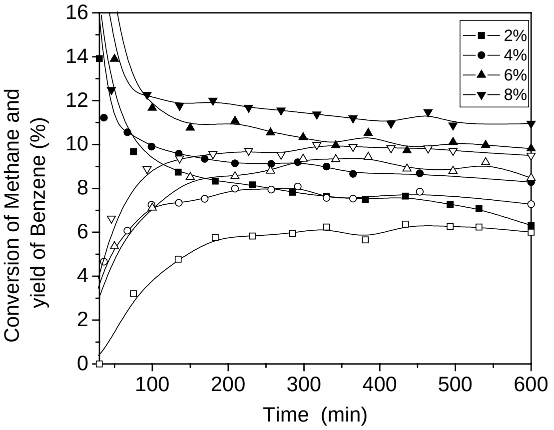

Fig. 2. Effect of Mo contents upon conversion of methane and yield of benzene over Mo/HMCM-49 catalysts. Solid: conversion of methane; hollow: yield of benzene.

benzene product at the first 20 min. The yield of benzene increases and reaches the maximum after 200–400 min. The catalyst has a high selectivity of benzene in comparison with naphthalene, carbon deposit, while toluene, CO_x, C_2 hydrocarbons is trace amounts.

The catalytic performance of Mo/HMCM-49 catalysts for aromatization is influenced markedly by the amount of active spices. The results of the aromatization of methane over the Mo/HMCM-49 catalysts with different molybdenum contents are shown in Figs. 2 and 3. When the amount of MoO_3 loading is 4 wt.% or less, the methane conversion is only 9% after methane was on stream for 100 min and the benzene yield can not exceed 6% for all the time. Until the amount of MoO_3 loading is up to 6–8 wt.%, the catalyst behaves excellent performance for aromatization: the methane conversion is as high as 13% and the maximal yield of benzene is about 10%. When the content of MoO_3 is above 10%, both the yield and the selectivity of benzene all descend slightly but the selectivity of coke ascends. As verified, the optimum molybdenum content in the catalysts is about 6–8 wt.% for the dehydro-aromatization reaction of methane.

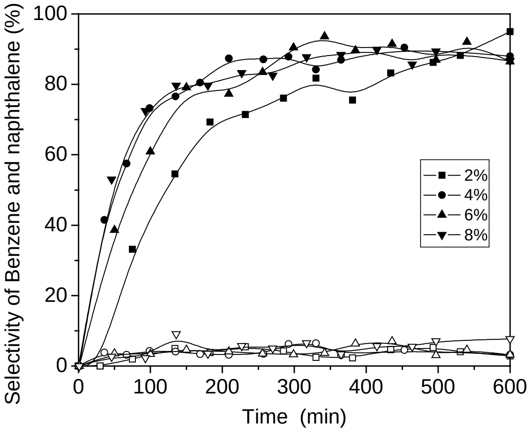

Fig. 3. Effect of Mo contents on the selectivity of aromatics over Mo/HMCM-49 catalysts. Solid: selectivity of benzene; hollow: selectivity of naphthalene.

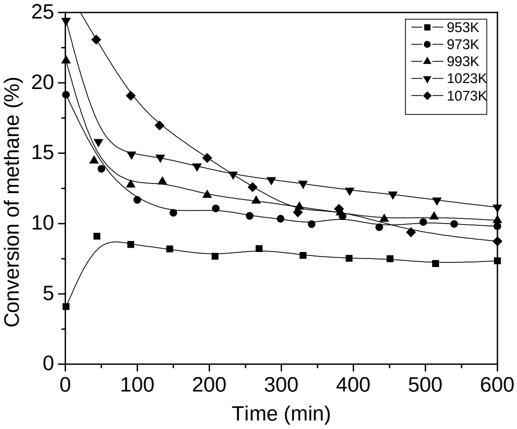

Fig. 4. Effect of reaction temperature upon conversion of methane over Mo/HMCM-49 catalysts.

3.3. Effect of temperature of reaction on the catalytic performance of Mo/HMCM-49 catalysts

The influence of temperature on the reaction over 6 wt.% Mo/HMCM-49 catalyst is shown in Figs. 4–6. As expected from kinetic and thermodynamic consideration, high temperature will be advantageous to the title reaction of aromatization. A significant increase of methane conversion can be observed when raising the reaction temperature from 953 to 1073 K. However, if the temperature is too high, e.g. 1073 K, serious carbon deposition occurs, and therefore the conversion of methane quickly decrease with the reaction time and the selectivity of aromatics becomes lower than that at lower reaction temperatures. The too short lifetime, high yield of coke and high consumption of energy are not worth the candle. As a comprehensive consideration, the proper temperatures range for the aromatization reaction of methane is actually between 973 and 1023 K in which we can easily obtain a steady methane conversion over 10%.

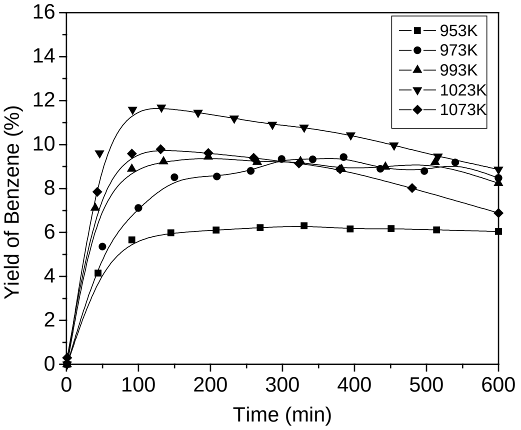

Fig. 5. Effect of reaction temperature upon the yield of benzene over Mo/HMCM-49.

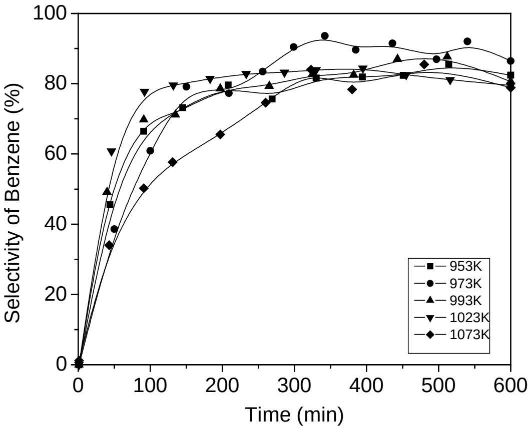

Fig. 6. Effect of temperature upon the selectivity of benzene over Mo/HMCM-49.

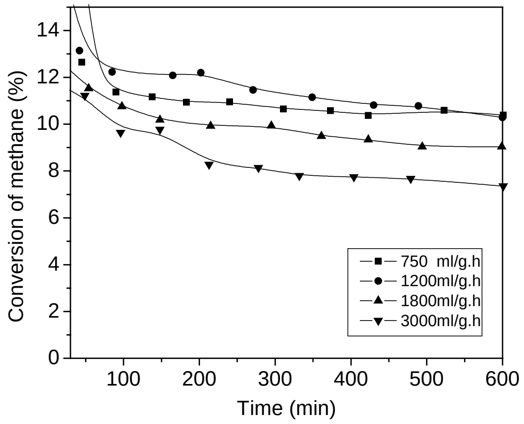

Fig. 7. Effect of feed space velocity upon conversion of methane over Mo/HMCM-49 catalysts.

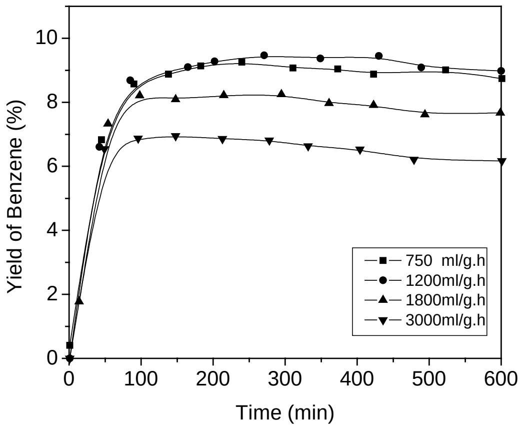

Fig. 8. Effect of feed space velocity upon yield of benzene over Mo/HMCM-49 catalysts.

3.4. Effect of feed space velocity of reaction on the catalytic performance of Mo/HMCM-49 catalysts

The feed space velocity of methane exerts significant influences on the reaction of methane. Figs. 7 and 8 reveal that with the increase in the space velocity methane (>1200 mL/g h), the conversion of methane decreases substantially while the selectivity of aromatics does not change. It is important to note that the conversion of methane reduces more quickly with the time on stream when increasing the space velocity of methane. It can prolong the lifetime of catalyst but is not more beneficial to the yield of aromatics. A proper scope of the space velocity is 1200–1800 mL/g h.

3.5. Test on lifetime of Mo/HMCM-49 catalysts

As mentioned in above paragraphs, the stability of catalyst is still a serious problem that could not be evasive for aromatization under non-oxidative conditions. The lifetime of Mo/HZSM-5 system is difficult to achieve 20 h despite the yield of benzene is on relatively low levels [7,14]. The stability behavior of Mo/HMCM-49 catalysts is clearly better than Mo/HZSM-5. Fig. 9 shows the long-term examination over a stochastically selected Mo/HMCM-49 catalyst sample for more than 150 h reaction. When the first 48 h reaction period was finished, the catalytic activity was obviously restrained. However, a simply calcination in air could

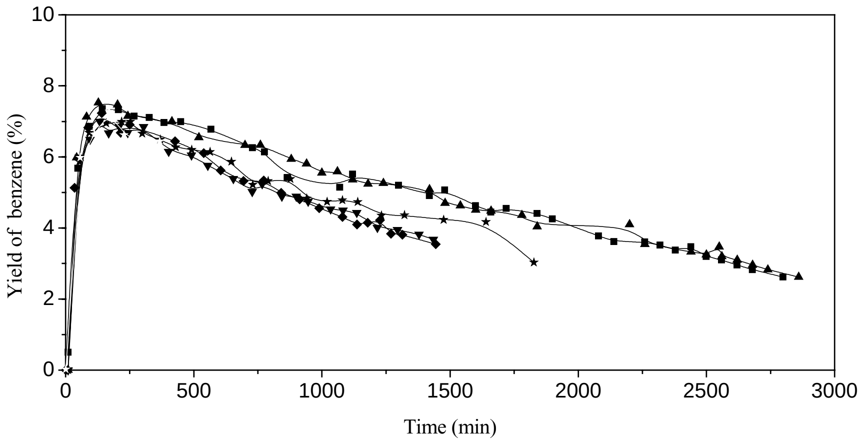

Fig. 9. Lifetime of 6 wt.% Mo/HMCM-49 catalyst.

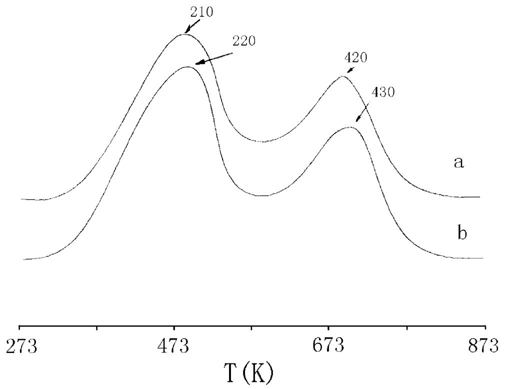

Fig. 10. TPD spectra of HMCM-49 and HZSM-5.

regenerate the used catalyst and then it has almost no distinction with the new catalyst. After two times of calcination the reactivation could not get a perfect recovery along with the sublimation losing of Mo spices during the long reaction at high temperature. Therefore, after the fourth calcination, 1 wt.% MoO_3 was added to reinforce the reborn catalyst through a straightforward mixing and fuming for 2 h. Although these simple treatments could not be equal to the aborative preparation of new catalyst in Section 2.1, they were assuredly effective to regenerate the catalytic activity.

The XRD patterns in Fig. 1 show that the zeolite has no significant loss of crystallinity after such a longtime reaction and those dispositions. The FT-IR spectra finger the –OH both on the surface or in the framework (1450, 1540, 3625 cm^{-1}) of zeolite were reduced as the reaction was carried out [26]. It indicates that more elaborate treatments, which included a hydrogen-ion-exchange once again, the reactivation will be more satisfactory.

3.6. Comparison of catalytic performance between Mo/HMCM-49 and Mo/HZSM-5 for methane aromatization under non-oxidative conditions

Possessing almost the same acid intensity and distribution with HZSM-5, as shown in NH_3-TPD spectra in Fig. 10, the HMCM-49 is to be expected also a fine zeolite support for non-oxidative aromatization of methane and the foregoing work has revealed that such is the case. However, the difference of catalytic performance for methane aromatization between the two zeolite supporting Mo are obvious. The Mo/HMCM-49 manifestly exceeded Mo/HZSM-5 in the selectivity of benzene, especially on the stability of catalyst as shown in Fig. 11. In fact, the selectivity of benzene over Mo/HMCM-49 is nearby 90% but Mo/HZSM-5 seldom reaches 70% [7]. The lifetime over Mo/HMCM-49 is around 48 h (single reaction).

Table 1
Carbon deposition on Mo/HMCM-49 and Mo/HZSM-5

Catalyst	4% Mo/ HZSM-5	6% Mo/ HMCM-49	6% Mo/ HMCM-49
Reaction time (min)	600	600	3600
Carbon deposit (%)	6.47	3.54	11.89

We consider that the difference of pore structure between HMCM-49 and HZSM-5 is the most important factor to influence the catalytic performance of the two catalyst systems. HMCM-49 has two types of pore channels: one is the two-dimensional sinusoidal channels and the other the supercage channels. The sinusoidal channels (0.41 nm × 0.51 nm) as the reaction location of aromatization are smaller than the channels of HZSM-5 (0.55 nm × 0.51 nm and 0.53 nm × 0.56 nm), which is perhaps the primary reason that Mo/HMCM-49 can get higher selectivity of benzene, lower selectivity of naphthalene and less coke than Mo/HZSM-5. On the other hand, HMCM-49 can load 6–8 wt.% Mo which is much higher than HZSM-5 with 2–4 wt.% molybdenum content, and therefore the aromatization active centers that are formed by molybdenum species located near the aluminum in the two-dimensional sinusoidal channels can be more effective. Moreover, the TG-DTA curves show the quantity of carbon deposit on the MCM-49 with a thin layer type crystal configuration is notably less than HZSM-5 (see in Table 1). This accords with the common theory considering carbon deposit causes catalyst deactivation and different behaviors between the two types of zeolite.

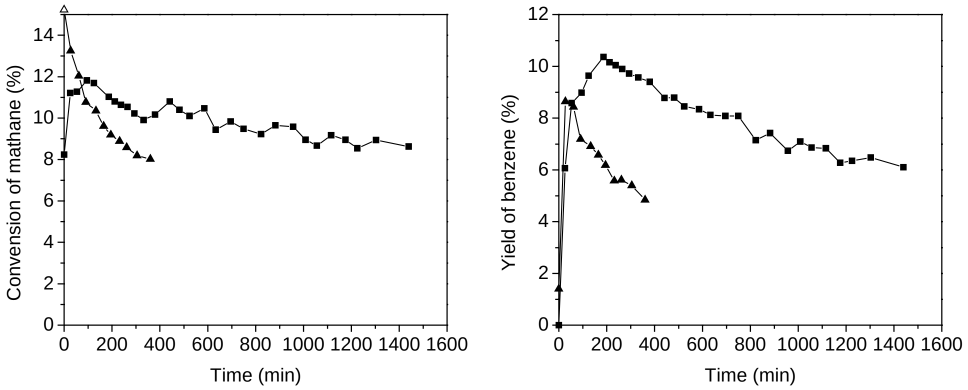

Fig. 11. Contrast of aromatization catalytic performance between Mo/HMCM-49 and Mo/HZSM-5. (■) 6 wt.% Mo/HMCM-49; (▲) 5 wt.% Mo/HZSM-5.

4. Conclusions

Nanosize MCM-49 zeolite of 300–500 nm diameter and 20–50 nm thickness was synthesized under the conditions of high temperature and low content of Na and water.

Catalytic performance of methane aromatization over Mo/HMCM-49 with different Mo contents was investigated in detail under various reaction conditions. The optimal methane conversion could reach 12% with benzene selectivity of 90% under following typical conditions: 6 wt.% Mo content catalyst, the reaction temperature is 973 K and feed space velocity is 1500 mL/g h. The optimal catalysts of Mo/HMCM-49 can maintain a lifetime over 150 h that has not been reported before. The particular performance of Mo/HMCM-49 on the improvement of methane aromatization reaction compared with HZSM-5 support metal, has shown more promising application value.

Acknowledgements

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