Synthesis of zeolite MCM-22 by vapor-phase transport method from different silica sources

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Abstract: Well-crystallized MCM-22 has been synthesized by a vapor-phase transport (VPT) method using three different silica sources. The products were characterized by means of powder XRD, SEM, and the effect of varying the silica source with different BET surface area on the structure of the dry inorganic gel and the crystallization behavior of MCM-22 was investigated. It was found that in the course of the dry gel preparation only partial framework structure unit was formed.

Key words: vapor-phase transport; zeolite MCM-22; synthesis; silica source
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A novel method of the synthesis of zeolites via the conversion of the parent gel was developed by Xu *et al*[1] in 1990 ——the vapor-phase transport (VPT) method, which has been used in the synthesis of various types of zeolites including MFI[1-2], FER[2], BEA[3], MOR[4] and so on. Compared with the hydrothermal synthetic (HTS) method, the VPT method is of great importance to practical application and has some advantages: when its crystalline period is equivalent to the traditional rotating synthesis, the products have higher crystallinity and the consumption of templates and Na^+ is lower. Zeolite MCM-22 was first synthesized via the VPT method by S. Inagaki *et al*[5] with fumed silica used as the only silica source. In this paper, well-crystallized MCM-22 was synthesized using different silica sources via the VPT method. Particularly, the influence of different silica sources on the product was discussed.

The process of synthesis of MCM-22 included the following two steps: the preparation of parent gel and the synthesis of zeolite MCM-22. The parent gel was prepared by mixing appropriate amount of sodium aluminate (96% puring, Al_2O_3 41%, Na_2O 37%) or aluminum sulfate (99%), sodium hydroxide (96%), deionized water and one of the silica sources: silicic acid (H_2SiO_3, AR), silica gel (SiO_2 40%, Na_2O 0.4%, H_2O 58%) and sodium silicate (SiO_2 20%, Na_2O 20%). The mixture [molar ratio: $n(SiO_2):n(Al_2O_3):n(Na^+):n(H_2O) = 1:x:y:44$] was dried at 393 K for 12 h after being stirred at the aging temperature for 1～4 h by a hot water bath. Dried gel powder (0.8 g) was placed in a Teflon cup in which the template and deionized water were poured as a source of steam at the bottom of the vessel. Crystallization of the dry gel went on at 423 K for 3～9 d. The products were washed, dried at 393 K overnight and calcined in air at 813 K for 10 h. The calcined samples were characterized by powder X-ray diffractometer (D/Max 2 500, Rigaku), field-emission SEM (LEO-435 VP) and BET micromeritics (ASAP 2010) and the crystallinities were determined by comparing the intensity of the major XRD peak (in the 2θ range 25°～27°) with that of a relative fully crystalline reference sample.

The XRD patterns of the typical samples prepared by the VPT and HTS methods using silicic acid

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as silica source are shown in Fig. 1. Fig. 1(b) corresponds quite well with that given in the Ref[6], and the diffraction peak at 26.01° is remarkable. Compared with Fig. 1(a), there are two diminutive diffraction humps at both 14.72° and 20.91°, which are indistinguishable by the traditional synthesis method (Fig. 1(a)) and the tip width of each peak is narrower. These results indicate that products prepared by the VPT method have higher crystallinity than those prepared by the HTS method. The comparison in the morphologies between the products synthesized by the VPT and HTS (under the rotating condition) methods is shown in Fig. 2 and 3. Usually the zeolite crystallizes as thin sheets or plates of shock layers about 2～3μm long, which are an agglomerate of thin plates. On the other hand, zeolite MCM-22 prepared by the HTS method appears in the form of round, thin and interpenetrating platelets with a diameter of 1μm.

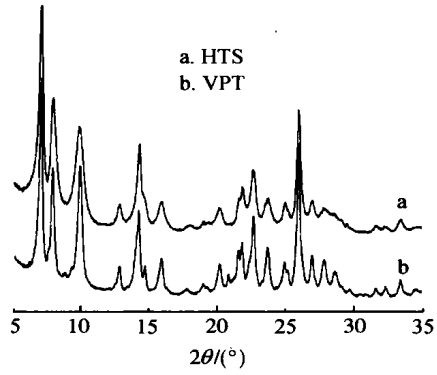

Fig. 1 XRD patterns of typical samples calcined in air at 813 K for 10 h

Fig. 2 SEM for the crystallized products prepared by the VPT method at 423 K for 5 d

The effect of the silica source on the crystallization of zeolite MCM-22 was tested through three different silica sources. A pure zeolite MCM-22 was obtained from all three silica sources, and the crystalline period was much shorter compared with that of the traditional static HTS method. However, different silica sources corresponded to different overall crystalline periods. It took 6 days to obtain 99.3 % zeolite MCM-22 from the sodium silicate parent gel with the highest specific surface area (S = 342.1 m^2/g). The silicic acid parent gel (S = 133.6 m^2/g) produced MCM-22 with the highest crystallinity (98 %) after 7 days. The colloidal silica parent gel had the lowest specific surface area of 117.1 m^2/g, and its crystallization was completed in about 5 days. The crystallinity increased with time during the first several days until it reached the highest crystallinity, after which other phase would be produced. The optimal crystalline period lasted from 5 to 7 days.

Fig. 3 SEM for the crystallized products prepared by the HTS method at 423 K for 5 d after aging 2 h at 313 K

The key to the synthesis of MCM-22 is the preparation of parent gel by the VPT method. Moreover, some polymers with a particuliar structural unit during this procedure make a higher crystallization rate compared with the static condition, and the crystallinity is improved than that prepared by the rotating synthesis.

In conclusion, highly crystallized zeolite MCM-22 can be obtained by the VPT method with different silica sources and the crystallization of raw materials could be completely accomplished. Sodium silicate is first used to prepare crystallized pure zeolite MCM-22. The consumption of templates and Na^+ is much lower than that in the hydrothermal synthesis. These

results show a promising prospect to reduce the cost in industrial production of zeolite MCM-22.

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汽相转移法合成不同硅源的 MCM-22 分子筛

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摘 要: 采用汽相转移(VPT)法合成出结晶度较高的纯 MCM-22 分子筛,并首次将硅酸钠应用于 VPT 法合成 MCM-22 分子筛;合成过程模板剂和 Na^+ 用量与水热合成法相比明显减少。用 X 射线衍射仪、扫描电子显微镜及 BET 比表面测定对产物作了表征,并重点对不同硅源对结晶产物的影响作了讨论。

关键词: 汽相转移;MCM-22 分子筛;合成;硅源

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(上接第 5 页)

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Simulation of catalytic combustion flows in honeycomb reactors

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Abstract: Reactive flow characteristics of a honeycomb catalytic reactor were studied under reaction conditions with the catalytic combustion of methane as the model reaction. A two-dimensional reactor model including the balance equations of mass, heat and momentum transport is solved by utilizing a CFD method. Based on the simulation results, the effects of the process parameters such as feed composition, inlet velocity and inlet temperature on the reactive flows were investigated. The results show that under the simulated conditions, the velocity profiles in channels are parabolic as in the case of laminar flows. Comparison of the model prediction with evaluated values of the conventional Hagen-Poiseuille equation shows that the Hagen-Poiseuille equation under-estimates values of pressure drop in all simulated cases, while the relative deviation, around 40 % in most cases, is highly related to the conversion degree and rate of reactions of interest.

Key words: honeycomb catalysts for combustion; catalytic combustor; flow characteristics; reacting flow

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