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Communication

Controllable direct-syntheses of delaminated MWW-type zeolites

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ABSTRACT

A method for the direct syntheses of partially and fully delaminated **MWW** zeolites is reported herein. Two organic amines were introduced into the hydrothermal synthetic system: hexamethyleneimine (HMI), which acted as the structure-directing agent for the **MWW** layered structure; and dicyclohexylamine (DCHA), in the role of an in-situ delaminating agent. By varying the amount of DCHA, partially and fully delaminated **MWW** zeolites having two **MWW** structure layers and one single layer, respectively, were obtained. These were denoted as SCM-1 (Sinopec Composite Material) and SCM-6, respectively. The delaminated materials possess ultra-large external surface areas, and the transmission electron microscopy images illustrated their layered nature. In the reaction of liquid phase benzene alkylation with ethylene, SCM-1, the double-layered **MWW** zeolite, exhibited far superior catalytic performance compared to zeolite MCM-22.

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Zeolites are important catalytic materials that are widely used in industrial plants for the production of chemicals from oil and coal [1]. Currently, approximately 19 zeolites of the 248 framework types approved by the Structure Commission of the International Zeolite Association (IZA-SC) have been commercialized, including **FAU**, **MFI**, ***BEA**, **MOR**, and **MWW** [2,3]. MCM-22, a material with a **MWW**-type structure and a multi-layered framework, is used as a catalyst for the production of ethylbenzene through liquid-phase alkylation of benzene with ethylene [4,5]. However, the acidic sites located in the 12-membered ring (12-MR) supercages and 10-MR channels of MCM-22 contribute minimally to the overall activity in the eth-

ylation of benzene; exclusively those located in the semi-supercages on the external surface of the crystal are active in the formation of ethylbenzene [6]. Theoretical calculations also demonstrated that the acid sites at the external surface of MCM-22 were more active than those at the internal cavity in the ethylation of benzene to produce ethylbenzene [7]. Therefore, it is highly desirable to synthesize novel **MWW**-type zeolites with ultra-large external surface areas that can accommodate larger numbers of semi-supercages. ITQ-2, a two-dimensional (2D) zeolite, formed by single **MWW** layers with a thickness of 2.5 nm, is one delaminated **MWW**-type zeolite with such characteristics [8]. However, the method for the

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preparation of ITQ-2 requires several synthetic procedures, making it unsuitable for industrial applications. In recent years, the direct synthesis of layered **MFI**-type zeolites employing designed amphiphilic organic structure-directing agents (OSDAs) consisting of a quaternary ammonium head and an alkyl chain tail, has revolutionized the direct synthesis of layered zeolites [9]. The OSDA is bi-functional, such that the quaternary ammonium head directs the crystallization of zeolite layers, while the long alkyl chain prohibits the ongoing crystallization along the *b*-axis of the MFI crystal. Similar bi-functional synthetic systems have been developed for the direct synthesis of delaminated **MWW** zeolites [10–13]. However, OSDAs are not commercially available. Moreover, these delaminated **MWW**-type zeolites show marginal improvements on the catalytic performance of MCM-22, a conventional 3D **MWW**-type zeolite [12].

MCM-22 is invariably constructed via topotactic dehydroxylation between the layers of its 2D lamellar precursor, (MCM-22(P)) [14]. MCM-22(P) is ordinarily synthesized hydrothermally using hexamethylenimine (HMI) as the OSDA in the presence of NaOH. MCM-49, a 3D **MWW**-type zeolite analogue, which has less HMI in the interlayer region than MCM-22(P), is formed directly when the HMI/NaOH molar ratio is less than 2. This implies that excess OSDA is required in order to occupy the void spaces between adjacent layers, when the 2D precursor is the target material. Therefore, a 3D **MWW**-type zeolite, rather than MCM-22(P), can be directly synthesized without OSDA or the use of cyclohexylamine (similar in size to HMI) as the OSDA [15,16]. The interlayer cross-linkage between adjacent layers of the 2D precursor is relatively weak, such that expansion of the interlayer space can be realized through structural swelling with surfactants and insertion of a Si source, which enables the preparation of delaminated and interlayer-expanded zeolites [17–19]. Inspired by the construction of bi-functional synthetic systems, herein, we report a novel method for the direct synthesis of a delaminated **MWW**-type zeolite, achieved by the addition of dicyclohexylamine (DCHA) as an organic additive into the conventional system used in the synthesis of MCM-22 zeolite. The direct hydrothermal crystallization was carried out at 423 K for 5 d. The starting slurry was obtained by mixing a silica source (Si-sol), alumina source (NaAlO₂), alkali (NaOH), HMI, and DCHA with a composition of SiO₂:Al₂O₃:NaOH:HMI:DCHA:H₂O = 1.0:1/30:0.10:0.20:(0–0.60):18.0. As illustrated in Scheme 1, HMI acted as the OSDA to direct the formation of **MWW** layers, while DCHA acted as an organic additive that weakened the interaction between adjacent **MWW** layers, which in turn disturbed the alignment of the layers along the *c*-axis, resulting in the formation of delaminated **MWW**-type zeolites.

Figure 1 shows the powder X-ray diffraction (XRD) patterns of as-synthesized **MWW**-type zeolites with varying DCHA/SiO₂ molar ratios. Without the presence of DCHA, the sample presents three peaks in the 3.0°–7.5° 2θ range, corresponding to the (001), (002), and (100) lattice plane; ((001) and (002) are the interlayer reflections and (100) is the intralayer reflection) (Fig. 1c). The two discrete peaks at 2θ values of approximately 8.1° and 10°, which are due to the interlayer reflections (101)

Scheme 1. Illustration of the direct synthesis method for generating delaminated **MWW**-type zeolite nanosheets.

and (102), indicate that the layers are stacking in a typical 3D order seen in MCM-22 [4]. The XRD patterns obtained for the samples synthesized with DCHA (Fig. 1a and b), present partial or full overlap of two peaks in the 7.5°–10° 2θ range, along with the absence of the two peaks corresponding to the (001) and (002) lattice plane, confirming a decrease in the stacking order of their layers, much like MCM-56 and ITQ-2 zeolites [8,20]. Following calcination, all samples preserved their structures (Fig. S1). All samples were characterized by typical nanosheet-like morphology of **MWW**-type zeolites, with crystal sizes of 300–500 nm (Fig. S2). Evidence of partial amorphous phase can be seen in the image of the sample synthesized with the highest amount of DCHA. For the convenience of discussion, zeolites synthesized with DCHA/SiO₂ molar ratios of 0.4 and 0.6 are referred to as SCM-1 and SCM-6, respectively.

Figure 2 shows Argon adsorption-desorption isotherms of the **MWW**-type zeolites. All samples possessed typical adsorptions representative of microporous materials, at relative pressures below 0.9. In the relative pressure region above 0.9, the observed dramatic increase in adsorbed volume may arise from disordered mesopores formed by nanosheet crystal stacking. The adsorption isotherm of MCM-22 (Fig. 2a) in the low relative pressure region (below 0.1) exhibits inflection points corresponding to 10-MR channels and 12-MR supercages of MCM-22. A decrease in adsorbed volumes corresponding to these two types of pores were observed for SCM-1 and SCM-6, indicating the loss of micropore volumes, which is likely as a result of delamination. Indeed, SCM-1 and SCM-6 possess

Fig. 1. XRD patterns of **MWW**-type zeolites synthesized with DCHA/SiO₂ molar ratios of (a) 0.6, (b) 0.4, and (c) 0.

Fig. 2. Argon adsorption-desorption isotherms of calcined **MWW**-type zeolites, (a) MCM-22, (b) SCM-1, and (c) SCM-6. Inset shows the enlargement of the low relative pressure region.

lower micropore volumes than MCM-22 (Table S1). Moreover, the external surface areas of SCM-1 and SCM-6 are twice as large as that of MCM-22. The external surface area of SCM-1 is relatively close to the theoretical value of double layered **MWW**-type zeolites, and half of the calculated value of single layered **MWW**-type zeolites (approximately 500 m² g⁻¹) [10]. The low surface area of SCM-6 may be due to the poor crystallinity of the material. When excess DCHA was added into the synthetic system, crystallization was minimal, resulting in a near-amorphous phase (Fig. S3a). Without HMI, only the amorphous phase was obtained (Fig. S3b).

The delamination nature of SCM-1 and SCM-6 was corroborated by TEM characterization as shown in Fig. 3. The TEM micrographs revealed that all crystals possessed nanosheet morphologies with characteristic porosity. The thickness of MCM-22 is approximately 20 nm, while SCM-1 and SCM-6 thicknesses are approximately 5.0 nm and 2.5 nm, respectively. It is imperative to highlight the fact that the thickness of SCM-1 is equal to that of double-layered **MWW**-type zeolites, and SCM-6 thickness is equal to that of single layered **MWW**-type zeolites [12], which demonstrates that the methodology described herein is efficient for the direct synthesis of delaminat-

Fig. 3. TEM images of layered **MWW**-type zeolites (a–c) and cross-sections (d,e) of single and double layered **MWW**-type zeolites, (a,d) SCM-6, (b,e) SCM-1, and (c) MCM-22.

ed **MWW**-type zeolites. Indeed, this is the first report detailing the direct synthesis of **MWW**-type zeolites with a double layer structure. The degree of delamination can be rationally controlled by varying the amount of added DCHA. Delaminated **MWW**-type zeolites possess an abundance of terminal silanols, which is evidenced by the intense peaks at around 3747 cm⁻¹ for SCM-1 and SCM-6 (Fig. S4) [17].

The addition of DCHA did not disturb the incorporation of Al into the framework (Fig. S5) [12] and no Al species outside of the framework were detected, with the Al content in the products being nearly equal to starting gel content (Table S2). The acid content and strength of SCM-1 were comparable with those of MCM-22, while SCM-6 possessed lower acid content (Fig. S6). When tested in liquid-phase alkylation of benzene with ethylene under mild conditions, the conversion of ethylene over SCM-1 was comparable to that over MCM-22, while SCM-6 performance was inferior (Table S2). When the reaction was carried out at a lower temperature and the feeding ratio of benzene/ethylene was altered to a higher WHSV of ethylene, SCM-1 exhibited dramatically superior performance compared to MCM-22, and the rate of ethylene conversion was almost twice as that of MCM-22. Moreover, SCM-1 is considerably more stable than MCM-22. The conversion of ethylene over MCM-22 diminished dramatically after 64 h, while in the case of SCM-1, the decrease was minimal (Fig. 4). This improved catalytic performance of SCM-1 was attributed to enhanced diffusion performance and better accessibility of active sites located on the ultra-large external surface [7]. The used catalyst was recovered and characterized using thermogravimetric analysis (TGA) coupled with mass spectrometry. Overall, SCM-1 exhibited total weight loss to a lesser degree compared to MCM-22 (Fig. S7). Both catalysts exhibited almost equal weight loss (approximately 2.5 wt%) at a temperature of –370 K, corresponding to adsorbed water; the loss at 370–623 K was due to adsorbed organic species, while the loss at above 623 K was presumable due to coke. These results once more demonstrat-

Fig. 4. Catalytic performances of SCM-1 and MCM-22 in liquid-phase alkylation of benzene with ethylene at 473 K under 3.5 MPa with a feeding molar ratio of benzene/ethylene of 3.0 and WHSV of ethylene 6.0 h⁻¹.

ed that SCM-1 was a superior catalytic material compared to MCM-22, due to the partially delaminated nature of SCM-1. The catalytic result of SCM-1 is encouraging because the process of benzene alkylation is strategic in the production of ethylbenzene. Moreover, SCM-1 was tested in the catalytic cracking of 1,3,5-triisopropylbenzene (TIPB), and its performance was once more superior to MCM-22 (Fig. S8).

The herein applied bi-functional synthetic system constructed of HMI and DCHA was effective for the direct synthesis of delaminated **MWW**-type zeolites. Additional organic additives were tested for the synthesis, such as cyclopentylamine, cyclohexylamine, quinolone, *N,N*-dimethylaniline, and *N,N*-diethylcyclohexylamine (Table S3). It is noteworthy that additives with molecular sizes larger than that of HMI were effective for the synthesis of delaminated **MWW**-type zeolites, while those with comparable or smaller sizes did not work. In addition, piperidine and homopiperazine could likewise be utilized as OSDA for the synthesis of delaminated **MWW**-type zeolites. Evidently, the size of the organic agent is a crucial factor determining its effectiveness as an additive in the construction of these bi-functional synthetic systems.

In summary, we have developed a new method for the direct synthesis of delaminated **MWW**-type zeolites by simply adding DCHA into the traditional synthetic mixture for zeolite MCM-22. By adjusting the amount of DCHA, partially and fully delaminated **MWW**-type zeolites with thicknesses of approximately 5.0 and 2.5 nm, respectively, were directly synthesized. The newly obtained zeolite, SCM-1, with an ultra-large external surface area acts as a highly efficient catalyst for the alkylation of benzene and cracking of TIPB. The new method can be fully generalized and can potentially be applied in the synthesis of

other layered precursor-derived zeolites.

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Graphical Abstract

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Controllable direct-syntheses of delaminated **MWW**-type zeolites

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A straightforward method for the direct, controllable synthesis of delaminated **MWW**-type zeolites is reported. The new material with ultra-large external surface area exhibits excellent catalytic performance in the alkylation of benzene with ethylene and the cracking of 1,3,5-triisopropylbenzene.

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层剥离MWW结构分子筛的直接可控合成

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摘要: 分子筛是一类重要的催化材料, 在石油和煤制化学品工业中应用广泛。目前, 国际分子筛协会结构委员会确认的248种分子筛骨架结构中的19种已经商业化应用, 如FAU, MFI, *BEA, MOR和MWW。具有多层结构的MCM-22是MWW结构分子筛的典型代表, 已应用于苯与乙烯液相烷基化制乙苯。然而, 烷基化反应主要发生在位于MCM-22分子筛晶体外表面的半超笼内, 位于10元环孔道和12元环超笼内的酸性位对乙烯转化率几乎没有贡献。因此, 有必要制备能够容纳更多半超笼的具有超大外比表面积的新型MWW结构分子筛。厚度仅2.5 nm的单层MWW结构分子筛ITQ-2具备以上特征, 但是其较弱的酸性质及复杂的制备过程使其无法工业应用。受到采用具有长碳链的双季铵阳离子两亲性有机结构导向剂直接合成层状MFI分子筛的启发, 其有机结构导向剂同时起到导向MFI结构和抑制晶体沿 b 轴方向生长的作用。类似地, 层剥离MWW结构分子筛也被直接合成出来, 但所得材料的催化性能不理想, 且有机结构导向剂不易得。通过对MCM-22分子筛的结构分析发现, 其合成态是由多个MWW结构层有序组装而成, 可以通过溶胀处理增大层间距, 削弱层间相互作用, 经超声处理即可实现层剥离。鉴于此, 本文采用向合成MCM-22分子筛的常规体系中加入二环己基胺充当有机添加剂构筑“双功能”合成体系的策略, 开展层剥离MWW结构分子筛新材料的直接合成。

X射线衍射(XRD)结果表明, 与MCM-22分子筛相比, 在二环己基胺参与下合成的分子筛SCM-1 ($\text{DCHA}/\text{SiO}_2 = 0.4$)和SCM-6 ($\text{DCHA}/\text{SiO}_2 = 0.6$)的XRD谱中与MWW结构 c 轴方向有关的(101)和(102)晶面的衍射峰出现偏移和重叠的现象, 表明其沿 c 轴方向有序性降低。扫描电子显微镜显示, 所有样品均为片状形貌, 其中SCM-6含有少量无定形物种。氩气及氮气物理吸附结果表明, SCM-1和SCM-6具有超大外比表面积, 而微孔体积小于MCM-22分子筛。透射电子显微镜表征结果表明, MCM-22为多层结构, 厚度约为20 nm, 而SCM-1和SCM-6的厚度分别约为5.0和2.5 nm, 对应双层和单层结构, 表明在有机添加剂参与下直接合成了层剥离的新型MWW结构分子筛。值得注意的是, 通过调节添加剂用量, 可以调节剥离程度, 即实现可控层剥离, 得到完全(单层)或部分(双层)剥离的MWW结构分子筛。该方法所采用的添加剂的尺寸是关键因素, 选用尺寸大于有机结构导向剂的添加剂才能有效抑制晶体沿 c 轴方向的有序生长, 实现层剥离MWW结构分子筛的直接合成。

采用该方法合成的新型MWW结构分子筛具有超大外比表面积和更多的表面半超笼, 在苯与乙烯液相烷基化反应中, SCM-1催化的乙烯转化率明显高于MCM-22分子筛。SCM-6因结晶度低而未能表现出优势。进一步比较SCM-1和MCM-22的催化稳定性发现, SCM-1的稳定性更好, 经过64 h连续反应, 其吸附的有机物及积碳更少。在1,3,5-三异丙苯裂解反应中, SCM-1的催化性能也明显优于MCM-22。

关键词: 分子筛; MWW; 烷基化; 乙苯; 剥离; 催化

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