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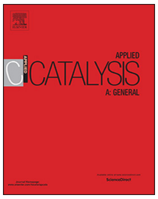

Fabrication of MIL-101(Cr/Al) with flower-like morphology and its catalytic performance

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ABSTRACT

The morphology and structure of metal organic frameworks (MOFs) are closely related to their properties. Herein, a flower-like morphology MOF (named as MIL-101(Cr/Al)$_{A\text{-}f}$) was rationally designed in a acid-free environment and the Al^{3+} was transformed into the framework by the substitution process of cation exchange. During the preparation process of MIL-101(Cr/Al)$_{A\text{-}f}$, we found that the acidity of the reaction mixture could regulate the morphology of MIL-101(Cr/Al)$_{A\text{-}f}$ by adjusting the coordination of the metal clusters and the ligand chains. The catalytic performance of MIL-101(Cr/Al)$_{A\text{-}f}$ was evaluated by the hydroxyalkylation of phenol with formaldehyde. Due to the larger surface area and high-density sites, MIL-101(Cr/Al)$_{A\text{-}f}$ showed a higher catalytic activity than the octahedron morphology MIL-101(Cr/Al)$_{A\text{-}0.5}$ which was prepared with traditional method in acidic environment. In approximately equal Al^{3+} content, the MIL-101(Cr/Al)$_{A\text{-}f}$ showed a remarkably high yield (97.1%) and a excellent selectivity (98.3%) to bisphenol F at 60 °C for 30 min. Finally, a possible mechanism for the synthesis of bisphenol F was proposed and the hydroxyalkylation of phenol with formaldehyde to bisphenol F was fitted by the Langmuir-Hinshelwood kinetic model.

1. Introduction

Porous solid materials are of great importance for catalysis [1], gas storage [2], liquid separation processes [3], sensing [4], drug delivery [5], luminescence [6] and magnetism [7]. Continuous efforts from both industry and academia have been committed to the search for novel types of porous materials. Among the various candidates explored in the past two decades, MOFs have attracted a wide range of interests due to its tailorable and versatile structures, extremely high surface areas and permanent nanoscale porosities [8–10]. As a relatively novel crystalline porous material, MOFs are promising for applications in the fields of catalysis [11–13]. The presence of coordinatively unsaturated metal sites in MOFs allows its use as a Lewis acid and, more important, allows its postfunctionalization via grafting of active species. Particularly, these high-density unsaturated metal sites can be uniformly distributed throughout the MOFs. Regarding the functionalization of MOFs, there have been four main approaches: a) functionalization of the organic linkers by pre-modified [14,15], b) functionalization of the linker sites or organic ligands by post-covalent modification [16,17], c) post-grafting of coordinatively unsaturated sites with chelators or metal clusters [18], (d) synthesis of multi-metal frameworks by one-step method [19–22]. Chui et al. reported that the ligands can be replaced by other chains, such as pyridine [23]. It has been also reported that the cavities of framework can be modified by chemical modification without change of the original crystal structure. Kitagawa and co-workers proposed that the introduction of functional groups decorates the sites of the framework. Cristina P. Krap and co-workers reported the incorporation of metal ions into the metal-organic frameworks by one-pot for catalysis [19]. In addition, various morphologies can be obtained by different synthetic approaches such as the Kirkendall effect, template method, microwave radiation method, chemical etching, ions doping and chemical vapor deposition method [24–30]. In order to maximize the structure advantage and realize beneficial functionalities, the rational design of morphology with high-density accessible sites is highly desirable.

We chose MIL-101-Cr as the platform material because of its high water/chemical stability and readiness for functionalization via post-synthetic modification methods, and the morphology of MIL-101-Cr can be controlled by adjusting parameters during the preparation process. This hybrid material is composed of supertetrahedral building units, which are formed from trimeric metal octahedron clusters and rigid terephthalate ligands [31]. The resulting three-dimensional cage material possesses two types of quasispherical mesoporous cages formed by hexagonal windows and pentagonal windows, respectively. In

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addition, the presence of open metal sites and regular frameworks in MIL-101 contributes to postfunctionalization via grafting of active species [32]. The fully accessible porosity, the favorable structural morphology, together with a high chemical and thermal stability make MIL-101 an excellent potential for catalytic purposes.

In this paper, a novel strategy has been proposed for preparing MIL-101(Cr/Al)$_{\text{A-f}}$ in a acid-free environment and a substitution process by cation exchange was carried out to transform the Al^{3+} into MOFs. We compared the catalytic properties of the prepared MIL-101(Cr/Al)$_{\text{A-f}}$ with the MIL-101(Cr/Al)$_{\text{A-0.5}}$ in hydroxyalkylation of phenol with formaldehyde. In addition, the effect of acidity on the morphology of the framework during the preparation process was investigated. The MIL-101(Cr/Al)$_{\text{A-f}}$ exhibited a excellent catalytic activity due to its unique morphology, which was supported by BET, SEM and TEM. Finally, a possible mechanism for the synthesis of bisphenol F was proposed and the hydroxyalkylation of phenol with formaldehyde was fitted by the Langmuir-Hinshelwood kinetic model.

2. Experimental section

2.1. Chemicals

All chemicals were provided from commercially available resources and were studied without further processing. Chromium nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$), aluminum chloride hexahydrate, nitric acid, terephthalic acid (BDC, 98%), N,*N*-dimethylformamide (DMF, 99%), formaldehyde (37–40%) and phenol were obtained from Sinopharm Chemical Reagent Co. Ltd., China.

2.2. Synthesis of MIL-101(Cr/Al)$_{\text{A-X}}$

Typical synthetic process was carried out via hydrothermal synthesis and described as follows: BDC (1.66 g, 10 mmol), $Cr(NO_3)_3 \cdot 9H_2O$ (4.0 g, 10 mmol), deionized water (30 mL) and nitric acid from 0 to 0.5 g were mixed at room temperature, and then sonicated for 30 min. The mixture was transferred into a 50 mL Teflon-lined autoclave and heated at 220 °C for 18 h. The suspension was centrifuged and the precipitate was washed with DMF and ethanol. The obtained product was dried at 150 °C for 12 h. 1 g of sample was refluxed in 50 mL of 0.3 m/L $AlCl_3$ aqueous solution at 70 °C for 24 h. Then solid was separated by centrifugation and washed twice with ethanol. Finally, the samples were vacuum-dried at 150 °C for 12 h, and labeled as MIL-101(Cr/Al)$_{\text{A-X}}$, where X represents the quality of nitric acid in the preparation process (0.5 g, 0.3 g, 0.1 g and free).

2.3. Characterization techniques

The crystalline phases of the products were examined by X-ray diffraction (Bruker D8 Advance diffractometer) with Cu Ka radiation (working at 40 kV and current 40 mA). Diffraction data were recorded in the 2 h range from 1° to 8° and 10° to 80° (increment: 0.5°). The unit cell parameters were calculated with a standard least squares refinement technique. NH_3-TPD analysis was performed with a Micromeritics AutoChem II 2920 V3.05 instrument. Prior to analysis, the catalyst (100 mg) was enclosed in a quartz tube and treated at 300 ℃ under helium flow of 30 mL min^{-1} for 1 h. The magic angle spinning (MAS) NMR analysis was performed by a Bruker Avance-400 with a 5 mm zirconia rotor and a spinning frequency of 11 kHz. Spectra for ^{27}Al was obtained. The porosity was analyzed by N_2 adsorption at 77 K using an ASAP 2010 sorption system. UV–vis diffuse reflectance spectra were recorded at a Perkin–Elmer Lambda 900 spectrophotometer under 200–800 nm. The binding energies of C, O, Cr and Al of the composite microspheres were detected on X-ray photoelectron spectroscopy (Thermo Fisher, USA) using an Al-KX-ray source. Scanning electron microscopy (SEM) micrographs were obtained on a Hitachi S4800 microscope operated at 30 kV. Transmission electron microscopy (TEM) and elemental mapping analysis were collected using a high-resolution transmission electron microscope (HRTEM, TECNAI F20). Energy-dispersive X-ray (EDX) analysis was used to determine the chemical composition of the samples. Thermogravimetric analysis (TGA) was recorded on a Mettler-Toledo 1600HT thermoanalyzer under a nitrogen atmosphere at a heating rate of 10 ℃ min^{-1}. The concentration of aluminum was monitored by an atomic absorption spectrophotometer (Z-2000, Hitachi, Japan).

2.4. Catalytic activity tests

Hydroxyalkylation of phenol with formaldehyde to bisphenol F was carried out in reactor with magnetic stirring. Typical experimental processes were summarized as follows: 0.465 g (5.7 mmol) of formaldehyde solution, 8.12 g of phenol and 0.12 g of catalyst were added into the reactor and the reaction mixture was heated to the desired temperature. After a certain time interval, 0.03 g of the suspension was taken out and then diluted with 10 mL of methanol. The composition of the product was confirmed by HPLC with a Shimadzu LC-20AT system connected with a SPD-20A UV/Vis detector and a Phenomenex Luna C18 column (250 × 4.6 mm, 5 mm); A mixture of methanol and water with 65:35 v/v was used as the mobile phase with a constant flow rate of 0.6 mL/min. The injective volume of the sample was 100 μL.

The yield and selectivity of bisphenol F are calculated on the basis of formaldehyde. The calculation equations are as follows:

$$\text{Yield}(\%) = \frac{\text{Moles of bisphenol F formed}}{\text{Expected moles of bisphenol F formed based on formaldehyde consumed}} \times 100\%$$

$$\text{Selectivity}(\%) = \frac{\text{Moles of bisphenol F formed}}{\sum \text{Moles of all the products}} \times 100\%$$

The synthetic route for the formation of bisphenol F by hydroxyalkylation of phenol with formaldehyde is shown in Scheme 1.

3. Results and discussion

3.1. Catalyst characterizations

The morphological evolution of MIL-101(Cr/Al)$_{\text{A-X}}$ was conducted by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). MIL-101(Cr/Al)$_{\text{A-0.5}}$ (Fig. 1a and b) exhibits single octahedron morphology with a size around 300 nm, while the flower-like morphology of MIL-101(Cr/Al)$_{\text{A-0.3}}$ begins to appear in the vicinity of the octahedron morphology (Fig. S1a–c). With the acidity weakening, more deprotonated carboxyl groups are generated to accelerate coordination with metal clusters. The appearance of mixed octahedron/flower-like morphologies may be attributed to the heterogeneous nucleation in the patterns of MIL-101(Cr/Al)$_{\text{A-0.3}}$. During the heterogeneous nucleation process, the increased deprotonated carboxyl groups firstly form flower-like morphology and the remained deprotonated carboxyl groups with low concentration form octahedron morphology. The particle size of octahedron morphology in MIL-101(Cr/Al)$_{\text{A-0.3}}$ (~150 nm) is about half smaller than that of MIL-101(Cr/Al)$_{\text{A-0.5}}$ with single octahedron morphology, which may due to the presence of flower-like morphology in their adjacent areas. In addition, the particle size of original MIL-101(Cr)$_{\text{A-X}}$ is investigated. The particle size of flower-like MIL-101(Cr)$_{\text{A-f}}$ is slightly larger than that of octahedron MIL-101(Cr)$_{\text{A-0.5}}$ (Fig. S2), which is consistent with the reference [33]. As shown in Table S1 and Fig. S3, the average particle size of MIL-101(Cr)$_{\text{A-X}}$ is analysed using a GaussAmp model. With the decrease of acidity, the number of the deprotonated carboxyl groups of terephthalic acid increases, which speeds up the rate of coordination with metal ions. The increase of the coordination rate makes the coordination tend to irregular and outward growth, leading to larger particles. With the decrease of acid from 0.3 to 0.1 g, the growth of flower-like morphology is easier (Fig. S1d–f). When there is no nitric acid, we get a nearly perfect flower-like morphology (Fig. 1c–e). The HRTEM images (Fig. 1f)