Catalysis Communications 80 (2016) 24–27

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Temperature effect on the morphology and catalytic performance of Co-MOF-74 in low-temperature NH_3-SCR process

Haoxi Jiang, Qianyun Wang, Huiqin Wang, Yifei Chen *, Minhua Zhang

[a] Key Laboratory for Green Chemical Technology of Ministry of Education, R&D Center for Petrochemical Technology, Tianjin University, Tianjin 300072, China
[b] Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, China

ARTICLE INFO

Article history:
Received 11 December 2015
Received in revised form 25 February 2016
Accepted 23 March 2016
Available online 25 March 2016

Keywords:
Co-MOF-74
Temperature effect
Morphology
SCR
$DeNO_x$

ABSTRACT

Co-MOF-74 materials were synthesized at different temperatures using solvothermal method. The effect of the synthetic temperature on the structure and low temperature NH_3-SCR catalytic performance of Co-MOF-74 was systematically investigated. Co-MOF-74 synthesized at 100 °C has flower-like morphology, while hexagonal prism structures could be obtained at other temperatures. Co-MOF-74 with flower-like morphology has a larger specific surface area and pore volume compared with the hexagonal prism ones. The highest catalytic activity was obtained at 200 °C under the optimal synthesis temperature, which was attributed to the combination of special morphology, the highest specific surface area and Co content.

1. Introduction

Exhaust gases from stationary power plant and mobile vehicles contain nitrogen oxides (NO, NO_2, and N_2O) which contribute to photochemical smog, acid rain, ozone depletion and the greenhouse effect [1]. The extremely attractive and efficient technology for reducing NO_x emissions from power plants is selective catalytic reduction (SCR) of NO_x with ammonia [2]. The most widely used catalyst for this process in industry is V_2O_5–WO_3(MoO_3)/TiO_2, which has a narrow and high working temperature (300–400) [3]. Researchers are interested in developing the low-temperature (e.g., 100–250 °C) SCR catalyst, which is capable of working downstream of the dust removal equipment and desulfurization devices without reheating. It has been extensively reported that manganese oxides-based (MnO_x) catalysts exhibit promising catalytic performance in low temperature SCR reactions; however, it is not practical to be used without support due to the low specific surface area [4]. In addition, the performance of supported catalysts was largely dependent on the dispersion of MnO_x [5,6]. Therefore, a catalyst with high specific surface area and highly dispersed catalytic active sites is required.

Metal–organic frameworks (MOFs), as a new type of crystalline porous materials assembled by metal ions/clusters and polyfunctional organic molecules, have been attracting great interest in recent years. MOFs have controllable pore size, high surface area, and desired chemical functionalities, which make MOFs a promising material for gas capture [7], separation [8], and catalysis [9]. A considerable amount of catalytic reactions over MOFs has been reported [9–11].

Unsaturated metal centers, also known as open metal sites, exist in some MOF structures, such as $Cu_3(btc)_2$ (btc = benzene tricarboxylic acid) (HKUST-1) [12] and M_2(dhtp) (M=Zn, Ni, Co, Mg; dhtp = 2,5-dihydroxyterephthalate) (MOF-74) [13]. MOF-74 was reported to have the highest density of open metal sites in MOF materials [14]. The open metal sites in MOF-74 could be acting as Lewis acid sites for SCR reaction. In addition, MOF-74 has a relatively large surface area which could improve the adsorption of the reactant and finally benefit for the reaction. The crystal structure of M-MOF-74 is based on a honeycomb motif with pores of ~12 Å diameters. Each metal atom coordinates with three oxygen atoms from carboxylate and two oxygen atoms from the deprotonated OH group; whereas, the sixth coordinative site is normally occupied by a water molecule or a molecule of solvent (DMF), which can be removed by a mild thermal treatment, finally exposing unsaturated metal sites [15]. Samiran et al. [16] reported that both crystalline and amorphous Fe-MOF-74 have good activity for hydroxylation of phenol using H_2O_2 as an oxidant. It has been shown that the catalytic activity of MOFs depends on the amount of unsaturated coordination sites in the framework, where the catalytic reaction takes place. Wang et al. [17] reported that MIL-100(Fe) has good activity for the SCR of NO_x with NH_3. It exhibited more than 97% NO_x conversion at 245–300 °C. Although its NO_x conversion is higher than conventional V_2O_5–WO_3(MoO_3)/TiO_2 catalyst, the catalytic temperature(245–300 °C) is not in the low-temperature window entirely. Therefore, we are expecting MOF-74, which has more open metal sites, to have a better catalytic performance at low temperatures. Co-MOF-74 was tested,

---

* Corresponding author.
E-mail address: yfchen@tju.edu.cn (Y. Chen).

http://dx.doi.org/10.1016/j.catcom.2016.03.013

because Co_3O_4 was reported to have high activity for both NO oxidation and NO_x reduction at high space velocity and low temperature [1].

In this work, Co-MOF-74 was synthesized at different temperatures by solvothermal method. The effect of temperature on the topography and properties of Co-MOF-74 has been compared. Their potential application as a heterogeneous catalyst for low-temperature NH_3-SCR deNO_x was investigated in order to get the optimal conditions for Co-MOF-74 synthesis and application.

2. Experiment

2.1. Preparation of Co-MOF-74

Cobalt (II) nitrate hexahydrate (3.8032 g, purity of 99%, Tianjin Recovery Technology LLC) and 2,5-dihydroxy-1,4-benzenedicarboxylic acid (DHTP, 0.7712 g, purity of 98%, Heowns Biochem Technologies LLC) were dissolved in a mixture of N,N-dimethylformamide (DMF, 106.7 ml, purity of 99.5%, Tianjin Jiangtian Chemical Technology LLC), ethanol (106.7 ml, purity of ≥99.7%, Tianjin Jiangtian Chemical Technology LLC) and water (106.7 ml). All the materials were purchased without further purification. The resulting solution was loaded in Teflon-lined autoclaves (5 × 100 ml and 2 × 150 ml) and heated at 100 °C, 120 °C, 135 °C, and 150 °C, respectively, in an oven for 24 h for reaction. After cooling to room temperature, the mother liquor was decanted; the products were washed and soaked in methanol for 12 h. After that, methanol solvent was decanted and replaced. The methanol exchanges were repeated in the next three days. Finally, the products were filtered and stored in a dryer.

The metal contents in the products were determined by TGA analysis (Figure S3(b)) under air condition from 25 °C to 800 °C. The final product is Co_2O_3, with the metal contents of 26.33%, 25.09%, 25.44%, and 25.70% for Co-MOF-74-100 °C, 120 °C, 135 °C, and 150 °C, respectively.

2.2. Characterization

The crystallinity of all the samples was confirmed by powder X-ray diffraction (PXRD, Rigaku D/Max 2500) at 40 kV and 200 mA with Cu Kα radiation. Fourier Transform Infrared Resonance (FTIR, Nicolet 6700) spectra of the crystalline samples were directly recorded using KBr pellets. Morphological features were examined by Scanning Electron Microscope (SEM, Hitachi S-4800). The thermal stability of the samples was evaluated using a thermo-gravimetric analyzer (TGA, METTLER DSTA851) followed by mass spectroscopy (MS, Balzers PFEIFFER ThermoStarTM). The nitrogen adsorption–desorption isotherms were measured with a Micromeritics Tristar 3000 using nitrogen at 77 K after the samples were pretreated in a N_2 atmosphere at 250 °C for 8 h. The specific surface areas and pore sizes were calculated by the BET (Brunauer–Emmett–Teller) method and the BJH (Barrett–Joyner–Halenda) method, respectively.

2.3. Catalyst activity evaluation

The deNO_x activity of the catalysts in the present of NH_3 was measured in a fixed-bed reactor at atmospheric pressure with the following reactant gas composition: 1000 ppm NO, 1000 ppm NH_3, 2% O_2, and the balance Ar. Approximately 0.2 g of catalysts (60–80 mesh) and 0.4 g of quartz sand were mixed in each test. Under ambient conditions, the total flow rate was 100 $ml \cdot min^{-1}$ and the gas hourly space velocity was 50,000 h^{-1}. The reaction temperature was regulated from 100 to 220 °C and the system was maintained 1 h at each experimental condition. The concentrations of NO and NO_2 were continually monitored by a flue gas analyzer (KM9106 Quintox Kane International Limited). The effluent streams were also analyzed by gas chromatography at 30 °C (Agilent GC-6820, with a 5 Å molecular sieve column for N_2 and a Porapak Q column for N_2O analysis).

3. Results and discussion

3.1. Effect of synthetic temperature on the structure and properties of Co-MOF-74 catalyst

PXRD patterns (as shown in Figure S1) showed that Co-MOF-74 with intact crystalline structure can be synthesized at 100 °C, 120 °C, 135 °C, and 150 °C, named as Co-MOF-74-100 °C, 120 °C, 135 °C and 150 °C, respectively [18]. The change of temperature does not have a significant impact on the formation of crystal Co-MOF-74 in 100–150 °C.

Comparing the FTIR spectroscopy of Co-MOF-74, raw materials, and corresponding metallic oxide (as shown in Figure S2), it is confirmed that Co-MOF-74 can be synthesized at 100 °C, 120 °C, 135 °C, and 150 °C, which is coincided with PXRD result.

TGA profiles (Figure S3(a)) of Co-MOF-74 prepared at different temperatures under SCR conditions showed two steps of weight loss. The temperature of the framework collapse was >250 °C (284.5 °C), therefore, Co-MOF-74 can keep stable structure under the SCR conditions (low-temperature SCR < 250 °C).

Fig. 1(a–d) represents the SEM images of Co-MOF-74-100 °C, Co-MOF-74-120 °C, Co-MOF-74-135 °C, and Co-MOF-74-150 °C, respectively. The shape of Co-MOF-74 greatly depends on hydrothermal temperature. Co-MOF-74 synthesized at 100 °C has flower-like morphology, which is the result of small polyhedral crystal aggregates together, with a diameter of approximately 100 μm. The size of the crystals with hexagonal prisms varies with temperatures. In addition, the hexagonal prism-like morphology is identical to Co-MOF-74 synthesized in 24 h by solvothermal method reported by Cho et al. [19]. For Co-MOF-74-120 °C, it is about 25 × 5 μm (length × diameter). The sizes for Co-MOF-74-135 °C and Co-MOF-74-150 °C are 35 × 8 μm and 40 × 6.5 μm, respectively. The crystal size increased with the increasing temperature. Hence, we can control their morphology by changing the hydrothermal synthetic temperature.

Fig. 2 showed the nitrogen adsorption isotherms of Co-MOF-74. All isotherms were of type I, with a very sharp uptake at relatively low pressure, subsequently a steady increase of adsorbed nitrogen, showing a characteristic of microporous materials. For a detailed observation, isotherms of Co-MOF-74-135 °C and Co-MOF-74-150 °C showed hysteresis, indicating the property of mesoporous.

Table 1 summarizes the textural properties of Co-MOF-74. Co-MOF-74-100 °C exhibits a specific surface area of 928.9 m^2/g. Compared with the values reported in previous literatures of 1327 m^2/g [19] and 1372 m^2/g [20], our Co-MOF-74 does have lower specific surface area, even in our optimization experiments. This might be because the solvents in the samples were not fully removed. However, it is in a reasonable range [21]. With the increasing hydrothermal synthetic temperature, both the specific surface area and pore volume of Co-MOF-74 are gradually decreased; whereas, the average pore sizes are slightly increased from 1.80 to 2.17 nm. The average pore size of Co-MOF-74-150 °C is a little beyond the scope of microporous (<2 nm), which is identical to the property of isotherm. In general, BET decreases with the increasing pore size. The larger specific surface area could provide more exposed adsorption and catalytic active sites. In addition, Co content of Co-MOF-74-100 °C is 26.33%, which is the largest among the samples. Therefore, compared with Co-MOF-74-120 °C, 135 °C, and 150 °C, Co-MOF-74-100 °C had the largest specific surface area and pore volume, and the largest content of catalytic active sites, which could be more beneficial for the SCR reaction. The optimal hydrothermal temperature for synthesis Co-MOF-74 is 100 °C.

3.2. DeNO_x catalyst activity

The catalytic performance of Co-MOF-74-100 °C, 120 °C, 135 °C, and 150 °C for NO conversion as a function of reaction temperature was tested and the results are shown in Fig. 3. For all four catalysts, as the temperature increased, the NO conversions were of similar trend.