Fabrication of hierarchical channel wall in Al-MCM-41 mesoporous materials to promote the efficiency of copper modifier

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ABSTRACT

A new route to promote the efficiency of copper species in the Al-containing MCM-41, by anchoring the copper species into the artificial defects on the channel wall, was proposed and validated in this article. These artificial defects in Al-MCM-41 were fabricated by acid leach of framework alumina, and three different loading methods, dry impregnation and grinding as well as microwave irradiation methods were utilized to disperse the copper oxide of 0.6 wt.% on the mesoporous support. Al-MCM-41 itself was also modified with CuO through dry impregnation as the comparison. The influence of modification on the structure and performance of Al-containing MCM-41 was investigated by use of XRD and N_2 adsorption-desorption. A kind of volatile nitrosamine N-nitrosopyrrolidine (NPYR), the typical carcinogenic pollutant in environment, was used in both instantaneous adsorption and temperature programmed surface reaction (TPSR) to explore the adsorption and catalytic properties of these mesoporous composites. Besides, Mass spectrometer was employed to analyze the gaseous products of NPYR decomposed during TPSR procedure. The CuO modifier anchored in acid-leached sample possessed a higher activity in eliminating volatile nitrosamines, in comparison with those located on the parent Al-containing MCM-41.

1. Introduction

Synthesis of the efficient selective adsorbent and catalyst is not only the requirement of environment protection, but also the challenge of material science. Zeolite is widely used in petrochemical, chemical industries and environmental protection due to its unique selectivity, but the sole presence of micropores in zeolites often imposes diffusion limitations due to restricted access and slow intra-crystalline transport to/from the active site, provoking low catalytic and adsorptive effectiveness [1]. Consequently, mesoporous materials became the valuable candidate in many applications, and their wide channel is the advantage enabling them to adsorb bulky molecules such as proteins, overcoming the limitation of pore size in zeolites or some other microporous materials [2]. However, ordered mesoporous materials lack not only the geometric confinement towards small molecules such as volatile nitrosamine [3], but also the cations to electrostatic induce the target [4], so their modification is necessary. There are various efforts to improve the adsorption and catalytic properties of ordered mesoporous materials, and one of them was the introduction of guest metal species such as copper, zinc and iron, either by one-pot synthesis or post-modification method, in order to form active

sites in the ordered mesoporous matrix [5–10]. However, increasing the metal modifier content of mesoporous material to improve their adsorption and catalytic abilities will inevitably increase the cost and sometimes even lower the performance of the composites owing to congregation of the modifiers [11,12], hereby we came up with a question how to form the active sites with high efficiency in the channel wall of ordered mesoporous materials. That is to say, how to maximize the utilization of the metal modifiers?

It is well known that the dispersion and distribution of modifier affect the actual properties of final composites [11,13,14], involving not only the accessibility and state such as the particle size of active sites [9,13], but also the interaction between the guest species and the support [15]. In our opinion, the activity of metal oxide should also involve the microenvironment provided by the support. With almost the same amount of CuO modifier, two catalysts with the same composition showed quite different activity in $CO + O_2$ reaction because their supports were synthesized with different methods and exposed different crystal plane [14]. As we previously reported [3], a mesoporous sample with a copper content of only 280 ppm exhibited a similar adsorption capacity to its textural analogue with a copper content of 1.01% [3], since the copper species on the former were anchored in kinks and vacancies while those of the latter were covered on framework. Clearly, the copper species located in the defects of support can improve the catalytic activity and selectivity of the resulting composites [15], because these defects act as anchoring sites to make the nanoparticles less mobile during the calcinations process [15], preventing the aggre-

gation of CuO particles. The narrow microenvironment of active sites, such as a newly formed pore, is beneficial for the capture of target molecules, because the movement of target will be limited within the newly formed pore. On the other hand, micropores and some defects can increase the effective collision of adsorbates with active site [16], and the variation of surface curvature provokes the whirling and swerving of flow to prolong the contact time of target with adsorbent [17]. For these reasons, the CuO species anchored in defects should have a high efficiency to capture target molecules in fast gas stream with a prolonged contact time due to the special microenvironment provided by the defects. For this aim we try to fabricate the hierarchical channel wall in Al-MCM-41 mesoporous materials, elevating the efficiency of copper modifier.

Leaching the Al-MCM-41 with acidic solution to tailor the channel wall is proven to be feasible [17], forming the abundant of surface flutes and micropores on the channel wall by eluting framework aluminum at a mild condition while keeping the mesostructure of MCM-41; at the same time, the distribution and location of framework Al species can be also changed. However, it is unknown whether this strategy can be utilized to promote the efficiency of guest metal modifier, which spurs us to assess the actual performance of CuO modifier in the treated mesoporous materials, especially in the instantaneous adsorption and catalytic decomposition of small carcinogen such as volatile nitrosamines. For this aim, the Al-MCM-41 with a low Al content is chosen to fabricate some defects for three reasons: the first, the framework aluminum can stabilize the structure of the sample [18], while the pure siliceous MCM-41 will lose its ordered structure in acidic solution due to the poor hydrothermal stability and uncontrolled hydrolysis of Si–O–Si bond in aqueous solution; The second, acid treatment rarely influenced the structure of Al-MCM-41 with a low Al content but caused framework collapse in the sample with high Al content [17]; The third, there is no micropore in Al-MCM-41, and thus a comparison can be made between the parent and the treated samples to explore the contribution of artificial defects on adsorption and catalysis. Subsequently, copper species are introduced into both the parent Al-MCM-41 and its acid leached analogue to examine the effect of artificial defects on the performance of copper modifiers. Besides, three loading methods, dry impregnation and solid state grinding as well as microwave irradiation, are utilized to investigate their influence on the dispersion and performance of copper species. *N*-nitrosopyrrolidine (NPYR), the typical volatile nitrosamine with a structure of five-member ring, was chosen as the probe to assess the actual adsorption and catalytic properties of the samples before and after modifications, since NPYR is a common carcinogen in tobacco smoke and environment [3,4].

2. Experimental

2.1. Materials and reagents.

N-nitrosopyrrolidine was provided by Sigma and dissolved in dichloromethane (A. R.) at the ratio of 1:19 (V/V) to get the solution of 0.54 mmol L^{-1}. Cetyltrimethylammonium bromide (CTAB) and silica aerosol were produced by Nanjing Chemical Reagents and Qingdao Haiyang (China), respectively. AlCl$_3$·6H$_2$O and Cu(Ac)$_2$·H$_2$O were purchased from Shanghai Meixing Chemical Plant and Shanghai Zhenxin Reagents, and other reagents with the AR purity were used as received

Fabrication of Al-containing MCM-41 and the acid treatment of the sample were performed according to literature [17]. Silica aerosol (3 g) was added to NaOH solution (0.5 mol L^{-1}, 45 mL) under stirring and heated at 333 K to dissolve the additive, and then a solution (25 mL) containing CTAB (4.5 g) was dropwise added with stirring at room temperature, subsequently, a certain amount of

AlCl$_3$ solution was put into the resulting mixture and the pH value of the solution was adjusted to 10 using HCl solution (2 mol L^{-1}). After being stirred for 6 h, the gel mixture was heated statically in autoclave at 403 K for 72 h, and the product was recovered by filtration, washed with distilled water, air dried and calcined in air at 823 K for 5 h to give the sample named as M70 where 70 represented the actual molar ratio of Si/Al. Acid treatment of the M70 sample was performed as follows: the M70 powder was stirred in 0.05 mol L^{-1} hydrochloric acid for 2 h at room temperature with a liquid to solid ratio of 100 mL g^{-1}; and then the solid product was filtrated, washed thoroughly with distilled water, and dried to give the sample of TM70 (Abbreviation of Treated M70). Subsequently, copper acetate was introduced on the mesoporous support by dry impregnation, solid state grinding and microwave irradiation methods, respectively. Dry impregnation was carried out with a liquid to solid ratio of 5 mL g^{-1} while in the grinding method copper acetate was ground with TM70 powder for 30 min at ambient temperature. For the microwave irradiation method, copper acetate and TM70 powder were ground for 15 min followed by an irradiation for 20 min with an output power of 850 W at 2450 Hz in a Mega1200 microwave laboratory system. In general, the resulting homogeneous powder was calcined at 773 K in air for 5 h (heating ramp of 2 K min^{-1}) to obtain CuTM70n (n = i, g, m, representing dry impregnation, grinding, microwave method, respectively), in which the content of CuO was fixed to 0.6 wt.%. For comparison, part of the TM70 sample had been treated in the same procedures without copper acetate to give TM70n (n = i, g, m), meanwhile, the copper modifier was also loaded on M70 by impregnation to attain CuM70i sample. At the same time, CuO was mechanically mixed with TM70 to obtain the mechanical mixture. The resulting powder sample was pressed into a plate at a 769YP-15A tablet machine and then sifted into 20–40 meshes for succeeding experiments.

2.2. Methods

The X-Ray diffraction (XRD) patterns of samples were recorded on an ARL XTRA diffractometer with Cu Kα radiation in the 2θ range of 0.5°–7° or 10°–80°, and the chemical composition of them was detected by X-ray Fluorescence (XRF) method using ARL-9800 X-ray fluorescence spectrometer [17]. Nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020 volumetric adsorption analyzer prior to the activation of sample at 573 K for 4 h. The Brunauer–Emmett–Teller (BET) specific surface area was calculated using adsorption data in the relative pressure range from 0.04 to 0.2. The total pore volume of sample was determined from the amount adsorbed at a relative pressure of about 0.99, and the pore size distribution curves were calculated from the analysis of the adsorption branch of the isotherm using the Barrett Joyner Halenda (BJH) algorithm. The primary mesopore volume, V_p, and micropore volume, V_{mic}, were calculated by the *t*-plot method.

Temperature-programmed reduction (TPR) was utilized to determine the state of CuO on CuTM70i and CuM70i [14]. The experiment was carried out in a quartz U-tube reactor, and 100 mg sample was used for each measurement. Before reduction, the sample was activated in N$_2$ stream at 773 K for 1 h and then cooled to room temperature. After that, a H$_2$–Ar mixture (7% H$_2$ by volume) with a flowrate of 40 mL min^{-1} was switched on and the temperature was increased linearly at a rate of 10 K min^{-1}. A thermal conductivity detector was used to detect the consumption of H$_2$ on stream.

Instantaneous adsorption of nitrosamines was carried out by using gas chromatography method [4], in which 5 mg samples (20–40 meshes) were filled in a stainless steel microreactor with one end inserted deeply into the injector port and the other end