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**SYNTHESIS OF TERNARY MESOPOROUS Cu-Zn-SiO₂ MATERIALS
AT AMBIENT TEMPERATURE AND THEIR APPLICATION FOR THE
WATER GAS SHIFT REACTION**

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Abstract

A series of ternary mesoporous CuZnMCM-41 materials has been synthesized at ambient temperature and their structure was characterized by XRD, N₂ physical adsorption and TPR techniques. Their catalytic applications in CO water gas shift reaction were studied.

Keywords: CuZnMCM-41, mesoporous materials, water gas shift, catalyst

INTRODUCTION

Polymer electrolyte fuel cell (PEFC) systems have received much attention as a compact generator for stationary applications and automotive applications in vehicles. In this system, hydrogen is used as fuel, coming from the partial oxidation of methanol or hydrocarbons followed by steam reforming. The problem is that the reformed gases contain CO at a level of 1-3% which adsorbs irreversibly on the Pt electrode of the PEFC at the operating temperature (*ca.* 80°C), and hinders the electrochemical reaction [1-3]. Therefore, CO must be

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removed from the reformed gases to less than 10-20 ppm before feeding the gas mixture to the Pt electrode. Water gas shift reaction (WGSR) is a desirable reaction for the removal of a large amount of CO because it is a moderately exothermic reaction and the reaction temperature is easy to control. Cu-ZnO/Al₂O₃ catalysts are the most common catalysts used for this process and they have been widely studied [4-6]. The catalysts were generally prepared by the coprecipitation or impregnation method.

Mesoporous material is a kind of material with a regular channel structure and high surface area. Since it is discovered by research group at Mobil corporation in 1992 [7], various synthesis methods have been developed and a large progress have been made. Its application in heterogeneous catalysis is a promising field, while the pure silica MCM-41 showed very limited catalytic activities. It is necessary to incorporate metals into the silicate framework to create active sites for catalytic reactions, such as Al, Ti, Cr, V, Sn, Co, Pd, Fe, Ga, Zr, Mn and Cu, [8-15]. Hartmann *et al.* synthesized CuZnMCM-48 at 373 K [16]. In the present study, a series of CuZnMCM-41 ternary mesoporous materials were synthesized at ambient temperature and their application for water gas shift reactions was studied.

EXPERIMENTAL

Preparation

The ternary mesoporous materials (CuZnMCM-41) were prepared by direct synthesis at ambient temperature. Cetyltrimethylammonium bromide (CTAB) and sodium silicate (Na₂SiO₃) were dissolved in distilled water (the concentrations of CTAB and Na₂SiO₃ were 0.1 M and 0.4 M, respectively). A mixture of Cu(NH₃)₄²⁺-Zn(NH₃)₄²⁺ solution (Cu:Zn (mole ratio)= 2:1) was quickly added to the CTAB-Na₂SiO₃ solution with vigorous stirring at 20°C, followed by the addition of diluted sulfuric acid (2 M) to adjust the pH value to 10, and continuous stirring was performed for another 30 min. The resultant slurry was transferred into a plastic bottle and aged at 20°C for 72 h. Then the precipitate was separated by centrifugation and washed with distilled water. The powder product was recovered by filtration and dried at 298 K. The surfactant was removed by calcination at 550°C in N₂ and then in air for 5 h. The products were designated as MCM-41, CuZnMCM-41(5), CuZnMCM-41(10), CuZnMCM-41(15), where 5, 10 and 15 indicate the (Cu+Zn) content (wt.%) in the products.

Characterization

All the as-synthesized and calcined samples were characterized by powder X-ray diffraction (Shimadzu XRD 6100 X-ray powder diffractometer, CuKα

radiation). Nitrogen sorption isotherms were obtained on a Quantachrome NOVA 3000 Instruments. Temperature-programmed reduction (TPR) was performed using a TP5000 multifunction absorber. 50 mg catalyst of a particle size of 40-60 mesh was reduced by a mixture gas of H₂/N₂ (1:9) in the temperature range of 100-500°C at a heating rate of 10°/min.

Catalytic testing

The catalytic activity of the catalysts for water gas shift reaction was evaluated in a fixed-bed flow reactor at atmospheric pressure with a space velocity of 10000 h⁻¹. The catalyst particle size was 40-60 mesh. The gas mixture of a composition of V(CO)/V(CO₂)/V(H₂)/V(He) = 2.1/3.4/25/69.5 was fed, and the gas to steam ratio was 1. Before the reactants were introduced, the catalyst was reduced in a diluted hydrogen gas (10%) under atmospheric pressure. The temperature was increased from room temperature to 200°C with a temperature ramp of 5°C/min, and then to 350°C with a temperature ramp of 2°C/min. The final temperature was kept for 2 h. After the catalyst reduction, the temperature of the reactor was lowered to the reaction temperature, and the feed gas was switched to test the catalytic activity. The products were analyzed by on-line gas chromatography.

RESULTS AND DISCUSSION

Ternary meso-structured materials

X-ray diffraction (XRD) patterns of the as-synthesized samples are illustrated in Fig. 1. Four reflection peaks appeared in the patterns which were in accordance with the typical XRD patterns of MCM-41. The XRD patterns of calcined samples showed no evident difference from the patterns in Fig. 1. As the metal content increased, the peak intensity decreased, which was different from the results of Guo *et al.* [15]. According to their report, the samples with copper incorporation had to some extent a more regular structure than the pure silica sample. This difference may stem from the different synthesis conditions. As shown in Fig. 1, with the increase of the metal content the reflection peak moved to lower angles indicating that the unit cell size of synthesized samples increased with the metal content.

The N₂ adsorption-desorption isotherms of these samples showed that all the curves were type IV isotherms. Detailed structural properties indicated that as the metal content increased, the surface area and pore size of the calcined samples decreased and the lattice parameters (a_0) and wall thickness increased monotonously.

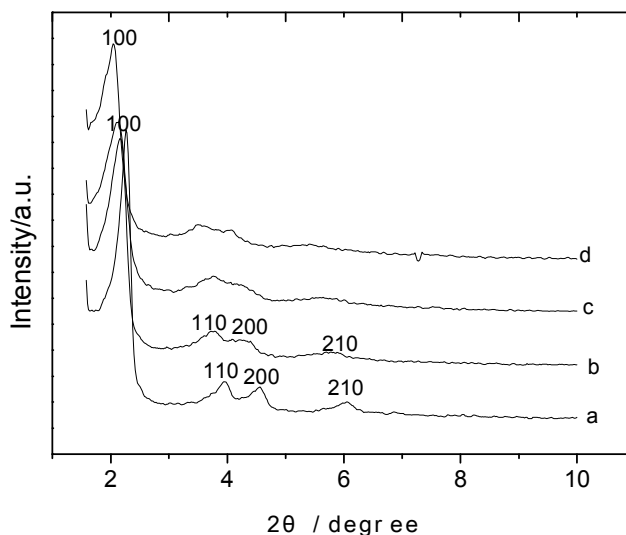


Fig. 1. X-ray diffraction patterns of as-synthesized MCM-41 and CuZnMCM-41s (a) MCM-41, (b) CuZnMCM-41(5), (c) CuZnMCM-41(10) and (d) CuZnMCM-41(15)

Reducibility

The TPR profiles (Fig. 2) showed that all the three samples had single reduction peaks. In addition, the TPR reduction temperature was much higher than that of CuZnMCM-48 [16] with the reduction temperature of 197°C, which indicated that CuO and ZnO were homogeneously dispersed in the mesoporous materials, and a strong interaction existed between the copper species and silica. Comparing the three samples prepared in the present study, the reduction of CuZnMCM-41(5) occurred at the highest temperature implying the strongest metal-molecular sieve interaction. Most of the metal species may incorporate into the lattice of MCM-41 in low metal content samples. The molecular sieves would strongly influence the metal properties of the catalysts.

Catalytic performance

The water gas shift reaction was carried out on the three calcined CuZnMCM-41 materials and the results were illustrated in Fig. 3. The CO conversion varied with reaction temperature and high temperature favored the reaction. The increase in the metal content enhanced the conversion of CO. This

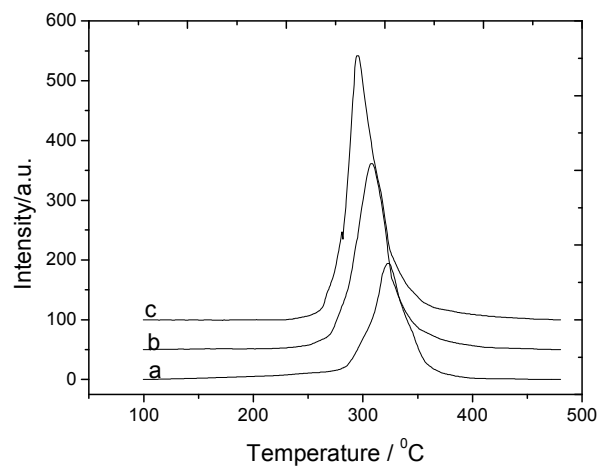


Fig. 2. TPR profiles of calcined CuZnMCM-41s
(a) CuZnMCM-41(5), (b) CuZnMCM-41(10) and (c) CuZnMCM-41(15)

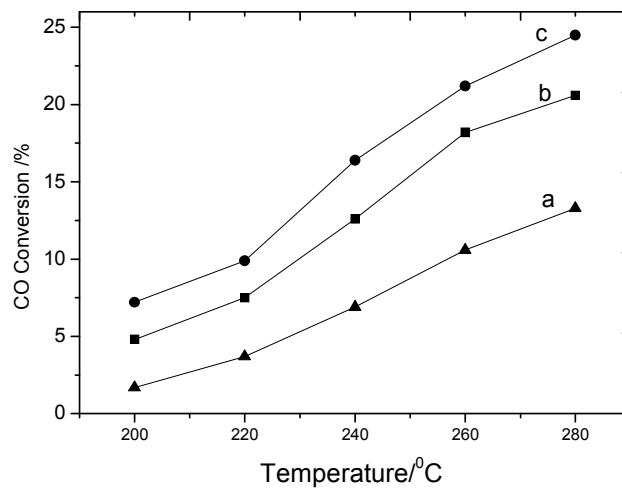


Fig. 3. Evolution of CO conversion with reaction temperature
(a) CuZnMCM-41(5), (b) CuZnMCM-41(10) and (c) CuZnMCM-41(15)

difference in the activity may stem from the difference in the reducibility of the three samples. The catalyst with lower metal content was difficult to be reduced indicating that the metal properties of CuAlMCM-41(5) was suppressed by the molecular sieve as the chemical environment of the Cu species. The work of Guo *et al.* also proved that Cu and ZnO were embedded in the framework of the mesoporous materials so that the content of copper on the surface is much lower than that in the bulk [15]. The higher metal content with possibly more Cu species on the surface and a relatively weak interaction between the metal and the molecular sieve resulted in performances with higher CO conversion.

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