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COPPER-MODIFIED MCM-22 AS CATALYSTS FOR HYDROCARBONE SELECTIVE CATALYTIC REDUCTION OF NO_x.

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Abstract

Cu modified-MCM-22 has been prepared by hydrothermal crystallization from the resource of copper acetate solution. The properties of Cu-MCM-22 was characterized by XRD, SEM, TEM, TPR-H₂ measurements. The catalytic activity of Cu-MCM-22 was tested DeNO_x by propene. The result shown that Cu-MCM-22 contains two positions of copper after ion-exchange Cu²⁺ ions and CuO particles nanosize, this catalyst has high activity in DeNO_x by propene process from 260°C to 400°C.

1. Introduction

Nitrogen oxides (NO_x) are emitted primarily from transportation and other industrial sources and significantly contribute to a variety of environmental, *e.g.* the formation of acid rain and the resultant acidification of aquatic systems, ground-level ozone, and general atmospheric visibility degradation. Therefore, legislation requires that the emission of NO_x is strictly limited. The most interesting catalytic method for removing NO_x from engine exhaust gases is hydrocarbon selective catalytic reduction (HC-SCR). Several series of catalytic materials including supported noble metals [5], metal oxides [6], pillared clays [7], Cu-ZSM-5 zeolite [8],... were investigated as catalysts for HC-SCR of NO_x. The catalysts, which are based on metal ion exchanged ZSM-5 zeolite, show very good activity and high selectivity towards nitrogen. However these materials have shown limited hydrothermal stability.

MCM-22 zeolite invented by Mobil researcher in 1990 [1,2] is a novel zeolite molecular sieve that has a unique and unusual crystal structure. Its internal structure is composed of two different independent pore systems. One of the pore systems consists of 2-dimensional sinusoidal channels (4.1 x 5.1 Å⁰), the other comprises large supercages (innerdiameter of 7.1 Å⁰ defined by 12-MR, height of 18.2 Å⁰), each connected to six others through 10-MR apertures (4.0 x 5.5 Å⁰). A certain amount of external zeolitic pockets correspond to half of supercages (7.1 x 7.1 x 7.0 Å⁰). MCM-22 has high thermal stability (up to 1198 K), much more stable than ZSM-5 and the other zeolite, high BET surface area and very large sorption capacity for many substances [3,4]. It has estimated an interesting potential to act as catalysts in petrochemical process such as alkylation (Mobil-Badger Ethylbenzene), CDTech (Catalytic Distillation Technology of cumen)...[4]. In the other hand, material of MCM-22 which is modified by transition metals are observed to be active catalysts in particularly interesting due to its special redox properties. Thus, the main goal of this work is to prepare and characterize Cu-Modified MCM-22 with different characterization techniques aiming to determine the effect of the copper metal on the properties of catalyst DeNO_x by C₃H₆.

2. Experimental.

2.1. Materials

MCM-22 material (total Si/Al ratio of 30) was prepared by hydrothermal method using Hexametylenimine (HMI) as structure directing agent (SDA).

Hydro-thermal synthesis was conducted at 150°C for 48h using teflon-coated stainless steel autoclave in static condition. After being filtered, the calcined sample was ion-exchanged with 0.01M copper (II) acetate solution at 80°C, followed by calcination in air flow at 773K for 8h. The solid product was washed repeatedly with distilled water and then dried at 60°C in a vacuum oven.

2.2. Characterization.

The synthesized materials were characterized by X-ray diffraction (XRD) on a Brucker D8 Advance diffractometer operating with CuK α radiation ($\lambda = 1.54056\text{\AA}$) at 40kV, 30mA and parameter setup: angles range 10° - 50°, step 0.02°, time step 2s.

SEM image was taken by JEOL-JSM 5410-Lv(Japan) machine under vacuum condition at room temperature.

TEM image was recorded by the JEM-1010 equipment with accelerating voltage from 80 to 100 kV, enlarging 300000 - 450000 times, angle analysis density 2A°. Hydrogen temperature programmed reduction (H₂ -TPR) experiments were carried out in a gas flow system equipped with a quartz microreactor, using a custom-made setup attached with a TCD detector.

2.3. Activity measurements

The reduction of NO_x by C₃H₆ over CuO/CuMCM-22 were performed in TPSR (temperature programmed surface reaction), raising the reactor temperature by steps of 10°C/min from 50°C to 600°C. The gas feeds were controlled by mass flow meters to yield an inlet mixture containing 580 ppm C₃H₆, 340 ppm NO_x 2% O₂, balanced with N₂, at a total flow rate of ml/min. The effluent gases (CO, CO₂, NO, NO_x) were analyzed using a gas chromatograph of TPSR with three detectors: - IR

- TCD
- Chemiluminescence

3. Results and discussions.

X-ray diffraction.

The XRD pattern of the calcined product obtained taken as a reference material is given in Fig. 1. For Si/Al = 30, MCM-22 can be obtained as a pure phase and generally with a good yield.

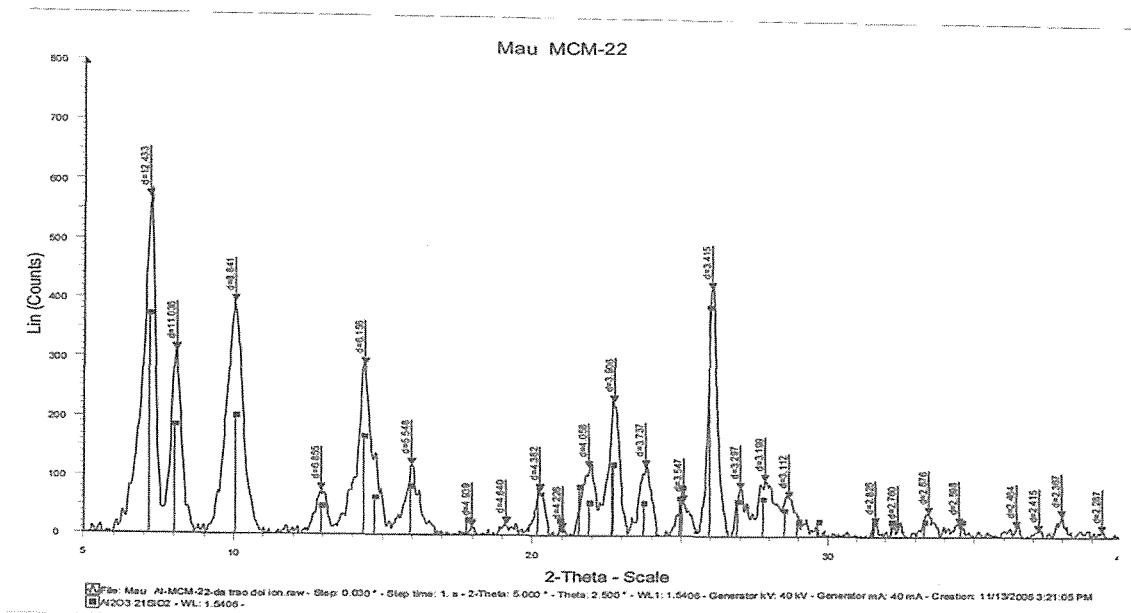


Figure 1. XRD patterns of the products obtained by hydrothermally treating the mother gel with the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 60

Zeolite MCM-22 contains two pore systems : the first one is a channel composed of circular 10-member rings, the other is the two dimensional supercage with 12-member rings and this material has many characters the same zeolite ZSM-5 and Mordenite, so it can be confused when indentifying the characterization of these materials. The typical peaks of MCM-22 appear at the angle $2\theta = 25, 26, 27^\circ$ sharply. The XRD patterns of the obtained materials are in good agreement with those previously reported by many researchers, which demonstrates that MCM-22 was prepared successfully.

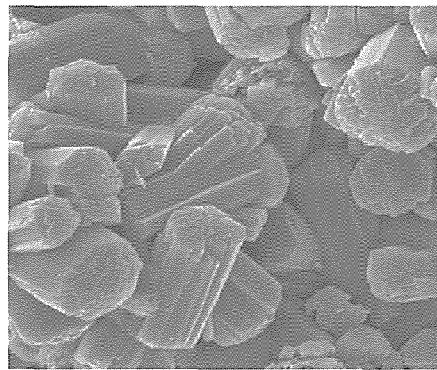


Figure 2. SEM images of MCM-22 materials

Scanning electron microscopy(SEM).

These MCM-22 samples appear under the scanning electron microscope as small, thin platelets, when changing the Si/Al ratio, occasionally forming circular aggregates, or as spherical cylinder with channels.

Temperature programmed reduction Hydrogen experiments(H-TPR).

Several types of copper species can co-exist after synthesis and thermal treatment. TPR-H₂ is shown the interesting information about the kinds of copper appearing in material and the amount of each kind. During synthesis via ion-exchanged, Cu²⁺ species in the aqueous acetate solution can replace Na⁺ cations as a solvated { Cu²⁺(OH)⁻ } ions. After the subsequent mal treatment, each of two Cu²⁺ monomers can combine with each other to form Cu²⁺ dimer, two kinds of Cu²⁺ ions interact with framework Al sites in MCM-22. beside Cu²⁺ ions, that CuO species also appear on the surface of MCM-22 is confirmed by TPR-H₂.

Table 1. Table of the temperature region of Copper reducing progress

Reducing progress	Temperature (°C)	Amount of Cu (mmol/g)
CuO → Cu	145	0.009
Cu ²⁺ → Cu ⁺	268	
Cu ⁺ → Cu	332	0.46

According to TPR-H₂ results, the two peaks H₂ consumption peaks entered at 268°C and 332°C. The ratio of two peaks was ~1, which indicated that all the Cu²⁺ ions had undergone a two electron reduction to Cu. The first peak at lower temperature stands for the reduction of Cu²⁺ to from Cu⁺ and the second peak at higher temperature was considered to be the continuous reduction process from Cu⁺ to Cu.

In the other hand, there was very tiny peak at lowest temperature 145°C, it is suggested that CuO particles would co-existed on the surface of this material. The low temperature region was explained for the small size of CuO species.

Transmition electric microscopy (TEM).

The TEM image exhibits the side view of the plate-like crystal, indicating the layered-like structure of the material, in good agreement with the proposed structure viewed along with c-direction. The shape of each sample MCM-22 matches the theoretical value. The TEM measurement was being used to obtain the images of CuO species on the surface of catalyst. the micrograph indicated how copper oxide particles appeared in sample very clearly. The CuO species have the size of nano particles and disperse steadily on the silica oxides support. Thus, the exitance of CuO particles were demonstrated. It is stated that contained two species of copper: Cu²⁺ ion on the zeolite framework and CuO species which play different roles in the catalytic properties.

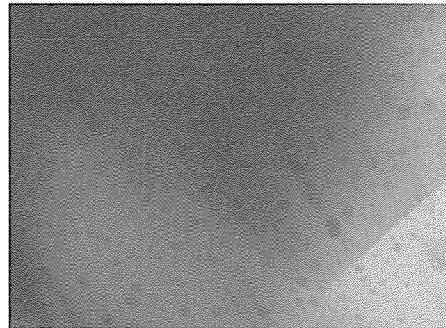


Figure 3. The TEM image of the MCM-22

Activity tests: TPSR of DeNOx by C3H6:

The result of TPSR of NO_x de sopption under C₃H₆/N₂ flow test over CuO/CuMCM-22 is presented in Fig 4 .

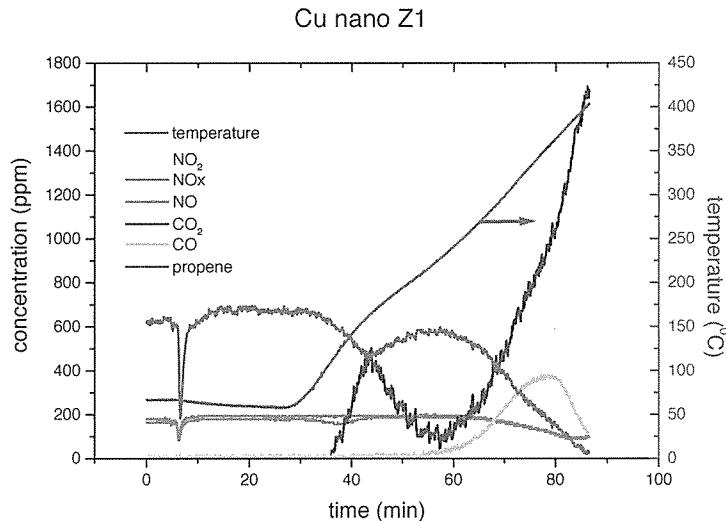


Figure 4. TPSR of NO_x de sopption under C₃H₆/N₂ flow test over CuO/CuMCM-22.

Obvious C₃H₆ oxidation conversion starts at 260°C and increases reaching total oxidation C₃H₆ at 400°C. Catalytic reduction of NO_x by hydrocacbons starts at 260°C, NO_x generated during reaction with a yield of 50% at 400°C. At the same temperature, conversion of CO₂ was maximum. The appearance of CO₂ coincides with the disappearance of C₃H₆.

From the result of catalyst physicochemical characterization with determination of CuO nano size and Cu²⁺ in MCM-22 and catalytic properties oxidation of C₃H₆ and reduction NO_x of CuO/CuMCM-22 pointed out their potential application for NO_x reduction.

4. Conclusion

1. Cu-MCM-22 was obtained by ion exchanging process of MCM-22 zeolite in the diluted copper acetate solution.
2. Cu-MCM-22 was characterized by using many mesurements, such as XRD, H₂-TPR, TEM mesurements confirmed that Cu-MCM-22 contained two positions of copper after ion-exchange Cu²⁺ ions and CuO particles nanosize over exelent HC and redox NO_x.
3. Cu-MCM-22 was tested in the oxidation of C₃H₆ and reduction NO_x in order to determine the catalytic properties of this material.
4. A more detailed discusion about the startes of copper and a mechanism NO_x reduction by propene is under way.

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