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# COPPER-MODIFIED MCM-22 AS CATALYSTS FOR HYDROCARBONE SELECTIVE CATALYTIC REDUCTION OF NO<sub>x</sub>.

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## Abstract

Cu modified-MCM-22 has been prepared by hydrothermal crytalization from the resource of copper acetate solution. The properties of Cu-MCM-22 was characted by XRD, SEM,TEM, TPR-H<sub>2</sub> measurements. The catalytic activity of Cu-MCM-22 was tested DeNO<sub>x</sub> by propene .The result shown that Cu-MCM-22 contains two positions of copper after ion-exchange Cu<sup>2+</sup> ions and CuO particles nanosize, this catalyst has high activity in DeNO<sub>x</sub> by propene process from 260°C to 400°C.

## 1. Introduction

Nitrogen oxides (NO<sub>x</sub>) 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<sub>x</sub> is strictly limited. The most interesting catalytic method for removing NO<sub>x</sub> 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<sub>x</sub>. The catalysts, which are based on metal ion exchanged ZSM-5 zeolite, show very good activity and high selectivity towards nitrogen. However theses 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 stucture is composed of two different independent pore systems. One of the pore systems consists of 2-dimensional sinusoidal channels (4.1 x 5.1 Å<sup>o</sup>), the other comprises large supercages (inerdiameter of 7.1 Å<sup>o</sup> defined by 12-MR, height of 18,2 Å<sup>o</sup>), each connected to six others through 10-MR apertures (4.0 x 5.5 Å<sup>o</sup>). A certain amount of external zeolitic pockets correspond to half of supercages ( 7.1 x 7.1 x 7.0 Å<sup>o</sup>). 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 observered 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<sub>x</sub> by C<sub>3</sub>H<sub>6</sub>.

## 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 after dried at 60°C in a vacuum oven.

### 2.2. Characterization.

The synthesized materials were characterized by X-ray diffraction (XRD) on a Bruker D8 Advance diffractometer operating with CuK $\alpha$  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, enlargement 300000 - 450000 times, angle analysis density 2A°. Hydrogen temperature programmed reduction (H<sub>2</sub> -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<sub>x</sub> by C<sub>3</sub>H<sub>6</sub> over CuO/CuMCM-22 were performed in TPSR (temperature programmed surface reaction), raise 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 C<sub>3</sub>H<sub>6</sub>, 340 ppm NO<sub>x</sub>, 2% O<sub>2</sub>, balanced with N<sub>2</sub>, at a total flow rate of ml/min. The effluent gases (CO, CO<sub>2</sub>, NO, NO<sub>x</sub>) were analyzed using a gas chromatograph of TPSR with three detectors: - IR

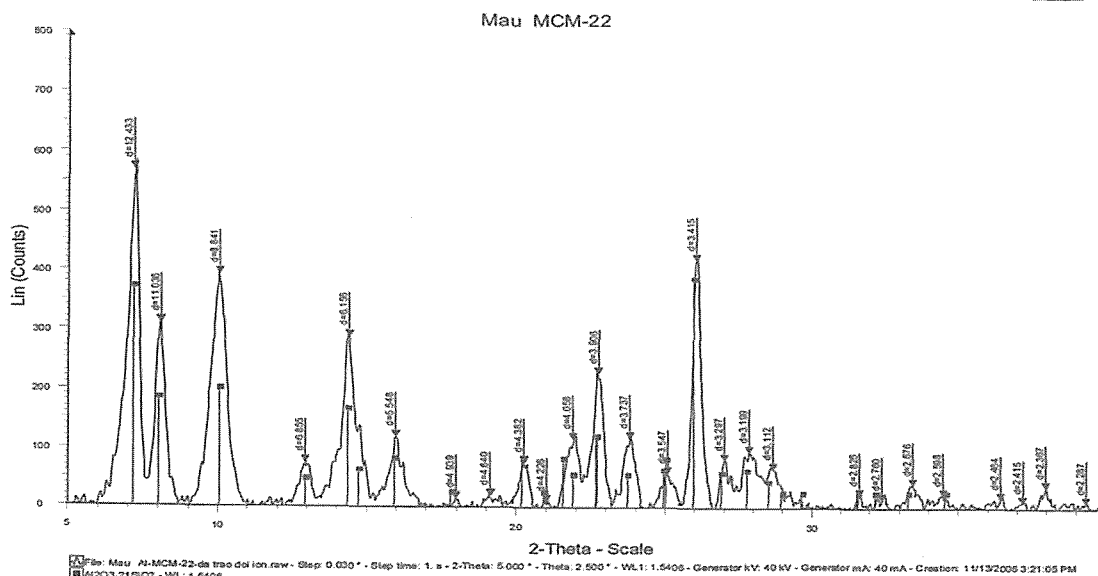
- TCD

- Chemiluminescence

## 3. Results and discussions.

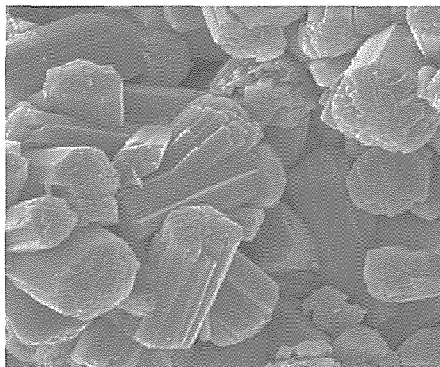
### *X-ray diffraction.*

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 Mordenit, so it can be confused when indentifying the charaterization 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 reseachers, 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-H<sub>2</sub> is shown the interesting information about the kinds of copper appearing in material and the amount of each kind. During synthesis via ion-exchanged, Cu<sup>2+</sup> species in the aqueous acetate solution can replace Na<sup>+</sup> cations as a solvated { Cu<sup>2+</sup>(OH)<sup>-</sup> } ions. After the subsequent thermal treatment, each of two Cu<sup>2+</sup> monomers can combine with each other to form Cu<sup>2+</sup> dimer, two kinds of Cu<sup>2+</sup> ions interact with framework Al sites in MCM-22. beside Cu<sup>2+</sup> ions, that CuO species also appear on the surface of MCM-22 is confirmed by TPR-H<sub>2</sub>.

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

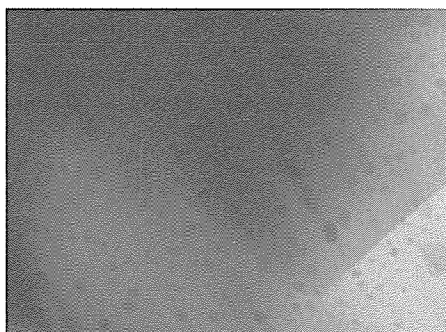
Reducing progress	Temperature (°C)	Amount of Cu (mmol/g)
CuO → Cu	145	0.009
Cu <sup>2+</sup> → Cu <sup>+</sup>	268	0.46
Cu <sup>+</sup> → Cu	332	

According to TPR-H<sub>2</sub> results, the two peaks H<sub>2</sub> consumption peaks entered at 268°C and 332°C. The ratio of two peaks was ~1, which indicated that all the Cu<sup>2+</sup> ions had undergone a two electron reduction to Cu. The first peak at lower temperature stands for the reduction of Cu<sup>2+</sup> to form Cu<sup>+</sup> and the second peak at higher temperature was considered to be the continuous reduction process from Cu<sup>+</sup> to Cu.

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

### *Transmission electric microscopy (TEM).*

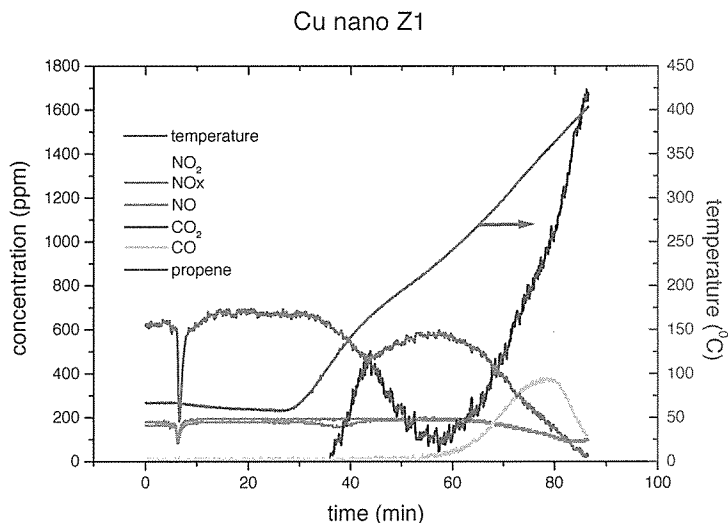
The TEM image exhibits the side view of the plate-like crystal, indicating the layered-like structure of the material, in good agreement with the proposed structure viewed along with c-direction. The shape of each sample MCM-22 matches the theoretical value. The TEM measurement was being used to obtain 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 existence of CuO particles were demonstrated. It is stated that contained two species of copper: Cu<sup>2+</sup> 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 DeNO<sub>x</sub> by C<sub>3</sub>H<sub>6</sub>:*

The result of TPSR of NO<sub>x</sub> de sopption under C<sub>3</sub>H<sub>6</sub>/N<sub>2</sub> flow test over CuO/CuMCM-22 is presented in Fig 4 .



**Figure 4.** TPSR of NO<sub>x</sub> de sopption under C<sub>3</sub>H<sub>6</sub>/N<sub>2</sub> flow test over CuO/CuMCM-22.

Obvious C<sub>3</sub>H<sub>6</sub> oxidation conversion starts at 260°C and increases reaching total oxidation C<sub>3</sub>H<sub>6</sub> at 400°C. Catalytic reduction of NO<sub>x</sub> by hydrocarbcons starts at 260°C, NO<sub>x</sub> generated during reaction with a yield of 50% at 400°C. At the same temperature, conversion of CO<sub>2</sub> was maximum. The appearance of CO<sub>2</sub> coincides with the disappearance of C<sub>3</sub>H<sub>6</sub>.

From the result of catalyst physicochemical characterization with determination of CuO nano size and Cu<sup>2+</sup> in MCM-22 and catalytic properties oxidation of C<sub>3</sub>H<sub>6</sub> and reduction NO<sub>x</sub> of CuO/CuMCM-22 pointed out their potential application for NO<sub>x</sub> 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 measurements, such as XRD, H<sub>2</sub>-TPR, TEM measurements confirmed that Cu-MCM-22 contained two positions of copper after ion-exchange Cu<sup>2+</sup> ions and CuO particles nanosize over exelent HC and redox NO<sub>x</sub>.
3. Cu-MCM-22 was tested in the oxidation of C<sub>3</sub>H<sub>6</sub> and reduction NO<sub>x</sub> in order to determine the catalytic properties of this material.
4. A more detailed discussion about the startes of copper and a mechanism NO<sub>x</sub> reduction by propene is under way.

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## References

1. Miky Niwa, Kazu Amutara at al . Acid properties and catalysis of MCM-22 with different Al concentrations . Journal of catalysis ,206(2003), p 23-28.
2. Zinrong Zhu, Quingling Chen, Wei Zhu, Dejin Kong, Can Li. Catalytic performance of MCM-22 zeolite for alkylation of toluene with methanol.Catalysis Today 93-95(2004), Pages 321-325.
3. Andrea Krejci, Jiri Cejka at al. Acitivity of zeolit MCM-22 and MCM-58 in the alkylation of toluene with propylene. Microporous and mesoporous Materials 53 (2003), p. 121-133.
4. Takashi Tatsumi. High selectivity of MCM-22 for cyclopentanol formation in liquid phase cyclopentene hydration. Journal of catalysis 213(2003), p 272-280.
5. A.A. Nikolopoulos, E.S. Stergioula, E.A. Efthimiadis, I.A. Vasalos, Catal. Today 54 (1999) 439.
6. Y. Okamoto, T. Kobuta, Y. Ohto, S. Nasu, J. Catal. 192 (2) (2000) 412
7. Y. Wan, J.X. Ma, Z. Wang, W. Zhou, S. Kaliaguine, J. Catal. 227 (1)(2004)242.
8. M.Iwamoto, Catal. Today 29 (1996)29.