Journal of Chemistry, Vol. 45 (3), P. 368 - 372, 2007

Fe-MCM-22 ZEOLITE: SYNTHESIS AND STUDY ABOUT THE STATES OF IRON

Received 13 June 2006

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SUMMARY

The Fe-MCM-22 zeolite was successfully synthesized with hexametylenimine template. Several physicochemical techniques (XRD, SEM, BET, AAS, IR and ESR) have been used to characterize this zeolite. Iron exists under three states: isolated ions in tetrahedral lattice positions, in octahedral coordination as isolated ions at cationic positions and as aggregated oxide species or hydroxide phases.

Keywords*: Fe-MCM-22 zeolite, synthesis, characterization, framework iron.*

I - INTRODUCTION

MCM-22 zeolite is a new patent given by Cooperation Mobil Oil [1]. In the last ten years, its properties were thoroughly investigated. The framework topology of MCM-22 has been shown to consist of layers linked together along the *c*-axis by oxygen bridges and contain two independent pore systems. Within the layers are two-dimensional sinusoidal 10-MR channels (4.1 × 5.1 Å), and between two adjacent layers are 12-MR supercages (~7.1 × 7.1 × 18.2 Å) communicating each other through 10-MR apertures (4.0 × 5.5 Å). In addition, its typical thin platelet morphology results in high external surface area [2]. Dealuminated acid forms of MCM-22 have been characterized, concluding that the acidic properties are very similar to H-ZSM-5 zeolite [3]. Nowadays, the synthesis parameters for the preparation of MCM-22 zeolite have been optimized [4].

Formerly, zeolite used to be known as an acidic catalyst. It is well known that the addition of transition metals, especially iron, in initial gel for zeolite synthesis was enormously studied. The presence of different iron species in zeolite created several new activities for this kind of material. This material, besides the known Bronsted acidic properties, shows such a lot of special catalytic activities in oxidation reaction. Until now, there are some researches which studied the synthesis of Fe-MCM-22 zeolite [5, 6]. In this work, we have successfully prepared Fe-MCM-22 zeolite. Several physicochemical techniques were used to characterize the extraframework and framework irons. The capacity of each technique for verifying the states of iron was discussed in detail.

II - EXPERIMENTAL

Fe-MCM-22 was synthesized according to the procedure given by *F. Testa et al* [5], it may be summarized as presented in Fig. 1. The general composition of the initial gel leading to Fe-MCM-22 was $6Na_2O$-$60SiO_2$-$1.5Fe(NO_3)_3$-30HMI-$2320H_2O$. The white crystallized was washed until reaching neutral pH and calcited in dry air at temperature of 500°C for 6 h to remove all HIM templates.

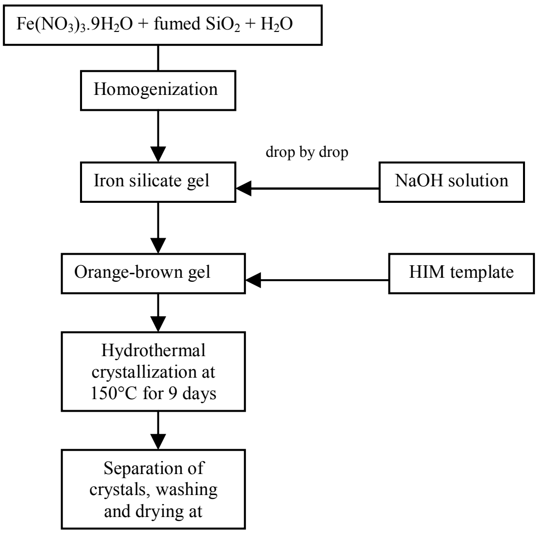

Figure 1: Synthesis procedure of Fe-MCM-22

Instrumentation

Powder X-ray diffraction (XRD) patterns were recorded on a Siemens D5005 diffractometer with a Cu*K*α radiation. Chemical composition of sample was analyzed by a Perkin–Elmer AAS instrument. SEM image was taken by JSM 54102V machine under vacuum condition at room temperature and ESR spectrum was recorded at room temperature on a Brucker ER200D ESR spectrometer equipped with a dual cavity and a 100-kHz modulation unit.

III - RESULTS AND DISCUSSION

MCM-22 structure of our zeolite sample was confirmed by comparing the XRD spectra with the reference spectrum of MCM-22 sample taken as standard. Its X-ray diffractogram was similar to those reported by P.Chu et al [1] (not shown in this article). According to F. Testa et al [5], the typical peak of MCM-22 standard (d= 3.42 and 2θ of 26.0) appeared in all sample with high intensity (figure 2). SEM photograph of as-synthesized zeolite was shown in figure 3, crystal MCM-22 has form of thin plate. It is similar to that of Fe-MCM-22 reported by F. Testa et al [5] while surface area (286 m^2/g) measured by BET method was slightly smaller than surface area of Fe-MCM-22 reported (308 m^2/g). Some main characteristics of this material were presented in table 1.

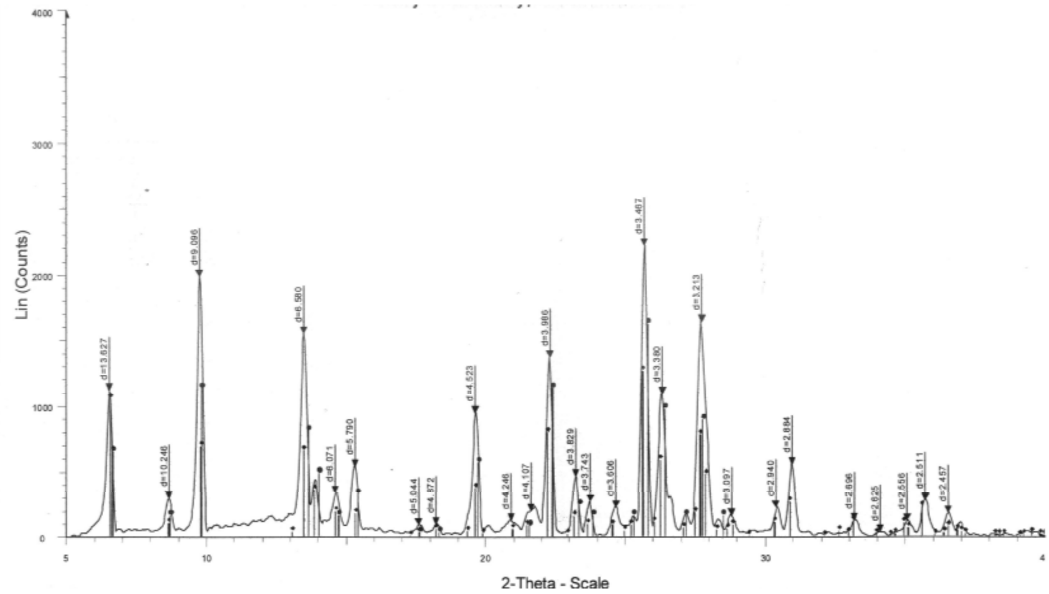

Figure 2: X-ray diffractogram

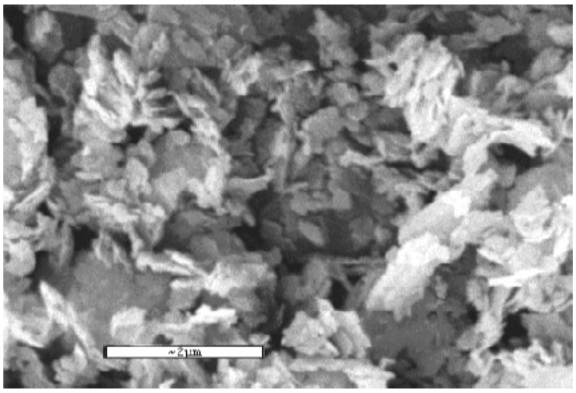

Figure 3: SEM image of as-synthesized zeolite

Table 1: Main characteristics of as-synthesized zeolite

Structure	MCM-22
Color	White
Surface area	286 m^2/g^*
Si/Fe	40
Fe wt.	0.70 (%)

$^{(*)}$Measured by BET.

Infrared spectroscopy is a useful means to study material surface. It has been more and more extended in the characterization of zeolite.

Meaningful information concerning the iron structure in the zeolite framework has been obtained by exploring both the hydroxyl stretching (3800 - 3400 cm^{-1}) and framework (1350 - 400 cm^{-1}) regions [7]. Figure 4 presents the typical framework bands of Fe-MCM-22 sample. The band at 550 cm^{-1} is assigned to the vibration of double-rings in MFI lattice [8]. In particular, the absorption in the range of 1250 - 950 cm^{-1} can be interpreted as deriving from the asymmetric modes with T_2 symmetry in the isolated [SiO_4] units. Because of characterizing for the asymmetric valence vibration in the tetrahedral TO_4, this band depends on the amount of transition metal in zeolite framework. Bordiga et al [7] found a shoulder at 1006 cm^{-1} partially overshadowed by the strong absorption centered at 1150 cm^{-1} on the IR spectrum of iron-substituted silicate and assumed that the bands at 1006 cm^{-1} can be explained on the basis of a fully ionic model: in this case the local structure surrounding the framework Fe^{3+} species is described by 4 [O_3Si-O^-] units. Returning to Fe-MCM-22, a band at 950 cm^{-1} partially overshadowed by the strong absorption centered at 1100 cm^{-1} was also observed (Fig. 4). Bordiga et al [7] hypothesized that these new bands at 950 cm^{-1} are mainly associated with the vibrational modes of the O_3SiO^- units surrounding the Fe^{3+} centre.

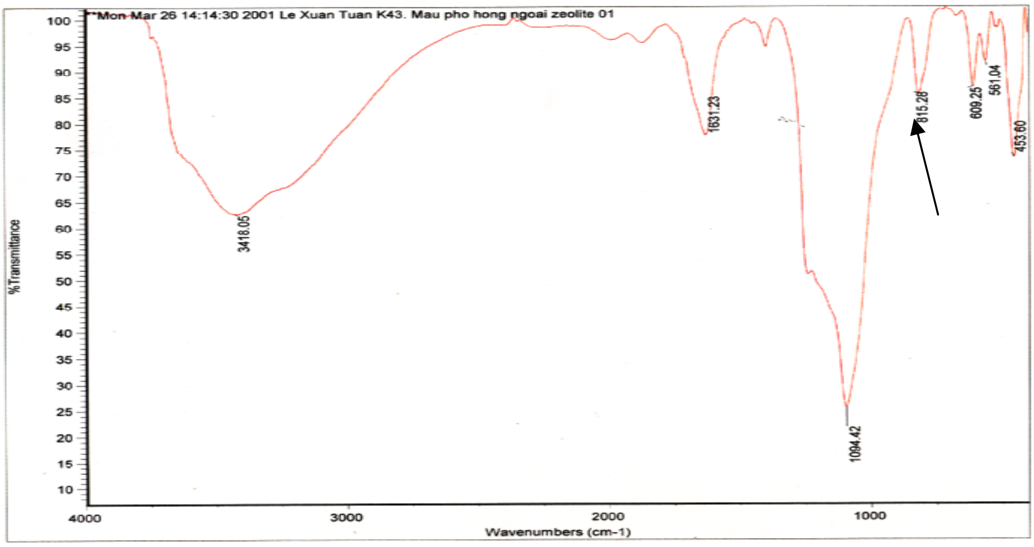

Figure 4: IR spectra of as-synthesized Fe-MCM-22

The first visual indication of location of iron species at framework positions in as-synthesized zeolite is the white color of crystallized product [9]. Information about the state of iron in as-synthesized Fe-MCM-22 was obtained by further ESR investigations. It is easy to observe that ESR spectra of the sample at room temperature are very similar to those of Fe-ZSM-5 and Fe-MFI zeolites published elsewhere [9, 10]. Three characteristic features can be recognized at g = 4.35, g = 2.35 and g = 2.03. We did not detect any other signals in ESR spectra of our sample. Assignment of these three signals appeared in zeolite containing iron was discussed in the literature [5, 7 - 12]. The commonly accepted assignment of these signals is as follows: (g = 4.35) framework iron, (g = 2.35) iron in interstitial oxide or hydroxide phases, and (g = 2.03) iron in cation-exchange sites, respectively [9,10]. ESR is nowadays predominantly used to check the g ~ 4.3 signals in order to confirm the tetrahedral substitution [13]. The intensity of this signal is lower at high temperature [5]. This may be explained basing on the state transformation of iron from framework to extra-framework with increasing of temperature of heat treatment procedure [14]. F. Testa et al [5] said that the framework iron tetrahedral species can be included in the ESR signal observed at low magnetic field, where only the middle of the spectrum was computed to be between 4.23 and 4.56, the latter species are considered as deformed tetrahedral species. The signal at g ~ 2.0 is known to be strongly affected by the water vapor content and it diminishes with water vapor for FAPO-5 whereas it grows with water vapor for Fe-ZSM-5 [11, 12].

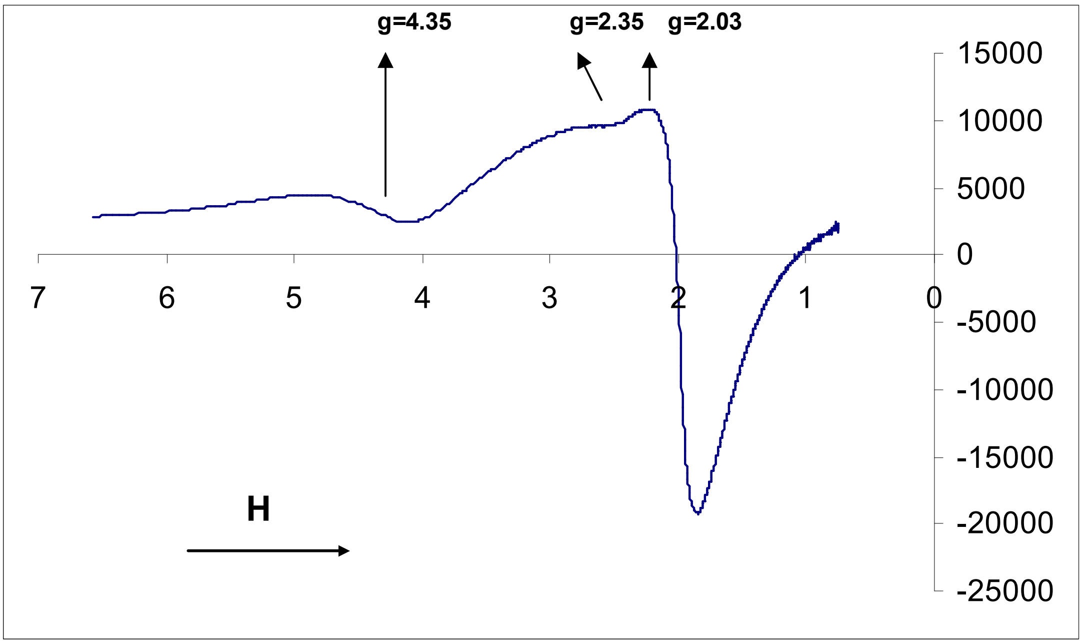

Figure 5: ESR spectrum of as-synthesized Fe-MCM-22

IV - CONCLUSIONS

1. Successful synthesis of Fe-MCM-22 under hydrothermal condition using HMI template was confirmed by XRD.

2. As-synthesized zeolite has relatively high surface area, 286 m^2/g (BET). Its white colour and a band at 950 cm^{-1} partially overshadowed by the strong absorption centered at 1100 cm^{-1} in IR spectra suggested a location of iron species at framework positions.

3. ESR results showed that iron exists under three states in as-synthesized: Fe-MCM-22 framework iron, iron in interstitial oxide or

hydroxide phases and iron in cation-exchange sites corresponding with g = 4.35, g = 2.35 and g = 2.03, respectively.

4. A more detailed discussion about the states of iron in this catalyst by means of XPS and Mossbauer spectroscopy is under way.

Acknowledgements: *This research was supported by Vietnam National University, Hanoi-Asia Research Center. The authors wish to thank Mr. P. Q. Nghi (Universite du Maine, Le Mans-France) for measuring ESR and his helpful discussions.*

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