

Chemistry

THE PHASE TRANSFORMATION IN THE CRYSTALLIZATION PROCESS OF Fe-MORDENITE ZEOLITE

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Abstract. In the present paper, we reported the influence of the crystallization time on the crystallinity of the Fe-mordenite zeolite (Fe-MOR). The obtained results showed that, in order to reach the high crystallinity of zeolite the optimal duration of crystallization was about 36 h.

When crystallization time increased from 48h to 72h, there was phase transformation from MOR zeolite to ZSM-5 zeolite. However, if crystallization time decreased (< 24 h) the obtained samples had low crystallinity.

1. INTRODUCTION

There is a current interest in the isomorphous substitution of Si and Al by tri-valent elements such as B, Ga, Mo, ..., and Fe into the framework of zeolite. The substitution of other elements in zeolite structure for Si- and Al- site is expected to develop the novel catalytic properties and expand the application of synthesized zeolites. For example, various types of zeolite substituted by transition metal cation were synthesized in order to modify their chemical and catalytic properties and so they could be applied in numerous redox catalytic reactions [1-5].

In recent years, isomorphous substitution of Si by Fe in the framework of zeolite by several methods has been studied. Fe-incorporated metallosilicate (ferrisilicate) with several types of zeolites (such as MFI, β eta, FER, and MCM-22, ...) have been reported by several authors [5, 6]. However, for Fe-substituted mordenites only a few studies have been reported [6].

In this study, Fe-MOR zeolite was synthesized hydrothermally by using the tetraethylammonium hydroxide (TEAOH) template. The influence of the crystallization time on the crystallinity of the Fe-MOR zeolite was discussed.

2. EXPERIMENTAL

2.1. Synthesis of Fe-MOR

Starting materials:

Glass water (23% SiO₂, 8% Na₂O)

Fe(NO₃).9H₂O

NaOH

H₂SO₄ (98%).
 TEAOH (20%).
 (COO)₂H₂

Condition of synthesis: the gels were crystallized in autoclave, at 170°C, pH= 10.5 with the different crystallization time ranging from 24 to 72 hours.

After crystallization the samples were washed by deionized water then heated at 120°C for 3 hours and calcined at 500°C for 3 hours.

The results of characterization were obtained by means of XRD, IR and SEM techniques. The states of iron cations in the framework of Fe-MOR zeolite were clarified by visible diffuse reflectance spectroscopy (UV- vis).

2.2. Characterization

X ray diffraction (XRD): for XRD patterns the Siemen D5005 XRD instrument was used with $K_{\alpha} = 1.54014$, 30KV, 0.01A, scanning rate of 1°/min.

Infrared (IR) analysis was conducted on IMPACT-410 (Germany) with wavenumber ranging from 400 - 1300 cm⁻¹.

SEM analysis was performed on Joel-JSM-5.300 (Japan).

2.3. UV-VIS analysis

To determine the states of iron ions in framework, the UV-VIS analysis was carried out on Shimadzu UV-2101/3101PC at room temperature with $\lambda = 200$ -8000nm.

3. RESULTS AND DISCUSSION

3.1. IR analysis

Table 1. *The change in structure with the crystallization time (at temperature 170 ° C)*

Sample	Gel composition		Crystallization time (h)	Structure identified by IR, XRD
	SiO ₂ /Fe ₂ O ₃	Na ₂ O/SiO ₂		
M1	40	0.898	24	MOR
M2	40	0.898	36	MOR
M3	40	0.898	48	MOR
M4	40	0.898	72	MOR+ ZSM-5

The samples with different crystallization time were denoted as M1, M2, M3, and M4), (Table 1). The crystallization time ranged from 24 to 72 hours, the SiO₂/Fe₂O₃ and Na₂O/SiO₂ ratios was 40 and 0.898 respectively.

From Table 1, it was noted that, when the crystallization time passed 72 h beside mordenite phase, there was ZSM-5 zeolite structure formed in the solid product.

Indeed, Fig.1 shows the IR spectra of the synthesized Fe-MOR zeolites. As reported previously [6-8], the characteristic bands of mordenite zeolite were 560-580 cm⁻¹, 618-627 cm⁻¹, 1220-1225cm⁻¹. The length of Fe-O bond is longer than that of Al-O (Fe-O = 1,85 Å and Al-O = 1,66 Å), so the bands in the IR spectra of Fe-MOR zeolite were shifted to the lower wavenumber than those

of Al-MOR. Especially, the two bands at around $560 - 580 \text{ cm}^{-1}$ and $618 - 627 \text{ cm}^{-1}$ approached closely to each other so that it was difficult to identify them separately. Thus the band at about 598 cm^{-1} was considered as the indicative band of Fe-MOR structure.

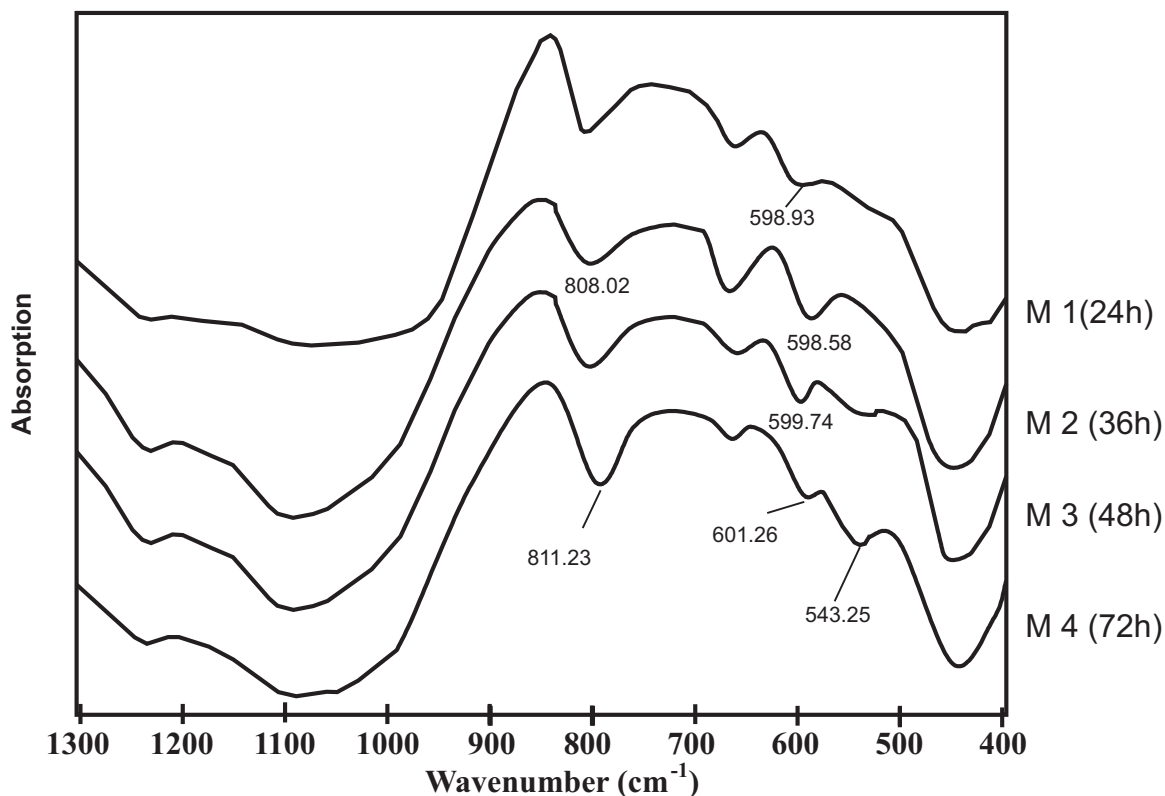


Fig. 1. IR spectra of samples with different crystallization time

It was observed in Fig. 1 that the intensity of the band $\sim 598 \text{ cm}^{-1}$ increased when the crystallization time increased from 24 to 36 hours. This is maybe related to the increase in crystallinity of Fe-MOR. But when the crystallization time increased from 48 to 72 hours the intensity of the band $\sim 598 \text{ cm}^{-1}$ decreased, showing the reduction of Fe-MOR crystallinity. In addition, it was noticed that there was the appearance of the band $\sim 543 \text{ cm}^{-1}$ in the samples with crystallization time from 48-72 hours. According to [10, 12], it was the characteristic band of Fe-ZSM-5. Thus there was the transformation from Fe-MOR to Fe-ZSM-5 type with the prolonged crystallization time.

Fig. 2 showed the shift of the band $\sim 1100 \text{ cm}^{-1}$ to the higher wavenumber (when crystallization time was prolonged). According to [4], the band at around $950-1200 \text{ cm}^{-1}$ is attributed to the asymmetric TO_4 vibration, so it was sensitive to the Si/T ratios ($T = \text{Al, Fe, B, Ga}$), the higher T content, the lower the band wavenumber is. Thus it was concluded that when crystallization time increases the Fe content substituted into framework decreases. This was in agreement with [12].

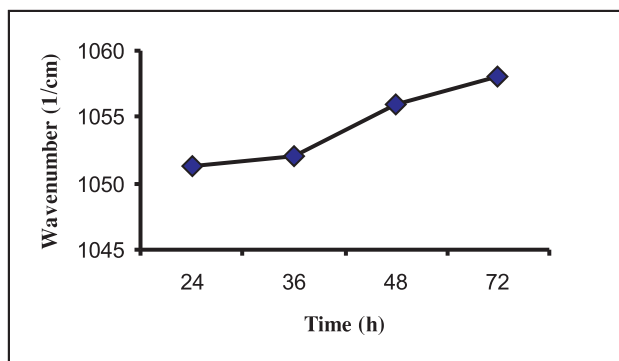


Fig. 2. Dependence of the band $\sim 1100\text{cm}^{-1}$ on crystallization time

3.2. XRD analysis.

The discussed remarks above were also confirmed by XRD patterns (Fig. 3). Fig. 3 showed the XRD patterns for the samples with different crystallization time. The patterns all indicated the Fe-MOR structure with high intensity, had the high crystallinity of mordenite. There were no strange peaks in the patterns for samples M1 (24h), and M2 (36h). It revealed that the samples are pure. In the samples with crystallization time, which was longer than 48 hours, there were small peaks at 2θ of 20° - 25° and 6° , according to [11] these two peaks were specified to Fe-ZSM-5 (M3, M4), showing a presence of Fe-ZSM-5 in these samples. In the patterns the specific peaks of Fe-MOR existed together the peaks of Fe-ZSM-5, however the peak intensity of Fe-ZSM-5 zeolite was still low.

Thus when the crystallization time was prolonged from 36-72 hours, there was the transformation of Fe-MOR to Fe-ZSM-5. This conclusion was in agreement with the results derived from the IR analysis presented above.

Furthermore, as discussed previously [8], the ratios of peak intensity characteristic of such planes as (111), (130), (511), and (530), sensitively depend on $\text{SiO}_2/\text{Fe}_2\text{O}_3$ value. A ratio between peak intensities of (111) and (130) planes, R1, and that of (511) and (530), R2, increased with increasing $\text{SiO}_2/\text{Fe}_2\text{O}_3$ value. Especially, the linear relationship was held only if samples did not contain impure crystals. If impurities coexist, the linearity is broken. Fig.4 shows the relation between R1, R2 of the samples ($\text{SiO}_2/\text{Fe}_2\text{O}_3$ ratio of 40 (table 1)) and crystallization time. It was observed that the R values of M4 sample (crystallization for 72h) do not lie on the straight line of the linear relationship. It was clear that M4 sample contains Fe-ZSM-5 phase as impure crystals.

So that, the crystallization time ranging from 36 to 48 hours was optimal for synthesis of Fe-MOR zeolite.

This conclusion was also confirmed by the intensity of the peak at 2θ of $21,8$ - $22,8^\circ$, which is the typical peak of mordenite structure [5,6]. In fig.5 it was seen that, the intensity of the (150) peak reached the maximum value when the crystallization time was 36 hours.

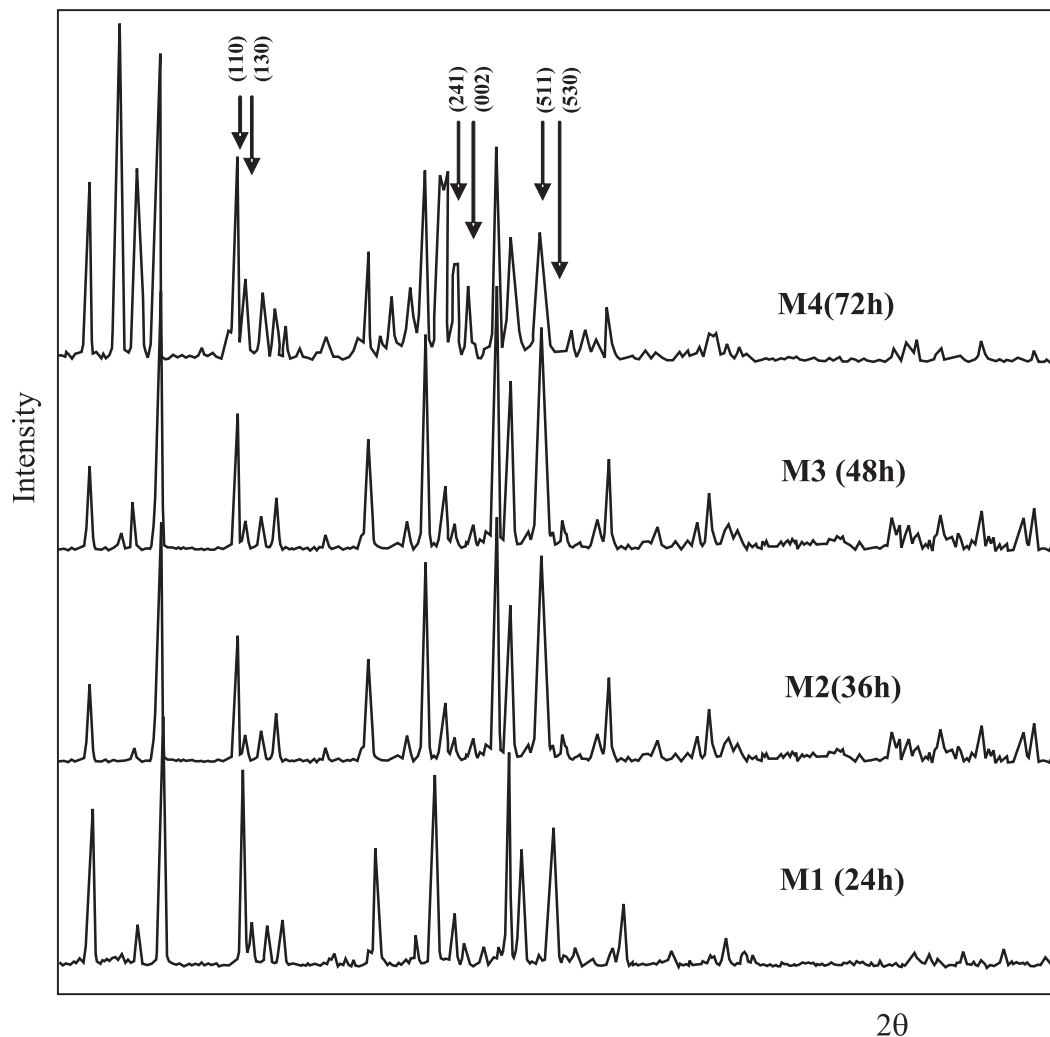


Fig. 3. XRD patterns of the samples

3.3. SEM image

Fig. 6 showed the SEM image for samples M2. All of the crystals in fig. 6 were of leaf-shaped form with the crystal size of $\sim 10 \times 25 \mu\text{m}$. There were no phase impurities in the obtained solid product.

3.4. Determination of Fe states in Fe-MOR framework

Fig. 7 shows the UV-VIS spectra for Fe-MOR samples crystallized from 24 to 72 hours and Al-MOR sample.

The substitution of Fe into the mordenite framework led to the appearance of adsorption bands that did not appear in the spectra for Al-MOR.

The spectra for Fe-MOR had two remarkable features as belows:

The strong adsorption band appeared in the range of 200-300 nm. According to [8, 9, 12], it might be assigned to the $d\pi$ to $p\pi$ charge-transfer between the

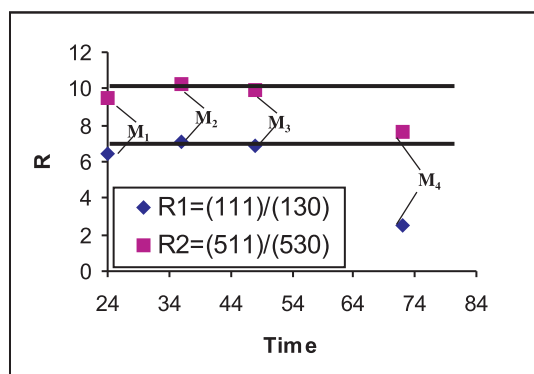


Fig. 4. Dependence of the R on crystallization time for the investigated samples

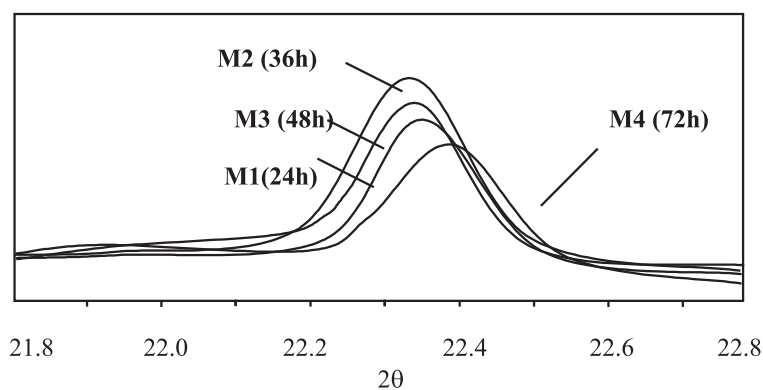


Fig. 5. XRD (150) peak of the M4 sample

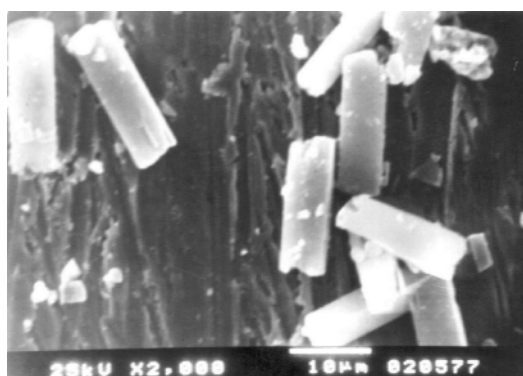


Fig. 6. SEM image of the Fe-MOR

iron and oxygen atoms in the framework of Fe-O-Si in zeolite. This band is used to identify the presence of Fe in framework.

The weaker band was observed in the range of 370-450 nm. This band implied different states of Fe in zeolite due to the d-d transfer of Fe³⁺ ions.

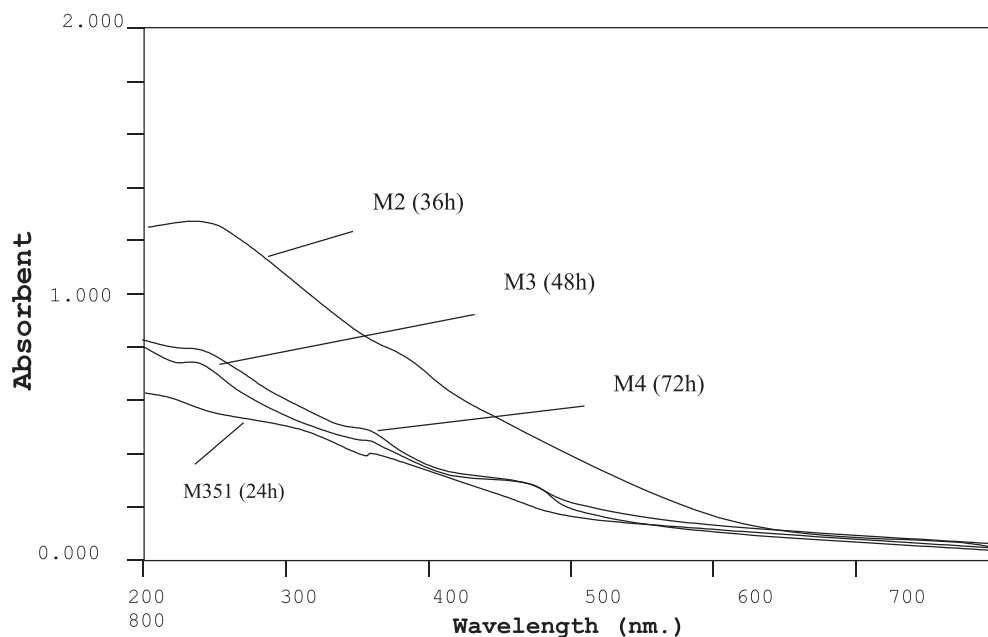


Fig. 7. UV-VIS spectra of the samples

It was seen from Fig. 7 that the strong band (200-300 nm) reached the maximum value at sample 36h (M2). When the crystallization time was prolonged from 48 to 72 hours (M3-M4), the band at about 500 nm was observed. According to [12], this band is attributed to the presence of Fe_2O_3 . By XRD analysis and IR it is known that when crystallization time was prolonged the transformation of Fe-MOR to the more stable phases (Fe-ZSM-5) occurred. In that case some Fe^{3+} might change into the oxide state, which reduced the crystallization efficiency for Fe-MOR.

Thus the optimum crystallization time for synthesis of Fe-MOR was 36 hours.

4. CONCLUSIONS

Crystallization time played the important role in the formation of Fe-MOR. In the synthesis of Fe-MOR there was the transformation of Fe-MOR to Fe-ZSM-5 when crystallization time was prolonged from 48 to 72 hours. The optimum crystallization time was 36 hours.

The UV-VIS method could identify the states of Fe in framework, in particular, in the following two states:

The state of Fe substituting into the Fe-MOR framework. The amount of Fe in this state was considerable, which produced the adsorption band around 200-300 nm (charge-transfer band).

The state of extra framework Fe. The amount of Fe in this state was negligible, which produced the adsorption band at about 500 nm (Fe_2O_3) and

the d-d transfer band around 370-450 nm (the octahedron coordinated or other states).

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Received December 21, 2004.

