

Degradation of EDTA using Different Percentages of Fe Encapsulated inside Mordenite

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Summary. Fe was incorporated inside mordenite by ion exchange technique in aqueous solution. The loaded Fe was (25-100 wt%), the iron precursor ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and the mordenite starting material (HM and Na-M). The prepared Fe-M samples were characterized by XRD, FTIR and N_2 adsorption measurements. It was found that Fe incorporated mordenite retain the same structure as that for Na-mordenite that may indicate that Fe well dispersed into mordenite channels. BET indicates Fe-M samples possess higher surface areas than the parent Na-M. Photocatalytic degradation of EDTA was carried out in the presence of the prepared Fe loaded mordenite catalysts. Effect of catalyst concentration and temperature were also studied. Thermodynamic parameters were calculated for 50 % Fe-M only because it shows the highest catalytic activity toward EDTA degradation.

Introduction

In recent years zeolites are extensively used in catalytic reactions.⁽¹⁾ Many authors have been carried out some modifications for zeolites framework by introducing some metal cations in order to enhance the catalytic activity. Mo-impregnated zeolites catalysis has been studied by XRD, IR, diffuse reflectance spectroscopy, surface area and water content.⁽²⁾

Recently, Fe loaded zeolites have been attracted the attention of many authors especially for environmental catalysis due to its activity and selectivity for many reactions such as Photo-Fenton. It was found that, the incorporation of Fe into MCM-41 increased the catalytic activity of MCM-41 by about 60 % for the photo-catalytic degradation of chlorinated phenols.⁽³⁾ The catalytic activity of Fe incorporated zeolites were also investigated on the photo-catalytic degradation of some azo dyes.⁽⁴⁾

It is well known that EDTA is one of the best and common chelating agents that used on a large scale of many industries. The removal of EDTA from waste water by using conventional techniques is not simple because it is not easily biodegradable and several recalcitrant compounds are formed during the degradation.⁽⁵⁻⁹⁾

The main objective of this study was to examine the influence of Fe loaded mordenite on the photo-degradation of EDTA. Fe was encapsulated inside mordenite in different percentages for improving the photo-degradability of EDTA as one of the common organic pollutants.

Experimental

Synthesis of Fe-M

The prepared Na-M was stirred in aqueous solution of different FeSO_4 concentrations to give Fe loaded mordenite with 25, 50, 75 and 100 wt%.⁽¹⁰⁾

Characterization

The X-ray diffraction patterns of various zeolite samples whereby measured using a Philips diffractometer (type PW 1390). The diffraction patterns were run with Ni-filtered copper radiation ($\lambda = 1.5404 \text{ \AA}$) at 30 KV and 10 mA with a scanning speed of $2\theta = 2^\circ \text{ min}^{-1}$. The Fourier transform infrared (FTIR) spectra were recorded on a Bruker (Vector 22), single beam spectrometer with a resolution of 2cm^{-1} .

Specific surface areas of various samples were obtained by the BET method at the liquid N_2 temperature (77K) using a conventional volumetric apparatus. The samples were outgassed at 573 K for 3h before measurement.

Photocatalytic experiment

The photoreactivity experiments were carried as described in reference.⁽⁴⁾

Results and discussion

Catalyst characterization

The XRD results (Table 1) revealed that the Fe-containing mordenite samples exhibit the typical lines of the Na-M zeolite, indicating that the structure of the zeolite

remains intact after the treatment procedure. Figure 1 shows the absence of any diffraction line characteristic of Fe species that may suggest that the loaded Fe is finely dispersed inside mordenite channels.

FTIR spectra of Fe-containing mordenite (25-100 wt%) were depicted in Figure 2 in comparison with the parent Na-mordenite. The data indicate that Fe-containing mordenite exhibit the same bands as that of H-mordenite, indicating that Fe-mordenite retain the same zeolite structure as that of H-mordenite even after the exchange process.

Measurements of BET surface area (Table 1) of the above mentioned samples showed a marked increase in their total surface areas if compared with the parent Na-mordenite.

Application of Fe-M for Photocatalytic degradation of EDTA

Different initial concentrations of EDTA solutions were subjected to UV irradiation (254 nm) under a constant flow of oxygen. The data obtained indicates that EDTA is degraded under the influence of light only but consumes a large time as depicted in Figure 3a. The percentage of degradation ranging from 92-100% depending on the concentration of EDTA used (Figure 3b).

The additions of 0.05 gm of encapsulated Fe-mordenite to EDTA solutions have a great influence on the degradation process if compared with Na-M itself (Fig 4a). It was found that, the degradation is very fast in the initial periods of reaction due to the adsorption of EDTA on the catalyst surface at the start of degradation reaction with respect to all samples. The percentage of degradation reaches 100% with all samples but at different periods except 100% Fe-M which show a different behavior that the degradation reaction was stopped after 60 min from the start of irradiation (Fig. 4b). It is clear that, the increasing of iron loading into mordenite increase the rate of degradation of EDTA and this may be due to the incorporation of iron into mordenite leads to the formation of new active sites from the incorporated iron on the surface of mordenite which improve the activity toward photodegradation process. On contrary to the above results despite 100% Fe-M sample contain large amount of

incorporated iron but give the lowest EDTA degradation this may be due to, as the amount of incorporated iron increase, this increasing the amount of leached iron (non-framework) as depicted in Table 1 which react with EDTA to form a stable complex especially in basic medium. The formed Fe-EDTA complex did not affected by UV irradiation so the degradation process did not furnished to the end.

Conclusion

- 1- Incorporation of Fe into mordenite increases its surface area.
- 2- Iron exchanged mordenite show high catalytic activity toward EDTA degradation.
- 3- 50% Fe-M samples show the highest catalytic activity.
- 4- The increase of Fe in solution leached from catalyst surface stopped the degradation of EDTA due to the formation of stable Fe-EDTA complex which does not affected by the used UV wavelength.
- 5- Temperature change has a great effect on the rate of EDTA degradation.

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References

1. R. M. Mohamed, A. A. Ismail, I. Othman and I. A. Ibrahim, *J. of Molecular Catalysis A; Chemical*, **151-157**, 238 (2005)
2. R. Cid, F. J. Gileambias, J. L. G. Fierro, A. L. Agudo and J. Villasenor, *J. Cata*, **478**, 89 (1984),

3. M. M. El-Moselhy; Ph. D. Thesis, Chemistry Department, Faculty of Science, Al-Azhar University, (2004).
4. M. M. Emara, A. M. S. Tourky and M. M. El-Moselhy, (in press)
5. M. M. Mohamed, N. S. Gomaa, M. El-Moselhy and N. A. Essa, *J. Colloid and Interface Science*, **331-337**, 259 (2003).
6. P. A. Babay, C. A. Emilio, R. E. Ferreyra, E. A. Gautier, R. T. Gettar and M. I. Litter, Kinetics and Mechanisms of EDTA Photocatalytic Degradation with TiO₂ under different experimental conditions, *Int. J. Photoenergy*, **193-199**, 3 (2001).
7. M. Sorensen and F. H. Frimmel, Photochemical degradation of hydrophilic xenobiotics in the UV/H₂O₂ process: influence of nitrate on the degradation rate of EDTA, 2-amino-1-naphthalenesulfonate, diphenyl-4-sulfonate and 4,4' diaminstilbene-2-2'-disulfonate, *Water Res.*, **2885-2891**, 31 (11) (1998).
8. J. K. Yang and A. P. Davis, Photocatalytic Oxidation of Cu (II)-EDTA with illuminated TiO₂: Kinetics, *Environ. Sci. Technol.*, **3789-3795**, 34 (17) (2000).
9. C. W. Schapher, N. N. Vlasova, S. K. Poznyak and A. I. Kokoring, *J. Colloid Interface Sci.*, **200**, 239 (2001).
10. M. M. El-Moselhy, Master Thesis, Al-Azhar University, (2001).

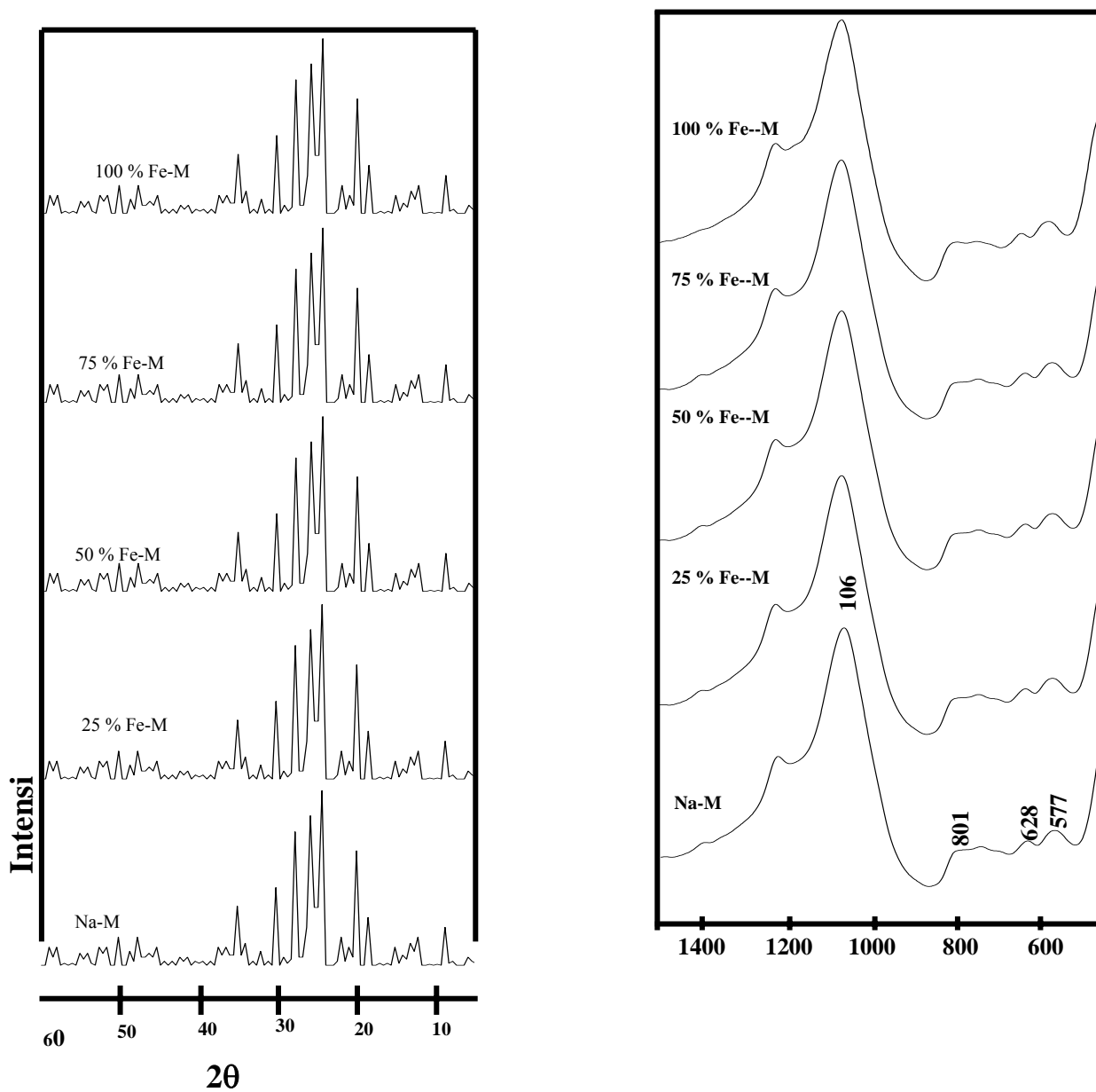


Fig. (1): X-ray diffraction patterns of the calcined Fe-M catalysis at varying loading of Fe (25-100 wt%) in comparison with the Na-M support

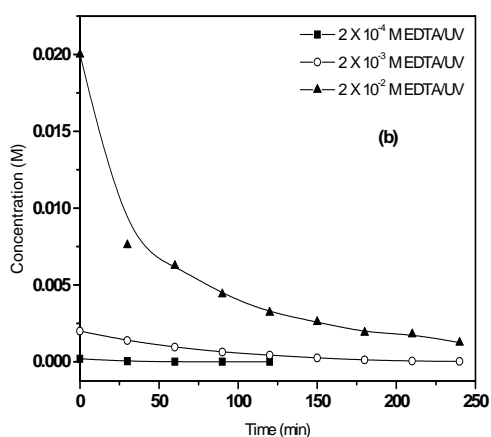
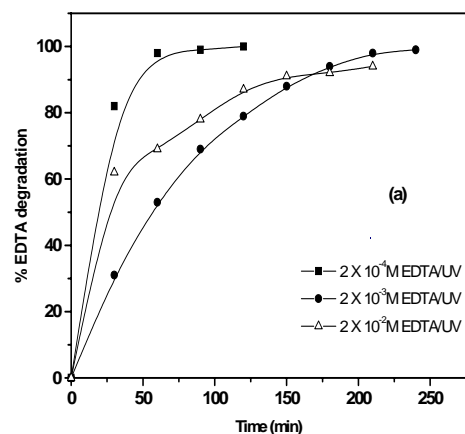
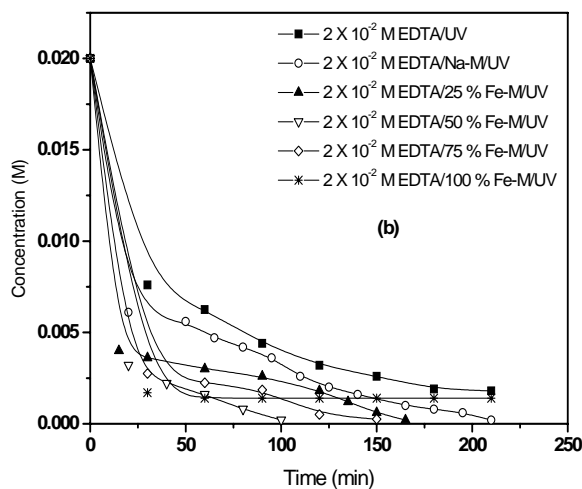
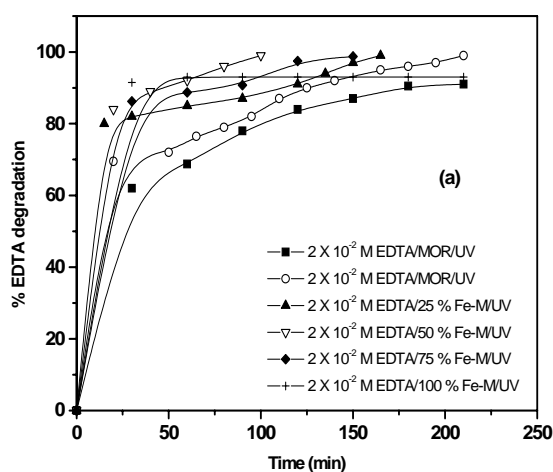


Fig. (3):

- a) % Degradation of EDT versus time,
 b) Different concentrations versus time for Degradation of EDTA.



- Fig. (4):** a) % Degradation of EDTA versus time over different Fe encapsulated mordenite,
 b) Different concentrations versus time for degradation of EDTA over different Fe encapsulated mordenite

Sample Name	Cell constants Å			Cell volume Å ³	Crystallinity %	S _{BET} (m ² /g)	Fe content	
	a	b	c				Fe _f	Fe _{non f}
Na-M	18.11	20.53	7.53	2798	100	340	-	-
25% Fe M	18.24	20.38	7.52	2795	90	378	0.73	0.92
50% Fe M	18.33	20.30	7.52	2798	86	416	1.7	2.3
75% Fe M	18.55	20.22	7.53	2823	82	485	3.4	4.8
100%FeM	18.98	19.91	7.53	2852	77	564	5.2	6.8

Table 1: The XRD unit cell parameters of mordenite (Na-M) loaded Fe catalysts.

