

Research Paper

SYNTHESIS AND CHARACTERIZATION OF MAGNESIUM MODIFIED MOBIL FIVE (MFI) ZEOLITE

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Mobil Five (MFI) zeolites were synthesized hydrothermally with silica to alumina ratio (SAR) of 50, 100 and 200. The synthesized MFI zeolites were used to exchange with 0.5%, 1.0% and 2.0% $\text{Ca}(\text{NO}_3)_2$ solutions for modification to Ca-MFI zeolite. XRD and FT-IR analysis were used to identify the MFI zeolite phases. The thermal stability of the samples was analyzed by TGA. UV-Vis (DR) spectra were used to analyze the successful exchange of the parent samples. The specific surface area, pore volume and pore size of the synthesized samples were investigated by the nitrogen adsorption-desorption isotherm, while morphology was examined using scanning electron microscopy.

Keywords: MFI, Magnesium, Ion-exchange, Microporous

INTRODUCTION

Zeolite cages can accommodate large cations such as Na^+ , K^+ etc. as well as transition metal cations and even relatively large molecules and cationic group such as water, ammonia, carbonate ions and nitrate ions, etc., due to their unique molecular architectures. According to necessity these ions can readily be exchanged for others in a contact solution as they are loosely bound. These cations are primarily present in the structure of the zeolite to counter balance the negative charge generated during isomorphous substitution of silicon atoms by other trivalent

metal atoms in the tetrahedral sites (Dyer, 2007). As a result the zeolites have high Cation Exchange Capacity (CEC) and it increases with the increase in aluminium content (Pless *et al.*, 2005). Zeolite molecular sieves have found extensive applications in ion-exchange, separation and Catalytic processes, particularly in the chemical and petroleum industries. Synthesis of magnesium and other alkaline-earth zeolites has not received much attention since the inception of the systematic investigation of zeolite synthesis some 35 years ago. Of the approximate 50 natural zeolites discovered to

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date, over 20% have eluded synthesis and another 10% have proven exceedingly difficult to synthesize at typical hydrothermal conditions.

Due to structural diversity of the Zeolites as well as possibility of insertion of ions by cation exchange, the various properties of zeolites can be modified. One of the properties that we are trying to modify here is the basicity of the zeolites to make it a suitable catalyst to carry out some base catalyzed organic reactions. So far, as the history of Mg- modified zeolites are concerned the synthesis of magnesium and other alkaline-earth metal zeolites has not received much attention since the inception of the systematic investigation of zeolite synthesis some 35 years ago. A general rule may be considered for the exchange of Cations in zeolite structures: in zeolites with very high SAR, complete ion exchange of divalent ions for monovalent ions becomes very difficult but the selectivity as well as the degree of exchange increases with increasing size of the divalent ion and decreasing SAR.

The objective of the work is to develop a novel approach for the modification of parent MFI zeolite to Mg-MFI by ion-exchange with $\text{Mg}(\text{NO}_3)_2$.

MATERIAL AND METHOD

Source of Chemicals

Chemicals used for the synthesis of MFI Zeolites and modified MFI Zeolites are sodium aluminate (Kemphasol), tetrapropylammonium bromide (Lancaster), sodium hydroxide (Fluka Chemika 99%), magnesium nitrate hexahydrate (Aldrich 99%), fumed silica (BDH) and de-ionized water.

Synthesis of MFI zeolite

Three samples of MFI Zeolites were synthesized

in the silica to alumina ratio (SAR) of 50, 100 and 200 by hydrothermal process using hydroxyl medium. A typical procedure for the synthesis of MFI zeolite with SAR of 100 is given below:

$\text{Si}/\text{Al} = 50$, $\text{NaOH}/\text{SiO}_2 = 0.15$, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$, $\text{TPA-Br}/\text{SiO}_2 = 0.07$, $\text{H}_2\text{O}/\text{SiO}_2 = 30$

Calculated amount of NaOH was dissolved slowly to 33 mL of de-ionized H_2O . To this solution required amount of TPA-Br was added slowly with continuous stirring. The solution was stirred for 15 min and a part of the required SiO_2 was added slowly to this mixture. The resulting mixture (A) was stirred for another half an hour. Calculated amount of NaAlO_2 was dissolved in 102 mL of de-ionized water slowly. To the solution the remaining part of required SiO_2 was added slowly with continuous stirring. The resulting mixture (B) is stirred for another half an hour. The mixture A was added to mixture B slowly and stirred continuously for 3 h at pH 11-12 to get homogeneous gel. The whole mass was then autoclaved in a teflon-lined stainless steel vessel maintained at 473 K inside an oven for 15 h. It was then cooled, filtered (Whatman No. 42) and washed with de-ionized water several times. The sample was dried in the filter paper at room temperature for about 12 h and at 383 K for 6 h. This was then calcined at 753 K to remove the template.

The same procedure was applied for the synthesis of other MFI zeolite (S50 and S 200). Table 1 shows the molar ratios of the components in the initial gel and other conditions maintained during the synthesis of the zeolite samples.

Modification of MFI zeolite by ion exchange with $\text{Mg}(\text{NO}_3)_2$ Solution

Synthesis of Mg modified MFI zeolite

Five samples of Mg modified MFI zeolite were

Table 1: Molar Ratios Of The Components in the Gel and Other Conditions Maintained During The Synthesis Of The MFI Zeolite Samples

Sample Designation	SiO ₂ : Al ₂ O ₃	TPA-Br: SiO ₂	NaOH: SiO ₂	H ₂ O: SiO ₂	Autoclavation Time (h)	pH of the Gel
S50	50	0.07	0.15	30	15	12
S100	100	0.07	0.15	30	15	12
S200	200	0.07	0.15	30	15	12

prepared by exchanging Calcined parent MFI Zeolite (SAR= 50, 100 and 200) with 0.5%, 1.0% and 2% Mg(NO₃)₂.

A typical procedure for the exchange of a Calcined parent MFI zeolite (SAR 100) with 0.5% Mg(NO₃)₂ Can be depicted as:

5 g of parent MFI zeolite was taken in a round bottomed flask and 150 mL (30 mL/g) of 0.5% Mg(NO₃)₂ was added to it . The solution was refluxed at 363 K for 3 h. The solution was decanted and again the above procedure was repeated 2 more times adding 150 mL (30 mL/g) of 0.5% Mg(NO₃)₂ to it. The solution was then filtered (with Whatman 42 Filter Paper), washed with distilled water 3 times, dried overnight at room temperature and then Calcined at 753 K to get Mg-MFI.

Similar procedure is repeated to exchange the Na-MFI samples with SAR 50 and 200 with 1%

and 2% Mg(NO₃)₂ solution to get other samples of Mg modified MFI zeolite. The various samples with different SAR and exchanged with different percentage of Mg(NO₃)₂ solutions are shown in Table 2.

The decanted solutions were studied with flame photometry to study the extent of ion-exchange of Na⁺ by Mg²⁺ and the results were found to be quite satisfactory.

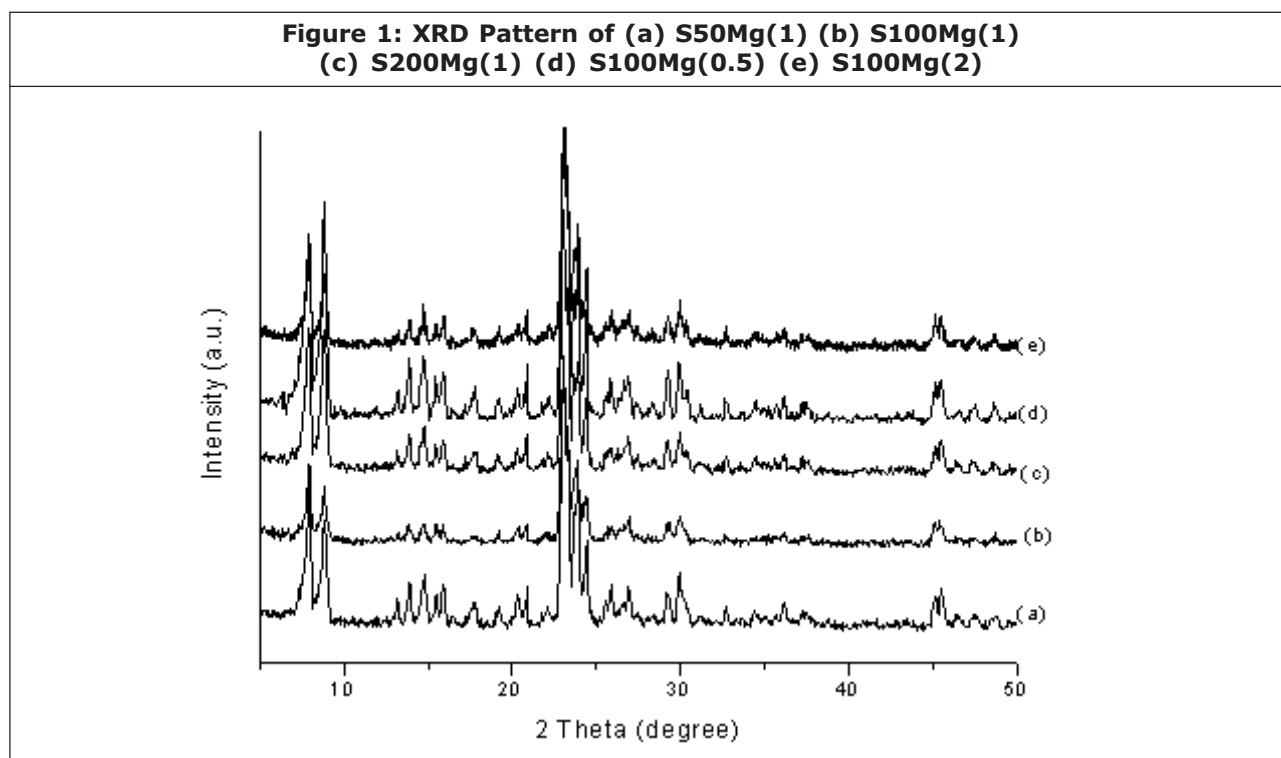
RESULTS AND DISCUSSION

Characterization of Mg modified of MFI zeolite

Five samples of Parent MFI with SAR 50, 100 and 200 were exchanged successfully with 0.5%, 1.0% and 2.0% Mg(NO₃)₂ solution. The modified MFI samples were identified by XRD. The XRD patterns of various modified samples are shown in Figure 1.

Table 2: The Various Samples with Different SAR and Exchanged with Different Percentage of Mg(NO₃)₂ Solutions

Sample Designation	SiO ₂ : Al ₂ O ₃	% of Mg(NO ₃) ₂ Solution	Exchanged Time (h)	Temperature (K)
S50 Mg(1)	50	1.0	9	363
S100 Mg (0.5)	100	0.5	9	363
S100 Mg (1)	100	1.0	9	363
S100 Mg (2)	100	2.0	9	363
S200 Mg (1)	200	1.0	9	363



The characteristic peaks are observed in 2θ values around 6.5 and 22.5 with a few additional shoulder peaks in all the Mg modified MFI samples suggesting formation of pure phase of the zeolite (Treacy and Higgins, 2001).

Crystallinity of the MFI samples is calculated using the relation

$$\%C = 100 \times I_{hkl} / (I_b + I_{hkl})$$

where, I_{hkl} is the corrected integral XRD peak intensity and I_b is the integral background intensity

for the same plane. The percentage of crystallinity with reference to one of the most significant peaks (501) is presented in Table 3. All the samples under the present investigation were found to exhibit high crystallinity ~93%.

The crystallite size of the synthesized samples was calculated using the relation.

$$D_{hkl} = K\lambda / (\beta \times \cos \theta)$$

Here, β is the full width at half maximum; K is the shape factor (taken to be 0.9); θ_{hkl} is the Bragg

Table 3: Crystallite Size and Percentage of Crystallinity (% C)_{hkl} of the Mg-modified MFI Sample

Sample Designation	SAR	% of Mg(NO ₃) ₂ Solution Exchanged	Crystallite size (nm) (501)	(%C) ₅₀₁ from XRD	% C from IR
S50 Mg (1)	50	1	56	94.82	90.3
S100 Mg (1)	100	1	53	93.27	89.4
S200 Mg (1)	200	1	51	92.26	89.2
S100 Mg (0.5)	100	0.5	53	93.86	89.6
S100 Mg (2)	100	2	53	93.71	89.3

angle and θ is the wavelength of $\text{Cu K}\alpha_1$ (1.5418Å). Relation 2. The crystallite size of the samples ranges from about 51 to 56 nm (Table 3). The crystallite sizes of the samples were found to increase with decreasing SAR.

FT-IR spectra of the Mg modified MFI zeolites are shown in Figure 2. IR results confirm the formation of MFI zeolite in all Cases showing distinct absorbance bands near 1080 (internal asymmetric stretch), 790 (external symmetric stretch), 540 (double ring vibration) and 450 cm^{-1} (T–O bending). The absorption bands near 550 cm^{-1} have been assigned to the presence of double 5-member rings in the structure (Szoztak, 1998). The IR method of finding relative crystallinity of the samples is achieved by calculating the Optical Density (OD) ratio of the peaks near 540 and 450 cm^{-1} . The results are given in Table 3 and are found to be in good agreement with those calculated from XRD studies.

The TGA curves of Mg -MFI zeolites samples are shown in Figure 3. The initial mass loss up to 423 K is attributed to physically adsorbed water in the porous materials (Guth *et al.*, 1989). The mass loss in the temperature range 423-630 K is attributed the loss due to the evolution of NO_2 produced from $\text{Mg}(\text{NO}_3)_2$ used during the ion-exchange process. Beyond 630 K, a little loss of mass was observed that might be due to those NO_2 , which were trapped strongly inside the cages and hence lost at higher temperature. In the present work, it is observed that the mass loss in the temperature range 423-630 K as well as beyond 630 K was found to increase with increase in the % of $\text{Mg}(\text{NO}_3)_2$ solutions with which the parent MFI samples were exchanged that might be due to higher concentration of NO_3^- in the samples. The percentage weight losses for various temperature ranges for different samples are presented in Table 4.

Figure 2: FT-IR Spectra of (a) S50Mg(1) (b) S100Mg(1) (c) S200Mg(1) (d) S100Mg(0.5) (e) S100Mg(2)

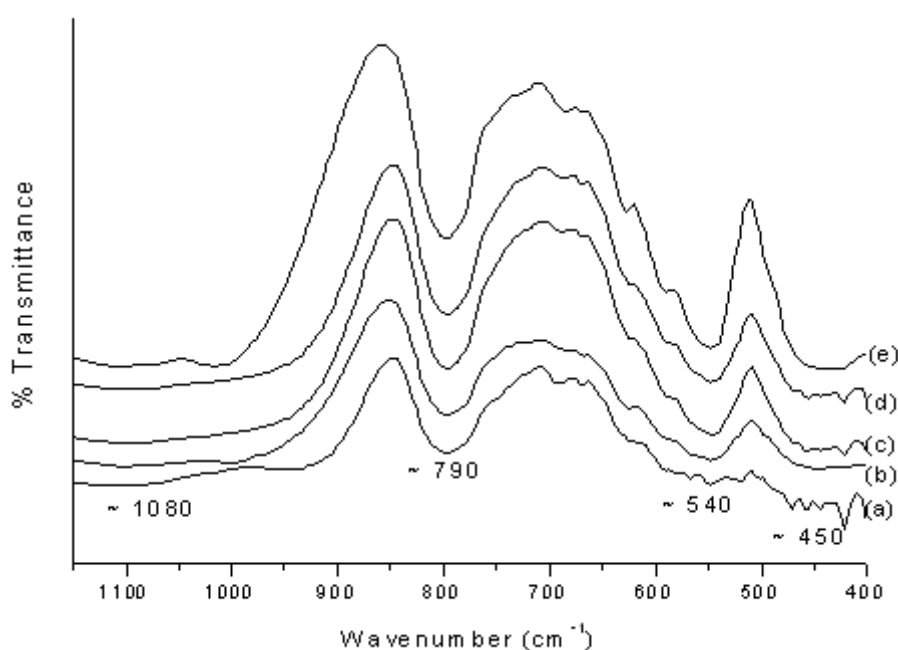


Figure 3: TGA Curve of (a) S50Mg(1) (b) S100Mg(1) (c) S200Mg(1) (d) S100Mg(0.5) (e) S100Mg(2)

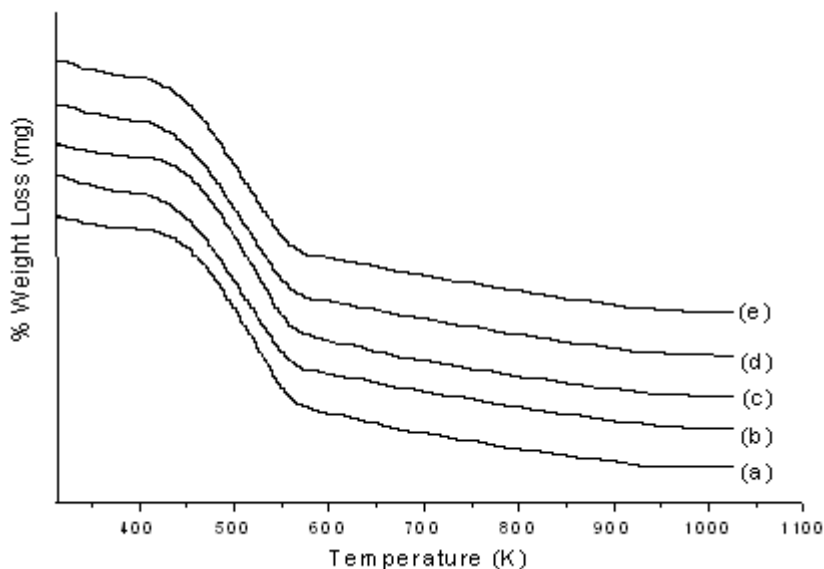


Table 4: Percentage of Weight Loss of the Mg Modified MFI Samples Observed During TG Analysis

Sample	% of Mg	Temperature Range (K)	% Weight Loss	Total % Weight Loss as Synthesized Samples
S50 Mg (1)	1.0%	273-423	0.98	13.38
		423-630	11.23	
		630-1023	1.17	
S100 Mg (1)	1.0%	273-423	1.37	13.60
		423-630	11.04	
		630-1023	1.19	
S200 Mg (1)	1.0%	273-423	2.31	14.62
		423-630	11.09	
		630-1023	1.22	
S100 Mg (0.5)	0.5%	273-423	1.84	13.28
		423-630	10.12	
		630-1023	1.32	
S100 Mg (2)	2.0%	273-423	1.96	13.82
		423-630	10.44	
		630-1023	1.42	

The UV-Vis-DR spectra of the parent and Mg -MFI samples are shown in Figure 4. The UV-Vis-DR spectra of the parent and Mg -MFI samples indicate the existence of a band at around 230 nm. The band was found to be more intense for Mg-MFI samples showing greater sensitivity of Mg for UV light.

Nitrogen adsorption-desorption isotherms of calcined Mg-MFI samples are depicted in Figure 5. The N₂ adsorption-desorption isotherms of the Mg modified samples have type H-1 type hysteresis loops with almost vertical adsorption desorption branches at P/P₀ = 0.12 to 0.21, which come from agglomerates of uniform particles. These types of hysteresis loop at these relative pressures are an indicative of microporosity along with some mesopores (Prez *et al.*, 2005). The analysis also showed that the specific surface area ranged from ~361 to ~363 m²g⁻¹ and pore

volume ranged from 0.182 to 0.191 cm³g⁻¹. The surface area as well as the pore volume of the synthesized samples were found to increase with increase in the % of exchanged Mg (NO₃)₂. The specific surface area, pore volume and pore size of the synthesized samples are shown in Table 5. The pore sizes of the synthesized samples were found to be both in mesoporous (~47 nm) and microporous range (~1.7 nm).

The morphology of the modified Mg - MFI samples was investigated by SEM analysis. SEM micrographs of synthesized Mg -MFI samples are shown in Figures 6 to 10. From the micrographs of Mg-MFI samples it can be seen that quite uniform cubical and twinned cubical shaped MFI particles were formed and the size of the particles was found to be nearly 10.2 μm. No major changes in the morphology of the samples were observed for Mg-MFI while comparing with the morphology of parent MFI (Jansen, 2001).

Figure 5: N₂ dsorption-desorption isotherms of (a) S50Mg(1) (b) S100Mg(1) (c) S200Mg(1) (d) S100Mg(0.5) (e) S100Mg(2)

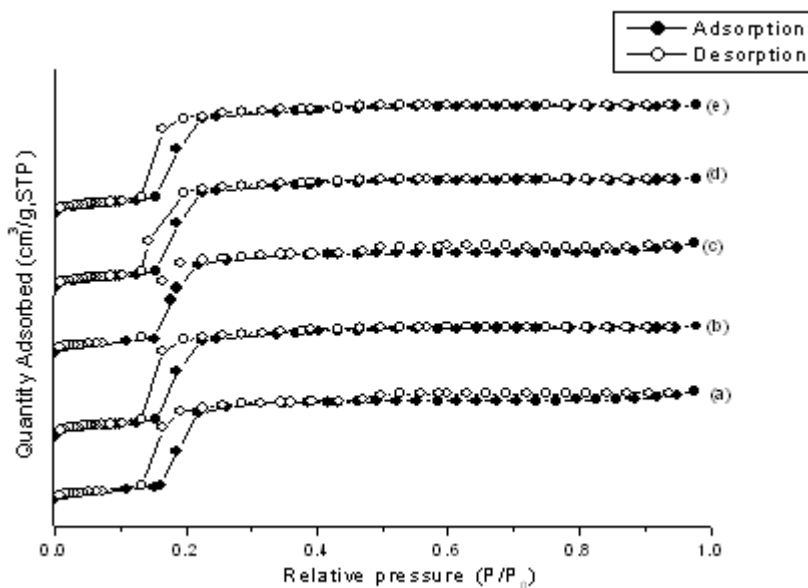


Table 5: Specific Surface Area, Pore Size and Pore Volume of Modified Mg-MFI Samples

Sample Designation	% of Mg	Surface Area (BET,m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)	Mesopore Size (nm)	Micropore Size (nm)
S50 Mg (1)	1	363.24	0.191	47.5	1.8
S100 Mg (1)	1	362.72	0.185	46.8	1.7
S200 Mg (1)	1	361.22	0.182	48.1	1.8
S100 Mg (0.5)	0.5	361.47	0.183	47.5	1.9
S100 Mg (2)	2	363.57	0.187	46.6	1.9

Figure 6: SEM Picture of S50 Mg (1)

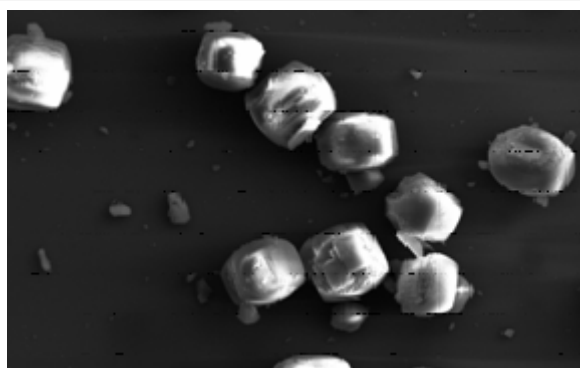


Figure 7: SEM Picture of S100 Mg (1)

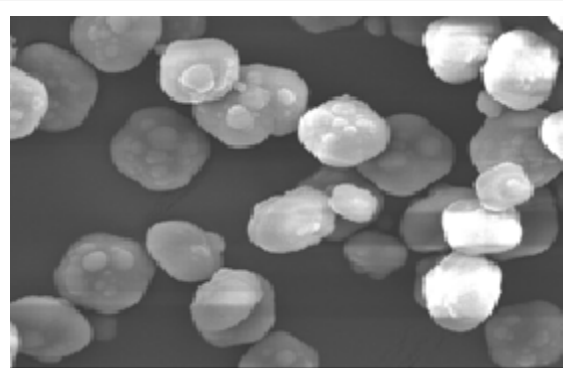


Figure 8: SEM Picture of S200 Mg (1)

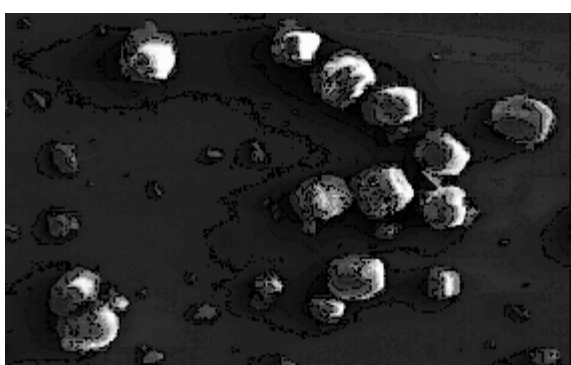
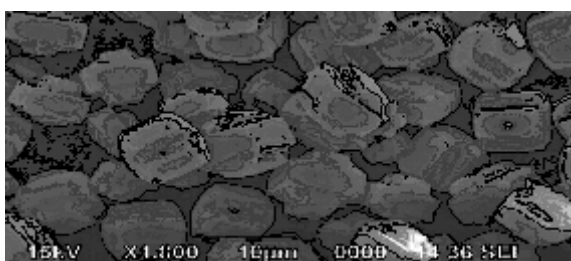


Figure 9: SEM Picture of S100 Mg (0.5)



Figure 10: SEM Picture of S100 Mg (2)



CONCLUSION

The parent MFI zeolites were exchanged successfully with Mg (NO₃)₂ solution with three different W/V % (0.5%, 1% and 2%). The modified samples were characterized by XRD. The crystallinity of the samples was found to decrease slightly to values ~93% while the crystallite size increased slightly to values 51 to 56 nm. The FT-

IR results supported that the zeolite phase remained intact even after the ion-exchange. TG analysis of the samples indicated the mass loss in three different steps. In the present work it is observed that the mass loss in the temperature range 423-630 K as well as beyond 630 K was found to increase with increase in the % of Mg (NO₃)₂ solutions with which the parent MFI samples were exchanged that might be due to higher concentration of NO₃⁻ in the samples. The UV-Vis-DR spectra of the parent and Mg -MFI samples indicate the existence of a band at around 230 nm. The band was found to be more intense for Mg -MFI samples showing greater sensitivity of Mg for UV light. The adsorption-desorption studies revealed that the surface area as well as pore volume of the modified samples increased slightly to values ~363 m²g⁻¹ and 0.182 to 0.191 cm³g⁻¹ respectively. The pore sizes of the samples remained almost same even after modification. The morphology studied from SEM analysis was found to be almost same while the particle size increased slightly to 10.2 μm.

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