

Ca-modified MFI zeolite: A study on its synthesis, characterization and catalytic activity

Kishor Kr Shah^{a,*}, Jitu Saikia^b

^aDepartment of Chemistry, ADP College, Nagaon, Assam- 782002, India.

^bRajiv Gandhi Govt. Polytechnic, Itanagar, Arunachal Pradesh 791113, India.

Received 30 August 2018; received in revised form 14 February 2019; accepted 3 June 2019

ABSTRACT

Using hydrothermal synthesis process a series of Mobil Five (MFI) zeolites were synthesized 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% Ca(NO₃)₂ solutions for modification of MFI zeolites to Ca-MFI zeolite. The formation of MFI zeolite phases was identified by XRD and FT-IR analysis. TGA studies reveal the thermal stability of the synthesized samples. The successful exchange of the parent samples with Ca was confirmed by UV-Vis (DR) spectra. The specific surface area, pore volume and pore size of the synthesized samples were investigated by the nitrogen adsorption-desorption isotherm. The morphology of the synthesized samples was examined using the scanning electron microscopy. O-methylation of phenol was carried over different synthesized catalysts to produce anisole as the major product.

Keywords: MFI, Calcium, Ion-exchange, Microporous, Anisole.

1. Introduction

Porous materials play an important role in the field of catalysis. The pores increase the surface area of the materials taking part in catalytic reactions. Zeolite is an important example of this type of material. The cages present in zeolites can lodge some important cations such as Na⁺, K⁺, etc. It is also possible to incorporate transition metal cations in those cages. The zeolite cages are sufficiently large enough to incorporate neutral molecules like H₂O, NH₃, etc. and also large anionic groups such as CO₃²⁻, NO₃⁻ etc. [1]. These cations being loosely bound can readily be exchanged with other suitable cations from their solution, to modify the properties of the zeolites desired level. When a Silicon atom is isomorphously substituted by a trivalent atom, a negative charge is generated in the tetrahedral site, which is counterbalanced by the cations in the cages [2]. As the aluminum content in the framework increases, the cation exchange capacity (CEC) of the zeolites also increases [3].

Zeolites have a wide range of applications, particularly in the chemical and petroleum industries [1].

Although a huge number of researches have been done in the fields of zeolite synthesis, the synthesis of calcium and other alkaline-earth metal zeolites have not received much attention. A large number of researches can be done on zeolites and these become possible only because zeolites have diverse structures. Moreover, the cations present in the cages of zeolites can be exchanged by other necessary metal cations, to modify their properties as necessary.

In the present study, we tried to synthesize a mild basic catalyst suitable for carrying out organic reactions. To fulfill this, the paper will provide a green method for the modification of parent MFI zeolite to Ca-MFI by ion-exchange with Ca(NO₃)₂. The catalytic activity of the synthesized samples was examined for O-methylation of phenol with dimethyl carbonate (DMC).

2. Experimental

2.1. Source of chemicals

The following chemicals were used for the synthesis of MFI zeolites and modified CaMFI zeolites – sodium aluminate (Kemphasol), tetrapropylammonium bromide (Lancaster), sodium hydroxide (Fluka Chemika 99%),

*Corresponding author.

E-mail address: kishoreshah14@gmail.com (K.K. Shah)

calcium nitrate tetrahydrate (Aldrich 99%), fumed silica (BDH) and deionized water.

2.2. Synthesis of MFI zeolite

In this study, we synthesized three samples of MFI zeolites in the silica to alumina ratio (SAR) of 50, 100 and 200. The hydrothermal synthesis process was carried out in basic medium. A typical procedure for the synthesis of MFI zeolite with SAR of 100 is given below:

Si/Al = 50, NaOH/SiO₂ = 0.15, SiO₂/Al₂O₃ = 100, TPA-Br/SiO₂ = 0.07, H₂O/SiO₂ = 30

First, a solution of NaOH was prepared by dissolving the calculated amount of NaOH in 33 mL of deionized H₂O. To this solution, the required amount of TPA-Br was added slowly with continuous stirring [4]. The solution was stirred for 15 min and a part of the required SiO₂ was added slowly to this mixture. The resulting mixture (A) was stirred for another 30 minutes.

Second, a solution of NaAlO₂ was prepared by dissolving the calculated amount of NaAlO₂ in 102 mL of deionized H₂O. To the solution, the remaining part of required SiO₂ was added slowly with continuous stirring. The resulting mixture (B) is stirred for another 30 minutes. The mixture A was added to mixture B slowly and stirred continuously for 3 h to get the homogeneous gel. During stirring the pH of the gel was maintained in the range of 11-12. The whole mass was then transferred to a Teflon-lined stainless steel autoclaved. It was then heated at 473 K inside an oven for 15 h. It was then cooled, filtered (Whatman No 42) and washed with deionized water several times. The sample was dried 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.

Using the same synthesis procedure, other samples of MFI zeolite (S50 and S 200) were also prepared. Table 1 shows the molar ratios of the components in the initial gel and other conditions maintained during the synthesis of the zeolite samples.

2.3. Modification of MFI zeolite by ion exchange with Ca(NO₃)₂ Solution

By exchanging calcined parent MFI zeolite (SAR= 50, 100 and 200) with 0.5%, 1.0% and 2% Ca(NO₃)₂, we prepared 5 samples of Ca modified MFI zeolites.

The procedure for the synthesis of CaMFI zeolite by the exchange of parent MFI zeolite (SAR 100) with 0.5% Ca(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% Ca(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% Ca(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 CaMFI.

For the exchange the NaMFI samples with SAR 50 and 200 with 1% and 2% Ca(NO₃)₂ solution to get other samples of Ca modified MFI zeolite, a similar procedure was adopted. The various samples with different SAR and exchanged with different percentage of Ca(NO₃)₂ solutions are shown in Table 2.

The extents of ion-exchange of Na⁺ by Ca²⁺ were studied with flame photometry using the decanted solution and the results were found to be quite satisfactory.

The reaction was carried out in the liquid phase in a three-necked round bottom flask equipped with a reflux condenser.

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

Table 2. The various samples with different SAR and exchanged with different percentage of Ca(NO₃)₂ solutions.

Sample designation	SiO ₂ : Al ₂ O ₃	% of Ca(NO ₃) ₂ solution	Exchanged time (h)	Temp.(K)
S100 Ca (0.5)	100	0.5	9	363
S100 Ca (1)	100	1.0	9	363
S100 Ca (2)	100	2.0	9	363

The reaction was studied in the temperature range of 338 to 358 K. All the catalysts were activated at 393 K for 4 h, prior to use in the reaction. The temperature of the reaction was maintained by a thermostated oil bath. After each experiment, the catalyst was separated by filtration and then dried at 383 K for 12 h. The dried catalysts were then calcined in air at 753 K for 6 h and reused. It was observed that the performance of the catalyst was not significantly affected even after two runs. The reaction products were identified by GC-MS (Perkin Elmer, Clarus - 500). The products obtained were anisole and methanol.

3. Results and Discussion

3.1. Characterization of Ca modified of MFI zeolite

In these studies, we used three different concentrations (0.5%, 1.0% and 2.0%) of $\text{Ca}(\text{NO}_3)_2$ solution for exchanging 5 different samples of parent MFI with SAR 50, 100 and 200. XRD analysis was carried out for determining the zeolite phases. The XRD patterns of various modified and parent MFI samples are shown in Fig. 1.

The formation of pure zeolite phase in all cases has been confirmed by XRD analysis. The XRD curves show peaks at 2θ values around 6.5 and 22.5 with a few additional shoulder peaks [5], they are characteristic peaks for zeolite phases.

The crystallinity of the MFI samples is calculated using this equation:

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

Where, I_{hkl} is the corrected integral XRD peak intensity and I_b is the integral background intensity for the same plane [1]. The percentage of crystallinity with reference to one of the most significant peaks (501) is indicated in Table 3. All the samples under the present investigation were found to exhibit high crystallinity, ~95%.

The crystallite size of the synthesized samples was calculated using this equation:

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

Here, β is the full width at half maximum; K is the shape factor (taken to be 0.9); θ_{hkl} is the Bragg angle and λ is the wavelength of $\text{Cu K}\alpha_1$ (1.5418 Å) [1]. The crystallite size of the samples ranges from about 51 to 56 nm (Table 3). In this study, it is found that with decreasing SAR, the crystallite sizes of the samples increased.

FT-IR results confirm the formation of zeolite phases in all cases. FT-IR results show absorbance bands at wavenumbers 1080 cm^{-1} , 790 cm^{-1} , 540 cm^{-1} and 450 cm^{-1} . These absorbance bands may be assigned as characteristic bands for T-O-T (Si-O-Al) internal asymmetric stretch, T-O-T (Si-O-Al) external symmetric stretch, double pentasil ring vibration and T-O-T bending respectively. The presence of tetrahedral framework in ZSM-5 was confirmed by Yokomori et al [6]. The T-O-T bending indicates the $\text{SiO}_3\text{-O-AlO}_3$ bending. In addition to these bands one band is observed at wavenumber 550 cm^{-1} , which indicates the presence of double 5-member rings in the structure [7]. The relative crystallinity of the samples was calculated by the optical density (OD) ratio of the peaks near 540 and 450 cm^{-1} [1]. Crystallite size and percentage of crystallinity (% C) $_{hkl}$ of the Ca-modified MFI samples calculated both from XRD and IR are given in Table 3. FT-IR spectra of the Ca modified MFI zeolites are shown in Fig. 2.

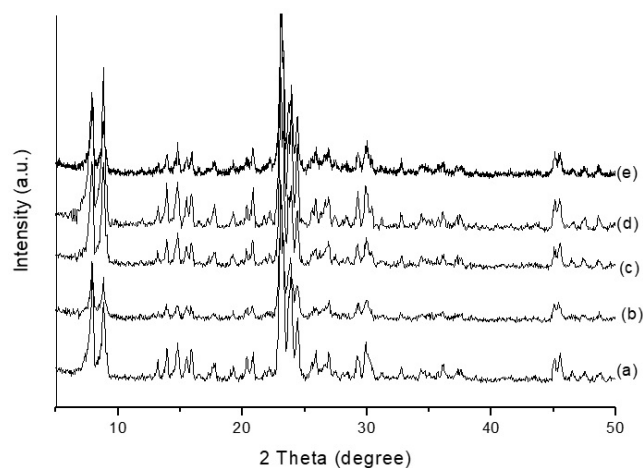


Fig. 1. XRD Pattern of (a) S50, (b) S100, (c) S100Ca(0.5), (d) S100Ca(1) and (e) S100Ca(2).

Table 3. Crystallite size and percentage of crystallinity (% C) $_{hkl}$ of the parent as well as Ca-modified MFI sample.

Sample designation	SAR	% of $\text{Ca}(\text{NO}_3)_2$ solution exchanged	Crystallite size (nm) (501)	(%C) $_{501}$ from XRD	% C from IR
S50	50	-	54	94.30	92.9
S100	100	-	52	95.61	92.3
S100 Ca (0.5)	100	0.5	56	94.63	90.9
S100 Ca (1)	100	1	55	94.47	91.4
S100 Ca (2)	100	2	57	94.62	91.3

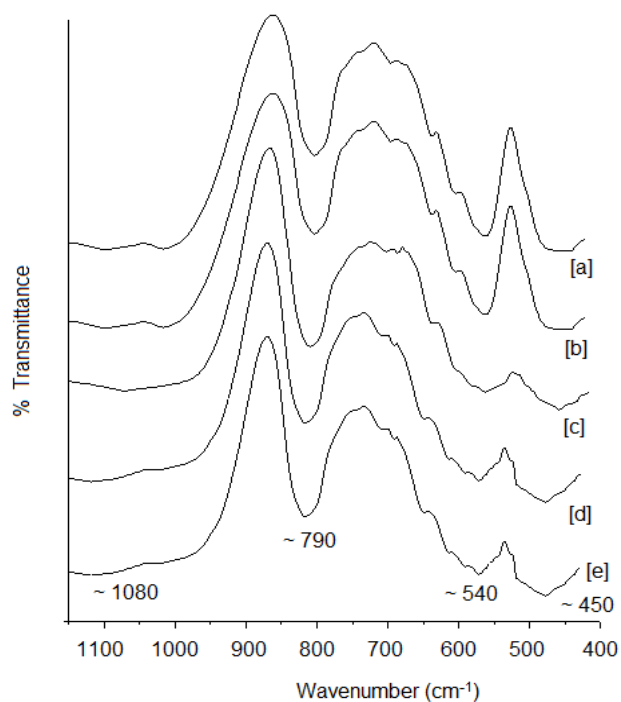


Fig. 2. FT-IR Spectra of (a) S50, (b) S100, (c) S100Ca(0.5), (d) S100Ca(1) and (e) S100Ca(2).

In TGA, it is suggested that all the samples show mass losses in three steps. Water molecules are adsorbed in the pores of the samples which are lost as an initial mass loss on heating the samples up to 423 K [8]. The second mass loss in the temperature range 423-630 K is due to the evolution of NO_2 , that is produced from $\text{Ca}(\text{NO}_3)_2$

used during the ion-exchange process. Finally, the mass loss beyond 630 K is due to strongly trapped NO_2 inside the cages [1]. The TGA curves of CaMFI zeolites samples are shown in Fig. 3.

This study reveals that with an increase in the % of $\text{Ca}(\text{NO}_3)_2$ solutions used for exchanging the parent MFI samples, the mass loss in the temperature range 423-630 K and beyond 630 K increased. The reason for increased mass loss may be due to the higher concentration of NO_3^- in the samples [1]. The percentage of weight losses at various temperature ranges for different samples are summarized in Table 4.

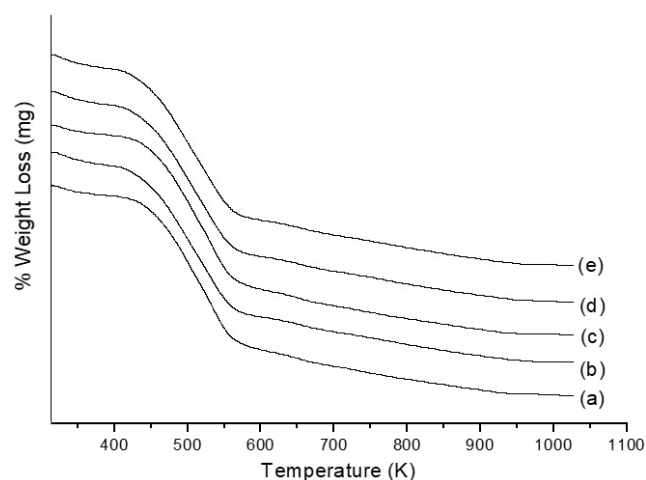


Fig. 3. TGA Curve of (a) S50, (b) S100, (c) S100Ca(0.5), (d) S100Ca(1) and (e) S100Ca(2).

Table 4. Percentage of weight loss of the Ca modified MFI samples observed during TG Analysis.

Sample	% of Ca	Temperature range (K)	% Weight loss	Total % weight loss as synthesized samples
S50	-	273-423	0.916	7.986
		423-893	6.264	
		893-1023	0.806	
S100	-	273-423	0.833	8.372
		423-893	6.855	
		893-1023	0.684	
S100 Ca (0.5)	0.5%	273-423	1.84	13.63
		423-630	10.34	
		630-1023	1.45	
S100 Ca (1)	1.0%	273-423	2.37	15.25
		423-630	11.36	
		630-1023	1.52	
S100 Ca (2)	2.0%	273-423	1.76	16.06
		423-630	12.33	
		630-1023	1.97	

A band is observed at ~ 230 nm, after analyzing the parent and Ca-MFI samples by UV-Vis-DR spectrometry [1]. The Ca-MFI samples have stronger bands than those of the parent MFI. The intense bands for CaMFI samples may be due to the greater sensitivity of Ca for UV light. Fig. 4 shows the UV-Vis-DR spectra of the parent and Ca -MFI samples.

The Ca-MFI samples are reported to have H-1 type hysteresis loops. These loops have adsorption desorption branches at $P/P_0 = 0.12$ to 0.2 . An indication of microporosity along with some mesopores is obtained from these types of hysteresis loop at these relative pressures [9].

The N_2 adsorption-desorption isotherm analysis showed that the specific surface area ranged from ~ 361 to ~ 364 m^2g^{-1} and pore volume ranged from 0.180 to 0.189 cm^3g^{-1} .

The pore volume and also the surface area of the Ca-MFI samples increased with an increase in the % of exchanged $Ca(NO_3)_2$ [1]. Table 5 shows the specific surface area, pore volume and pore size of the synthesized samples. The synthesized samples were found to have pore sizes in both mesoporous (~ 47 nm) and microporous ranges (~ 1.8 nm).

Fig. 5 shows the nitrogen adsorption-desorption isotherms of calcined Ca-MFI samples.

SEM studies were used to analyze the morphology of the Ca-MFI samples. Fig. 6a-e shows the SEM micrographs of synthesized Ca-MFI samples. The SEM analysis showed that the synthesized samples have quite uniform cubical and twinned cubical shape. From the SEM studies, the particle sizes are found to be ~ 10.2 μm . Morphologically, the parent and Ca-MFI samples are almost the same [10].

The synthesized samples were used to carry out O-Methylation of phenol with dimethyl carbonate (DMC). The reaction is shown in Scheme 1.

In case of all the catalysts, the conversion was found to increase with time on stream (TOS). Table 6 shows the

effect of reaction time on O-Methylation of phenol at 358 K with phenol to DMC ratio 1:2 and catalyst amount of 2 (W/W) % with respect to the total substrate.

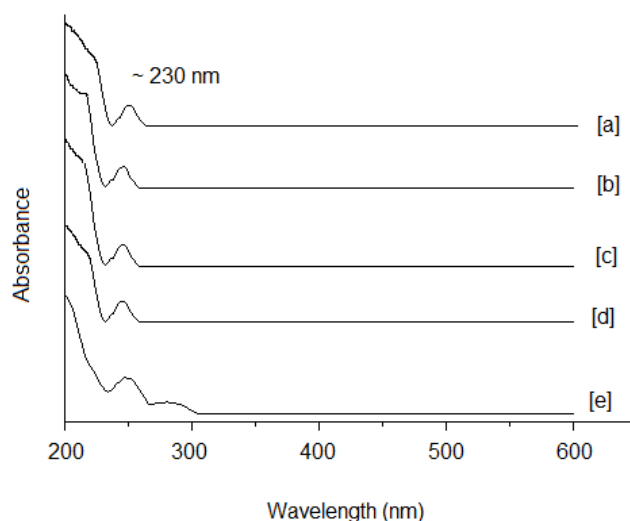


Fig. 4. UV-Vis (DR) Spectra of (a) S50, (b) S100, (c) S100Ca(0.5) and (d) S100Ca(1) (e) S100Ca(2).

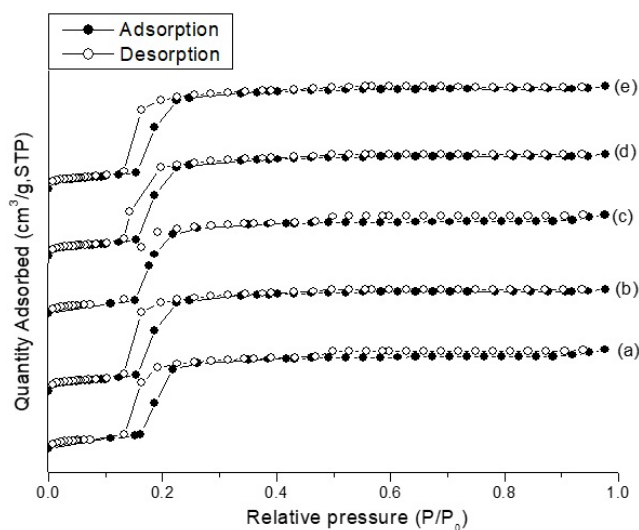


Fig. 5. N_2 Adsorption-desorption isotherms of (a) S50, (b) S100, (c) S100Ca(0.5), (d) S100Ca(1) and (e) S100Ca(2).

Table 5. Specific surface area, pore size and pore volume of modified Ca-MFI samples.

Sample designation	% of $Ca(NO_3)_2$	Specific surface area (BET, m^2g^{-1})	Pore volume (cm^3g^{-1})	Mesopore size (nm)	Micropore size (nm)
S50	-	361.67	0.186	47.2	1.9
S100	-	361.21	0.180	46.4	1.8
S100Ca(0.5)	1	361.72	0.185	46.9	1.8
S100Ca(1)	0.5	363.52	0.187	47.2	1.8
S100Ca(2)	2	364.25	0.189	47.6	1.9

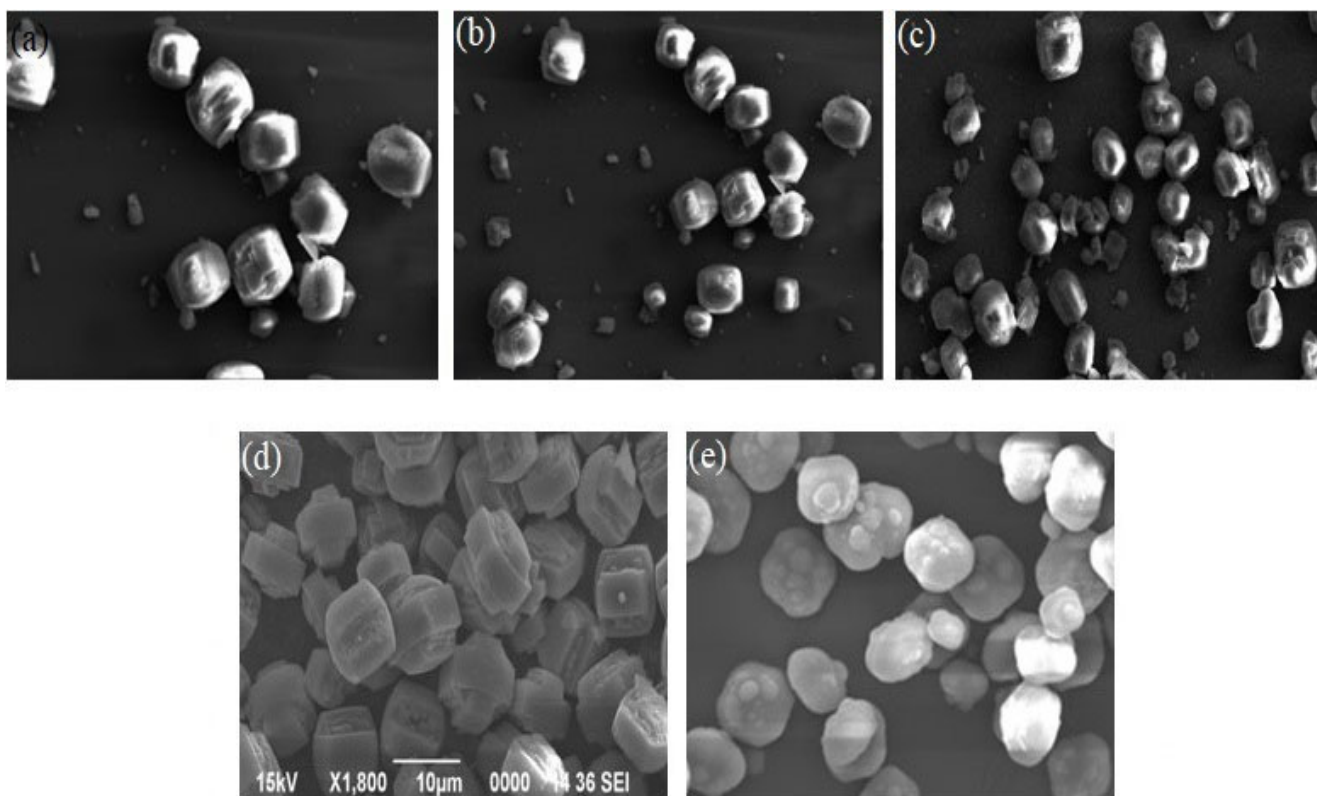


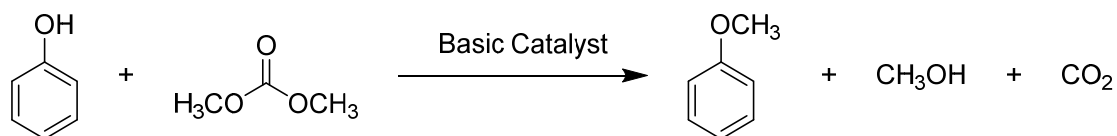
Fig. 6. SEM picture of (a) S50, (b) S100, (c) S100Ca(0.5), (d) S100Ca(1) and (e) S100Ca(2).

Results showed that the yield of anisole for different DMC/Ph molar ratios increased continuously with the reaction time to a maximum value after 3-7 h and then was steady over a 24 h reaction period. On introduction of Ca to the parent MFI, the conversion of phenol was found to be lowered; this may be due to decrease in basicity of the samples. However, the selectivity of anisole increased with decrease in basicity i.e. with increase in the % of Ca in the samples. Fig. 7 shows the effect of reaction time on O-methylation of phenol.

In order to study the effect of phenol and DMC mole ratio on O-methylation of phenol the reaction was carried out in three different phenol: DMC (1:1, 1:1.5 and 1:2) over different catalysts at temperature 358 K and with catalyst amount 2 (W/W) % with respect to the total substrate in DMSO. The products were withdrawn at 7 h interval and were analyzed by GC-MS.

The results are shown in Table 7 and depicted in Fig. 8.

With other Phenol/DMC molar ratios (1:1 and 1:1.5), the yield of anisole was reduced and never exceeded 40%. For these ratios, the selectivity decreased with reaction time to values close to 59% with a phenol conversion around 63%. When the phenol concentration increases, with a higher phenol/DMC molar ratio, the anisole formation decreases. This fact could be caused by the strong adsorption of phenol on the surface of the MFI zeolite which avoids the DMC adsorption [11]. Furthermore, a high concentration of phenol would produce the hydrogen-bonding formation among the molecules of phenol, inhibiting the phenolate formation by the action of the catalyst. A similar phenol/DMC molar ratio was reported by Ouk et al. in the methylation of phenol with DMC employing tetrabutylammonium bromide as the catalyst [12].



Scheme 1. O-methylation of phenol with dimethyl carbonate to produce anisole.

Table 6. Effect of reaction time on O-Methylation of phenol.

Catalyst	Reaction time (h)	Conversion of phenol (%)	Selectivity of anisole (%)
S100	1	14.6	74.5
	3	32.2	74.6
	5	47.6	74.8
	7	62.3	74.7
	9	63.4	74.6
S100Ca(0.5)	1	13.7	75.1
	3	31.4	75.9
	5	45.7	77.0
	7	61.6	77.2
	9	61.9	77.8
S100Ca(1)	1	13.2	75.7
	3	30.9	76.4
	5	45.1	77.6
	7	60.4	77.9
	9	61.1	78.3
S100Ca(2)	1	12.8	75.9
	3	30.1	76.8
	5	44.7	77.9
	7	59.7	78.4
	9	60.2	78.6

Phenol conversion and the selectivity of anisole were calculated using equations 1, and 2 respectively.

$$\% \text{ Phenol conversion} = \frac{(\text{Mole phenol}_{\text{inlet}} - \text{Mole phenol}_{\text{outlet}})}{\text{Mole phenol inlet}} \times 100 \text{ --- (1)}$$

$$\% \text{ Selectivity for Anisole} = \frac{(\text{Mole of Anisole}/\text{Mole of Anisole} + \text{Mole of } \text{CH}_3\text{OH}) \times 100 \text{ --- (2)}$$

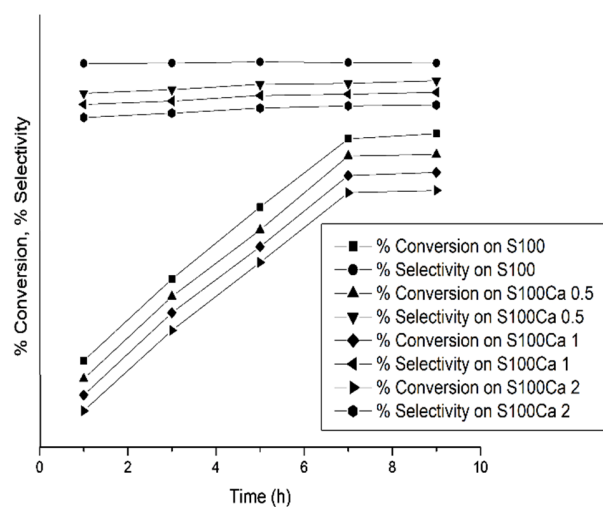


Fig.7. Effect of reaction time on O-methylation of phenol.

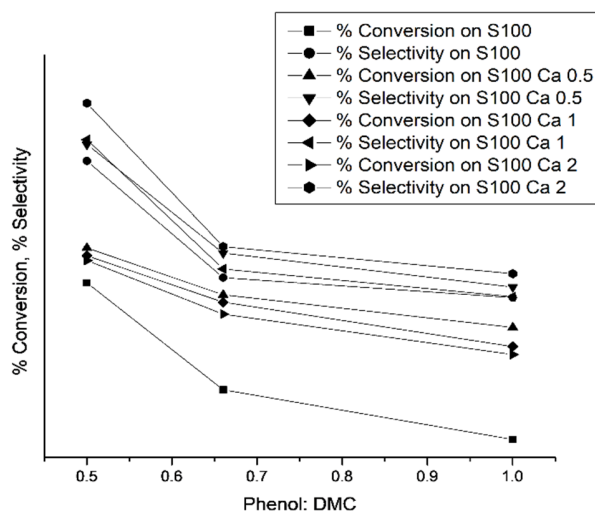


Fig. 8. Effect of phenol and DMC ratio on O-methylation of phenol.

Table 7. Effect of phenol and DMC mole ratio on O-methylation of phenol.

Catalyst	Phenol: DMC	Conversion of phenol (%)	Selectivity of anisole (%)
S100	0.5	62.3	74.7
	0.66	46.2	57.1
	1	38.7	54.1
S100Ca(0.5)	0.5	61.6	77.2
	0.66	54.5	60.8
	1	49.6	55.7
S100Ca(1)	0.5	60.4	77.9
	0.66	53.4	58.4
	1	46.7	54.2
S100Ca(2)	0.5	59.7	78.4
	0.66	51.6	56.8
	1	45.5	52.7

Phenol conversion and the selectivity of anisole were calculated using equations 1, and 2 respectively.

$$\% \text{ Phenol conversion} = \left[\frac{\text{Mole phenol}_{\text{inlet}} - \text{Mole phenol}_{\text{outlet}}}{\text{Mole phenol}_{\text{inlet}}} \right] \times 100 \text{ --- (1)}$$

$$\% \text{ Selectivity for Anisole} = \left[\frac{\text{Mole of Anisole}}{\text{Mole of Anisole} + \text{Mole of CH}_3\text{OH}} \right] \times 100 \text{ --- (2)}$$

4. Conclusions

The synthesized parent MFI zeolites were exchanged successfully with $\text{Ca}(\text{NO}_3)_2$ solution with three different W/V % (0.5%, 1% and 2%). The formation of zeolite phases as well as incorporation of Ca in samples were determined by XRD, FTIR, TGA, UV-Vis, N_2 adsorption-desorption isotherm and SEM. The synthesized samples were used to carry out O-methylation of phenol with dimethyl carbonate. In case of all the catalysts, conversion was found to increase with time on stream. It was suggested that, the yield of anisole for different dimethyl carbonate: phenol molar ratios increased continuously with the reaction time. The effect of phenol and dimethyl carbonate mole ratio on product formation was also evaluated. In this study, a good catalyst has been synthesized that is selective towards synthesis of anisole at quite low temperature in comparison to others that have already been reported. Moreover, the samples contain quite low amount of Ca. Thus, it may be concluded that the noble catalyst for selective production of anisole is S100Ca (2).

Acknowledgments

The authors acknowledge the Centre for Nanotechnology and CIF of IIT, Guwahati, Department of Physics, Tezpur University, Tezpur, NEHU, Shillong and Department of Instrumentation & USIC, Gauhati University for characterization of the samples.

References

- [1] J. Saikia, K.K. Shah, A.K. Talukdar, *Int. J. Eng. Sci. Res. Technol.* 3 (2014) 191-199.
- [2] A. Dyer, *Stud. Surf. Sci. Catal.* 168 (2007) 525-553.
- [3] J.D. Pless, R.S. Maxwell, M.L.F. Philips, K.B. Helean, M.Y. Axness, T.A. Nenoff, *Chem. Mater.* 17 (2005) 5101-5108.
- [4] R. Kawase, A. Lida, Y. Kubota, K. Komura, Y. Sugi, K. Oyama, H. Itoh, *Ind. Eng. Chem. Res.* 46 (2007) 1091-1098.
- [5] M.M.J. Treacy, J.B. Higgins, *Collection of Simulated XRD Powder Patterns for Zeolites*, 1st Ed., Elsevier Science, Amsterdam, 2001.
- [6] Y. Yokomori, S. Idaka, *Microporous Mesoporous Mater.* 28 (1999) 405-413.
- [7] R. Szostak, *Molecular Sieves: Principles of Synthesis and Identification*, 2nd Ed., Blackie Academic and Professional, London, 1998.
- [8] J.L. Guth, H. Kessler, J.M. Higel, J.M. Lamblin, J. Patarin, A. Seive, J.M. Chezeau, R. Wey, *Zeolite Synthesis in the Presence of Fluoride Ions: A Comparison with Conventional Synthesis Methods*. ACS Symp. Ser., Vol. 398, American Chemical Society, Washington DC, 1989.
- [9] J. Perez-Ramirez, J.C. Groen, A. Brückner, M.S. Kumar, U. Bentrup, M.N. Debbagh, L.A. Villaescusa, *J. Catal.* 232 (2005) 318-334.
- [10] K. Jansen., H. Robson, *Verified Syntheses of Zeolitic Materials*, 2nd Ed., Elsevier Science, Amsterdam, 2001.
- [11] T.J. Beutel, *J. Chem. Soc. Faraday Trans.* 94 (1998) 985-993.
- [12] S. Ouk, S. Thiebaud, E. Borredon, P. Le Gars, *Appl. Catal. A* 241 (2003) 227-233.