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Catalytic polymerization of *N*,*N*-diethanol acrylamide with phthalic anhydride in the presence of H-mordenite and Fe-mordenite zeolites

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Abstract

The H-mordenite zeolite catalyzes the polymerization of *N*,*N*-diethanol acrylamide (DEAA) with phthalic anhydride (PA) yielding polyesteramide (PEA) resin. The Fe modified mordenites showed lower activity than that of H-mordenite that presented high stability on multiple recycling. The formation of DEAA; the principal step in forming PEA, was occurred through the condensation reaction of diethanol amine (DEA) and acrylic acid (AA) with 91% selectivity in addition to 9% devoted for the corresponding ester (diethanol amine monoacrylate; DEMA). The IR spectroscopic study of DEAA formation in the presence of mordenite zeolite reveals the greater affinity of the reactants specifically AA to protons that are likely to be the initiators of the DEAA formation. The formation of ester was confirmed through the appearance of a band at 1735 cm^{-1} attributed to the stretching vibration of C=O of ester groups. A possible reaction mechanism is proposed based on data reported in the literature and the results of the present investigation. The activation energy of the DEAA formation was found to be 35.5 $kJ\,mol^{-1}$, for non-catalyzed and 11.46 $kJ\,mol^{-1}$, for the H-mordenite catalyzed one. The acidic and textural properties of the catalytic samples have been measured using NH_3 adsorption (at 150 °C) and N_2 adsorption (at −196 °C), respectively. The results obtained indicate the importance of the zeolite acid selectivity towards amide and ester formation.

Keywords: H-mordenite; *N*,*N*-Diethanol acrylamide; Polyesteramide formation; Spectroscopic measurements

1. Introduction

Polymeric systems based on polyesteramides (PEA) are high performance material, which combine the useful properties of polyester and polyamide resins, and finds many applications most importantly as protective surface coatings [1,2]. Diethanolamine derivatives of fatty acids were used in the preparation of polyesteramide and alkyd/polyesteramide resins [3,4]. Most alkylolamides are derived from ethanolamine and fatty acids [5,6]. The above-mentioned derivatives are used as the ingredient source of dihydric alcohol for polycondensation.

Various catalysts including inorganic oxides and salts have been employed for the preparation of polyesteramide such as MgO, Al_2O_3, ZnO, TiO_2 and LiOH. Many of these compounds are incorporated in the preparation of vehicles for paints. Acid catalysts, on the other hand, such as sulfuric acid or P-toluene sulfonic acid increase the rate of polyesteramidification, but usually cause color formation and other detrimental side reactions [7]. For this reason the latter catalysts are generally not used in high-temperature cooks. In addition, some of highly price organometallic compounds are used as catalysts for direct polyesteramidification [8]. Thus, according to the disadvantages of homogeneous catalysts in practical applications [9] heterogeneous ones are favorably required in polymerization processes for the purpose of producing uniform polymer particles with narrow particle size distribution and a high bulk density [10]. In addition, the raised difficulties to separate the catalyst from the product, that are inherent to homogeneous catalysts, used to cause serious drawbacks together with the possibility of the catalyst decomposition. On the other hand, the heterogeneous catalysts present easy separation and reuse.

The present work presents an investigation of using mordenite zeolite as a potential catalyst for the preparation of polyesteramide by the reaction of diethanolamine and acrylic

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acid (AA) followed by the addition of phthalic anhydride (PA). The effectiveness of mordenite zeolite catalyst in promoting the polymerization reaction is evaluated and discussed with the help of some spectroscopic measurements including FTIR, MS and UV-Vis in addition to gas chromatography and N_2 adsorption measurements. A comparative study between mordenite and Fe modified mordenite catalysts towards polyesteramide formation was carried out and rationalized in the light of their ammonia adsorption and texturing properties. In addition, particular information regarding the kinetics and mechanism of the intermediate *N*,*N*-diethanol acrylamide (DEAA) formation and stability of H-mordenite in the sense of its multiple uses in the polymer formation are reported.

2. Experimental

2.1. Materials

Diethanol amine (DEA) and acrylic acid were obtained from Merck (Germany). All solvents were of the purest grade (Analytical grade) and were used as received. Because of the easy polymerization of AA when exposed to light or heat, a polymerization inhibitor was added (methoxy phenol) at 200 ppm to prevent strong exothermic polymerization.

2.1.1. Synthesis of N,N-diethanol acrylamide (DEAA), step I

A mixture of freshly distilled diethanol amine (10.5 g, 0.1 mol), acrylic acid (7.2 g, 0.1 mol); xylene (10 ml) and catalyst (0.1 g) was placed in 250 ml round bottom flask fitted with Dean and Stark apparatus. The mixture was allowed to reflux at 140 °C by heating mantle until 0.1 mol (1.8 ml) of water was liberated.

2.1.2. Synthesis of polyesteramide resin (PEA), step II

The *N*,*N*-diethanol acrylamide was esterified with calculated amount of phthalic anhydride in the presence of catalyst (0.1 g) and xylene solvent (10 ml). The reaction mixture was refluxed (140 °C) using Dean and Stark trap and the course of the reaction was followed by determining the acid value as well as observing the amount of water liberated.

2.1.3. Catalyst preparation

The H-mordenite (extrudates) was of Conteka brand of the SiO_2/Al_2O_3 ratio 10.8. The Na form $[Na_8(AlO_2)_8(SiO_4)_{86}\cdot 24H_2O]$ was obtained from the H form using 0.1 M NaOH solution. Prior to exchange Na-mordenite into Fe^{3+}-form, the zeolite was thermally pretreated at the rate of $2.0^\circ\ min^{-1}$ where it was then kept at 300 °C for 3 h. The Na-form mordenite was stirred in aqueous solutions of $FeSO_4\cdot 7H_2O$ to give Fe loadings of 10, 15, 20 and 25 wt.%. Each loading was performed three times for accomplishing the required Fe content. The Fe-mordenites were dried at 110 °C for 6 h and finally calcined at 550 °C for 6 h. The percentages of exchanged Fe in Na-mordenite were determined spectrophotometerically by UV absorption of the thiocyanate-Fe complex in the presence of CTAB at 308 nm; the process is sensitive to Fe concentration as low as 0.6 ppm Fe [11]. For comparison purposes, another H-mordenite sample of SiO_2/Al_2O_3 ratio 203 was used and purchased from Strem Chemicals (Japan).

The used TiO_2 catalyst, supplied from Degussa, of surface area $50\ m^2\ g^{-1}$ and pore volume of $0.9\ cm^3\ g^{-1}$ indicated the presence of both anatase [$2\theta = 25.3^\circ$ (1 0 1)] and rutile [$2\theta = 27.4^\circ$ (1 1 0)] with a percentage ratio of 85:15.

2.2. Measurements: methods of testing and structural elucidation

2.2.1. Determination of acid value (ASTM, D-1639-96)

The course of polyesteramide reaction can be followed by titration of the total free carboxyl in the samples removed from the reaction at time intervals against alcoholic KOH (in 95% ethyl alcohol), using phenolphthalein as indicator.

2.2.2. Determination of hydroxyl value (ASTM, D-1957-95)

The free OH groups that are determined at time intervals were accomplished through acetylation (1 volume of acetic anhydride + 3 vol. of pyridine) and refluxing for 30 min. Then, allowing the system to cool and determine the free acetic acid by titrating with 1 N sodium hydroxide using methyl orange as indicator.

2.2.3. Elemental analysis

Elemental analyses were determined on a Perkin-Elmer 240 C micro-analyzer and the results for the indicted elements were within ±0.3% of the calculated values.

2.2.4. Ultraviolet visible spectroscopy

Colorimetric methods for analyses of Fe modified mordenites (for determining the actual amount of encapsulated Fe inside the zeolit channels) and the polymer produced were adopted, based on the formation of colored complexes with thiocyante [12] with the former and determining the extent of the reaction for the latter based on calibration curves. The analyses were accomplished by means of a Perkin-Elmer Lambda 3 spectrophotometer.

^1H NMR spectra were measured on a Varian Gemini (300 MHz) instrument.

2.2.5. Gas-mass spectrometer

GC-MS analyses of the reaction products were performed on a Shimadzu GC-MS QP 1000 Ex instrument.

2.2.6. FTIR spectroscopy

FTIR spectra of the polymeric catalysts were recorded as KBr pellets on a Brucker IR spectrometer in the range $400–4000\ cm^{-1}$.

XRD analyses for Fe-zeolite samples were recorded on a Philips (PW 1390) diffractometer, using Cu Kα radiation.

The samples were measured in the 2θ range of 05–60° at 30 kV, 10 mA and a scanning rate of 2° in $2\theta\,\text{min}^{-1}$.

2.2.7. Mossbauer analysis for the nature of Fe incorporated in mordenite

Mossbauer spectra (MS) were recorded, using a constant acceleration spectrometer of 100Ci ^{57}Co radioactive source in a Cr matrix. Iron metal was used for the calibration. Mossbauer spectra were analyzed using a program based on the distribution of hyperfine magnetic field (HMF) and quadrupole splitting (QS).

2.2.8. Acidity of the modified zeolite samples

The Fe-mordenite samples were pressed into self-supporting wafers and mounted in an IR cell of CaF_2 windows and pretreated at 10^{-4} Torr/400 °C. The zeolite acidity was measured for the pretreated samples after exposition to NH_3 gas at 150 °C for 30 min followed by NH_3-desorption at 10^{-4} Torr/200 °C for 15 min. The spectra were measured using a 2 cm^{-1} resolution Jasco FTIR 5300 spectrometer.

2.2.9. Surface area and pore structure analysis

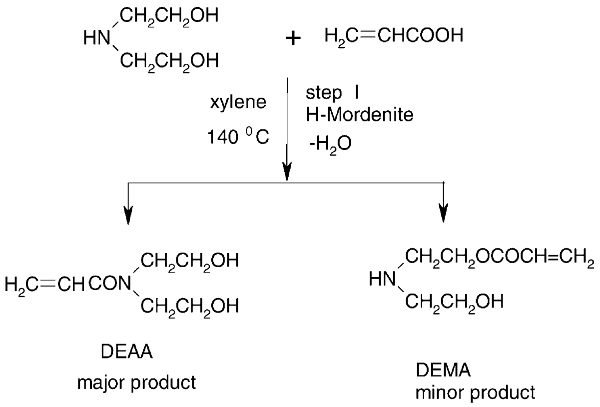
Different surface characteristics of the catalysts investigated were studied using nitrogen adsorption isotherms conducted at −196 °C. The BET surface area (S_{BET}), total pore volume (V_P) and mean pore radius (r_H) were computed. Each sample was degassed by heating at 300 °C under reduced pressure of 10^{-4} Torr for 3 h.

3. Results and discussion

3.1. Preparation of N,N-diethanol acrylamide as an intermediate for the polyesteramide

The polyesteramide resin is prepared by condensation polymerization between phthalic anhydride and the diol *N,N*-diethanol acrylamide in the presence of H-mordenite catalyst. The diol formation was performed by reacting diethanolamine (DEA) and acrylic acid in the presence of the latter catalyst in addition to Fe-mordenites using *o*-xylene as a solvent (bp 140 °C). The diol (DEAA) was the major product produced according to the expected strong interaction of the amine (DEA) with the carboxyl group of the acid [3–6]. This reaction was followed up by monitoring the amount of water liberated. Unexpectedly, another product was also detected, as traced by GC-MS, and it was diethanol amine mono-acrylate (DEMA) ester. The reaction proceeds to completion in forming DEAA and DEMA with selectivities 91 and 9%, respectively. It is noteworthy mentioning that the majority of the work used to prepare dihydric amino alcohol derivatives of fatty acids claimed the absence of the ester formation [1–6].

The IR spectrum (will be shown later) of the products indicates C=C stretching frequencies at 1628 cm^{-1}, νCO at 1732 cm^{-1}, νCH aliphatic at 2934 cm^{-1} and νOH at 3381 cm^{-1} [13]. Accordingly, the structure of DEAA [5,6] and DEMA can be formed as follows:



Further confirmation for DEAA formation was obtained from hydroxyl value measurements (705.6 mg KOH/g versus theoretical 700 mg KOH/g), Elemental analysis [(carbon; calc. 52.81; found 52.76, hydrogen; calc. 8.23; found 8.12 and nitrogen; calc. 8.79; found 8.86)] and UV-Vis spectroscopy that revealed intense absorption band at 222 nm ascribed to $\pi \rightarrow \pi^*$ in addition to two small bands at 240 and 330 nm ascribed to $n \rightarrow \pi^*$. On the other hand, the mass spectrometry confirmed the presence of DEAA and DEMA products through the appearance of two molecular ion peaks at $m/z = 159$ and 213, respectively. The presence of the molecular ion peak at 213 ($C_{10}H_{15}O_4N$) emphasized the suggestion that some of the diol product (DEAA) was just about to share in the ester formation through one OH groups of the diol. More details concerning this point will be elaborated later.

3.2. Effect of the catalyst

A set of experiments was conducted between acrylic acid (0.1 mol) and diethanolamine (DEA; 0.1 mol) in the presence of H-mordenite zeolite and TiO_2 (conventional) catalysts (0.1 g) in comparison with a blank experiment. The yield of the reaction was calculated on the basis of the theoretical amount of water (1.8 ml; 0.1 mol) that was collected with time after ensuring that DEAA and DEMA were the only products. The reactants and the catalyst were introduced into the reactor simultaneously without any activation for the catalysts in advance. The mordenite catalyst was found to be the most active one, whereas the yield in the absence of catalyst (blank) showed the lowest activity with a very long induction period (Fig. 1). As it can be seen, the latter self-catalyzed reaction takes 175 min to complete the reaction while the acid catalyzed one (H-mordenite) takes only 25 min.

In order to check the durability of the H-mordenite catalyst, after its use in the former run, it was recycled three times under the same experimental conditions, i.e. by adding fresh equimolar amounts of AA and DEA for each run. As can be seen in Fig. 2, the activity of the catalyst was

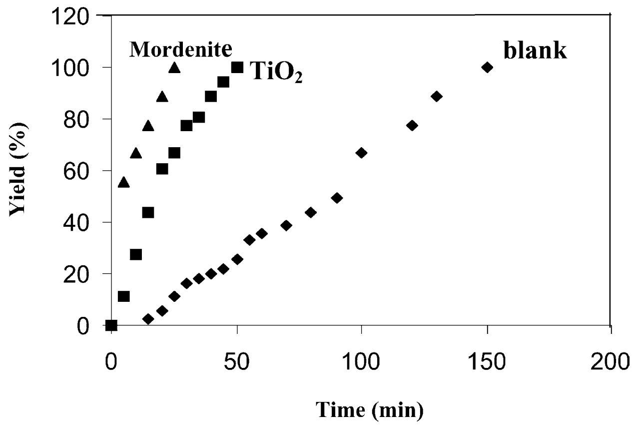


Fig. 1. Kinetic curves for the condensation reaction of diethanol amine and acrylic acid in the presence of mordenite and TiO_2 catalysts in comparison with the blank experiment. Initial AA concentration is 0.10 mol, DEA is 0.105 mol, catalyst amount 0.1 g, 30 ml total volume with *o*-xylene as a solvent; temperature 140 °C.

neither decreased nor influenced on going from the first cycle till the third one. Performing the same reaction on Fe modified mordenites with Fe contents varying from 10 into 25 wt.% showed that Fe containing mordenite at the 25 wt.% loading was the most active catalyst (Fig. 3). The kinetic curves of Fe-mordenite catalysts was accompanied by an increase in the reaction rate with increasing Fe contents together with a parallel decrease in the induction period, which was followed by a steady state rate acceleration and finally unchanging products yield was reached for all samples. Of particular importance, the kinetic curve of the 25 wt.% Fe-mordenite (Fig. 3) catalyst was similar to that of Fe free mordenite (Fig. 1) in the sense that the reaction takes 25 min for completion, apart from the noticed delay in the induction period devoted for the 25 wt.% Fe-mordenite sample comparatively.

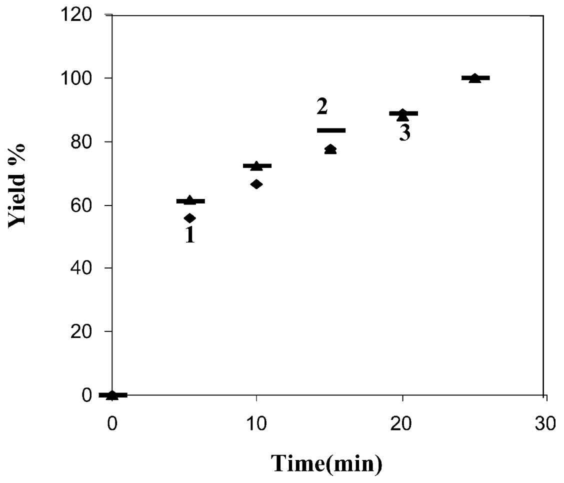


Fig. 2. Durability of the mordenite zeolite catalyst during DEAA and DEMA formations using 0.1 g amount of the catalyst for the three run cycles: (1) first run; (2) second run; (3) third run. The rest of the reaction conditions as in Fig. 1.

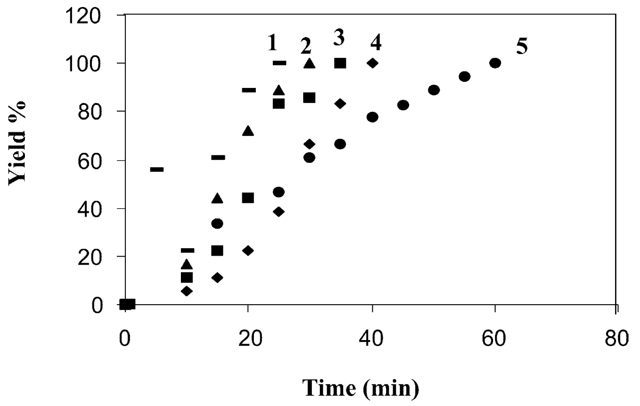


Fig. 3. Kinetic curves of DEAA and DEMA formation in the presence of Fe modified mordenites in comparison with α-Fe_2O_3: (1) 25% Fe mordenite; (2) 20% Fe mordenite; (3) 15% Fe mordenite; (4) 10% Fe mordenite; (5) α-Fe_2O_3. The rest of the reaction conditions as in Fig. 1.

Figuring out whether or not Fe takes part in the reaction, a fresh run was performed on a pure form of α-Fe_2O_3 catalyst (Fig. 3) that showed a slow rate comprises 60 min necessary for reaction completion. This may indicate that Fe is active when incorporated inside mordenite zeolite (heterogeneous phase) and its share in the reaction activation may come following that of mordenite. This was ascertained from the shorter induction period in the kinetic curve of the mordenite sample (Fig. 1) when compared with those of Fe-mordenite ones (Fig. 3).

More emphasis on the role of different Fe species can be evident from Mossbauer results that presented in Table 1. The Mossbauer parameters and percentages of different Fe components indicate the presence of two iron species, namely octahedral Fe^{3+} (Fe^{3+}oct) and tetrahedral Fe^{3+} (Fe^{3+} tet), at low loadings (10 and 15 wt.%) where at the loadings of 20 and 25 wt.% one more species of α-Fe_2O_3 was obtained.

As is revealed, the highest yield for Fe-mordenite catalysts was found over the 25 wt.% Fe-mordenite catalyst that contains major amounts of non-framework Fe species (86%). This result indicates the importance of extra-framework Fe as active sites for the reaction and probably the small sized α-Fe_2O_3 encapsulated inside mordenite channels. The well dispersion of the latter species was elaborated from XRD patterns of the samples (data not shown) that revealed the absence of any Fe species. These findings points to varying the morphology and thus the activity of α-Fe_2O_3 species, that prepared in the pure form and takes 60 min to complete the reaction, from that when it is encapsulated inside zeolites [14]. The presence of homogeneous Fe derived from α-Fe_2O_3 (in the pure form) substantiate the rapid deactivation and thus affected the activity. This could lead us to propose that the leached Fe (homogeneous Fe species) from Fe-mordenites does not contribute significantly to the catalytic activity. On the other hand, the encountered high activity devoted for H-mordenite than that found for Fe-mordenites could be due to the lower strength of acid

Table 1
Mossbauer parameters of Fe incorporated mordenite zeolites

Sample	Ferric octa				Ferric tetra				α-Fe_2O_3				
	IS (mm s^{-1})	QS (mm s^{-1})	LW (mm s^{-1})	Area (%)	IS (mm s^{-1})	QS (mm s^{-1})	LW (mm s^{-1})	Area (%)	IS (mm s^{-1})	QS (mm s^{-1})	LW (mm s^{-1})	H_{eff} (KOe)	Area (%)
10 wt.% Fe-mordenite	0.4	0.56	0.26	29	0.25	0.93	0.66	77					
15 wt.% Fe-mordenite	0.4	0.56	0.32	41	0.23	0.91	0.73	59					
20 wt.% Fe-mordenite	0.37	0.6	0.32	45	0.19	1.1	0.8	35	0.36	−0.23	0.31	516	20
25 wt.% Fe-mordenite	0.37	0.6	0.32	60	0.18	1.07	0.83	14	0.38	−0.20	0.51	516	26

IS, isomer shift; QS, electric quadrupole; *H*, mean hyperfine field.

sites of ferrisilicates than that in aluminosilicates, as proposed before by Parillo et al. [15] in similar reactions. Thus, it was indeed essential having an idea about the acidity of the used catalysts.

3.3. IR spectroscopic identification of the intermediate N,N-diethanol acrylamide and acidity of the mordenite zeolite

The important role of the intermediate DEAA in the PEA synthesis and the active sites involved on the catalyst surface are of interest to be evaluated. The IR spectra at increasing time intervals during the interaction of diethanolamine (DEA) with acrylic acid (1:1 molar ratio) on H-mordenite are presented in Fig. 4 in comparison with the spectrum of H-mordenite. The IR absorption spectra of Fe-mordenites taken at time intervals in the range of lattice vibrations (1300–450 cm^{-1}) only suffer a decrease in intensity when compared with the parent sample. Absorption bands at 1800–1300 cm^{-1} characterize bond vibrations of the products obtained on mordenite surface. This type of products shows absorption bands at 1735, 1627–1637 and 1366 cm^{-1}. The band at 1735 cm^{-1} can not be ascribed to νCON species [3–5] but rather due to νC=O of ester [16] where that of amide νC=O that used to appear in the region 1650–1610 cm^{-1} [17] presumably overlapped by the tail of the ester and the νC=C band (1627–1637 cm^{-1}). The broadness of the latter band (1627–1637 cm^{-1}) give emphasis to the previous assignment concerning the amide C=O band. On the other hand, the band at 1366 is ascribed to δC–H.

Interestingly, the νC=O at 1735 is intensified with time characterizing the surface bound esters. Increasing the latter band intensity with time indicates the preferable interaction of the acid carboxyl groups with OH ones of diethanol amine. Since we are working at stoichiometric ratios, a clue about involving some of the OH groups of the diol produced (*N*,*N*-diethanol acrylamide) in the formation of ester can be evident from the coming results. The measured hydroxyl value at the end of the reaction comprises about 1.6OH groups (not 2.0 any more). On the other hand, the presence of an acid catalyst initiates the removal of OH groups of DEAA as water, leaving behind an electrophile; $^+CH_2$, that can attack the polarized oxygen of the acid (AA) forming ester moieties. The 1735 cm^{-1} band cannot be due to the νC=O derived from carboxyl groups since the calculated

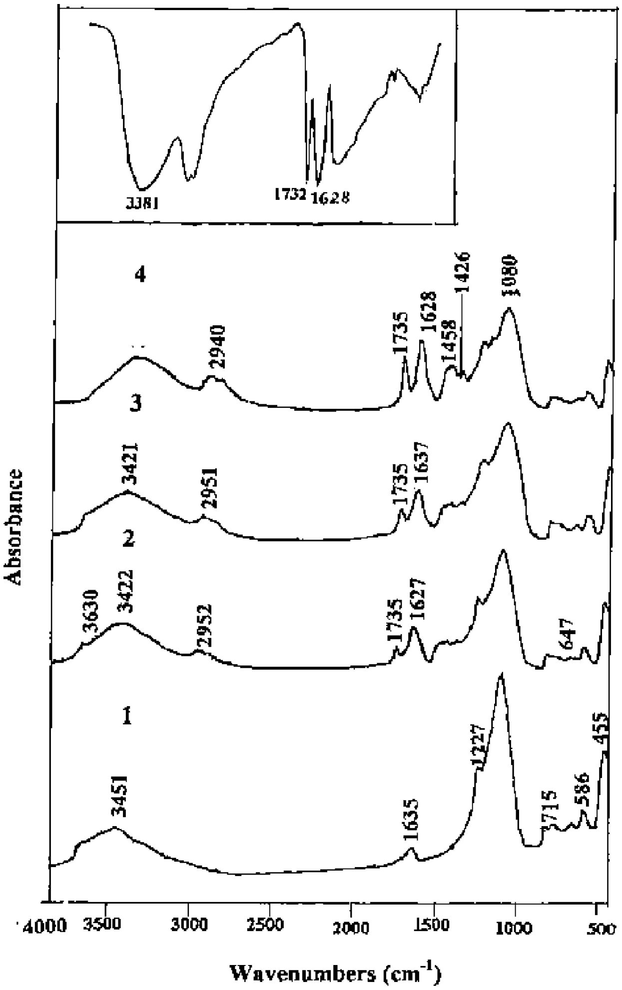


Fig. 4. FTIR spectra of H-mordenite sample prior to polymerization reaction (1) and after performing the reaction at time intervals 5 min (spectrum 2), 15 min (spectrum 3) and 25 min (spectrum 4). In the inset the outcome spectrum of the reaction product between DEA and AA.

acid value was zero at the end of the reaction. This points to vanishing the carboxyl groups through amidification and then esterification. This result further invalidates that the reaction can proceed through the addition of diethanol amine on the double bond of AA due to increased fractions of water produced during the reaction time.

Additionally, the gradual shift of the $\nu(\mathrm{OH}\cdots\mathrm{O})$ mode at 3451 $\mathrm{cm^{-1}}$ in wavenumbers (3388 $\mathrm{cm^{-1}}$, spectrum 4) with time indicates the greater affinity of the reactant specifically AA to proton affinity, i.e. very high HB perturbations. As can be seen, with increasing time, a monotonic decrease in the concentration of the acidic bridged and silanol OH groups was obtained and ultimately they almost disappear. The involvement of the former OH groups (acidic Bronsted [Si(OH)Al]) explains the importance of these strong acid sites in the reaction performance. The νCH aliphatic positioned at 2952 $\mathrm{cm^{-1}}$ showed a shift at the extent of the reaction (2940 $\mathrm{cm^{-1}}$). This means that the hydrogen bond perturbation may perhaps responsible for the downward shifts of 12 $\mathrm{cm^{-1}}$. Comparing the spectrum obtained at the extent of the reaction with that of the inset devoted for the product obtained without catalyst, they are indeed similar.

Regarding the reaction mechanism of DEAA and ester formation from AA and DEA, there has been several studies suggest that the acidity of the catalyst plays an important role [4,5,7]. Revealing the acid sites on the catalysts and their relation to the DEAA (DEMA) formation was achieved using NH_3 adsorption. This was essential because of the proton transfer process that must be correlated with the acidic characteristics of the zeolite surface and specifically the Bronsted sites that take part in proton acceptor–donor reactions.

Fig. 5 shows the IR spectra of NH_3 adsorbed on the H-mordenite catalyst and when loaded with different Fe contents. After the catalysts were exposed to NH_3, bands due to adsorbed NH_3 species appear at 1647 and 1405 (1445) $\mathrm{cm^{-1}}$. Similar bands have been reported previously [18], and they can be assigned to strongly bonded ammonia probably as asymmetric bending of coordinated NH_3 and asymmetric bending vibration of NH_4^+; $\delta_{as}(NH_4^+)$, respectively. The bands at 1647 and 1405 $\mathrm{cm^{-1}}$; which corresponds to $\delta_{as}(NH_3)$ and $\delta_{as}(NH_4^+)$, respectively, decrease in intensity with increasing the Fe contents. This indicates that the number of either Bronsted or Lewis sites decrease with increasing amounts of Fe on mordenite zeolite. It can also be seen that the decrease of the ammonium ions on Bronsted acid sites (1405 $\mathrm{cm^{-1}}$) was faster than that of coordinated ammonia attached to Lewis ones (1647–1637 $\mathrm{cm^{-1}}$). However, the decrease in the former was paralleled to an increase of the one at 1445 $\mathrm{cm^{-1}}$ that ascribed to another Bronsted acid sites probably correlated with Fe (OH) Si moieties of more covalent character than that of Al (OH) Si ones. The fairly high stability of the Lewis acid sites may be correlated to the confirmed Lewis acidity devoted for α-Fe_2O_3 species [19]. The synergistic effect of Bronsted acid sites either devoted from 1405 to 1445 $\mathrm{cm^{-1}}$ bands are very important in assisting the activation of AA to form DEAA and DEMA via DEA.

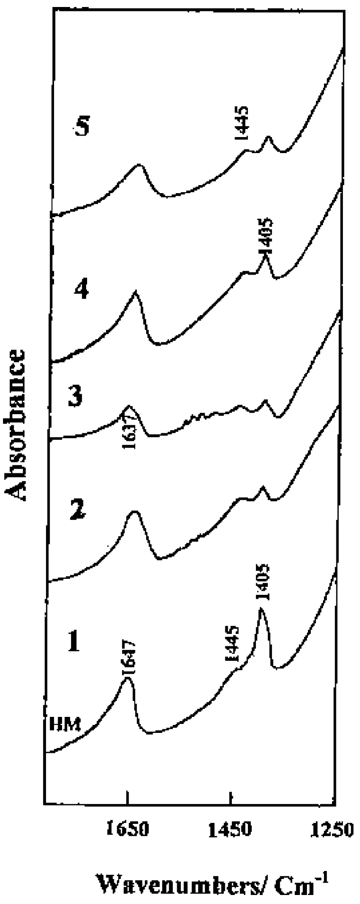
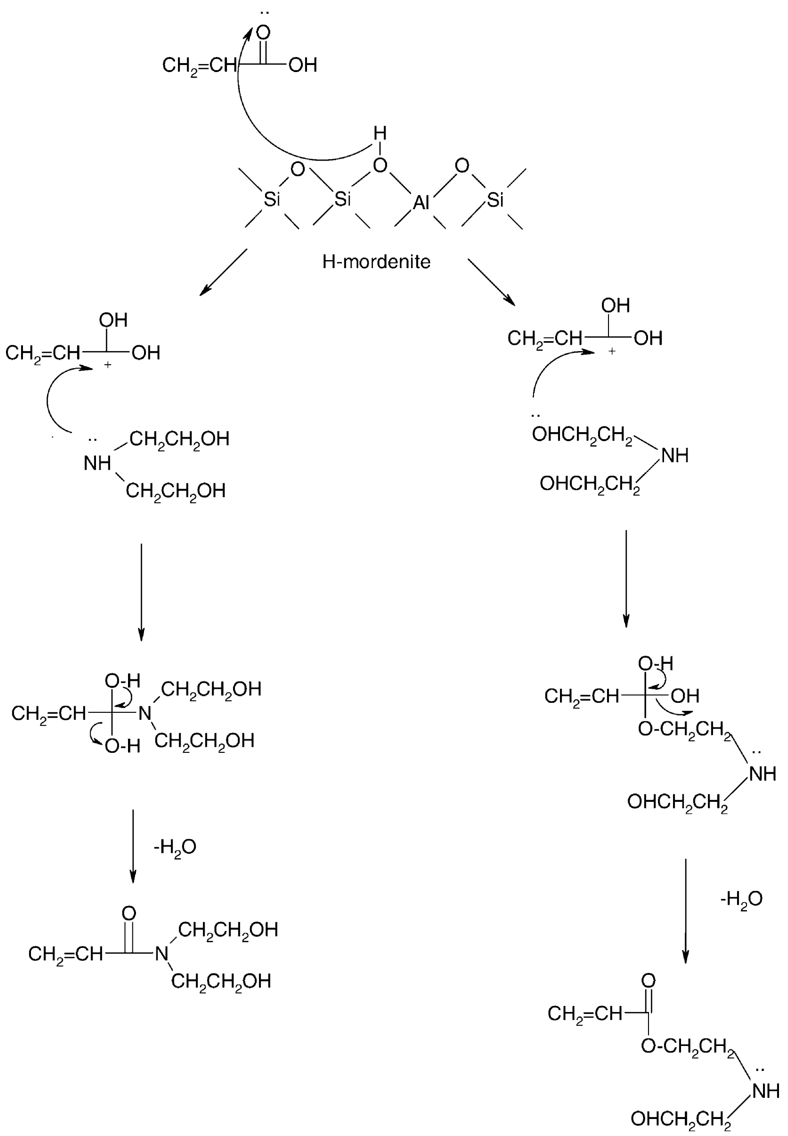


Fig. 5. FTIR spectra of NH_3 adsorption on Fe-mordenites with different Fe contents in comparison with H-mordenite after exposure to NH_3 at 150 °C: (1) H-mordenit; (2) 10 wt.% Fe-mordenite; (3) 15 wt.% Fe-mordenite; (4) 20 wt.% Fe-mordenite; (5) 25 wt.% Fe-mordenite.

Thus, the encountered delay in activity of the 25 wt.% Fe-mordenite sample when compared with H-mordenite can be due to increasing the acid strength of Al-mordenite over that of Fe-mordenites [20]. This indeed will facilitates the deprotonation process for the former than that for the latter.

Accordingly, based on the above results the suggested mechanism of the synthesis of DEAA and DEMA from AA and DEA using either mordenite or Fe modified mordenite catalysts is as follows:

The formation of 100% amide in the absence of any catalyst and in presence of some oxide catalysts such as Fe_2O_3 and TiO_2; as has been evidenced by some authors [1–6], provokes the importance of the unshared electron pair on the amine nitrogen; which can be shared with electron deficient carbonyl group. Such unshared pair on nitrogen is less tightly held than that on the corresponding oxygen atom of alcohol based on electronegativity consideration. The only difference between the non-catalyzed and oxide catalyzed reaction could be related to promoting the electron deficiency (carbocation) of latter ones. Thus, the application of oxides



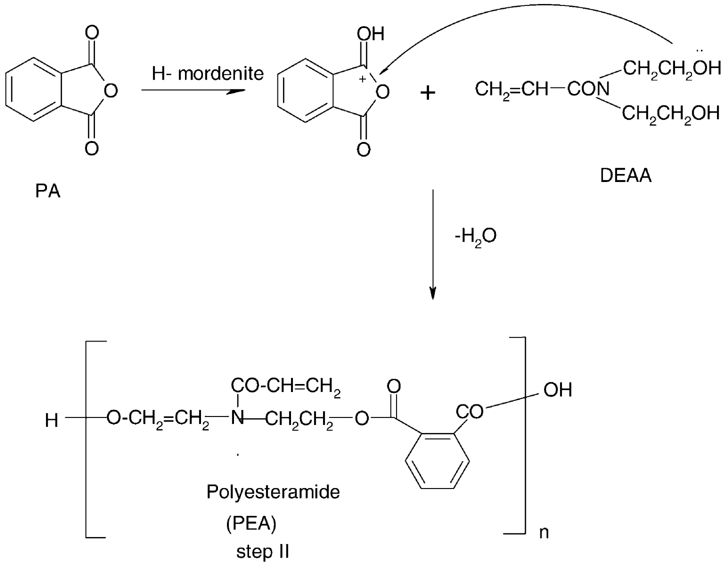
in such reactions are expected to depend on surface properties and chemical compositions of the surface (deficient sites and polarity). On the contrary, increasing the acidity of mordenite zeolite, when compared with those of oxides, specifically Bronsted sites will give chances to the lone pair of nitrogen; in amine, to be attacked by hydrogen and thus decreasing the probability of amide formation in favor of forming appreciable amounts of ester, which requires strong acid sites.

3.4. Catalytic polymerization of DEAA using phthalic anhydride

After the successful preparation of *N*,*N*-diethanol acrylamide (with selectivity of 91%) under the above-mentioned experimental conditions, attention was directed towards its incorporation with dibasic acid such as phthalic anhydride to produce polyesteramide resin in the presence of H-mordenite catalyst. This was done for the purpose of producing polyesteramide resin of highly modified properties than those used to be prepared using fatty acid/anhydride system [21]. This can be achieved by reacting the product mainly the polyol (DEAA) with phthalic anhydride using stoichiometric amounts as follows (step II):

The course of the polyesterification reaction was followed by monitoring the amount of water liberated. Fig. 6 shows that the reaction proceeds to completion 100% towards the formation of (PEA) in only 30 min. The formation of PEA was confirmed by means of IR and ^{1}H NMR spectroscopies similar to what has been elucidated before by Kemp [22]. It is of interest to notice that this reaction was very slow in the absence of a catalyst yielding 41.5% at 200 min reaction time.

To find out whether or not the ratio of Si/Al of H-mordenite can affect on the polymerization of DEAA with PA to give PEA, a similar experiment was conducted using another H-mordenite (HM1) of varying SiO_2/Al_2O_3 ratio (203). Direct comparison (Fig. 6) indicates that the higher



activity was obtained for the sample of higher Si/Al ratio. This indicates that the hydrophobicity of the zeolite play a role probably in the non selective adsorption step at the very beginning of the reaction towards the reactants specifically AA. In addition, the higher yield of PEA is obtained regardless of the expected lower acidity of HM1 [23]. This is because increasing the Si/Al ratio will in turn causes a decrease in the number of Bronsted acid sites but, on the other hand, will increase the acid strength of the remaining [24]. In addition, this could give a clue about the importance of hydrophobicity-hydrophilicity of the zeolite when dealing with reactants of different polarities as in our case. Besides, the HM1 sample presented an increase in S_{BET} higher than HM by about 43% (Table 2). On the other hand, the total pore volume suffers a slight decrease, thus the observed net increase in the S_{BET} for HM1 could be due to the effective pore narrowing. As a result, one can conclude that the adsorption property of the catalyst is of prime importance (high S_{BET}) and specifically the hydrophobicity/hydrophilicity ratio followed by the global acidity of the catalyst.

From what has been presented, it appears that there is a considerable blocking of the micropore as devoted from loss of the micropore volume. In addition, one has to bear in mind that blocking the internal pores with non-framework species could impose diffusional limitations of organic substrate in the mono-dimensional channel in mordenite and thus restricting the reaction to sites present at the external particle surface and rather substantiate the role of acidity as mentioned earlier. On the other hand, rising the Si/Al ratio (HM1) will increase the number of adsorbed molecules due to the strength of the electrostatic field located in the pores of the zeolite [25].

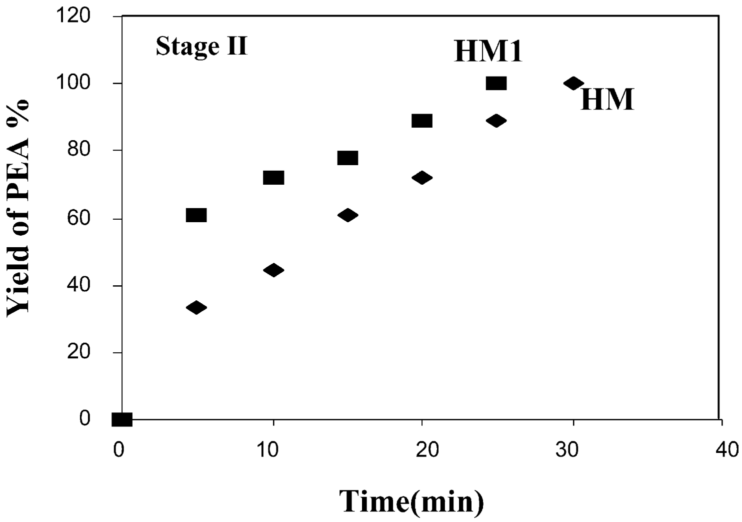


Fig. 6. Kinetic curves of the polyesterification of *N*,*N*-diethanol acrylamide by phthalic anhydride to produce polyesteramide in the presence of mordenite catalysts of varying Si/Al ratios. The reaction conditions as in Fig. 1.

Table 2
Surface characteristics of H-mordenite and Fe-mordenite zeolite samples

Sample	Si/Al[a]	S_{BET} ($m^2 g^{-1}$)	V_p ($ml g^{-1}$)	r_H (Å)	C constant
H-mordenite (HM)	10.8	380 (371)	0.699	57.9	134
10 wt.% Fe-mordenite		422 (412)	0.53	30.8	120
15 wt.% Fe-mordenite		438 (440)	0.50	29.4	115
20 wt.% Fe-mordenite		450 (450)	0.47	27.6	105
25 wt.% Fe-mordenite		464 (466)	0.43	25.6	99
H-mordenite (HM1)	203	543 (516)	0.557	21	165

V_p is the total pore volume, r_H the value of the average pore radius, S_{BET} the BET surface area.

[a] Molar ratio: values between brackets (S_t) are surface area values derived from $V_l - t$ plots.

Table 3
Film performance of various prepared polyesteramides

Type of resin	Gloss at 60° (%)	Cross-cut adhesion	Rocker hardness (s) at 30 μm	Flexibility mandrel	Chemical resistance				
					Water	5% Na_2CO_3	5% H_2SO_4	5% NaCl	O solvent
SC-PEA	72	GT1	85	Pass	Excellent	Good	Excellent	Excellent	Excellent
HM-PEA	66	GT0	120	Pass	Good	Good	Excellent	Good	Excellent
UM-PEA	82	GT2	94	Pass	Excellent	Fair	Good	Good	Excellent

SC-PEA, HM-PEA and UM-PEA represent self-catalysed, H-mordenite catalyzed and unmodified polyesteramide resin, respectively; and GT0 > GT1 > GT2; gloss was measured according to ASTM, D-523-93 a (Rapproved, 2001); adhesion was measured according to ASTM, D-3359 (1995); hardness was measured according to DIN-53157; flexibility was measured according to ASTM, D-522 (1993); chemical resistance was measured according to ASTM, D-1308-87 (Rapproved, 1993).

The Arrhenius equation was found to be obeyed since straight lines were obtained for both catalyzed and non-catalyzed reactions (Fig. 7). The calculated activation energy for catalyzed reaction was markedly lower (11.46 kJ mol^{-1}) than that of uncatalyzed one (30.5 kJ mol^{-1}) in the studied temperature range 165–120 °C when using mesitylene (bp 165 °C) as a solvent. This suggests that the reaction is more facile when mordenite zeolite is used as a catalyst but rather reveals that the reaction is catalyzed and not only acid promoted.

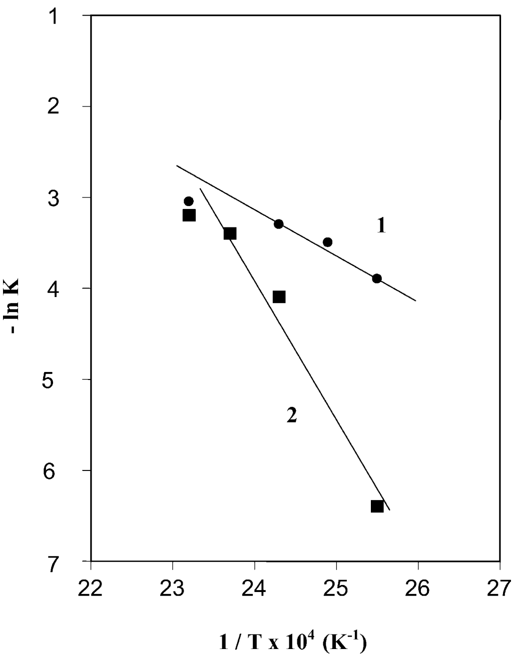


Fig. 7. Arrhenius plots of ln K vs. $1/T$ for uncatalyzed (2) and H-mordenite (1) catalyzed reaction for DEAA (and DEMA) formation.

The presence of about 10% ester may change the properties of the produced polymer so that modified polyesteramides, either the self-catalysed [SC-PEA] or H-mordenite catalyzed [HM-PEA]), were compared with that unmodified polyesteramide (UM-PEA), prepared by linseed oil fatty acid (Table 3). The prepared resins were diluted with xylene to 50% solid, filtered and followed by the addition of driers combination (0.04% cobalt and 0.02% manganese as octoate) to get the varnish. The resulting varnishes were applied on glass and tin panels and backed at 110 °C for 1 h. The films formed were evaluated as surface coating according to standard techniques (Table 3). The preliminary evaluation indicates the high hydrophlicity and hardness of the produced polymer obtained upon using H-mordenite as a catalyst when compared with those obtained by conventional methods (SC-PEA and UM-PEA). In conclusion the former resin can be used as a vehicle for surface coatings.

4. Conclusion

It was shown that H-mordenite zeolite promotes the polymerization of *N*,*N*-diethanol acrylamide and phthalic anhydride producing polyesteramide resin. The catalytic activity of H-mordenite does not change on multiple recycling in the formation of polyesteramide resin. Comparison of H-mordenite samples of varying Si/Al ratios indicate the important role of moderate number of Bronsted acid sites in the polymerization process as well as the zeolite hydrophobicity. Spectroscopic evidence of a proton transfer via hydrogen bonding formation gives a clue about the reaction mechanism. It was also concluded that Fe modification resulted in the total elimination of strong Bronsted acidity accompanied by the formation of new Bronsted type sites with reduced acid strength. On the basis of the results devoted for the HM1 sample, an evidence for the importance of the acid strength was revealed. Promoting the ester formation and rather keeping the selectivity in favor of amide formation was mainly due to the high acidity provoked by the mordenite zeolite.

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