

Silica–Alumina Catalysts for Polymerization of Cyclic Siloxanes

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ABSTRACT: Silica–alumina catalysts of varying acidity were used for polymerization of hexamethyl cyclotrisiloxane and octamethyl cyclotetrasiloxane monomers (cyclic trimer and tetramer, respectively). Acidic sites of silica–alumina are responsible for the polymerization and variation in the acidity of the catalyst were shown to influence the polymerization significantly. Mordenite type zeolites with low silica-to-alumina ratio (~ 5) gave low yields of polymer from tetramer and zeolite ZSM-5 with a much higher silica-to-alumina ratio (~ 40) was found to be a very efficient catalyst for polymerization. Studies on the effect of water on the polymerization suggested that the polymerization (rate and yield) depended to some extent on the amount of water present in the system. The products were characterized using FTIR, $^1\text{H-NMR}$, $^{29}\text{Si-NMR}$, and GPC techniques. A plausible mechanism for polymerization of cyclic siloxane monomers on silica–alumina catalysts was proposed. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 629–635, 1998

Key words: cationic polymerization; cyclic siloxane; trimer; tetramer; silica–alumina catalyst

INTRODUCTION

Polymerization of cyclic siloxane monomers is generally carried out using acidic and basic catalysts.¹ Catalysts that have been reported to initiate cationic polymerization of siloxane include protonic acids like H_2SO_4 , HClO_4 , a variety of lewis acids, and trifluoro methane sulfonic acid.¹ Cationic as well as anionic catalysts, in general, are soluble in the reaction medium and therefore pose problems of separation from the product and lead to issues related to effluent treatment. A recent trend in chemical reactions is in arriving at processes which are environmentally friendly and devoid of effluent treatment problems. Substitution of soluble catalysts with insoluble and there-

fore easily separable catalysts is a possible option in the case of polymerization of cyclic siloxanes. Aluminosilicates, natural or synthetic, could serve as environmentally friendly catalysts used for polymerization/oligomerization of alkenes.^{2–6}

Pike patented a method of polycondensation of silanol oligomer to give high molecular weight organosilicon polymer using zeolite.⁷ In the case of ring opening polymerization of cyclic siloxanes there are some reports of using clays like kaolinite, montmorillonite, and zeolite as catalysts.^{8,9} The acid sites in these aluminosilicates are known to be responsible for the polymerization. However, the effect of varying acidity of the catalysts have not been studied so far. In addition, the polymer product had not been thoroughly characterized except by viscosity measurements.

Our efforts were directed in arriving at silica–alumina catalysts for polymerization of cyclic siloxanes. The acidic sites of silica–alumina which are responsible for the polymerization were varied

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and were shown to influence the polymerization significantly. In addition, the effect of addition of water on the polymerization rate and molecular weight of the product was also studied in detail. Our mechanistic investigation suggested that when cyclic siloxanes were treated with silica–alumina (amorphous and crystalline) catalysts, the cyclic monomer is first converted into a silanol-terminated monomer/oligomer which in turn polycondensed to form a polymer. A plausible mechanism for polymerization of cyclic siloxane using silica–alumina catalyst was proposed.

EXPERIMENTAL

Materials

(1) Materials used were octamethyl cyclotetrasiloxane (D₄), purity = 97.85%, Ex. Reliance silicone, Bombay, India; (2) hexamethyl cyclotrisiloxane (D₃), purity = 90%, Ex. Aldrich chemicals; (3) zeolan-100 Na, Ex. Union Carbide U.S.A.; (4) ZSM-5 S/A = 40, Ex. United Catalyst of India, Baroda; (5) neutral sodium silicate 40% solution (commercial gr.); and (6) aluminum sulfate, purity = 98%, L.R. grade.

Methods

Catalyst Preparation

Silica–Alumina Catalyst. Sodium silicate solution (40%, 325 mL) was taken in a 3 L beaker and diluted with 500 mL water. The pH of the solution was adjusted to 1 by dropwise addition of 1 : 1 HNO₃ under vigorous stirring. The solution was heated to 90°C and to this a hot solution of aluminum sulfate in 25 mL water was added. The

mixture was stirred for 60 min and the solution was allowed to stand for 16 h. The pH of the solution was adjusted to a value between 5 and 6 by dropwise addition of ammonia solution. The gel formed was filtered and washed with water until the filtrate became free of sulfate ions. The catalyst gel was extruded and heated at 100°C for 12 h. The sample was then subjected to sintering at 750°C for 6 h.

H-Exchanged Silica–Alumina Catalyst. The catalyst prepared by the above procedure will have the Na⁺ ions, which have to be exchanged with H⁺ to improve the acidity. Calcined silica–alumina (100 g) catalyst in sodium form was taken in a 1 L beaker and 10 mL of 1 : 1 HCl was added. The resultant solution was heated to 80°C and 300 mL of ammonium acetate solution (1M) was added. The mixture was stirred for 6 h at 80°C and the pH was adjusted to 3 using 1 : 1 ammonia solution. The product was then filtered and the procedure was repeated three times. The catalyst was finally dried at 120°C and sintered at 450°C for 5 h.

Pretreatment of Zeolite Catalyst. SA-V (ZSM-5) (100 g) and 250 mL distilled water were taken in a 2 L beaker and the contents were stirred vigorously. The pH of the solution was adjusted to 1 by 1 : 1 HCl and the solution was heated to 90°C. To the hot solution, ammonium acetate (250 mL; 1M solution) was added. The mixture was then stirred for 5 h and then allowed to stand for 15–16 h. The pH of the solution was adjusted to 3 by addition of ammonia solution. The resultant catalyst was recovered by filtration and the filter cake was reslurried in water. This procedure was repeated twice. The filtered cake was finally washed with distilled water until it was free from chloride ions. The resultant catalyst was dried at

Table I Characteristics/Synthetic Conditions for the Various Catalysts Used to Study Polymerization of Cyclic Siloxane

Catalyst	Na-Silicate	Amt. of Al Sulfate	S/A Ratio	H-exchanged	Nature ^a
SA-I (Na form)	130 g	50 g	5.22	No	Amorphous
SA-II (H-form)	130 g	50 g	5.22	Yes	Amorphous
SA-III (H-form)	130 g	5 g	52	Yes	Amorphous
SA-IV	Zeolan-100 Na (Mordenite type, commercial sample)		5	Yes	Crystalline
SA-V	ZSM-5 (commercial sample)		50	Yes	Crystalline

^a Catalysts were characterized by XRD. S/A = SiO₂/Al₂O₃.

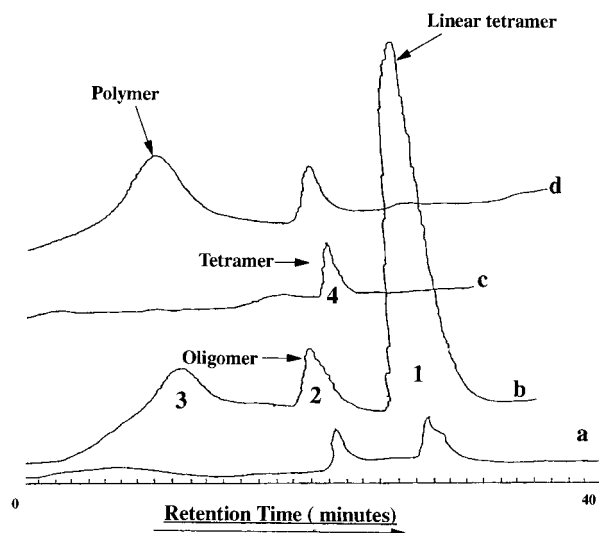


Figure 1 GPC of products from the polymerization of cyclic tetramer catalyzed by (a) SA-II [i.e., H-exchange silica-alumina (S/A = 5.2)]; (b) SA-IV [i.e., H-exchanged Zeolan-100 Na (Mordenite Type S/A ~ 5)]; (c) SA-I [i.e., silica-alumina in Na⁺ form (S/A = 5.2)]; and (d) SA-V [i.e., H-ZSM-5 (S/A ~ 40)].

110°C for 12 h and the sample was sintered at 500°C for 6 h. The synthetic conditions for the various catalysts used for the polymerization reaction are shown in Table I.

Polymerization of Cyclic Siloxane. In a 50 mL dry R.B. flask 10 g octamethyl cyclo tetrasiloxane and 1 g catalyst in powder form were taken and the reaction mixture was refluxed at 175°C for 7 h. The reaction mixture was then cooled to room temperature and diluted with toluene. The catalyst was recovered by filtration. The polymer was recovered after removing the solvent by vacuum

distillation and was characterized by GPC. The above reaction was repeated in the presence of varying amounts of water.

Determination of Acidity of Catalyst

The acidity of the catalysts used was determined by ammonia sorption technique. Fifteen mg of the catalyst sample was placed in a sample pan and was heated up to 500°C to remove moisture. Ammonia was continuously injected into the carrier gas stream and then equivalents of ammonia adsorbed on the catalyst were quantified.

Characterization

NMR spectra were recorded using a Bruker ACP 200 spectrometer in CDCl₃. IR spectra were recorded using a Bomem Hartmann and Braun FTIR spectrometer. GPC analyses were carried out using a Shimadzu GPC instrument with Ultrastayragel column (Waters) combination of linear, 10⁴ Å, and 500 Å with toluene was used as the mobile phase.

RESULTS AND DISCUSSION

Ring Opening Polymerization Using Silica-Alumina Catalysts of Varying Acidity

Polymerization of the cyclic tetramer on various silica-alumina catalysts (details of the catalysts are given in Table I) were carried out at 175°C and the progress of the reactions were monitored using GPC. The chromatograms of the reaction products after 3 h of reaction with each catalyst system are given in Figure 1. In general, peaks

Table II Effects of Catalysts of Varying Acidity on Polymerization of Trimer and Tetramer

Catalyst	S/A Ratio	Acidity ^a (mmol/g)	% Yield of Polymer from Tetramer	% Linear Monomer from Tetramer	% Yield of Polymer from Trimer
SA-I	5.2	0	0	0	0
SA-II	5.2	47.5	0	58.6	0
SA-III	52	73.33	0	69	80
SA-IV	5	272	16	74.39	84
SA-V	40	906.6	81	0	90.6

S/A I, II, III = amorphous silica-alumina catalysts. SA-IV = Zeolan-100 Na (H form), SA-V = ZSM-5.

^a Acidity expressed in terms of ammonia gas adsorbed in mmol/g of catalyst.

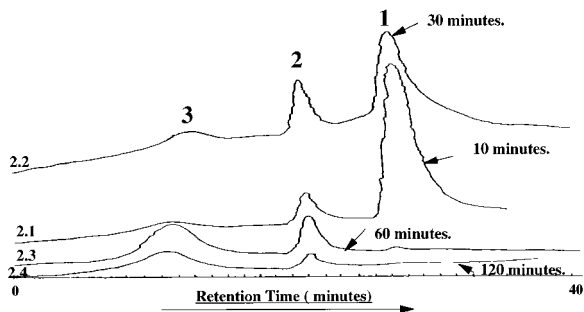


Figure 2 Polymerization of tetramer using SA-V. GPCs after 10, 30, 60, and 120 min of reaction. (Curves 2.1–2.4, respectively.)

appear in the regions indicated as 1–4. Of these, the peak indicated as 4 matches the retention time for the starting cyclic tetramer. Peak 3 corresponds to the polymer with molecular weight 20,000 to 30,000. Peak 1 observed in the case of figures (b) and (a) suggests the presence of a species lower in molecular size as compared to the cyclic tetramer, whereas peak 2 in the case of (b), (d) suggests the presence of linear oligomer. The results given in Figure 1 (curve c, a) indicate that the amorphous silica–alumina catalyst without sodium exchange (SA-I) and its H-exchanged form (SA-II) did not have any catalytic activity for the polymerization. In the latter case, however, part of the tetramer was converted into a product having a lower retention volume (peak 1). This was considered to be the linear tetramer (characterized by $^1\text{H-NMR}$). In the case of zeolite (SA-IV i.e., Zeolan-100 Na in H-form) catalyst, there was significant conversion of tetramer into the linear product (peak 1), oligomer (peak 2), and to some extent into a polymer (peak 3, $M_w = 25,000$, curve b). The most efficient polymerization catalyst was found to be SA-V (Zeolite ZSM-5, curve d). The molecular weight of the polymer was in the same range as that obtained from SA-IV. The results along with the compositions and acidity of the catalyst in each case are given in Table II.

The data shown above suggested a trend where the ability of the catalysts to polymerize cyclic siloxanes increased with increasing acidity. It is interesting to note that in the case of SA-II the cyclic tetramer is converted into the linear molecule and this conversion is more significant in the case of SA-III, which has a higher acidity (high silica-to-alumina ratio, Table II). $^1\text{H-NMR}$ of the product after reaction showed the presence of the

Si-OH group at 1.5δ . Thus it appears that in such cases the conversion of cyclic tetramer into the linear molecule takes place and subsequently the linear molecule undergoes condensation, leading to the polymer. Polymerization of cyclic trimer was also carried out using the same catalyst and the results are given in Table II. Compared to the tetramer, polymerization of cyclic trimer could be catalyzed to give high yields using catalysts with lower acidity values. The easier polymerization of trimer is explained to be due to the more strained nature of the ring.

Kinetics of Polymerization

The kinetics of ring opening polymerization of tetramer and trimer catalyzed by the most efficient catalyst (SA-V) was studied using GPC. The GPCs of the reaction mixture (tetramer) at various intervals of time are given in Figure 2. As we mentioned earlier during the initial stages (10 min) the tetramer gets converted into a species having a lower retention time (peak 1) and no polymer was formed. Subsequently, polymerization takes place and the intensity of this peak 1 decreases, whereas peak 2 is due to oligomer. This was indicated to be due to the conversion of cyclic tetramer into the linear molecule and subsequent condensation of the linear molecule into the polymer (peak 3).

The extent of polymerization is indicated in Figure 3. The rate of polymerization is extremely low up to 20 min of the reaction. It is likely that the active acidic sites on the catalyst are in contact with the cyclic monomer initially (when the concentration of the cyclic monomer is very high) and convert them into the linear molecule. On the depletion of the cyclic monomer in the reaction mixture, the catalyst is then effective in condensa-

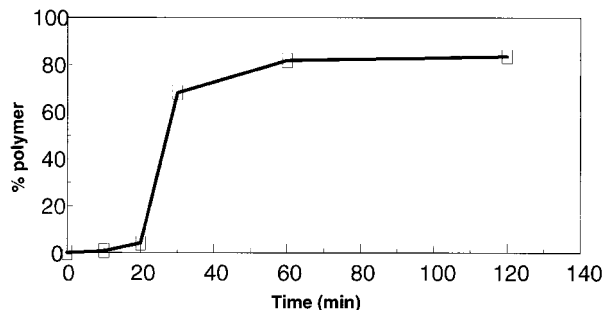


Figure 3 Polymerization of tetramer using SA-V. Plot of polymer yield versus time.

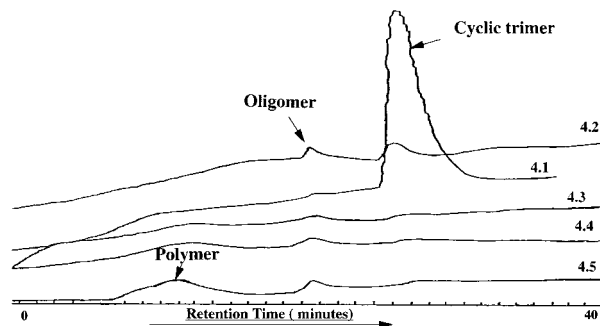


Figure 4 Polymerization of trimer using SA-V GPCs after 0, 10, 20, 30, and 60 min of reaction. (Curves 4.1–4.5, respectively.)

tion of the linear molecules into the polymer. The total conversion of the cyclic monomer into polymer by SA-V was found to be 80 to 90%. The GPCs for polymerization of cyclic trimer on SA-V catalyst is given in Figure 4. The extent of conversion of cyclic trimer to polymer and oligomer is given in Figure 5. The difference here is that the trimer gets converted into oligomers (as compared to the linear tetramer in the case of cyclic tetramer) and subsequently to the polymer.

The ^{29}Si spectra of the cyclic trimer and the oligomer are given in Figure 6. The linear structure of the oligomer is confirmed by FTIR, ^1H -NMR and ^{29}Si -NMR. The presence of peaks due to $-\text{OH}$ groups (3700 cm^{-1}) and the splitting of the peak due to $\text{Si}-\text{O}-\text{Si}$ linkages ($\sim 1050\text{ cm}^{-1}$) in FTIR spectra and ^1H -NMR peak at 1.5δ (due to $\text{Si}-\text{OH}$) suggested ring opening to form a linear oligomer. ^{29}Si -NMR of oligomeric siloxane shows $-\text{Si}-\text{O}-\text{Si}$ and $\text{Si}-\text{OH}$ at -21δ and -19δ ppm. The oligomer concentration is high during the initial stages, and finally all the oligomer was converted into the polymer. The trend of ring opening and subsequent condensation of the linear $-\text{OH}$ terminated oligomers is the same for the cyclic tetramer as well as trimer.

Effect of Water on the Polymerization of Cyclic Siloxanes

Wilczek, Rubinsztajn, and Chojnowski¹⁰ have reported an initial increase in the rate of reaction with increase in the water concentration. With very high levels of water, the rate decreased. We have now studied the effect of water on molecular weight of polymer and polymer yield in the case of ZSM-5 (SA-V) catalyst. The acidity of silica-

alumina catalysts is known to be influenced by the amount of water present. The results are shown in Figure 7. There was an initial increase in the extent of polymerization (molecular weight as well as weight of polymer), followed by a regular decrease with increasing addition of water.

These results can be explained based on the change in the acidity of zeolite catalyst due to incorporation of water. Binding of water on the zeolite¹¹ surface is explained in Figure 8. Water can interact with the $\text{Si}-\text{OH}-\text{Al}$ group and bind as H_3O^+ [Fig. 8(A)] thereby increasing the acidity, hence polymer yield increases. However, higher amounts of water would lead to solvation of H_3O^+ [Fig. 8(B)], or bind as unprotonated water [Fig. 8(C and D) are rarely observed] and decrease availability of acid sites. In addition, permanent loss of acidity¹² of zeolites due to collapse of the zeolite framework on interaction with high amounts of water will also lead to reduced catalytic activity.

A systematic reduction in acidity is thus observed and this explains the decreasing extent of polymerization with further increase in water content. The molecular weight of the polymer formed also follows a similar trend (see Fig. 7).

Mechanism

A polymerization mechanism in the case of montmorillonite was proposed by M. T. Bryk (ref. 9) based on ring opening followed by polycondensation of silanol catalyzed by acidic sites located on the external surface of the catalyst. Our results also revealed formation of oligomer/linear monomer in the silica-alumina catalyzed polymerization of cyclic trimer or tetramer prior to the formation of the polymer. In the case of cyclic tetramer

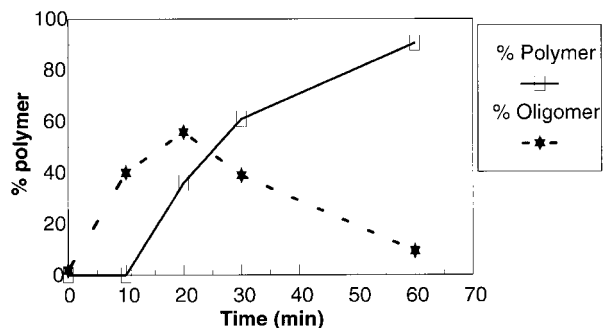


Figure 5 Polymerization of trimer using SA-V. Plot of polymer yield versus time.

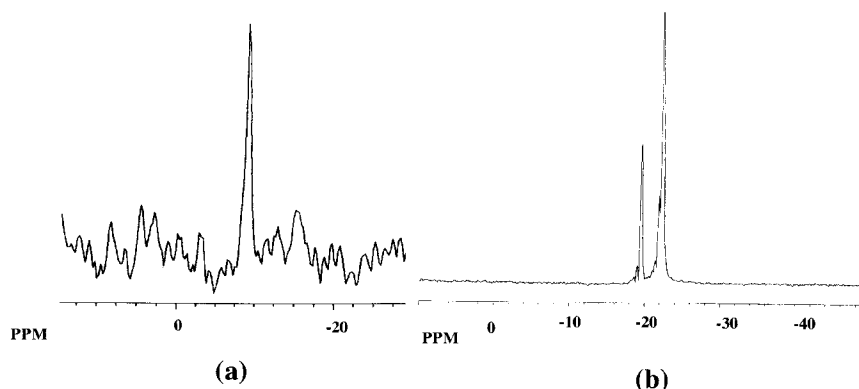


Figure 6 ^{29}Si -NMR of (a) cyclic trimer, (b) oligomer after reaction.

(Fig. 2) linear tetramer (rather than oligomer) was preferentially formed which then polycondensed into polymer. Cyclic trimer, however, was converted into oligomer first and subsequently to polymer. The formation of oligomer (as compared to linear monomer for D_4), could be due to the strained nature of the molecule due to which siloxonium ions attack another trimer before being hydrolyzed into silanol. These results are schematically represented in Figure 9.

The active sites for ring opening and polycondensation are produced by silica-alumina catalyst and correlation between total acidity of the various silica-alumina catalysts on the polymerization of cyclic trimer and tetramer was indicated earlier. The acidity of silica-alumina systems arises out of the polarizability of the Si—O—Al linkage leading to deprotonation of water molecules and generation of protons associated with the oxygen of the Si—O—Al linkage. In the case of zeolites the polarizability of the Si—O—Al

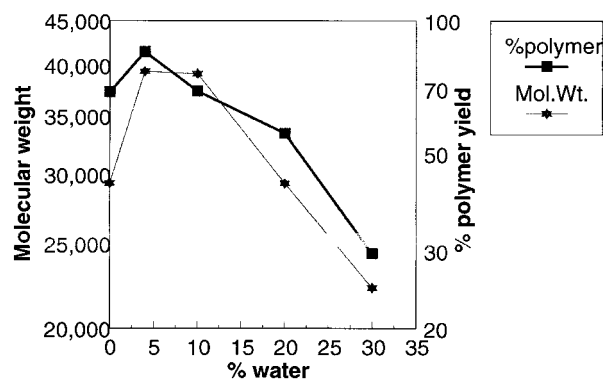


Figure 7 Effect of water on polymerization of tetramer. Plot of polymer yield and molecular weight versus water concentration.

linkages are more pronounced due to the higher Si—O—Al bond angle as compared to amorphous silica-alumina, and therefore zeolites show a higher acidity as compared to their amorphous counterparts having identical composition. This explained the high activity of ZSM-5 for polymerization of cyclic siloxane. Amorphous silica-alumina usually contains a few sites where tetrahedral coordinate silica and alumina tetrahedra share an oxygen bridge. These Bronsted acidic sites are considered to be zeolitic. Therefore acidity of amorphous silica-alumina is low.¹³

CONCLUSIONS

Cyclic siloxanes can be polymerized using silica-alumina catalysts having varying silica-alumina ratios. Variation in silica-to-alumina ratios affects the acidity of the silica-alumina systems and this was shown to have a profound effect on their catalytic activity to polymerize. Crystalline zeolites are more acidic than amorphous silica-alumina and thereby give higher polymer yield. Mordenite type zeolites with low silica-to-alumina ratio (~ 5) gave low yields of polymer from tetramer and zeo-

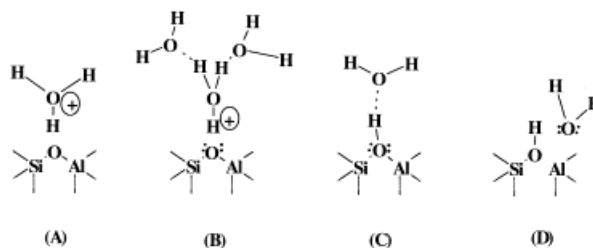


Figure 8 Binding of water on zeolite surface.

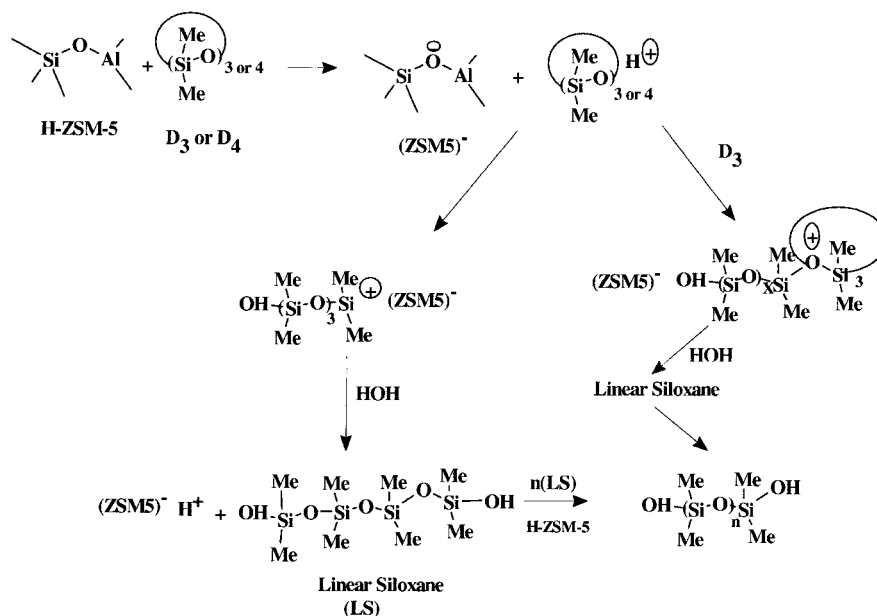


Figure 9 Mechanism of cationic polymerization of cyclic siloxane using ZSM-5 catalyst.

lite ZSM-5 with a much higher silica-alumina ratio (~ 40) was found to be very efficient. Yield and molecular weight of polymer was found to depend upon concentration of water present in the reaction medium. The extent of polymerization reaction decreases with further addition of water.

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