

Synthesis of ZSM-5 Zeolites in the $C_2H_5OH-Na_2O-Al_2O_3-SiO_2-H_2O$ System

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ZSM-5 type zeolites have been synthesized using ethanol as template. The effect of initial gel composition (in terms of molar ratios H_2O/SiO_2 , SiO_2/Al_2O_3 , OH^-/SiO_2 , and C_2H_5OH/SiO_2 , with Na_2O/SiO_2 constant), temperature, stirring velocity, and seeding has been investigated. A semiempirical mathematical model for the kinetics of zeolite growth has been developed, reproducing the experimental data with deviations of less than 10%. © 1987 Academic Press, Inc.

INTRODUCTION

Zeolites have become very important in recent years due to the wide range of industrial applications in catalytic processing (fluid catalytic cracking, methanol to gasoline process, etc.) and separation operations (adsorption, ion exchange, etc.). Countries with a well-developed petrochemical industry but still depending on zeolite importation are therefore interested in developing zeolite synthesis.

A research program for zeolite synthesis was begun in our Department in 1973, starting with the synthesis of zeolites X, A, and Y. From experience gained in earlier years (1-4), the synthesis has now been extended to the "Pentasil" zeolites (with an Si/Al ratio higher than 10), and more particularly to the ZSM-5 zeolites, which are probably the most representative.

The nonchiral ZSM-5 zeolite structural unit consists of 12 primary units (SiO_4 , AlO_4^-) connected by oxygen atoms. These units are linked by corners to produce first chains and then linked structures by an inversion process. The combination provides a three-dimensional network, with a two-channel systems, namely, a straight one with an elliptical cross section and a

sinusoidal one with a nearly circular section perpendicular to the former (5, 6). This special structure provides unique catalytic properties, showing high selectivity for isomerization and aromatization processes, resistance to poisoning and thermal stability. For these reasons, their application to chemical processes of industrial interest is continuously increasing (7-11).

During the past 15 years, these Pentasil zeolites have been synthesized from highly reactive aluminosilicate gels, by adding organic templates. Ample information on ZSM-5 synthesis using salts and hydroxides of quaternary ammonium ions, amines, and diamines can be found in the literature (12-15). These organic templates, however, are poisonous and industrially expensive. Therefore in order to extend the use of ZSM-5 zeolite into different fields of application it is necessary to develop additional advantageous methods, using more economical templates such as, e.g., alcohols, for which the data in the literature are more scarce.

EXPERIMENTAL

The syntheses have been carried out in two different reactors, at autogenous pressure. Kinetic experiments were carried out in a stirred reactor of 500-cm³ capacity provided with a sampling device, whereas

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the fixed-time experiments were done in a static autoclave with seven stainless-steel tubes of 150-cm³ capacity. Reactants used were sodium silicate (27 wt% SiO₂, 8 wt% Na₂O) and aluminum sulfate.

Two aqueous solutions with the required amount of water for the synthesis were prepared: first an alkaline solution with silicate, the selected template (with the exception of ethanol) and the crystal seeding, if used, and second an acid solution containing aluminum sulfate, sulfuric acid (in order to obtain the proper pH for the synthesis), and ethanol, if used, as template. Both solutions were homogeneously mixed for gel formation and then placed in the reactor, raising the temperature until the desired value was attained. At that moment, reaction time was assumed to be zero. Periodic samples and final product were filtered, washed with distilled water, and dried at 110°C. Using X-ray diffraction (Siemens Kristalloflex D 500 powder diffractometer, with CuK α radiation and Ni filter), the crystalline phase (x_c) present in a sample was determined quantitatively by comparing the peak area of $2\theta = 22\text{--}25^\circ$ of solid product with a standard end sample (14).

RESULTS AND DISCUSSION

Previous Experiments

First series of experiments was carried out to select the reactants and the template, and to establish the convenience of a previous aging time for the initial gel.

Different compounds were used as templates: two amines (*n*-butyl and *n*-hexyl amines) and seven alcohols (ethanol, propanol, isopropanol, butanol, isobutanol, pentanol-2, and allylic alcohol). These templates were tested using the same composition of the initial gel (H₂O/SiO₂ = 40, SiO₂/Al₂O₃ = 90, OH⁻/SiO₂ = 0.11) and a molar ratio template/SiO₂ of 0.33 for amines and 2.5 for alcohols.

High yields of ZSM-5 zeolite were obtained in all cases, the yields being higher

for amines than for alcohols. Primary straight-chain alcohols were better templates than secondary or branched alcohols, the chain length being less significant (14). Ethanol, being a low-priced available product, was selected as template for the rest of the experimental work.

Gel reactivity and the reaction mechanism of zeolite crystallization are highly dependent on the nature of the reactants used (15, 16). Therefore two pairs of reactants of industrial importance were tested using ethanol as template: these were sodium silicate/aluminum sulfate and amorphous silica/sodium aluminate. The first system was more reactive, requiring only half the time for total conversion to zeolite compared to the second system, as shown in Fig. 1.

The effect of aging time on gel reactivity was also studied, as in other zeolite syntheses previously investigated (2). For the reactants and template selected, aging times in the range 0–64 h showed no effect on gel reactivity (Fig. 2).

Influence of Variables

The effect of the following variables on the synthesis of ZSM-5 zeolites was studied.

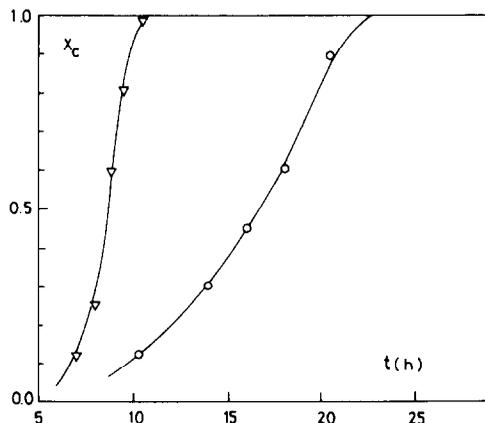


FIG. 1. Effect of the nature of the reactants on the formation of ZSM-5 (SiO₂/Al₂O₃ = 90; H₂O/SiO₂ = 40; OH⁻/SiO₂ = 0.11; C₂H₅OH/SiO₂ = 1.5; 180°C; 300 rpm): ∇ , sodium silicate/aluminum sulfate; \circ , amorphous silica/sodium aluminate.

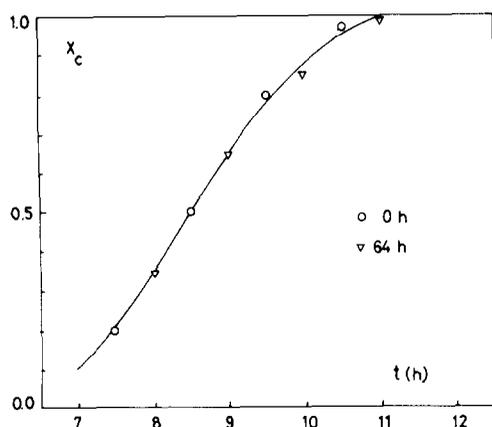


FIG. 2. Effect of aging time on ZSM-5 formation ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 90$; $\text{H}_2\text{O}/\text{SiO}_2 = 40$; $\text{OH}^-/\text{SiO}_2 = 0.11$; $\text{C}_2\text{H}_5\text{OH}/\text{SiO}_2 = 1.5$; 180°C ; 300 rpm).

Initial composition of the gel. Gel composition was established as a function of four molar ratios: $\text{H}_2\text{O}/\text{SiO}_2$, $\text{SiO}_2/\text{Al}_2\text{O}_3$, OH^-/SiO_2 , and $\text{C}_2\text{H}_5\text{OH}/\text{SiO}_2$. The molar ratio $\text{Na}_2\text{O}/\text{SiO}_2$ was constant and equal to 0.287 since sodium silicate was used as one of the reactants.

It was impossible to form the initial gel with molar ratios $\text{H}_2\text{O}/\text{SiO}_2$ below 40 because in these conditions the reactant mixture became an amorphous solid. By increasing the molar ratio $\text{H}_2\text{O}/\text{SiO}_2$, the reaction rate and zeolite yield decreased. At molar ratios above 80, dilution of reactant mixture resulted in negligible yields. Therefore, a constant value of 40 was established for this molar ratio for the rest of the experiments (14).

Values of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio varied from 10 to ∞ , but the only range useful for ZSM-5 zeolite synthesis, using ethanol as template, was 40–180. Values higher than 180 led to crystalline silica (Y variety (17)), whereas mordenite (18) and analcime (19) were obtained at values lower than 40. By seeding the mixture with ZSM-5 zeolite crystals, the amount of such impurities was reduced, but pure ZSM-5 was never obtained.

Alkalinity of the gel was controlled by the OH^-/SiO_2 molar ratio. Values of this

ratio were varied from 0.080 to 0.200, keeping the rest of the variables constant for reaction times of 16 and 21 h (Fig. 3). Maximum conversion x_c was obtained for $\text{OH}^-/\text{SiO}_2 \approx 0.11$. Increasing amounts of $\text{SiO}_2\text{-Y}$ appeared for higher values of this ratio, this impurity becoming, for very high values, the only solid phase present in the reaction mixture. The optimum value of this ratio turns out to be dependent on $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{C}_2\text{H}_5\text{OH}/\text{SiO}_2$ ratios.

Concerning the molar ratio $\text{C}_2\text{H}_5\text{OH}/\text{SiO}_2$, different values were tested in the range 0–4, keeping the rest of the variables constant for reaction times of 16 and 20 h. Figure 4 shows how the reaction rate increases with this ratio, until a maximum conversion x_c is reached, this value being a function of both the $\text{SiO}_2/\text{Al}_2\text{O}_3$ and OH^-/SiO_2 ratios. Beyond this point of maximum conversion the influence of the molar ratio $\text{C}_2\text{H}_5\text{OH}/\text{SiO}_2$ vanishes and even at high values of this ratio, $\text{SiO}_2\text{-Y}$ can result as the predominant phase.

The influence of the last two molar ratios considered, OH^-/SiO_2 and $\text{C}_2\text{H}_5\text{OH}/\text{SiO}_2$, can be explained in terms of the chemical reaction involved. Even small variations in their values give rise to important changes in the reaction rate and in the nature of the crystalline phases as well. Within these

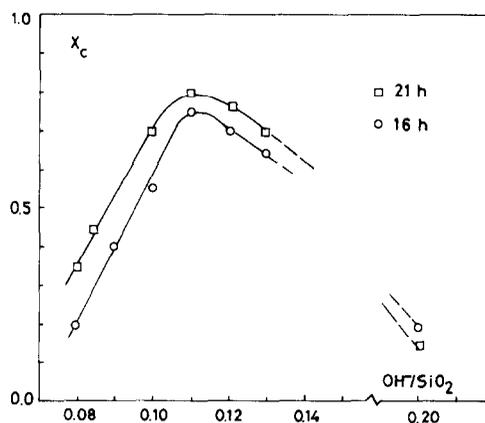


FIG. 3. Effect of OH^-/SiO_2 molar ratio on ZSM-5 formation rate ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 90$; $\text{H}_2\text{O}/\text{SiO}_2 = 40$; $\text{C}_2\text{H}_5\text{OH}/\text{SiO}_2 = 1.5$; 170°C ; 0 rpm; ---, $\text{SiO}_2\text{-Y}$ impurity).

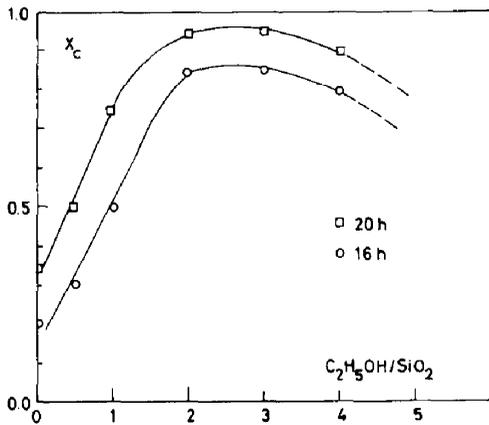


FIG. 4. Effect of C_2H_5OH molar ratio on ZSM-5 formation rate ($SiO_2/Al_2O_3 = 90$; $H_2O/SiO_2 = 40$; $OH^-/SiO_2 = 0.11$; $170^\circ C$; 0 rpm; 10% seeding; ---, SiO_2 -Y impurity).

types of synthesis, carried out in highly alkaline media, the formation of very reactive gels is favored by increasing alkalinity and template concentration (20).

In the synthesis of the ZSM-5 zeolite, it was observed that for a given SiO_2/Al_2O_3 ratio, there was always a pair of values, one for the OH^-/SiO_2 ratio and the other for the C_2H_5OH/SiO_2 ratio, that lead to a maximum reaction rate with no presence of SiO_2 -Y impurities. Therefore, a new variable was defined, the "initial gel reactivity" R being the product of both molar ratios, so that it should show an optimal value, regardless of the particular values of the individual molar ratios:

$$R_{op} = \left(\frac{OH^-}{SiO_2} \right) \left(\frac{C_2H_5OH}{SiO_2} \right) = f \left(\frac{SiO_2}{Al_2O_3} \right) \quad (1)$$

When increasing the SiO_2/Al_2O_3 ratio, the optimum gel reactivity also increases ($R_{op} = 0.120$ for $SiO_2/Al_2O_3 = 40$; $R_{op} = 0.180$ for $SiO_2/Al_2O_3 = 90$), but the ranges allowed for OH^-/SiO_2 and C_2H_5OH/SiO_2 decrease accordingly. Finally, for a value of $SiO_2/Al_2O_3 = 180$ only one value of each ratio provides the optimum for reactivity.

Figure 5 shows the ZSM-5 zeolite "synthesis volume" in a three-dimensional

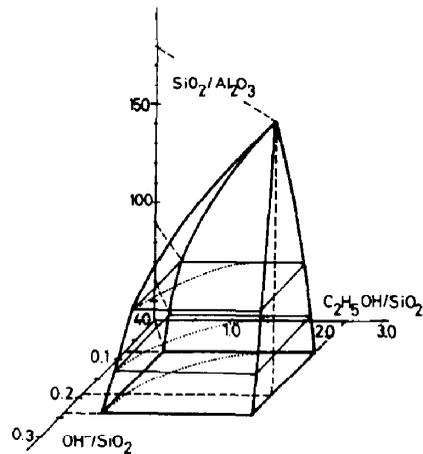


FIG. 5. ZSM-5 zeolite "synthesis volume" for the ratio $H_2O/SiO_2 = 40$ and with ethanol as template.

space of coordinates ($x = OH^-/SiO_2$, $y = C_2H_5OH/SiO_2$, $z = SiO_2/Al_2O_3$) for a ratio $H_2O/SiO_2 = 40$ and ethanol as template. Planes parallel to the xy plane (constant ratio SiO_2/Al_2O_3) determine synthesis surfaces whose area decreases progressively when increasing the SiO_2/Al_2O_3 ratio, until it reduces to a point for a value of $SiO_2/Al_2O_3 = 180$. Optimum reactivity curves have been represented on three of these surfaces. For gel reactivity values slightly different from optimum, pure ZSM-5 zeolite can also be obtained, but it requires longer reaction times.

Temperature. Figure 6 shows some ki-

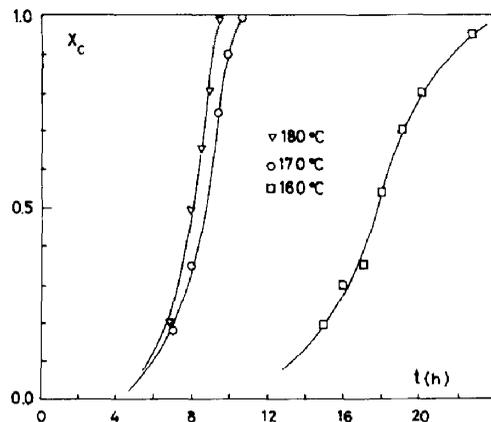


FIG. 6. Effect of temperature on ZSM-5 formation ($SiO_2/Al_2O_3 = 90$; $H_2O/SiO_2 = 40$; $OH^-/SiO_2 = 0.12$; $C_2H_5OH/SiO_2 = 1.5$; 300 rpm).

netic experiments at three different temperatures, with identical conditions for the rest of the variables. Kinetic curves show that the initial nucleation period decreases with temperature, this effect being more important at low temperatures. Thus, when changing from 160 to 170°C the nucleation period reduces from 15 to 7 h, whereas changing from 170 to 180°C only implies a 1-h reduction. At the same time, the crystallization rate increases with temperature, as shown by the shape of the kinetic curves.

Stirring velocity. Figure 7 represents a group of kinetic experiments carried out at five different stirring velocities, with identical conditions for the rest of the variables.

It is observed that stirring velocity only influences the initial nucleation period, which shows a decrease for increasing stirring velocity. There is no significant effect on the reaction rate, since all the kinetic curves have nearly the same slope. Maximum synthesis rate for this zeolite (minimum total time for nucleation and crystallization) was achieved for 450 rpm. Above this value excessive stirring seems to render the nucleation phenomenon difficult, thus requiring a longer nucleation period, which is in any case shorter than that corresponding to no stirring.

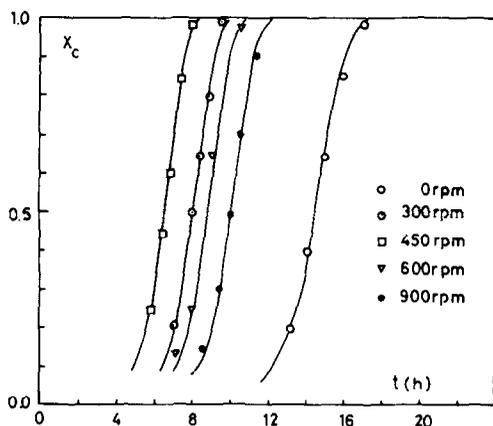


FIG. 7. Effect of stirring velocity on ZSM-5 formation ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 90$; $\text{H}_2\text{O}/\text{SiO}_2 = 40$; $\text{OH}^-/\text{SiO}_2 = 0.12$; $\text{C}_2\text{H}_5\text{OH}/\text{SiO}_2 = 1.5$; 300 rpm).

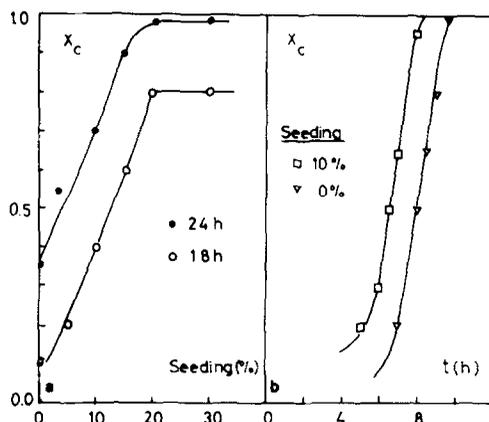


FIG. 8. Effect of seeding on (a) formation rate and (b) formation curve for ZSM-5.

These results are in agreement with those observed previously found for zeolite A synthesis (a).

Seeding. Figure 8a shows the results of two series of fixed-time experiments carried out at six different percentages of seeding (wt% of SiO_2 present in the initial gel) with identical conditions for the rest of the variables. Figure 8b shows the kinetic experiments at two percentages of seeding with identical conditions.

Figure 8a shows that seeding increases zeolite formation rate up to a certain limit ($\approx 20\%$), its effect being negligible beyond this point. Figure 8b shows that seeding only affects the initial nucleation period, as in the case of the stirring velocity.

The influence of this variable agrees with the results obtained for other low-ratio Si/Al zeolites (3), it being possible to obtain a higher zeolite yield when alternative phases are also possible products.

Furthermore, using seeding techniques (about 20%), ZSM-5 zeolite was obtained in the absence of template. In such cases, the reaction rate was slightly lower, the OH^-/SiO_2 molar ratio becoming a critical variable for obtaining pure zeolite. Thus, e.g., when $\text{SiO}_2/\text{Al}_2\text{O}_3 = 90$, this molar ratio is equal to 0.210.

A series of 24 experiments following a factorial design 2^3 for the three last vari-

ables ($T = 160\text{--}180^\circ\text{C}$; $N = 0\text{--}300$ rpm; seeding = 0–10%) for three different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios allowed determination of the interactive influences among them, thus obtaining useful information for ZSM-5 synthesis (14).

Kinetic Study

Kinetic curves of ZSM-5 zeolite formation (Figs. 6, 7, and 8b) have a sigmoid shape, typical of other zeolites with a lower Si/Al ratio (1–3), showing an initial nucleation period, followed by another period of crystal growth. These curves also show the autocatalytic behavior of the reaction, with a rate that increases with temperature and gel reactivity, this last having a maximum value which depends on the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio.

The mechanism of the formation of zeolite is not well understood. Assuming that zeolite formation follows two steps (15, 16), namely, dissolution of amorphous solid (S) from the initial gel to give the active dissolved species (D^*) and autocatalytic conversion of these active species (D^*) to give the zeolite (Z), the following reactions can be written:



We have developed three semiempirical mathematical models, based on the following three hypotheses: (a) the first step (expression (2)) is faster and reversible, attaining an equilibrium state, (b) the rates of both steps (expressions (2) and (3)) are similar, so that a quasistationary concentration of active species (D^*) is attained, and (c) there is a simultaneous zeolite formation step from solid substrate (S). Comparing our experimental results with theoretical predictions from these hypotheses, the best agreement was obtained for hypothesis (b). Thus, from expressions (2) and (3) we obtain

$$\begin{aligned} \frac{d(\text{D})}{dt} &= k_1(\text{S})R^x - k_2(\text{D}) - k_3(\text{D})(\text{Z}) \\ &= 0 \\ (\text{D}) &= \frac{k_1(\text{S})R^x}{k_2 + k_3(\text{Z})} \end{aligned} \quad (4)$$

where x is a constant related to the initial gel reactivity R (since gel reactivity is practically impossible to measure in each moment), (D), (S), and (Z) are mass concentrations in the gel of the dissolved active species, amorphous solid substrate, and zeolite, respectively, and k_1 , k_2 , and k_3 are velocity constants for the individual reactions (2) and (3).

TABLE I
Kinetic Study of Zeolite Formation^a

$T = 160^\circ\text{C}$				$T = 170^\circ\text{C}$				$T = 180^\circ\text{C}$			
$R = 0.16$		$R = 0.14$		$R = 0.16$		$R = 0.14$		$R = 0.16$		$R = 0.14$	
$t(\text{h})$	x_c	$t(\text{h})$	x_c	$t(\text{h})$	x_c	$t(\text{h})$	x_c	$t(\text{h})$	x_c	$t(\text{h})$	x_c
10.5	0.20	13.5	0.35	6.5	0.15	8.0	0.20	4.0	0.20	4.5	0.20
11.0	0.30	14.5	0.50	7.0	0.20	9.0	0.40	5.0	0.35	5.5	0.35
12.0	0.60	15.3	0.55	7.5	0.35	10.0	0.55	5.5	0.50	6.3	0.50
13.0	0.80	16.0	0.75	8.0	0.40	11.0	0.70	6.0	0.85	7.3	0.80
13.5	0.90	16.5	0.85	8.5	0.55	12.5	0.90	7.0	0.95	8.5	0.95
—	—	17.0	0.90	10.0	0.80	—	—	—	—	—	—
—	—	17.5	0.97	11.0	0.95	—	—	—	—	—	—

^a $\text{H}_2\text{O}/\text{SiO}_2 = 40$; $\text{SiO}_2/\text{Al}_2\text{O}_3 = 90$; $\text{C}_2\text{H}_5\text{OH}/\text{SiO}_2 = 1$; $N = 300$ rpm; seeding = 0%.

The zeolite reaction rate from the second stage, regarding the quasistationary concentration value of active species D (4), can be expressed as

$$\frac{d(Z)}{dt} = k_3(D)(Z) = \frac{k_1 k_3 (S) R^x}{k_2 + k_3(Z)} (Z) \quad (5)$$

When introducing the mass fraction $y = (Z)/((Z) + (S))$, $1 - y = (S)/((S) + (Z))$ and a new constant $K = (k_2/k_3)((Z) + (S))$, we obtain

$$\frac{dy}{dt} = \frac{k_1(1-y)y}{K+y} R^x \quad (6)$$

This rate equation is similar to those proposed for A, X, and Y zeolites (3) based on the Michaelis–Menten equation for fermentative processes (21).

Integrating the differential equation (6) with conditions $t = 0, y = 0, 2$ and $t = t, y = y$ (assuming for the nucleation period the limit $x_c = 0.2$) and considering that the initial gel reactivity R and solid mass concentration $((Z) + (S))$ remain nearly constant, we obtain

$$t = \frac{1}{R^x} \left[\frac{K}{k_1} \ln \frac{y}{0.2} - \frac{K+1}{k_1} \ln \frac{1-y}{0.8} \right] \quad (7)$$

Table 1 shows the data for six kinetic experiments carried out with the same values of all the variables, except for temperature and reactivity (always lower than optimum) and Table 2 summarizes the values of constants x , K , and k_1 obtained from the experimental data of Table 1 by nonlinear regression.

Figure 9 compares reaction times from experimental data (Table 1) and from Eq.

TABLE 2

Kinetic Parameters of Zeolite Formation

T (°C)	x	K	k_1
160	1.5	1531	32170
170	2.05	323	14310
180	2.39	865	99380

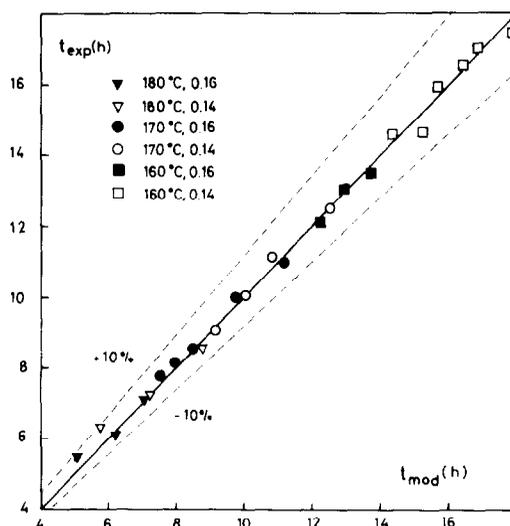


FIG. 9. Comparison of the theoretical model and the experimental results in zeolite formation.

(7) for identical conversions. As shown, the deviations are less than 10%.

Finally, the synthesized ZSM-5 zeolites were used as catalysts in the conversion of a variety of products derived from coal and biomass, showing in all cases excellent catalytic properties (22–25).

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