

Role of Basic and Acid Sites in the Bimolecular Dehydration of Alcohols Catalyzed by HY Zeolite

E. SANTACESARIA,* D. GELOSA,† E. GIORGI,† AND S. CARRÀ†

* CNPM, Centro Nazionale Propulsione ed Energetica and † Dipartimento di Chimica Fisica Applicata del Politecnico di Milano, Piazza Leonardo da Vinci, 32-Milan, Italy

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The dehydration of ethyl and methyl alcohol, catalyzed by Y decationized zeolite, has been studied in order to identify the sites active in promoting the reaction. The suppression of ether formation by the presence of acetic acid shows that acid sites coupled with vicinal basic sites are the main ones in the reaction. The number of these sites has been quantitatively evaluated by studying the adsorption of acetic acid on zeolite using thermogravimetric measurements. The number of the overall acid sites has been evaluated by poisoning the catalyst with pyridine. The order of the reaction under the experimental conditions used is about zero. A discussion of the mechanism of the reaction and of the kinetic results concludes the paper. © 1984 Academic Press, Inc.

INTRODUCTION

The reaction of ether formation by catalytic dehydration of alcohols has been extensively studied in the past over catalysts such as alumina (1-5) and silica-alumina (6-8). In some papers, also the use of catalysts as NaHX and NaHY zeolites (9-11) has been examined.

The remarkable interest given to this reaction is owed to the fact that catalytic dehydration of alcohol is strongly dependent upon the nature of the catalyst and therefore provides information about the catalytic behaviour and about the nature of the active sites present on the catalytic surface. Although the reaction described has been extensively studied, doubts still remain both on the kinetics of the reaction and on the mechanism pattern.

In a previous paper (12), dealing with the study of the kinetics of the esterification of acetic acid, with ethyl alcohol, catalyzed by Y decationized zeolite, it has been observed that ether was not present as a reaction product. Since the dehydration reaction is strongly promoted by the surface acidity of Y decationized zeolite, as reported in the literature (1-11), the absence of ether in the reaction products of esterifi-

cation suggests a strong poisoning effect of the acetic acid with respect to the dehydration reaction. In this paper, the effect of the acetic acid on the dehydration reaction has been quantitatively examined. To achieve this, kinetics of ethyl ether formation has been studied at low temperature, both on fresh Y decationized zeolite and on the same zeolite pretreated with acetic acid. Further, the characteristics of the adsorption of acetic acid on Y decationized zeolite have been investigated by employing both a differential scanning calorimeter (DSC) and thermobalance (TG). In agreement with the findings of Bielanski and Datka (13), which demonstrated the amphiprotic properties of OH groups in NaHY zeolites, it has been observed that a small amount of acetic acid is irreversibly retained on the basic sites of zeolite. This small quantity of acetic acid has a dramatic effect in lowering the catalytic activity of the zeolite. The simultaneous existence of both acid and base sites on the same solid surface has been mentioned by several other authors (15, 16). Furthermore, Correa *et al.* (17) have recently demonstrated that both Lewis acid and Lewis base sites are active on alumina. Uytterhoven *et al.* (18) have studied the structures of acidic and basic sites on decat-

ionized X and Y zeolites. Acid sites on zeolite can be poisoned by pyridine, but the effect of pyridine in lowering dehydration rates is less than the one of acetic acid. On the basis of these observations, the paper will demonstrate the kind of active sites which are effective in the reaction and the density of these sites will be quantitatively evaluated. Consequently, a kinetic law and a mechanism for the reaction will be described, discussed, and compared with previous findings by other authors.

METHODS

Kinetic runs have been performed in a stainless-steel tubular reactor, internal diameter 1 cm, thickness 0.125 cm, and length 36 cm, by feeding ethyl alcohol with rates in the range 0.35–0.90 mol/h. These feed rates were sufficient to prevent external mass transfer effects on the reaction rates. Preliminary runs, performed on pellets of different sizes, excluded the influence of internal diffusion when commercial pellets of 0.13 cm of equivalent diameter were employed (in the temperature range 125–175°C). On the basis of a previously reported treatment (12, 14), the influence of the intracrystalline diffusion can be ignored. The apparatus used is outlined in Fig. 1. The products and reagents were analyzed by gas chromatography using a column of Chromosorb 102 containing 15% of Carbowax 20 M. Helium has been used as carrier gas. Four types of kinetic runs have been made: the first on ethyl alcohol in order to evaluate the catalytic activity of the zeolite before and after the treatment with acetic acid; the second for the purpose of defining a suitable kinetic law for the etherification reaction; the third type of kinetic run was performed for the evaluation of the poisoning effect of pyridine and the last run was made on methyl alcohol, instead of ethyl alcohol, in order to determine the influence of the type of alcohol on the kinetics of the reaction.

The characteristics of the adsorption of

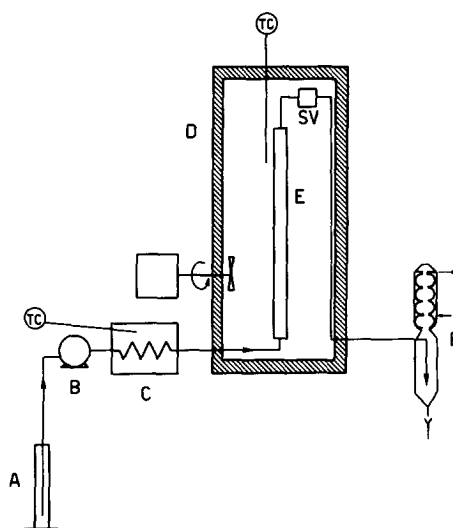


FIG. 1. Scheme of the apparatus used. A, Reagent reservoir. B, Micrometric pump. C, Preheater. D, Thermostatted chamber. E, Tubular reactor. F, Collecting vessel. TC, Thermocouple. SV, Sampling valve.

acetic acid on the Y decationized zeolite have been investigated by performing thermogravimetric and calorimetric runs. Two types of runs have been made for both the techniques mentioned, that is: adsorption and desorption. Both adsorption runs have been made, under isothermal conditions at 150°C by feeding a nitrogen stream of 30 cm³/min, saturated at 25°C with acetic acid, on a weighed sample of 20–30 mg of zeolite. The desorption runs on the same sample of zeolite followed the adsorption ones, and were performed by increasing the temperature at a constant rate from 150 up to 280°C, always in the presence of a nitrogen stream of 30 cm³/min but by-passing the acetic acid saturator. The thermobalance used was the DuPont Company 951 Model, while the differential scanning calorimeter (DSC) was the 910 Model by the same company.

Decationized Y zeolite has been prepared by ionic exchange of the commercial zeolite LZY-52 of the Linde Company with ammonium chloride. After three ionic exchanges about 80% of the sodium was replaced by ammonium. Thermal treatment of the ammonium-exchanged zeolite, at

about 450°C, gives the decationized zeolite in the usual way.

RESULTS

Kinetic runs have been performed at different concentrations of ethanol at different feed rates and temperatures in order to determine a kinetic law for the etherification reaction. Very small amounts of ethylene were obtained at the low temperature employed, ethyl ether was the main product of the reaction. The results obtained, expressed in terms of conversions of alcohol to ether, are reported in Table 1, together with the operative conditions adopted. As can be seen, and in agreement with the observations of other authors (1-11), the reaction roughly obeys a zero-order kinetic law with respect to the reagent. Another interesting observation is that the catalyst has the same activity in promoting the esterification reaction, as can be observed in the last line of Table 1, where data related to the esterification reaction are reported for comparison purposes (12).

Two questions arise. Why is ethyl ether formed only in negligible amounts during the esterification reaction? What is the

TABLE 1

Kinetic Data Collected for the Ethanol Etherification Reaction on Fresh Y Decationized Zeolite

T (°C)	F/W $\left(\frac{\text{mol}}{\text{h kg}}\right)$	Conversion $\times 100$	Molar fraction of $\text{C}_2\text{H}_5\text{OH}$	r $\left(\frac{\text{mol}}{\text{h kg}}\right)$
127	46.2	5.7	1.00	2.63
148	46.2	22.7	1.00	10.50
170	46.2	63.4	1.00	29.31
175	50.4	82.9	1.00	41.70
148	46.2	22.0	0.20	10.16
148	46.2	23.1	0.14	10.67
148	46.2	17.2	0.11	7.81
148	46.2	21.0	0.09	9.80
148	36.0	26.1	1.00	9.41
148	46.2	21.7	1.00	10.04
148	72.0	13.0	1.00	9.18
152 ^a	44.2	17.3	0.33	

^a The last data are related to the esterification reaction.

TABLE 2

Kinetic Data Collected for the Ethanol Etherification Reaction on Y Decationized Zeolite Pretreated with Acetic Acid

T (°C)	F/W $\left(\frac{\text{mol}}{\text{h kg}}\right)$	Conversion $\times 100$	Molar fraction of $\text{C}_2\text{H}_5\text{OH}$	r $\left(\frac{\text{mol}}{\text{h kg}}\right)$
127	46.2	0.83	1	0.38
150	46.2	4.51	1	2.08
170	46.2	16.83	1	7.78
150	46.2	6.05	0.20	2.79
150	46.2	5.90	0.14	2.73
150	46.2	6.00	0.11	2.77
150	46.2	5.75	0.09	2.65

mechanism according to which acetic acid seems to hinder the formation of ether? In order to answer these questions, we have repeated the kinetic runs reported in Table 1 on the same Y decationized zeolite, pretreated with acetic acid. The results obtained are reported in Table 2. As can be seen the reaction order is unchanged, but the activity is strongly depressed. The results of Tables 1 and 2 have been elaborated on the basis of zero-order kinetics. In Fig. 2 the resulting kinetic constants are ar-

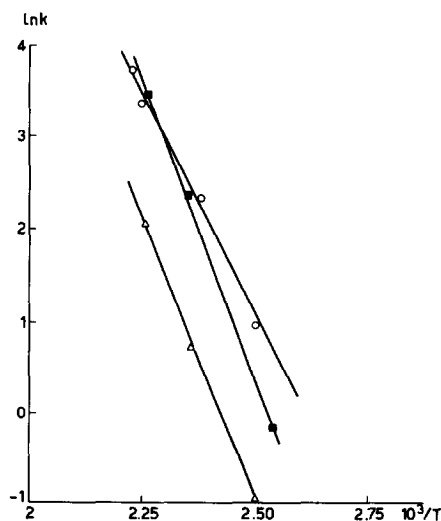


FIG. 2. The Arrhenius-type plots related, respectively, to the ethanol dehydration reaction, performed on fresh (O) and pretreated zeolite (Δ) and to methanol dehydration reaction (\blacksquare).

TABLE 3

Kinetic Parameters

Reagent	Catalyst	Preexponential factor	Activation energy (kcal/mol)
C ₂ H ₅ OH	Fresh zeolite	5.45×10^{10}	18.8
C ₂ H ₅ OH	Pretreated zeolite	4.13×10^{12}	23.8
CH ₃ OH	Fresh zeolite	4.16×10^{14}	26.5

ranged in an Arrhenius-type plot, while in Table 3 the kinetic parameters obtained for the two cases considered are reported. As can be shown the treatment of the zeolite with acetic acid produces a significant increase in the activation energy of the reaction, and in the preexponential factor.

It is interesting to follow the transient behavior of the alcohol-saturated zeolite, during the treatment at 150°C with acetic acid as seen in Fig. 3, and during the wash with ethyl alcohol to eliminate as much of the acetic acid adsorbed as possible (see Fig. 4). Details of the operative conditions are reported in the legend of the figures. By comparing Figs. 3 and 4, it is possible to observe that not all the acetic acid adsorbed

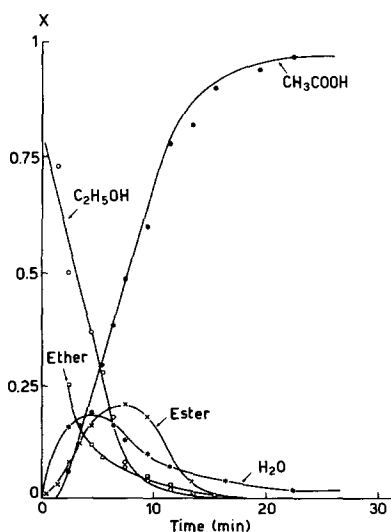


FIG. 3. Transient behavior of the catalytic bed saturated with ethyl alcohol during the pretreatment with acetic acid. The temperature was 150°C, the feed rates $0.46 \text{ cm}^3/\text{min}$, the amount of zeolite 10 g.

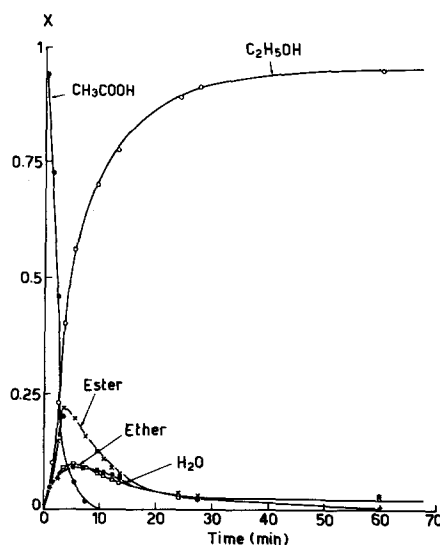


FIG. 4. Transient behavior of the catalytic bed during the wash with ethyl alcohol to remove acetic acid after the pretreatment. The temperature was 150°C, the feed rates $0.46 \text{ cm}^3/\text{min}$, the amount of zeolite 10 g.

in the treatment is removed by washing with alcohol. It can be roughly estimated that $5 \times 10^{-4} \text{ mol/g}$ of acetic acid are retained by the zeolite. In order to determine more exactly the quantity of acetic acid that remained anchored to the zeolite and the nature of the bond responsible for the adsorption, thermogravimetric and calorimetric runs have been performed. Figure 5 shows the thermogravimetric runs obtained

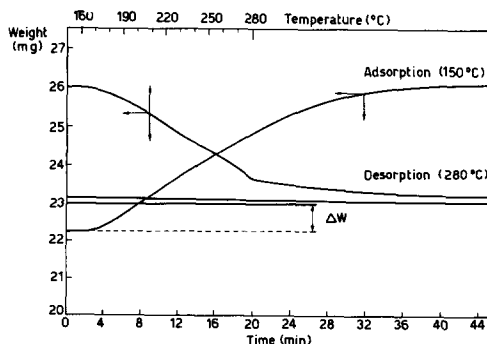


FIG. 5. Thermogravimetric runs obtained by adsorbing and desorbing acetic acid. Adsorption run has been performed isothermally at 150°C, while desorption run by scanning temperature in the range 150–280°C and then by keeping the sample at 280°C.

by adsorbing and desorbing acetic acid on zeolite, under the conditions already described. As can be observed in the desorption step, a certain amount of acetic acid cannot be removed even at 280°C. This is in agreement with the observations of Bielanski and Datka (13). According to these authors the appearance of the anion acetate characteristic infrared bands for the adsorbed acetic acid is the best demonstration of the existence of basic sites on zeolite. Furthermore, they show that adsorbed acetic acid cannot be removed from the zeolite even at 400°C under vacuum.

By considering the plots reported in Fig. 5 it is possible to give an exact evaluation of the number of basic sites, that is, 3.18×10^{20} sites/g which corresponds to a quantity of acetic acid, irreversibly bonded to the zeolite, of 5.29×10^{-4} mol/g.

In order to evaluate the energy involved in the acetic acid adsorption, calorimetric runs have been performed under the same conditions as adopted for the thermogravimetric runs. First of all, we have evaluated the overall adsorption heat for acetic acid on Y decationized zeolite, in isothermal conditions, at 150°C. The result was 229 J/g as can be seen in Fig. 6. The filling degree of the zeolite can be considered 1 at the end

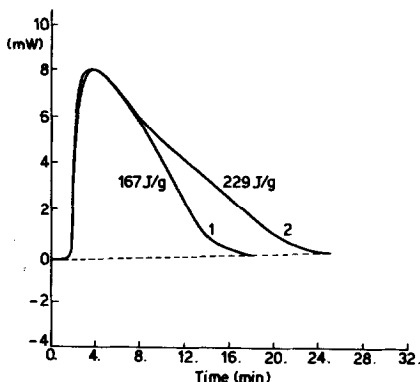


FIG. 6. Calorimetric runs, performed isothermally at 150°C for the adsorption of acetic acid on HY zeolite. Curve 1 is related to the adsorption from a nitrogen stream, saturated at room temperature on fresh zeolite while curve 2 has been obtained under the same conditions on pretreated zeolite.

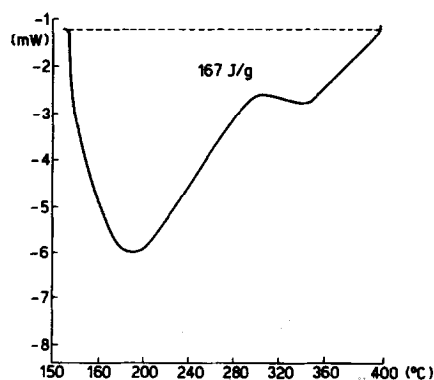


FIG. 7. Calorimetric run, for the acetic acid desorption from HY zeolite obtained by scanning temperature in the range 150–400°C, in the presence of a nitrogen stream.

of the run, being very high the adsorption equilibrium constant for acetic acid. A desorption calorimetric run was afterward made on the same sample by scanning the temperature from 150 up to 280°C at constant rate. The desorption heat was 167 J/g as can be seen in Fig. 7. By comparing the adsorption heat with the desorption heat, it is possible to calculate that 62 J/g is the heat for the adsorption of the acetic acid which cannot be removed from the zeolite by desorbing. This value corresponds to a bond energy for the type of adsorption considered of about 28 kcal/mole. These values have been confirmed by repeating another adsorption step (on the same sample after the desorption), always in isothermal conditions, at 150°C. The thermogram obtained is reported also in Fig. 6. By comparing the two thermograms of Fig. 6, a bond energy of about 30 kcal/mol can be evaluated, this is in satisfactory agreement with the previously determined value.

Kinetic runs have also been made by feeding a small amount of pyridine with the reagent. In Fig. 8, the decay of the catalytic activity for the poisoning effect of pyridine is reported. Because pyridine poisons acid sites, by considering the plot of Fig. 8 the number of acid sites can be calculated giving 1.16×10^{21} sites/g in satisfactory agreement with the values obtained by other au-

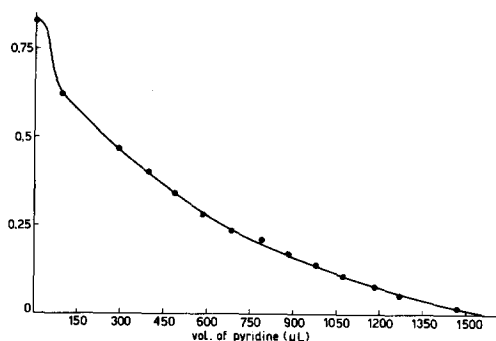


FIG. 8. The poisoning effect of pyridine on the reaction activity at 175°C. The amount of zeolite was 10 g.

thors (19). It is very interesting to observe that the poisoning action of acetic acid is more effective than that of pyridine. The effect of adding water to the reagent on the catalytic activity is reported in Fig. 9. The depressing action of water, represented in Fig. 9, has been previously observed by many other authors.

Finally, some kinetic runs have been performed also by employing methanol as reagent. The results obtained are reported in Table 4, while the corresponding Arrhenius plot is reported in Fig. 4 and the kinetic parameters obtained in Table 3. As can be seen in the case of methanol dehydration, the activation energy is higher than in the case of ethanol.

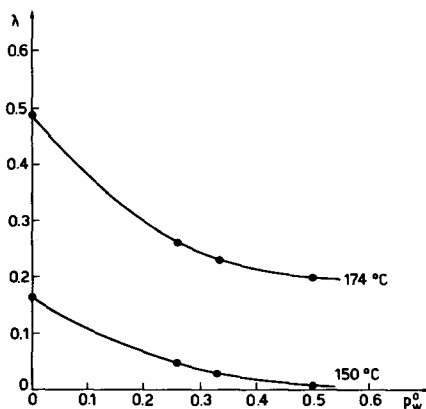


FIG. 9. The effect of water added to the reagent in depressing reaction activity.

TABLE 4

Kinetic Data Collected for the Methanol Etherification Reaction of Methanol on Fresh Y Decationized Zeolite

T (°C)	F/W ($\frac{\text{mol}}{\text{h kg}}$)	Conversion $\times 100$	Molar fraction of CH_3OH	r ($\frac{\text{mol}}{\text{h kg}}$)
120	82	1.06	1	0.86
151	82	14.70	1	11.90
168	82	40.15	1	32.74
151	82	11.58	0.2	9.44
151	82	10.81	0.14	8.86
151	82	10.90	0.11	8.74
151	82	10.81	0.09	8.82
151	55	15.85	1	12.90
151	75	11.82	1	9.64

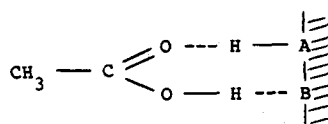
DISCUSSION

It has been shown that acetic acid, strongly bonded to the Y decationized zeolite, has a strong poisoning effect in the etherification reaction. In fact, at 150°C, reaction rate decreased by about 75% when zeolite was pretreated with acetic acid. On the other hand, pyridine also has a poisoning effect on the reaction and the catalytic activity can be zeroed if all the acid sites are neutralized. Another important observation is that the etherification reaction of methanol has an activation energy higher than the same reaction for ethanol. This fact could be justified by assuming that the formation of the carbocation is the rate-determining step in the reaction, the ethyl carbocation being more stable than the methyl carbocation. But carbocations can be formed only on acid sites, whereas we observed that basic sites seem to be more important in promoting the dehydration reaction.

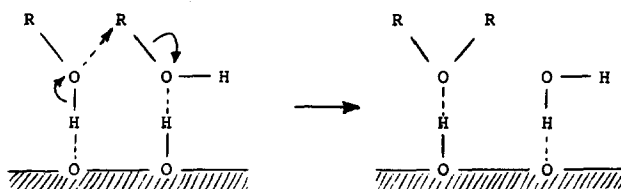
The influence of the basic sites on the reaction can be better appreciated if the turnover frequency related, respectively, to the basic and to the acidic sites is calculated. In this case, basic sites are proved to be 10 times more active than acid ones. On the other hand, the formation of the carbo-

cation can be obtained only on the acid sites. Furthermore, the complete poisoning of basic sites does not eliminate completely the catalytic activity.

The conclusion is that basic sites are promoters of the catalysis and their action favors the formation of the carbocation by stabilizing the precursor. Two acid–basic vicinal sites, therefore, would be the main catalytic sites. Acetic acid has the poisoning effect described because it interacts contemporaneously with both basic and vicinal acid sites according to the scheme

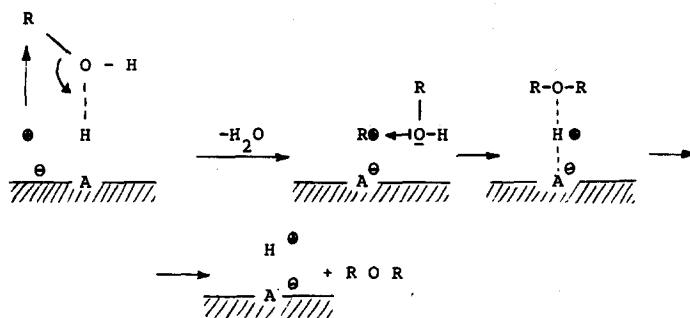


The difference in the activation energy among the reaction catalyzed by fresh zeolite and zeolite pretreated with acetic acid could be attributed to the difference in the energy required for the formation of carbocation in the absence or in the presence of basic sites. The formation of carbocation, in fact, is favored in the presence of basic sites according to the concerted mechanism



The situation described is the most favorable for the reaction because of the cooperative action of the two sites and because the ether molecules formed can be easily desorbed from the basic sites. Water, as has been shown, has an inhibiting effect on the

reaction. This effect could be attributed to the competitive adsorption of water both on the acid and basic sites. The reaction, catalyzed by the isolated acid sites, could be described in a simplified way by the mechanism



Water can inhibit the reaction also in this case, owing to the competitive adsorption on the acid sites.

All these facts clearly explain the reasons for which many different kinetic relations for this reaction have been proposed in the literature.

In fact, taking into account all the previously mentioned effects, the reaction rate expression should contain two terms: the main term, related to the behavior of the more active sites, the couple of basic sites plus vicinal acid sites and another term, related to the isolated acid sites which, as has

been shown, work with a higher activation energy. If free sites are negligible, in comparison with the sites occupied by alcohol and water and if ether adsorption does not affect the reaction rates, as has been experimentally observed, a Langmuir–Hinshelwood kinetic law of the type suggested by Jacobs *et al.* (10) seems to be the most suitable for representing both the two cases considered

$$r = r_b + r_a = k_b \frac{b_{ba} \cdot p_a}{b_{ba} \cdot p_a + (b_{bw} + b_w)p_w} + k_a \frac{b_a \cdot p_a}{b_a \cdot p_a + b_w \cdot p_w}$$

In the first term, the adsorption equilibrium constants for water consider the possibilities of adsorption of the molecules both on the basic and on the vicinal acid sites. The kinetic constant k_b is related to the number of basic sites, while k_a is related to the number of acid sites. For relatively low conversions, reaction order becomes zero and reaction rates correspond to the addition of the two kinetic constants as has been experimentally observed.

In conclusion, it has been shown that bimolecular dehydration of ethyl alcohol on Y decationized zeolite mainly occurs on acid sites vicinal to the basic ones. The catalytic activity on the isolated acid sites is about one order of magnitude lower than that on the acid–base couple reported.

In both cases, it has been assumed that the formation of the carbocation is a rate-determining step. Therefore, the difference in the catalytic activity is explained by assuming that basic sites have a stabilizing effect on the precursor of the carbocation.

A Langmuir–Hinshelwood kinetic law containing two terms, one for the reaction occurring on the vicinal couple acid–base and another for the reaction on the isolated acid centers has been suggested on the basis of the following observations:

(a) At relatively low conversions and at low temperature, the apparent reaction order is zero.

(b) If water is added to the reagent, the reaction rate is depressed.

(c) If zeolite is treated with acetic acid the first term of the kinetic law disappears due to the poisoning of the basic sites, but residual activity remains.

(d) By poisoning the catalyst with pyridine, activity is slowly depressed to a zero value when all the acid sites are neutralized.

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