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One-Pot Selective Synthesis of Ethyl Esters from Aromatic Nitriles Using Acid Faujasites as Catalysts

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In order to determine the potential of acidic zeolites as catalysts in the preparation of carboxylic esters from nitriles, faujasites, beta, and mordenite have been studied in a liquid ethanolic medium. From the results obtained, it can be concluded that the optimum zeolite for this reaction is the less acidic faujasite (Si/Al = 2.5). Competitive dehydration of ethanol takes place and, consequently, the two nucleophiles ethanol and water react with the nitriles. Zeolites with the strongest acid sites (beta, mordenite) show higher activity in a first step of the process, particularly towards amide formation. A linear relationship between activity and acidity is established in this step for a competitive attack of the nucleophiles. After the strong acid sites have been poisoned by the product, the reaction is performed over the remaining less acidic free sites. A consecutive reaction takes place leading to the ester with good selectivities (80%) over faujasites. The probable operating mechanism involves as the first step a fast protonation of the nitrile, the rate-determining step being, as in homogeneous conditions, the nucleophilic attack.

INTRODUCTION

The application of zeolites as catalysts for the synthesis of fine chemicals has been increasing rapidly (*1*). The use of a suitable zeolite catalyst should lead to a better selectivity of the desired compound (*2*) and avoid such drawbacks as the production of large quantities of salt by-products. The acidic form of zeolites can catalyse any organic reaction subject to conventional proton catalysis.

Furthermore, nitriles are interesting reactants which can undergo acidic (*3, 4*), basic (*5, 6*) or metallic (*7*) catalysis to enhance their reactivity in solvolysis or hydration reactions. New processes over metallic oxides have been developed (*8, 9*). The selectivity into amide or acid depends mainly on the nature of the catalyst.

Up to now there are only a few examples of nitrile reactions using zeolites as catalysts. For nitrile hydration, even in an alcoholic medium, the reported examples indicate only the amide formation whatever the nature of the zeolite, acidic (*10*), basic (*11*), or zeolite-supported metal (*12*). The most striking example (*10*) describes the reaction of acetonitrile with methanol over faujasites which leads to a mixture of mono- and dialkylated amides.

In homogeneous conditions very different results are obtained. By the Pinner synthesis, acid-catalyzed attack of a primary alcohol on the nitrile yields an imidate salt which undergoes an acid-catalyzed hydrolysis (*13, 14*). The mechanism of the hydrolysis of imidates has been studied extensively. The products as well as the rates of hydrolysis have been shown to be sensitive to pH. The typical products at low pH are ester and amine, while amide and alcohol are the products at high pH (*13, 15, 16*). However, in very strong acid solutions (up to 65% aqueous sulfuric acid) the products of hydrolysis of methylbenzimidates (*16*) have been shown to be the corresponding N-alkylbenzamides.

Contrary to the above results over acid zeolites and in accordance with the results

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in homogeneous conditions, we have shown in a preliminary study (*17*) that the reaction of benzonitrile, over acid zeolites in a liquid medium using ethanol as solvent, gives ethyl benzoate and benzamide. The selectivity of the reaction depends mainly on the acidic zeolite used, faujasite (Y), beta (β), or mordenite (M). For example, the ester selectivity varies from 80% over faujasites with different framework Si/Al ratios (2.5 to 15) to 50% over beta (Si/Al = 15) and 15% over mordenite (Si/Al = 9) for a typical conversion of 25% at 230°C.

Mechanistic studies are very scarce and consequently the mechanism of nitrile solvolysis or of nitrile hydration over zeolites is still to be established. The present paper deals with this study using acidic faujasites. The choice of these catalysts is determined by a preliminary study of the activity/acidity relationship for various zeolites characterized by their structure and their acidity.

EXPERIMENTAL

The $Y_{2.5}$ zeolite (faujasite, Si/Al = 2.5) was obtained by deammoniating NH_4Y (Linde SK 41 from Union Carbide). The Y_{15} zeolite (faujasite, Si/Al = 15) was provided by Zeocat (ZF 515).

The β_{15} zeolite (beta, Si/Al = 15) was synthesized in the laboratory according to the method described previously (*18*) and had the chemical composition determined by elemental analysis: $\%SiO_2 = 77.89$, $\%Al_2O_3 = 4.34$, and $\%Na_2O = 0.40$.

Zeolon 100 H (Si/Al = 6.9 from Norton Co.) was dealuminated by treatment of 8 g in 1 M HCl aqueous solution (500 ml) for 4.5 h at 80°C to obtain a mordenite M_9 (Si/Al = 9). The chemical composition was determined by elemental analysis: $\%SiO_2 = 69.86$, $\%Al_2O_3 = 6.42$, and $\%Na_2O = 0.40$.

The reactions were carried out in a 0.1 liter stirred autoclave operating in a batch mode and equipped with a system for sampling liquid during the reaction. The autoclave was charged with the organic reactant together with the solvent and the freshly calcined zeolite (calcination for 6 h at 500°C in air prior to use) and then heated to the desired temperature. The general conditions were: 2.5 g (0.4 mol.l^{-1}) of benzonitrile, 60 ml of EtOH (dried over molecular sieves), and 1.25 g of zeolite. A study of the effect of nitrile structure was carried out in the same conditions with 2.5 g of $Y_{2.5}$ zeolite. The total volume of ethanol (EtOH) and H_2O was 60 ml when water was added in the range from zero to 2.2 ml.

The course of the reaction was followed by gas chromatography (Delsi, Girdel 3000 apparatus with a flame ionization detector) using an OV_1 column (25 m), dodecane as external standard, and subsequent temperature programming: 55°C, 15°C min^{-1}, 180°C.

The products were identified by GC–MS chromatography.

RESULTS AND DISCUSSION

The reaction was performed over acidic $Y_{2.5}$, Y_{15}, β_{15}, and M_9 zeolites differentiated by their structure and their acidity. In a liquid medium, with EtOH as solvent, the benzonitrile reaction over acidic zeolites leads to a mixture of ethyl benzoate, benzamide, N-ethylbenzamide, and small amounts of benzoic acid. Ester selectivity is defined as %ester/% products.

Before discussing the mechanism, it is necessary to obtain a clear indication of the relationship between the characteristics of the zeolite and its catalytic activity in the nitrile reaction.

1. Relationship between Activity and Acidity of the Zeolite

In acid-catalyzed reactions, the activity of the catalyst will not necessarily be directly proportional to the total concentration of acid sites present on the catalyst as it may also be influenced by the concentration of acid sites with a given acid strength (*19, 20*). It is widely agreed that the acid strength of zeolites increases with the Si/Al ratio of the framework (*2, 21*). Moreover, the distribution of the strength of the acid sites varies with the structure (*22–24*). For example, Climent *et al.* (*22*) have stated that TOF

TABLE 1

Initial Rate of Benzonitrile Disappearance at 230°C, in General Conditions, as a Function of the Number of Strong Acid Sites (Desorption Temperature of NH_3 > 350°C)

Zeolite	Si/Al	eq H^+ g^{-1} $\times 10^3$	$r_0 \times 10^6$ (mol $liter^{-1}$ s^{-1} g^{-1})
Y	2.5	0.115	6.7
Y	15	0.160	7.0
β	15	0.292	13.0
M	9	0.452	26.0

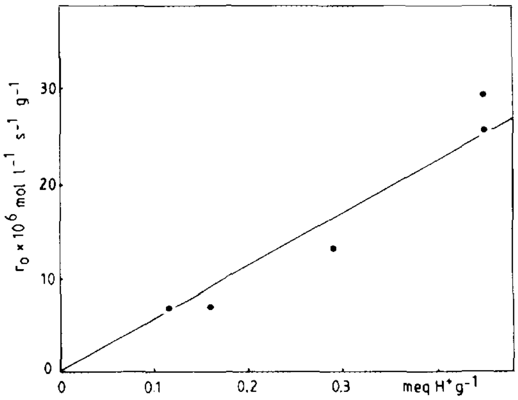


FIG. 1. Correlation of the initial rate of nitrile disappearance (mol $liter^{-1}$ s^{-1} g^{-1}) with the number of strong acid sites (meq H^+ g^{-1}).

values for β zeolites are in general slightly higher than those for dealuminated Y zeolites indicating that β has stronger acid sites than dealuminated Y zeolites.

This is emphasized by the study of the acid strength distribution of the sites of the zeolites evaluated by temperature programmed desorption of NH_3. Table 1 shows the number of strong acid sites per gram of catalyst or eq H^+ g^{-1} for sites which retain NH_3 at temperatures greater than 350°C.

In the reaction of benzonitrile over the various acid zeolites, at 230°C, the same behaviour is observed. The reaction can be broken down into two steps. During the first step, the relatively fast disappearance of the nitrile is accompanied by ester and amide formation. In the second step, the rate of nitrile disappearance diminishes, and the amide concentration shows a rapid stabilization while the ester concentration varies linearly with time. A relative deactivation of the catalyst takes place, more probably related to poisoning of the strong acidity than to diffusional constraints of organic compounds inside the channels of the zeolite. In fact, the same scheme is obtained for the large pore tridirectional faujasite, beta zeolites and for the unidirectional mordenite. Table 1 and Fig. 1 show that a good correlation is obtained between the initial rate of nitrile disappearance (r_0, first step) and the number of strong acid sites.

Our results fit well with differences in the acid strength distribution in terms of the structure of the catalyst, particularly if we compare the results for the two Y and β zeolites with the same Si/Al ratios. The faujasites with different Si/Al ratios exhibit practically the same activity, due to the related number of strong acid sites in the two catalysts with regard to the requirement of the reaction.

The effect of temperature upon nitrile reactivity has been studied (see Fig. 2 and Fig. 3). Figures 3 and 4 show the effect of temperature for the less acidic $Y_{2.5}$ zeolite. By increasing the temperature from 230 to 250°C, the first step appears more clearly. It seems that deactivation of the $Y_{2.5}$ zeolite

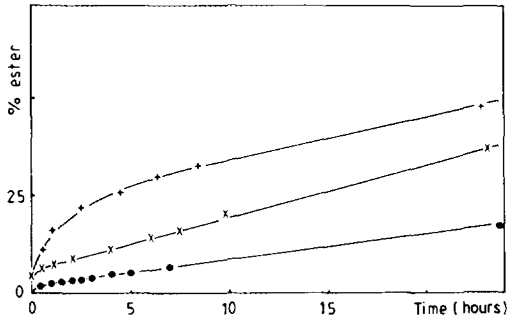


FIG. 2. Effect of the temperature on ester production: (●) 200°C, (×) 230°C, and (+) 250°C, in general conditions, over $Y_{2.5}$ zeolite (1.25 g).

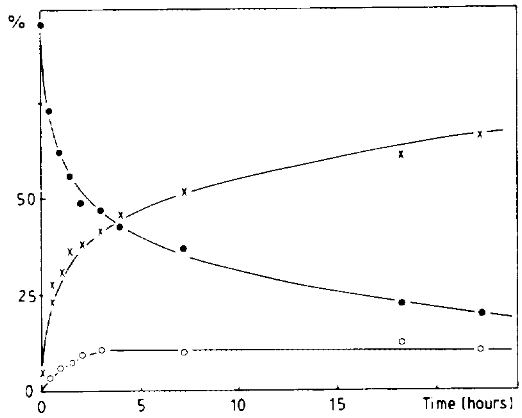


FIG. 3. Example of ester production over $Y_{2.5}$ zeolite (2.5 g), T = 250°C, in general conditions: (●) %benzonitrile, (×) %ethylbenzoate, and (○) %benzamides.

occurs later. It is known that in the case of molecules of different polarity, changes in the relative adsorption can be dramatic. Nitrile, ester, acid, ethanol, and amide have increasing basicities with pK_a values relative to water of -10, -7.4, -7, -2, and -1.5, respectively (*25*). During the reaction, ammonia is produced. However, saturation can be reasonably imputed to the basic amide with a higher boiling point than the more basic ammonia (*26*). Moreover, we do not observe saturation by NH_3 of the $Y_{2.5}$ zeolite, even when the conversion is high (80%). This specific interaction of amide with Brønsted acid sites has been noted for acrylamide over acid hydroxyl sites of MnO_2 (*9*).

The thermal effect leads to a weakened interaction between acid sites of the $Y_{2.5}$ zeolite and the products and, consequently to a lower saturation of the catalyst. For the other acidic zeolites, even for the Y_{15} zeolite, the same desaturation effect is not observed.

This effect of temperature on the activity of the zeolites shows the influence of the strong acidity on the two-step profile of the reaction. Under the circumstances the distribution of the acidity of the zeolite is of prime importance.

It has been shown that nitrile reactivity depends mainly on the strong acidity of the catalyst. In the first step of the process, reactivity is enhanced by strong acidity but, in the second step, after a rapid saturation of the strong acid sites by the formed amide, the ester synthesis is performed on the weaker free sites. Then, it is shown that the selectivity in the zeolite-catalyzed reaction depends on the step under consideration.

At 250°C (Fig. 4) when deactivation of the $Y_{2.5}$ zeolite occurs later, reaction selectivity does not vary with conversion nor with nitrile concentration. This observation leads to the conclusion that, in the first step, the two possible nucleophiles EtOH and H_2O attack the nitrile in competitive reactions.

At 230°C (Fig. 5) the change in reaction selectivity is the effect of the ester growth when amide concentration appears constant. Initial ester selectivity is evaluated from initial slopes of ester and amide formation. Initial selectivity in ester, 60, 27, and 13%, respectively, over Y, β, and M zeolites, reflects the activity of the catalyst toward ethanolysis or hydration of benzonitrile. In the second step, the ester can be obtained from the amide, in a consecutive scheme, on the weakest acid sites (Scheme 1).

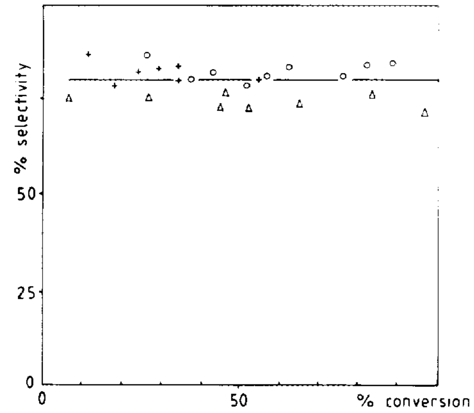


FIG. 4. Ester selectivity as a function of nitrile conversion over $Y_{2.5}$ zeolite, T = 250°C: (+) [Nit] = 0.4 mol liter^{-1}, m Cat = 1.25 g; (○) [Nit] = 0.4 mol l^{-1}, m Cat = 2.5 g; and (△) [Nit] = 0.8 mol liter^{-1}, m Cat = 2.5 g.

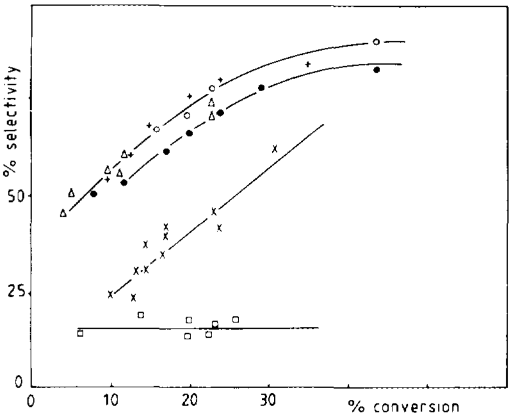


FIG. 5. Ester selectivity as a function of nitrile conversion over $Y_{2.5}$ zeolite, T = 230°C: (●) [Nit] = 0.2 mol liter^{-1}; (+) [Nit] = 0.4 mol liter^{-1}; (△) [Nit] = 0.8 mol liter^{-1}, m Cat = 1.25 g; (○) [Nit] = 0.4 mol liter^{-1}, m Cat = 2.5 g; and (×) over β_{15} zeolite and (□) over M_9 zeolite in general conditions.

TABLE 2

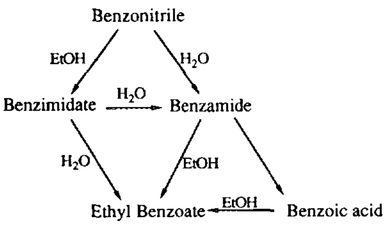
Initial Rate of Substrate[a] Disappearance at 230°C

Zeolite	$-[d[Am]/dt]_0$ × 10^5 (mol liter^{-1} s^{-1} g^{-1})	$-[d[Ac]/dt]_0$ × 10^5 (mol liter^{-1} s^{-1} g^{-1})	$-[d[Nit]/dt]_0$ × 10^7 (mol liter^{-1} s^{-1} g^{-1})
$Y_{2.5}$	1.5	10.7	13.0
β_{15}	0.7	7.7	5.0
M_9	0.15	4.6	2.8

[a] In the liquid phase, substrate = benzamide (Am), benzoic acid (Ac), at 0.1 mol liter^{-1} concentrations and benzonitrile (Nit) at 0.4 mol liter^{-1} with (mass substrate)/(mass catalyst) = 2.

The solvolysis of benzamide and the esterification of benzoic acid over the same zeolites have been studied and compared with ester formation from nitrile. In the second step of the process, when the amide concentration appears constant ([Am] < 0.1 mol liter^{-1}), the former reactions are easier than the latter one (Table 2). The overall zeolite-catalyzed ester process seems kinetically controlled by the conversion of benzonitrile into benzimidate or benzamide in a possible competitive nucleophilic attack by EtOH or H_2O on the substrate. Alternatively, ester can be obtained by a consecutive reaction of the alcohol on the amide or the acid preliminary formed (Scheme 1).

We observe (Table 2) that the relative order of catalyst activity obtained for ester production in a liquid alcoholic medium is the same whatever the reactant, be it amide, acid or nitrile. This noticeable result over $Y_{2.5}$ can be related to the lower water concentration over less acidic zeolites. It is known that ester production, at high temperatures, can be limited by reaction of ethanol to ethene and water (*27*).



SCHEME 1

The mechanism of the nitrile reaction has been studied over faujasites, which give the better selectivity for ester.

2. *Reaction Mechanism over Y Zeolites*

The effect of various parameters such as water or nitrile concentration and substituent effect on the aromatic ring have been studied. In the overall process it has been shown that the benzimidate or amide formation is the limiting change (Scheme 1, Table 2).

At 230°C, it can be considered that the concentration of added water (0 < $[H_2O]$ mol liter^{-1} < 2) has no effect on the observed rate for the $Y_{2.5}$ and the Y_{15} catalysts (Fig. 6). It is acknowledged that the competitive dehydration of ethanol over acid faujasites proceeds easily, giving olefin and water. In excess water, the rate law is pseudo-zero-order in H_2O and in EtOH. Therefore, it cannot be concluded whether the reaction fits the Langmuir–Hinshelwood or the Eley–Rideal mechanism.

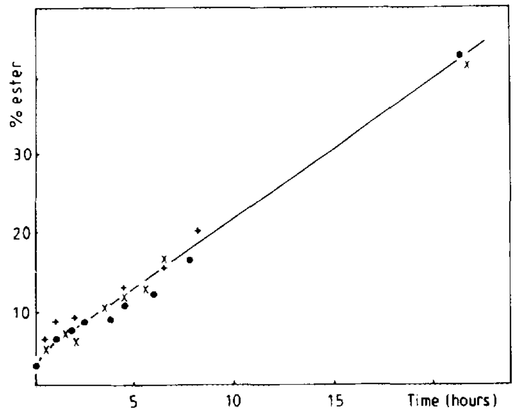


FIG. 6. %ester formation over Y_{15} zeolite as a function of added water, $T = 230°C$, $[Nit] = 0.4$ mol liter^{-1}: (●) in ethanol, (+) with 1.1 ml H_2O, and (×) with 5 ml H_2O.

Table 3 shows the effect of nitrile concentration on the initial rate over $Y_{2.5}$ zeolite. In general conditions, r_0 is first order for the two steps of the reaction for $0.2 < [Nit]_0$ mol liter^{-1} < 0.8, then, the results can be fitted to the rate law,

$$r = k_1\theta_{Nit},$$

$$\theta_{Nit} = \lambda_{Nit}[Nit]/D,$$

$$D = \lambda_{Nit}[Nit] + \lambda_p[p] + \lambda_s[s],$$

where Nit = nitrile, p = products, s = EtOH, H_2O; λ_{Nit}, λ_p, λ_s = adsorption constants for nitrile, product and solvent, respectively; [Nit], $[p]$, $[s]$ = concentrations for nitrile, product and solvent, respectively.

In the first step,

$$\lambda_p[p] \text{ is small, } \lambda_s[s] > \lambda_{Nit}[Nit]_0,$$

therefore,

$$\theta_{Nit} = \lambda_{Nit}[Nit]_0/\text{cte},$$

with cte $= \lambda_s[s]$, and $r_0 = k_1(\lambda_{Nit}/\text{cte})[Nit]_0$,

$$r_0 = k_{obs}[Nit]_0.$$

From the results in Table 3, $k_{obs} = 2.1 \times 10^{-5}$ s^{-1} g^{-1} ($r = 0.991$). In the first step, it has been verified that the observed initial rate of nitrile conversion varies with the weight of catalyst at 230°C (not shown) and at 250°C (Figs. 2 and 3). This result indicates that, for this reaction which requires strong acidity, diffusion limitations are avoided.

In the second step, there has been formation of amide and ammonia: $\lambda_p[p] > \lambda_s[s]$, the rate law would be described by the same equation but with saturation of the catalyst by the products:

$$r = k_1(\lambda_{Nit}/\text{cte})[Nit],$$

with cte $= \lambda_p[p]$,

$$r = k'_{obs}[Nit].$$

From the results in Table 3, $k'_{obs} = 3.3 \times 10^{-6}$ s^{-1} g^{-1} ($r = 0.999$). The effectiveness of the $Y_{2.5}$ zeolite is divided by 6.

Nevertheless, in this phase of the reaction no effect due to the weight of catalyst is observed, in accordance with a higher adsorption and a lower diffusion rate of benzamide. The study of the substituent effect on the aromatic ring on nitrile conversion shows this influence of amide basicity.

The effect on reactivity of a change in reactant structure is a good tool for elucidating the reaction mechanism.

In the case of nitriles, this effect was investigated with para-substituted benzonitriles at 250°C (Fig. 7) and 230°C (Fig. 8). Secondary reactions with p-NO_2 benzonitrile prevent the study of this compound at these temperatures. For all substituted com-

TABLE 3

Rates of Nitrile Conversion over $Y_{2.5}$ Zeolite for the Two Steps of the Reaction as a Function of Benzonitrile (Nit) Concentration at 230°C

$[Nit]_0$ (mol liter^{-1})	$r_0 \times 10^6$ (mol liter^{-1} s^{-1} g^{-1}) 1st step	$r \times 10^7$ (mol liter^{-1} s^{-1} g^{-1}) 2nd step
0.2	2.2	5.8
0.4	6.7	13.0
0.8	16	25.5

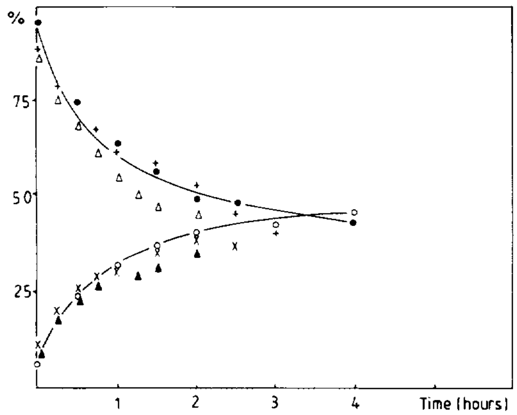


FIG. 7. Effect on reactivity of the change in nitrile structure over $Y_{2.5}$ zeolite, $T = 250°C$, in general conditions: (●) benzonitrile, (+) p-OCH_3 benzonitrile, (△) p-OH benzonitrile, (○) ethyl benzoate, (×) ethyl-p-methoxy-benzoate, and (▲) ethyl-p-hydroxy-benzoate.

pounds, a decarboxylation reaction takes place, especially at 250°C. The corresponding substituted aromatic hydrocarbons (chlorobenzene, phenol, anisole) are obtained (*28*).

It is clear, particularly at 250°C, that no effect of *para* substitution is observed in the first step of the reaction. It can be considered that electron donating to the reaction centre favours the heterolysis of the CN linkage but hinders the formation of the new bond with the nucleophile. Bond breaking is approximately as important as bond making in the rate-determining step, and substituents have an effect on both processes in opposite directions (Scheme 2) (*14*). This result agrees well with the mechanism of acid-catalyzed hydration of nitriles in homogeneous conditions (*3*).

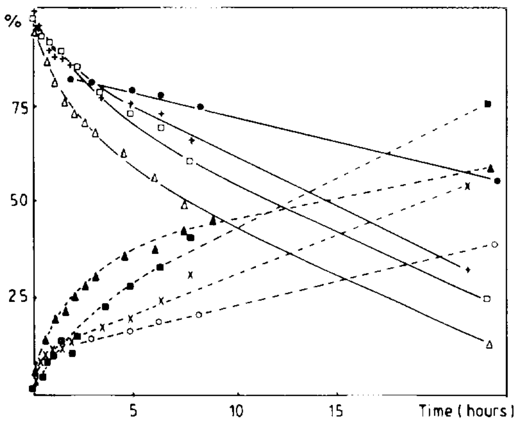
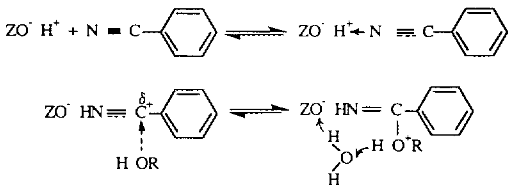


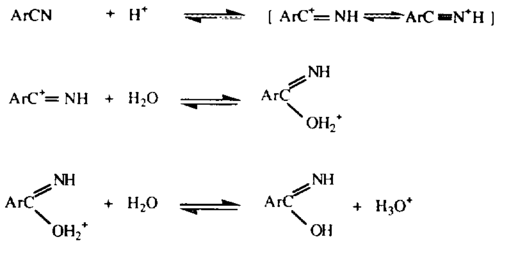
FIG. 8. Effect on reactivity of the change in nitrile structure over $Y_{2.5}$ zeolite, $T = 230°C$, in general conditions: (●) benzonitrile, (+) p-OCH_3 benzonitrile, (△) p-OH benzonitrile, (□) p-Cl benzonitrile, (○) ethyl benzoate, (×) ethyl-p-methoxybenzoate, (▲) ethyl-p-hydroxybenzoate, and (■) ethyl-p-chlorobenzoate.



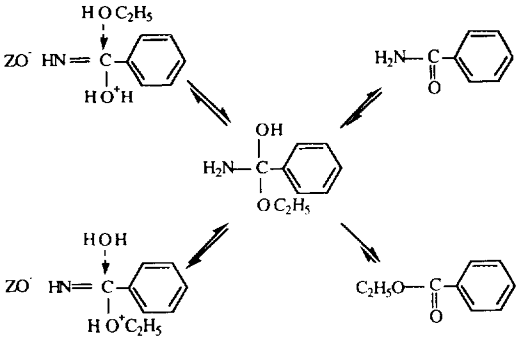
SCHEME 2

When the reactant functions as a nitrogen, sulphur or oxygen base, it seems likely that its protonation will usually be so rapid as not to be rate-determining (*29*). Thus, acid catalysis of nitrile hydration proceeds generally by a first rapid protonation step. The nucleophilic attack would in all probability be rate-determining (*30*). Possibly the best interpretation for the rate-determining step is a concerted process in which nucleophilic attack by water on the protonated nitrile, in a second step, is coupled with deprotonation by another water molecule in a consecutive step (Scheme 3).

The mechanism for nitrile reaction over acidic zeolites implies an equilibrium be-



SCHEME 3



SCHEME 4

tween the reactant and its conjugate acid at the surface of the catalyst. The correlation between the initial rate and the number of strong Brønsted-acid sites (Fig. 1) is consistent with a steadily increasing proportion of the protonated nitrile. The adsorption of nitriles on zeolites has been studied. The polarity of the CN bond results in a strong interaction, with the hydroxyl groups of the zeolite, readily detectable by IR spectroscopy (*31*). However, in homogeneous conditions, extensive protonation of nitriles occurs only in pure sulfuric acid (*32*). Attack of the nucleophile proceeds on the protonated nitrile adsorbed onto the catalyst leading to a transition state with a delocalized charge. Before desorption faster ethanolysis or hydrolysis can take place, leading to the products ester and amide (Scheme 4).

Alternatively, another molecule of water or ethanol can operate for catalyst regeneration (Scheme 2). These results emphasize the similarities that exist between zeolites and liquid acids (*33*).

Various studies on ester or amide hydrolysis, by an A2 mechanism, are in agreement with the above result. Thus, as for the acid-catalyzed hydrolysis of esters, substitution in the *meta* and *para* positions of benzamide has only a small effect on the rate regardless of polarity (*29*), lending further support to the mechanism suggested in heterogeneous catalysis.

In the second phase, the conversion is enhanced for *para*-substituted nitriles (Fig. 8). *Para* substitution of aromatic compounds by electron-withdrawing substituents (Cl) lowers amide basicity and, therefore, the adsorption constant on the Brønsted acid sites. The contrary is known for electron-donating substituents (OCH_3, OH). For *p*-OH and *p*-OCH_3 benzamides it can be considered that adsorption by the hydroxyl or the methoxy group lowers the basicity of the amide and hence, the deactivation of the strong acid sites of the zeolite by the formed amide diminishes. The formation of the ester is enhanced over the $Y_{2.5}$ catalyst.

There exist different routes to N-alkyl carboxyamides. In most of the reactions, a carboxylic acid is converted to a more reactive intermediate, e.g., the ester, which reacts with an amine. At this stage of our knowledge we consider that N-alkyl amides are obtained, by a consecutive way, from the acid or the ester (*34*) and N-alkyl amines. These amines can be formed in an acid-catalyzed process from the evolved ammonia and ethanol (*35*).

CONCLUSIONS

In the present work we have shown that acidic faujasites permit the one-pot synthesis of ethyl esters from nitriles in liquid ethanolic medium. A good correlation is obtained between nitrile reactivity and strong acidity evaluated by thermodesorption of ammonia. The reaction is broken into two steps. In a first step, catalytic activity is proportional to the strong Brønsted acidity. The reaction is first order with respect to nitrile and zero order with respect to ethanol and water concentration. Competitive attack of the two nucleophiles takes place. In a second step inhibition of nitrile reactivity by the amide is effective depending on the acid strength distribution of the zeolite. A consecutive pathway for ester formation is proposed. Taking into account these results, we have shown that the more effective zeolite for ester production with good selectivities is the less acidic $Y_{2.5}$ catalyst. The study of the mechanism indicates that, as in homogeneous conditions, the rate-limiting step is the nucleophilic attack on the protonated nitrile. The conversion depends mainly on the amide structure and, consequently on the nitrile structure.

REFERENCES

1. (a) Venuto, P. B., and Landis, P. S., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 18. p. 259. Academic Press, London and New York, 1968; (b) van Bekkum, H., and Kouwenhoeven, H. W., *in* "1st International Symposium on Heterogeneous Catalysis and Fine Chemicals, Poitiers, France, 1988;" *Stud. Surf. Sci. Catal.* **41,** 45 (1988); (c) Hölderich, W. F., *in* "1st International Symposium on Heterogeneous Catalysis and Fine Chemicals, Poitiers, France, 1988;" *Stud. Surf. Sci. Catal.* **41,** 83 (1988).

2. (a) Chiche, B., Finiels, A., Gauthier, C., Geneste, P., Graille, J., and Pioch, D., *J. Org. Chem.* **51,** 2128 (1986); (b) Pardillos, J., Brunel, D., Coq, B., Massiani, P., De Ménorval, L. C., and Figueras, F., *J. Am. Chem. Soc.* **112,** 1313 (1990).

3. Schaefer, F. C., *in* Rappoport H., "The Chemistry of The Cyano Group" (S. Pataï, Ed.). Interscience, New York, 1970.

4. Geneste, P., Kamenka, J. M., and Dessapt, P., *Bull. Soc. Chim. Fr.,* 187 (1980).

5. Wiberg, K. B., *J. Am. Chem. Soc.* **75,** 3961 (1953); **77,** 2519 (1955).

6. Taillades, J., Rousset, A., Laspéras, M., and Commeyras, A., *Bull. Soc. Chim. Fr.* **II,** 650 (1986).

7. (a) Hayashi, H., Nishi, H., Watanabe, Y., and Okazaki, T., *J. Catal.* **69,** 44 (1981); (b) Ravindranathan, M., Kalyanam, N., and Sivaram, S., *J. Org. Chem.* **47,** 4812 (1982); (c) Hirai, H., Wakabayashi, H., and Komiyama, M., *Bull. Chem. Soc. Jpn.* **59,** 545 (1986); (d) Sugiyama, K., Miura, H., Watanabe, Y., Ukai, Y., and Matsuda, T., *Bull. Chem. Soc. Jpn.* **60,** 1579 (1987); (e) Lee, J. C., Cant, N. W., Trimm, D. L., and Wainwright, M. S., *Appl. Catal.* **57,** 215 (1990); (f) Mseddi, S., Figueras, F., Moreau, C., and Pich, R., *in* "1st French-Maghreb Colloquium on Catalysis, Hammamet, Tunisie, 1990," in press.

8. Liu, K. T., Shih, M. H., Huang, H. W., and Hu, C. J., *Synthesis* **9,** 715 (1988).

9. Sugiyama, K., Miura, H., Nakano, Y., Suzuki, H., and Matsuda, T., *Bull. Chem. Soc. Jpn.* **60,** 453 (1987).

10. Konuma, K., Kaneko, T., and Nakanishi, A., *Jpn. Kokai Tokkyo Koho,* J.P. 62, 201, 853, 1987 [Amer. Chem. Abstr. 110 74838 r.]

11. Dzkumakaev, K. K., Isakov, Y. I., Fedolyak, G. T., Minachev, K. M., Isakova, T. A., and Kagarlitskii, A. D., *Kinet. Katal.* **28**(4), 856 (1987).

12. Miura, H., Hattori, T., Keitoku, K., Sugiyama, K., and Matsuda, T., *Nippon Kagaku Kaishi* **4,** 692 (1982).

13. Neilson, D. G., *in* "The Chemistry of Imidates and Amidines" (S. Pataï, Ed.), p. 422. Wiley, New York, 1975, and references therein.

14. March, J., *in* "Advanced Organic Chemistry," p. 792. Wiley, New York, 1985.

15. De Wolfe, R. H., and Augustine, F. B., *J. Org. Chem.* **30,** 699 (1965).

16. Smith, C. R., and Yates, K., *J. Am. Chem. Soc.* **94,** 8811 (1972).

17. Finiels, A., Geneste, P., Laspéras, M., Marichez, F., and Moreau, P., *in* "2nd International Symposium Heterogeneous Catalysis and Fine Chemicals, Poitiers, France, 1990"; *Stud. Surf. Sci. Catal.* **59,** 565 (1991).

18. Wadlinger, R. L., Kerr, G. T., and Rosinski, E. J., U.S. Patent 3,308,069 (1967).

19. Corma, A., *Stud. Surf. Sci. Catal.* **52,** 1 (1989).

20. Gao, Z., and Tang, Y., *Acta Chim. Sin.* **48,** 632 (1990).

21. (a) Mortier, W. J., *J. Catal.* **55,** 138 (1978); (b) Dwyer, J., *Stud. Surf. Sci. Catal.* **37,** 333 (1988); (c) Dwyer, J., *in* "Zeolite Microporous Solids: Synthesis, Structure and Reactivity" (E. G. Derouane, F. Lemos, C. Naccache, and F. R. Ribeiro, Eds.), NATO ASI Series C, Vol. 352, p. 303. Kluwer, Dordrecht, 1992.

22. Climent, M. J., Corma, A., Garcia, H., Iborra, S., and Primo, J., *Stud. Surf. Sci. Catal.* **59,** 557 (1991).

23. Boulet, M., Thesis, University of Montpellier II, France, 1990.

24. Lequitte, M., Figueras, F., Moreau, C., and Hub, S., *Appl. Catal. (A)* **84,** 155 (1992).

25. Ref. (*14*), p. 220.

26. Santilli, D. S., and Zones, S. I., *Catal. Lett.* **7,** 383 (1990).

27. Parker, L. M., Bibby, D. M., and Miller, I. J., *J. Catal.* **129,** 438 (1991).

28. Ref. (*14*), p. 507.

29. Long, F. A., and Paul, M. A., *Chem. Rev.* **57,** 935 (1957).

30. Ref. (*3*), p. 260.

31. Rabo, J. A., *in* "Zeolite Chemistry and Catalysis," ACS Monograph No. 171, p. 222. American Chemical Society, Washington, DC, 1976.

32. Liler, M., "Reaction Mechanisms in Sulfuric Acid and Other Strong Acid Solutions," p. 205. Academic Press, London/New York, 1971.

33. Coq, B., Durand, R., Fajula, F., Moreau, C., Finiels, A., Chiche, B., Figueras, F., and Geneste, P., *Stud. Surf. Sci. Catal.* **41,** 241 (1988).

34. (a) Nordahl, A., and Carlson, R., *Acta Chem. Scand. Ser. B* **42**(1), 28 (1988); (b) Castro, E. A., and Ureta, C., *J. Org. Chem.* **55,** 1676 (1990).

35. Rusek M., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), Vol. 3, p. 1138. The Chemical Institute of Canada, Ottawa, 1988.