

Modified Faujasite Zeolites as Catalysts in Organic Reactions: Esterification of Carboxylic Acids in the Presence of HY Zeolites

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Three partially exchanged NaHY and four dealuminated HYD zeolites have been studied as catalysts for the esterification of phenylacetic and benzoic acids with ethanol, isopropanol, tert-butanol, and *p*-cresol. From the results obtained it can be concluded that the optimum zeolite catalysts for this reaction must have a framework Si/Al ratio of greater than 15. These materials make it possible to overcome homogeneous equilibrium limitations, and show an average catalytic activity per proton very similar to that of sulfuric acid. The operating mechanism likely involves as the first step a fast protonation of the carboxylic acid, which is strongly adsorbed on the surface of the zeolite. From a preparative point of view, HY zeolites have been found especially valuable for the direct esterification of phenols with carboxylic acids. © 1989 Academic Press, Inc.

INTRODUCTION

The use of solid acid catalysts in organic reactions is a field of current interest (1, 2). Although zeolites have been largely employed in petrochemical processes (3), only in the last few years has wide attention been paid to these materials as acid catalysts for synthetic organic reactions (4, 5).

Besides the general advantages associated with solid catalysts, zeolites can be synthesized with different crystalline structure, acid exchange level, and framework Si/Al ratio, which allow design of those catalytic properties that depend mainly on pore size, acid strength distribution, and hydrophobicity, respectively.

The aim of the present study is to establish the relationship between the characteristics of HY zeolite and its catalytic activity in the esterification of carboxylic esters. A more precise understanding of the factors governing the catalytic properties of these inorganic materials has been obtained, and some progress has been made in the design of more adequate zeolites for general organic syntheses.

EXPERIMENTAL

Materials

The partially exchanged NaHY zeolites, where the number indicates the percentage of Na⁺ removed, were prepared starting from a NaY (SK-40, Union Carbide zeolite) in the following way.

The HY-21 zeolite was obtained by treating NaY with a 0.25 M solution of ammonium acetate, using a liquid-to-solid weight ratio of 4:1 at 25°C for 30 min, followed by drying at 110°C during 6 h and ulterior calcination at 550°C for 3 h.

The HY-50 zeolite was prepared from HY-21 by further exchange with 0.4 M aqueous solution of ammonium acetate and subsequent drying and calcination as above.

The HY-90 zeolite was obtained from the HY-50 by further exchange with 0.60 M aqueous ammonium acetate and a final deep bed calcination at 550°C for 3 h.

The series of dealuminated zeolites (HYD1-4) were achieved by dealumination with SiCl₄ (6, 7) and their unit cell size determined following a procedure previously described (7). The HYD samples were thoroughly washed with water and then ex-

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changed and calcined twice at the same conditions as those above.

The acidity of the zeolites by pyridine adsorption was measured in a Perkin-Elmer 580 B spectrophotometer equipped with a data station (8).

The water concentration in the solvent after 18 h reaction time with samples HY-90 and HYD-3 has been measured by the Karl-Fisher method. Water adsorption isotherms were performed on samples HYD-1 and HYD-4 at 100°C in a cahn microbalance.

Reaction Procedure

Before each experiment activation of the inorganic solids (1 g) was carried out by heating at 150°C under 1 Torr for 3 h, after which the system was cooled down to room temperature. Then a solution of the carboxylic acid and the alcohol or *p*-cresol in the corresponding solvent (50 ml) previously heated at the reaction temperature was poured onto the activated catalyst. The resulting suspension was magnetically stirred at the appropriate temperature. The course of the reaction was followed by gas chromatography until the ester yield ceased to increase. Then the catalyst was filtered and the solvent evaporated in vacuo.

Esterifications with sulfuric acid were carried out by heating a solution of phenylacetic acid (240 mg, 17 mmol) and ethanol (100 mg, 22 mmol) in chloroform (50 ml) at 61°C in the presence of 20 mg of H₂SO₄.

The gas chromatographic analyses were performed with a Perkin-Elmer 3920 B apparatus using a 1% SP-1240-DA column on 100:120 Supelcoport support. ¹H-NMR spectra were recorded in CDCl₃ solutions with a 60-MHz Varian 360 EM spectrometer, using TMS as an internal standard.

RESULTS AND DISCUSSION

In order to establish the influence of the catalysts we have chosen as a model reaction the esterification of phenylacetic acid with ethanol and performed this reaction in the presence of three partially exchanged Y

zeolites, HY-21, HY-50, and HY-90, as well as with a series of HYD zeolites with different framework Si/Al ratio. The main structural characteristics of the zeolites employed in our work are given in Table 1.

The advance of the reaction was periodically followed chromatographically at times ranging between 0.1 and 17 h. The final reaction mixture was also analyzed by ¹H-NMR. The initial reaction rates were calculated from the slope of the curves representing the yield of ethyl phenylacetate vs time.

The yields of ester obtained in the reaction of phenylacetic acid (1.7 · 10⁻² M) with ethanol (2.2 · 10⁻² M) in the presence of HY-21, HY-50, and HY-90 at four different reaction temperatures are summarized in Table 2.

From Fig. 1, where the initial esterification rates at 110°C are plotted vs the levels of Na⁺ removed from the zeolite, it can be seen that the catalytic activity does not increase linearly with the percentage of ion exchange. Since it is well known that HY zeolites have a wide distribution of acid strengths, this lack of linearity indicates that not all the protons introduced by exchange catalyze this reaction, but only the fraction which increases exponentially with the degree of sodium removal. On the other hand, it is obvious that not all acid-catalyzed reactions are equally demanding from the point of view of the acid strength of the catalytic sites.

TABLE I

Characteristics of the Dealuminated HY Zeolites

Zeolite	Unit cell size (Å)	Crystallinity (%)
HY-21	24.70	100
HY-50	24.70	100
HYD-1	24.45	100
HY-90	24.41	85
HYD-2	24.31	95
HYD-3	24.30	75
HYD-4	24.26	75

TABLE 2

Esterification of Phenylacetic Acid ($1.7 \times 10^{-2} M$) with Ethanol ($2.2 \times 10^{-2} M$) over HY Zeolites (1 g): $\text{PhCH}_2\text{COOH} + \text{CH}_3\text{CH}_2\text{OH} \rightleftharpoons \text{PhCH}_2\text{COOCH}_2\text{CH}_3 + \text{H}_2\text{O}$

Catalyst	Temperature (°C)	Solvent	Yield of ester ^a
HY-21	25	CHCl_3	0
	42	CH_2Cl_2	0
	61	CHCl_3	3
	110	$\text{C}_6\text{H}_5\text{-CH}_3$	32
HY-50	25	CHCl_3	0
	42	CH_2Cl_2	5
	61	CHCl_3	21
	110	$\text{C}_6\text{H}_5\text{-CH}_3$	69
HY-90	25	CHCl_3	0
	42	CH_2Cl_2	34
	61	CHCl_3	43
	110	$\text{C}_6\text{H}_5\text{-CH}_3$	20 ^b

^a Reaction time, 17 h.

^b 1-(4-methylphenyl)-2-phenylethanone (11%) was also present.

Therefore, in order to find out the requirements of this esterification we have measured the acid strength distribution in the three HY zeolites by means of the pyridine adsorption-desorption method based on the relative intensity of the IR band associated with pyridinium ions (1545 cm^{-1}) (8). The results obtained are represented in Fig. 2. Then, when the initial rate for esterification is plotted vs the relative intensity of the 1545-cm^{-1} band after pyridine evacua-

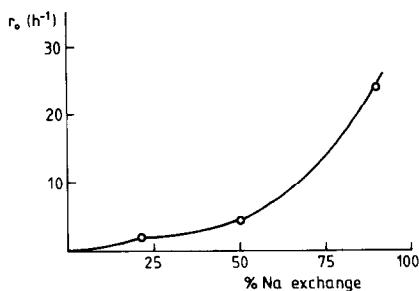


FIG. 1. Influence of Na^+ exchange level on the initial rate (h^{-1}) for the esterification of phenylacetic acid with ethanol at 110°C .

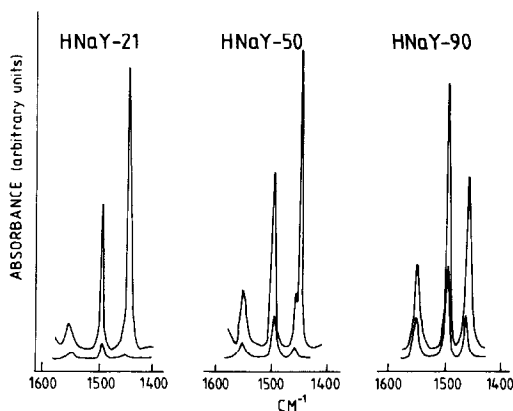


FIG. 2. Intensity of the 1545-cm^{-1} pyridinium IR bands of the three HY zeolites after desorption at 10^{-4} Torr at 180 and 350°C .

tion at 180°C and 10^{-4} Torr, which measures the pyridine adsorbed on Brønsted acid sites of medium and strong acidity (Fig. 3a), a correlation far from a straight line is observed. However, if the activity is related to the pyridine remaining after treatment at 350°C and 10^{-4} Torr (strong acid sites only), an almost linear correlation is obtained (Fig. 3b). We can then conclude that the esterification of phenylacetic acid by ethanol is catalyzed only by strong acid sites.

Taking into account the crystalline nature of the synthetic zeolites, it is possible to gain further knowledge of the characteristics of the specific sites involved in the esterification reaction. Indeed, it has been shown (9, 10) that the Brønsted acid strength of a given site decreases as the number of aluminums present on the second coordination sphere increases. Therefore, of all the different acid sites present in the zeolite, the strongest ones correspond to those where no aluminums are present as the next nearest neighbors (NNN). On the other hand, changes in the framework Si/Al ratio of the zeolite must produce variations in the relative number of the different centers with 0, 1, 2, 3, etc., aluminums as the NNN, and therefore it is clear that by dealumination of the zeolite, catalysts can be obtained where the relative number of

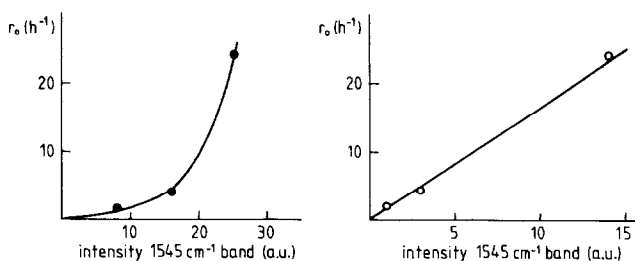


FIG. 3. Initial rates (h^{-1}) for esterification at 110°C of phenylacetic acid with ethanol catalyzed by HY zeolites versus the intensity of the pyridinium IR bands (1545 cm^{-1}) after desorption at 180°C and 10^{-4} Torr (●) or after desorption at 350°C and 10^{-4} Torr (○).

strong acid sites has been increased. Figure 4 shows the relative number of sites with different number of aluminums as the NNN vs the aluminums per unit cell for the HY zeolites.

In order to test the above point, esterification of phenylacetic acid with ethanol was also performed at 61°C in the presence of a series of zeolites (HYD) with different framework Si/Al ratios. Table 3 contains the turnover frequencies (TOF), which are calculated dividing the initial rates by the number of aluminums per unit cell.

In Table 3 it can be seen that a decrease in the number of aluminums per unit cell corresponds to an increase of the TOF up

to a certain value. Since the TOF is a measure of the average ability of the sites to catalyze a reaction, these results clearly show that zeolites with 9 or fewer aluminums per unit cell are much more active for the esterification of phenylacetic acid with ethanol. From the comparison of Fig. 4 with Table 3 it can be seen that with Al/unit cell ≤ 9 only the strongest acid sites, i.e., those aluminums supporting Brønsted sites with non and one aluminum as NNN, are present, and therefore these results corroborate what was observed above when working with NaHY zeolites, i.e., the esterification studied needs strong acid sites to be catalyzed.

Mechanism of the Reaction

The first step of all the mechanisms observed for the acid-catalyzed esterification

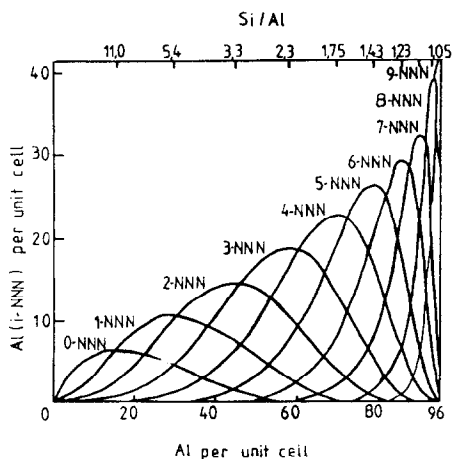


FIG. 4. Evolution of the proportion of the different types of Brønsted sites with the number of aluminums on the second coordination sphere (NNN) depending on the number of Al per unit cell.

TABLE 3

Esterification of Phenylacetic Acid ($1.7 \times 10^{-2} M$) with Ethanol ($2.2 \times 10^{-2} M$) in the Presence of a Series of HYD Zeolites (1 g) with Different Framework Si/Al Ratios at 61°C

Zeolite	Al/unit cell ^a	TOF (h^{-1} Al/u - c)
HYD-1	24	0.17
HY-90	20	0.19
HYD-2	9	1.55
HYD-3	8	1.87
HYD-4	3.5	2.28

^a Calculated from the unit cell size and Fitchner-Smittler's equation (19).

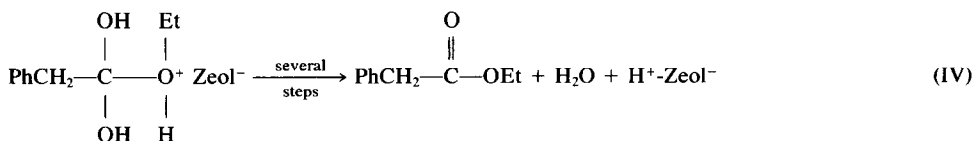
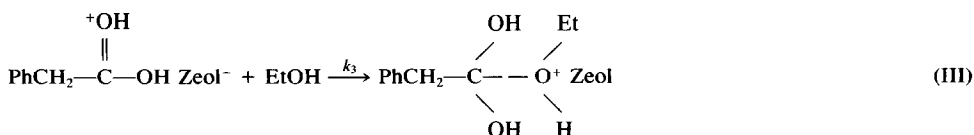
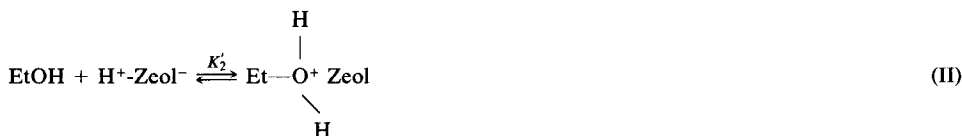
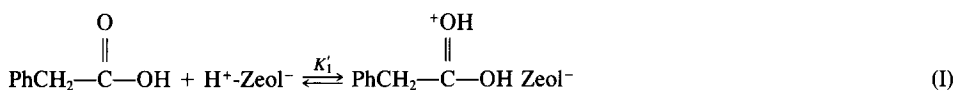
involves a fast protonation of one of the reagents, followed in subsequent steps by the nucleophilic attack of the other (11).

In the case of the zeolite-catalyzed esterification of phenylacetic acid, the reaction does not occur via protonation of the ethanol and subsequent attack on the acid. Indeed, it is well known that the dehydration of ethanol on acid zeolites can be catalyzed by sites of weak, medium, and strong acidity, and therefore the activity correlates very well with the global Sanderson's electronegativity of the zeolite (12). Thus, if protonation of ethanol is the initial step of the mechanism operating in our zeolite-catalyzed esterification, we should have found a linear correlation between the activity and the level of Na exchange, as well as a TOF independent of the framework Si/Al ratio. Since this is not the case, we must conclude that the initial step is the protonation of the acid. From thermodynamic data it can be inferred that protonation of a carboxylic acid would require strong acid sites, as in fact has been observed here.

Nevertheless, it is clear that the alcohol will compete with the phenylacetic acid for

the catalytic centers of the zeolite. This competition will tend to decrease the esterification rates and possibly favor other side reactions. Furthermore, taking into account the relative acidities of carboxylic acids and alcohols, it must be expected that in a nearly equimolar mixture of the reagents, most of the sites will be occupied by ethanol, unless the zeolite was able to stabilize the carboxylic acid by means of acid-base pairs present on the surface of the zeolite, thus enhancing the adsorption of the phenylacetic acid.

In order to progress in understanding the reaction mechanism, we have measured initial rates at different initial concentrations of ethanol and phenylacetic acid. A fast protonation step has been assumed and, therefore, the protonated species are assumed to be in equilibrium with the reagents on the surface of the zeolite. Then, from a Hougen-Watson-Langmuir-Hinshelwood formalism, Scheme 1 can be written as the reaction mechanism. Taking into account that the reaction will take place by an Eley-Rideal type process, i.e., a molecule of the adsorbed acid reacting with neu-



SCHEME 1. Mechanism of the esterification of phenylacetic acid with ethanol over HY zeolites.

tral ethanol in the liquid phase, and that the ethanol competes for the active sites, Eq. (1) can be written:

$$r = \frac{k_3[\text{H}^+ - \text{Zeol}^-]K'_1[\text{PhCH}_2\text{CO}_2\text{H}][\text{EtOH}]}{1 + K'_1[\text{PhCH}_2\text{CO}_2\text{H}] + K'_2[\text{EtOH}]} \quad (1)$$

If the initial rates are measured at different concentrations of ethanol while the concentration of phenylacetic acid is kept constant ($[\text{PhCH}_2\text{CO}_2\text{H}]_0$), and vice versa, Eq. (1) can be simplified and converted into Eqs. (2) and (3), respectively, where $a = [\text{H}^+ - \text{Zeol}^-]K'_1[\text{PhCH}_2\text{CO}_2\text{H}]_0$, $b = 1 + K'_1[\text{PhCH}_2\text{CO}_2\text{H}]_0$, $c = [\text{H}^+ - \text{Zeol}^-]K'_1[\text{EtOH}]_0$, and $d = 1 + K'_2[\text{EtOH}]_0$:

$$r_0 = \frac{k_3a[\text{EtOH}]_0}{b + K'_2[\text{EtOH}]} \quad (2)$$

$$r_0 = \frac{k_3c[\text{PhCH}_2\text{CO}_2\text{H}]_0}{d + K'_2[\text{PhCH}_2\text{CO}_2\text{H}]_0} \quad (3)$$

Linearization of Eqs. (2) and (3) yields Eqs. (4) and (5), where $m = b/k_3a$, $n = K'_2/k_3a$, $l = d/k_3c$, and $s = K'_1/k_3c$:

$$1/r_0 = m/[\text{EtOH}] + n \quad (4)$$

$$1/r_0 = 1/[\text{PhCH}_2\text{CO}_2\text{H}] + s \quad (5)$$

$$n/s = \frac{K'_2}{K'_1} \times \frac{[\text{EtOH}]_0}{[\text{PhCH}_2\text{CO}_2\text{H}]_0} \quad (6)$$

By least-squares fitting of the results given in Table 4 to Eqs. (4) and (5), the $K'_2/$

K'_1 ratio was calculated from Eq. (6), and the adsorption constant was found to be 1.6 times higher for phenylacetic acid than for the alcohol. This result clearly shows that the amount of protonated carboxylic acid on the surface of the zeolite is higher than the amount of protonated alcohol.

This fact could be explained if the existence of an acid-base pair effect were accepted. Thus, the adsorption of the acid is due not only to the protonation of the carbonyl group of the acid by the Brønsted sites of the zeolite, but also to the hydroxyl groups of the organic acid contributing to the adsorption by interaction with basic oxygen groups of the zeolite.

Another item which deserves consideration is the influence of the hydrophobicity of the dealuminated zeolites on the final yield of the ester obtained. Since the reported equilibrium constant for the reaction of acetic acid with ethanol in apolar solvents is 3.38 (13), and considering that in our case the α phenyl ring does not exert any appreciable inductive or mesomeric influence on the reaction, it could have been predicted that the equilibrium yield of phenylacetate here would be close to 65%. In order to establish a more valid comparison, esterification of the phenylacetic acid with ethanol was also carried out in chloroform using sulfuric acid as catalyst. In this case the ester yield extrapolated to zero reaction rate was found to be 69%. As can be seen from Fig. 5, if the same reaction is performed in the presence of highly dealuminated HYD-3, the yield obtained after 18 h is 87%, and the slope of the curve is still slightly positive.

Two hypotheses can be visualized to explain this behaviour. In the first one it is considered that the zeolite adsorbs the water formed and shifts the equilibrium to further hydrolysis. In the second, the hydrophobicity of the highly dealuminated zeolites (14) would play an important role in shifting the equilibrium. A consequence of this would be that the real reaction medium is the hydrophobic surface of the

TABLE 4

Initial Rates (h^{-1}) at 61°C Measured at Different Concentrations of Phenylacetic Acid and Ethanol

Concentration (mM)		Initial rate (h^{-1})
Phenylacetic acid	Ethanol	
35.2	21.7	2.8
35.2	43.5	3.8
35.2	87.0	4.3
35.2	174.0	6.6
70.4	43.5	4.1
140.8	43.5	4.8

Note. $n = 0.152$, $s = 0.198$.

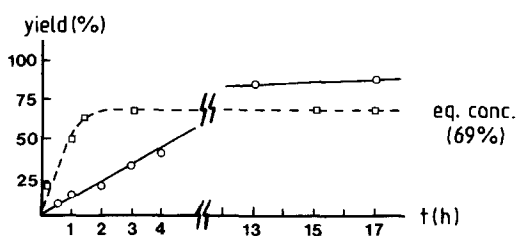


FIG. 5. Esterification of phenylacetic acid ($1.7 \times 10^{-2} M$) with ethanol ($2.2 \times 10^{-2} M$): HYD-3 (○); SO_4H_2 (□).

dealuminated zeolite, and the water concentration there would be very small. We have checked these two possibilities by measuring, on one hand, the water adsorption capacity of two zeolites dealuminated at different levels, and on the other hand, the water content in the solvent after 18 h of reaction, using as catalysts two zeolites dealuminated at different levels.

At 100°C and 300 Torr, the amounts of water adsorbed on zeolites HYD-1 and HYD-4 were 7.8 and 3.6 wt%, respectively, clearly indicating the increase in hydrophobicity upon dealumination. However, when the water content was analyzed in the solvent and in the solvent after reaction with HY-90 and with HYD-3, the amounts of water obtained were 0.04, 0.05, and 0.08 mg $\text{H}_2\text{O ml}^{-1}$ organic, respectively. From these results it appears that indeed the two zeolites are adsorbing a part of the water generated during the hydrolysis, even though the water in the organic phase is higher with the more dealuminated sample. We may then conclude that both factors, i.e., water adsorption by the zeolite and surface hydrophobicity, can influence the conversion values observed at long reaction times. In this way, the higher the Al content of the zeolite the more important will become the adsorption effect, while for zeolites with very low Al content the surface hydrophobicity can become the predominant factor in the shifting of the equilibrium.

Finally, it is worth mentioning that in the experiment carried out with sulfuric acid,

the catalytic activity per proton (initial rate divided by number of protons) was found to be $5.5 \times 10^4 \text{ h}^{-1} [\text{H}^+]^{-1}$, while for the HYD-3 zeolite the average activity per proton was $3.6 \times 10^4 \text{ h}^{-1} [\text{H}^+]^{-1}$, indicating that the average activity of all types of acid sites in this zeolite is very close to that of sulfuric acid, which is the catalyst most widely used for esterification reactions.

Influence of Structure of the Substrates on the Esterification

In order to determine the scope and potential of HY zeolites as catalysts in the preparation of carboxylic esters, we have carried out the esterification of phenylacetic and benzoic acids with ethanol, isopropanol, *t*-butanol, and *p*-cresol. Table 5 lists the results obtained under several conditions when these reactions are performed with nearly equimolar amounts of the reagents. While ethyl esters are readily formed using acid zeolites, the tert-butyl analogs could not be formed under any of the conditions used here. Isopropanol exhibits behavior intermediate between the primary and the tertiary alcohols, giving rise to isopropyl phenylacetate (conditions II in Table 5) but not to the corresponding benzoate.

These facts, and especially the reluctance of tert-butanol to undergo esterification, fit well into a reactive scheme where dehydration of the alcohol competes with the reaction with the carboxylic acid, as is well known to occur in homogeneous acid catalysis.

The presence of alkyl aromatic hydrocarbons as the only products when esterifications of isopropanol and tert-butanol were attempted in toluene at 110°C strongly supports the formation of intermediate carbenium ions, which is consistent with our mechanistic proposals (Scheme 2). The ability of these acid HY zeolites to catalyze electrophilic aromatic alkylations in related systems has been previously reported (15).

On the other hand, benzoic acid gives results similar to those of phenylacetic

TABLE 5

Heterogeneous Catalyzed Esterifications over HY Zeolites

Carboxylic acid (mM)	Hydroxy compound (43 mM)	Catalyst	Solvent	Temp. (°C)	Yield of ester (%)	Other products (%)
PhCH ₂ CO ₂ H (17)	Me ₂ CHOH	HY-50	Toluene	110	0	2-Cimene (13); 4-cimene (18)
			CHCl ₃	61	11	—
	Me ₃ COH	HY-50	Toluene	110	0	4-Tert-butyltoluene (25)
			CHCl ₃	61	0	—
	4-MeC ₆ H ₄ OH	HY-50	Toluene	110	35 ^a	—
			HYD-3	Toluene	110	20
PhCO ₂ H (20.4)	EtOH	HY-50	Toluene	110	5	—
	Me ₂ CHOH	HY-50	Toluene	110	0	2-Cimene (11); 4-cimene (15)
	Me ₃ COH	HY-50	Toluene	110	0	4-Tert-butyltoluene (31)
	4-MeC ₆ H ₄ OH	HY-50	Toluene	110	17 ^b	—

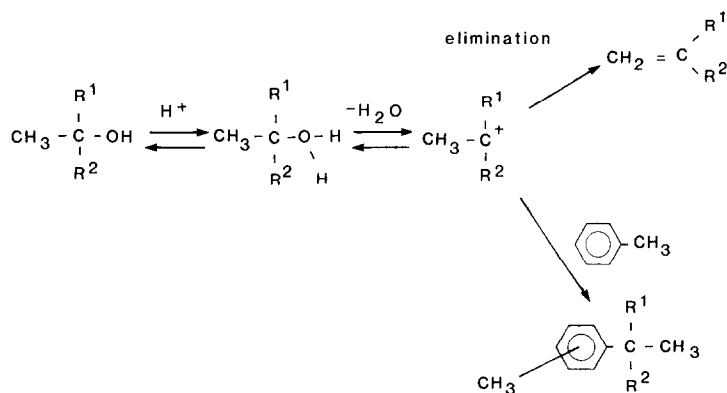
^a *p*-Cresol recovered, 61%.^b *p*-Cresol recovered, 81%.

acid, but the yields of benzoic esters are in all cases considerably smaller. This can be explained by the lower susceptibility to nucleophilic attacks of aromatic carbonyl groups due to the transfer of charge from the aromatic ring to the electron-deficient carbonyl carbon.

Finally, *p*-cresol reacts with phenylacetic and benzoic acids over HY-50 zeolite at 110°C, yielding the corresponding tolyl esters in moderate yields. It is noteworthy that the direct esterification of carboxylic acids with phenols under homogeneous acid catalysis is rarely used to pre-

pare aryl esters, due to the poor yields obtained. In addition, phenols may readily undergo aromatic electrophilic substitution with sulfuric acid and other acid catalysts, giving rise to undesired by-products. In this context it is especially worth mentioning the high selectivity observed for the formation of tolyl esters over HY-50 zeolite, indicating that esterification is the only process being catalyzed when dehydration cannot take place, as is the case with hydroxybenzenes.

In order to learn whether the formation of aryl esters can be increased and whether



SCHEME 2. Competitive reactions taking place on the HY catalyzed esterifications of carboxylic acids.

dealuminated HYD zeolites are the most active HY zeolite catalysts, esterification of *p*-cresol and phenylacetic acid was also carried out in the presence of HYD-3 at 110°C in toluene. As can be seen from Table 5, in addition to tolyl ester (20%), 1-(2-hydroxy-5-methylphenyl)-2-phenylethanone (16%) was also present in the final reaction mixture.

The selectivity curves (yields vs total conversion) for both products when the reaction is performed in the presence of HYD-3 are given in Fig. 6. They show that under these conditions the aryl ester is a primary and unstable product, while the *o*-hydroxyaryl ketone is a secondary one. These facts are consistent with an initial *o*-acylation of the *p*-cresol to give the ester, which in turn can undergo a 1,3-acyl migration leading to the aryl ketone. The intermediacy of aryl esters in other similar Friedel-Crafts acylations of phenols has been well established, and the Fries rearrangement of aryl esters to yield *o*- or *p*-hydroxyaryl ketones is in fact a reaction of substantial synthetic utility (16), which can be carried out with Lewis acids and Brønsted acids (17). The ability of Y zeolites to catalyze the related Friedel-Crafts acylations of aromatic hydrocarbons reactions has been previously reported (18).

CONCLUSIONS

In the present work we have shown that esterifications of carboxylic acids can be catalyzed by HY zeolites. Only the stron-

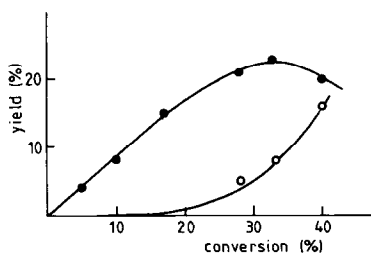


FIG. 6. Selectivity curves for the formation of tolyl acetate (●) and 1-(2-hydroxy-5-methylphenyl)-2-phenylethanone (○) at 110°C over HYD-3.

gest acid sites present in these materials, which correspond to those sites with non and one aluminums as next nearest neighbors, are active. The best materials are, therefore, obtained by dealuminating the zeolite to a framework Si/Al ratio of at least 15. These dealuminated materials have an average activity per acid site very similar to that found for sulfuric acid. Additionally these heterogeneous catalysts can overcome equilibrium limitations due to the hydrophobicity of their surfaces, where the concentration of water must be quite small. Finally, the reactivity pattern found in the HY zeolite catalyzed esterifications is the same as in homogeneous liquid phase esterifications. Changing from primary to tertiary alcohols or from aliphatic to aromatic carboxylic acid results in a decrease in the yield of ester. From a preparative point of view zeolite catalysts have been found to be especially valuable for the direct esterification of phenols.

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