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Influence of the Structural Parameters of Y Zeolite on the Transalkylation of Alkylaromatics

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A kinetic study of the transalkylation of *m*-xylene has been carried out on zeolites Y dealuminated at different levels and by two different procedures. For each sample the true kinetic rate constant, activation energy, adsorption constant, and entropy and enthalpy of adsorption have been obtained. These parameters, together with surface acidity characterization, have been used to discuss the reaction mechanism and the relative influence of different zeolite parameters on the reaction. © 1993 Academic Press, Inc.

INTRODUCTION

Fundamental catalytic studies on acid zeolites have the advantage with respect to other amorphous acid catalysts that the nature and structure of the acid sites are known in the former. One of the most important of the factors which control the carboniogenic activity of a zeolite is the number and distribution of Al atoms in the framework, since they control the number and strength of the associated Brønsted acid sites (*1*). Then, models have been derived to correlate framework Si/Al ratios with the distribution of Al in different surroundings, and these with an activity coefficient of the acid sites (*2*). Even though physicochemical technics such as NMR-MAS have strongly helped to give experimental evidence to accept or reject the different models, the final conclusions on their catalytic impact still rely on the use of test reactions.

However, due to the great experimental effort necessary when test reactions have to be applied properly, most of the authors compared catalyst activity on the basis, at most, of initial rates. It can be easily understood that in the initial rate, both adsorption and activity parameters are included. Therefore, if series of zeolites with different compositions have to be compared in order to see differences in the number and strength of acid sites, this comparison has to be carried out on the basis of kinetic parameters such as kinetic rate constant, true activation energy, and frequency factors.

In this work, the catalytic adsorption properties of two series of dealuminated Y zeolites for a bimolecular reaction, such as *m*-xylene transalkylation, are discussed on the basis of kinetic and adsorption parameters.

EXPERIMENTAL

Materials

A series of ultrastable Y zeolites (USY) were prepared by steam calcination of a NH_4NaY sample (80% Na exchanged) at 873 K, followed by two exchanges with NH_4^+ and ulterior steam treatment (100% steam) at 873–1023 K in order to obtain samples with different Si/Al frameworks (*3*) (Table 1). A second series of dealuminated Y zeolites (HYD) was produced by treating the original NaY sample (SK-40 Union Carbide) with $SiCl_4$ following a published procedure (*4*) at temperatures from 573 to 773 K in order to achieve different dealumination degrees (Table 1). The crys-

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TABLE 1

Physicochemical Characteristics of the Zeolite Samples

Sample	a_0 (Å)	Al/u.c.[a]	Framework Si/Al ratio[a]	Crystallinity (%)	Si/Al ratio[b]
HYD-1	24.55	36	4.3	100	1.87
HYD-2	24.43	22	7.7	100	2.25
HYD-3	24.35	13	13.8	85	2.75
HYD-4	24.29	7	29.0	85	
HYD-5	24.25	2	99.0	85	5.99
USY-1	24.55	36	4.4	100	2.40
USY-2	24.47	27	6.2	90	2.80
USY-3	24.36	14.8	12.0	90	2.70
USY-4	24.28	6	31.0	80	2.40

[a] Al per unit cell (u.c.) calculated from Fichtner-Schmittler equation (5).

[b] From chemical analysis.

tallinity of the samples was determined by XRD from the intensity of the [5,5,3] reflection peak using the NaY as reference. The framework Al content was deduced from the value of the unit cell size (a_0), using the correlation found by Fitchner-Schmittler *et al.* (5). The number of framework Al per unit cell and the crystallinities of the different samples are given in Table 1.

Infrared spectroscopic measurements were carried out in a convectional greaseless IR cell. Wafers of 10 mg · cm^{-2} were pretreated overnight at 400°C and 1.33×10^{-2} of Pa of dynamic vacuum. The spectra in the 4000–3300 cm^{-1} region were recorded at room temperature on a Perkin–Elmer 580B spectrophometer equipped with Data Station. For the pyridine adsorption experiments 666 Pa of pyridine was introduced into the cell at room temperature. After equilibrium the samples were outgassed at temperatures in the range 250–400°C under vacuum, and the spectra recorded at room temperature. Looking by IR at the HF and LF hydroxyl groups restored after desorption of pyridine at a given temperature, one can deduce the acidic sites which are not strong enough to retain the pyridine. Meanwhile, the difference between the spectra corresponding to HF and LF hydroxyls of the original zeolite before adsorbing pyridine and the spectra of the restored hydroxyls upon pyridine desorption does give acid sites strong enough to retain pyridine at a given temperature.

Catalytic Experiments

The catalytic experiments were carried out in a fixed bed, continuous, glass reactor. The dimensions of the reactor are 1.4×10^{-2} and 0.12 m internal diameter and length, respectively. *m*-xylene (0.037–0.216 mmol · s^{-1}), 99.5% purity (Scharlau), was fed by a positive displacement pump in a preheater zone together with N_2 (99%). The partial pressure of *m*-xylene was varied by changing the *m*-xylene/N_2 molar ratio between 0.1 and 4. The catalyst amounts used were varied between 15 and 500 mg in order to adjust the conversion levels.

When the catalyst was introduced into the reactor, air was passed through while increasing the temperature up to 723 K, and keeping this temperature for half an hour. Then, air was changed to N_2 and the temperature was conducted to the desired reaction temperature. When stabilized, *m*-xylene was fed, and accumulated liquid samples were taken at 30, 60, 120, 180, 300, and 420 sec. The analysis was carried out by G.L.C. using a packed column with 16% DC-200 methyl silicone oil and 3% Bentone 34 on 80–100 mesh Chromosorb W., in a Konic-200 C G.C. with F.I.D. detector. The conversion at zero time on stream, i.e., in the absence of deactivation, was obtained analytically by the decay equation

$$X = X_0 \exp(-k_d t^{1/2}), \qquad (1)$$

where X_0 is the conversion at zero time and k_d is the deactivation constant.

Preliminary experiments were done in order to establish the conditions in which no control by external or internal diffusion exists. From these experiments the following experimental conditions were selected: *m*-xylene flows greater than 0.037 mmol · s^{-1} and a catalyst particle size between 0.59 and 0.82 mm.

Initial rates were obtained from conversion values smaller than 8% by fitting conversion versus contact time to the equation

$$X_0 = r_0(W_{cat}/F_0). \quad (2)$$

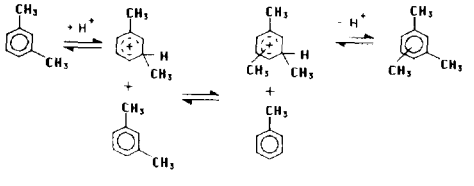
In this way, initial rates at different partial pressures of *m*-xylene (0.08–0.8 atm), and different temperatures (513–593 K) were obtained for each zeolite catalyst sample. The fitting of the experimental data to the different kinetic equations was carried out using as the optimization criterion the minimization of the square of the relative deviation between the experimental and calculated values. The nonlinear Marquardt's algorithm (*6*) was used to calculate the parameters; the mean relative deviation (MRD) and the Exner parameter (*7*) were used as statistical tests for the fitting.

RESULTS AND DISCUSSION

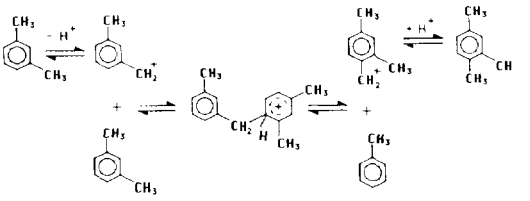
Reaction Scheme and Kinetic Models for m-Xylene Transalkylation

When secondary carbocations can be formed in the alkyl chains, then SN1 and SN2 transalkylation can occur (*8*). However, in the case of methyl groups, transalkylation only occurs by an SN2 mechanism (*9*), since an SN1 would imply the formation of unstable methenium ions. On these bases, two reaction schemes have been proposed in the literature. The first one (I) (*10, 11*) assumes that the methyl group of a substituted benzenium ion suffers a nucleophilic attack by another aromatic molecule and the methyl group is transferred to give a trisubstituted ionic species.

A second scheme (II) implies bencilium carbocations in diphenylalkane intermediates (*12–15*).



SCHEME I



SCHEME II

The formation of the different diphenilalkanes intermediates is limited by the nonsubstituted positions in the benzenic ring of the particular xylene. Consequently, this determines the trimethylbenzene isomers formed as primary products. In the case of the *m*-xylene studied here, any of the trisubstituted isomers can be obtained from the intermediate diphenylalkanes (*16*).

In any case, and from the proposed reaction intermediates, it becomes evident that a second-order kinetic equation should be applied. Then, and from a Langmiur–Hinselwood formalism (*17*), there are two possible bimolecular models:

(a) The two-site Langmuir–Hinselwood mechanism assumes that the reaction occurs between two adsorbed molecules, and under initial conditions, the corresponding kinetic equation can be written as

$$r_0 = \frac{k_0(Kp_0)^2}{(1 + Kp_0)^2}. \quad (3)$$

(b) An Eley–Rideal type mechanism considers that the reaction takes place between one adsorbed molecule and another in the gas phase. This can be translated into the kinetic expression

$$r_0 = \frac{k_0 K p_0^2}{(1 + Kp_0)}, \quad (4)$$

where k_0 is the kinetic rate constant, K is the equilibrium adsorption constant, p_0 is the initial partial pressure of *m*-xylene, and r_0 is the initial rate constant.

Extrapolating to the limit of the Langmiur–Hinselwood model and taking into account that Brønsted acids are the active sites for transalkylation, one would

have to assume that the reaction occurs between two molecules of xylene adsorbed on two Brønsted acid sites and therefore between two close carbocations. This assumption, which seems quite improbable, could be better interpreted by considering that the reaction occurs between one adsorbed carbocation and another molecule "retained" within the strong electric fields existing in the interior of the zeolite structure. In other words, the Langmiur–Hinselwood model will emphasize the importance of the adsorption characteristics of the zeolite with respect to an Eley–Rideal model.

When the initial rates for *m*-xylene transalkylation were obtained at different partial pressures (Figs. 1 and 2), and fitted to the models given in Eqs. (3) and (4) (see as an example the values obtained at 553 K which are given in Table 2), the high relative errors, as well as the fact that negative adsorption constants are obtained for most catalysts when using Eq. (4), made us reject the Eley–Rideal model as the most probable for the transalkylation of *m*-xylene. On the other hand, good fits are obtained with Eq. (3), and the kinetic parameters obtained are given in Tables 2 and 3.

Other transalkylation processes between alkylaromatics such as toluene (*18*) or 1,3,5 trimethylbenzenes (*19*) have also been correctly fitted by the Langmuir–Hinselwood model. Nevertheless, and despite the fact that the benzene ring can delocalize the

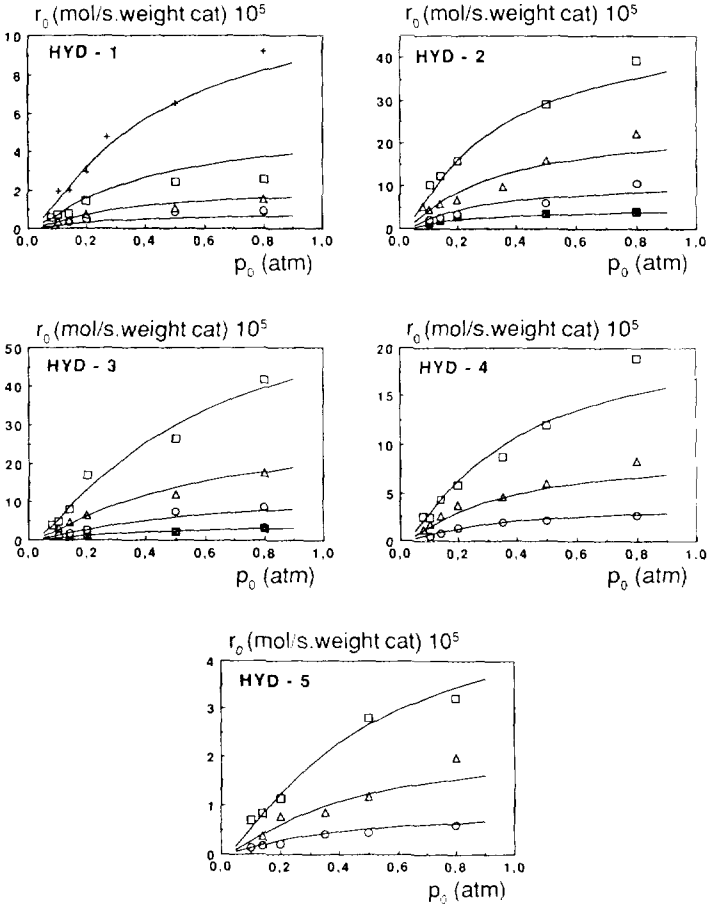


FIG. 1. Initial rates (r_0) as a function of partial pressures at several temperatures (■, 513; ○, 533; △, 553; □, 573; +, 593 K), for HYD samples. The curves are calculated from Eq. (3).

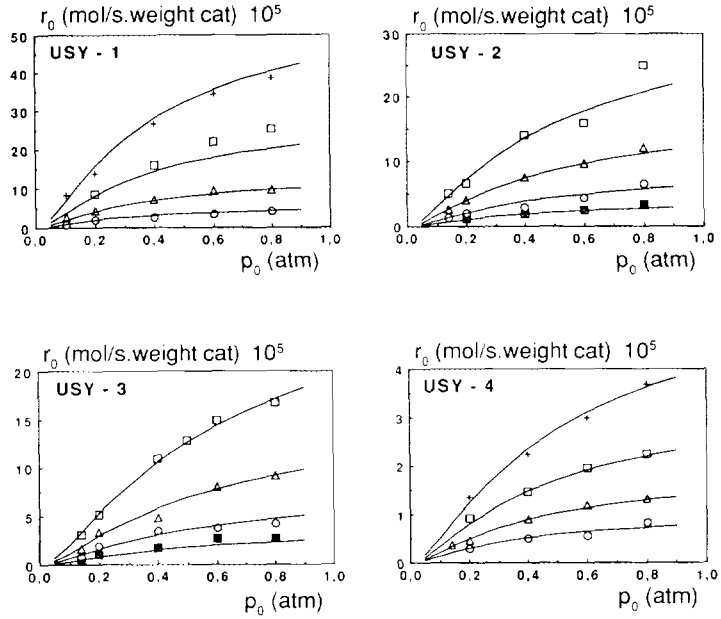


FIG. 2. Initial rates (r_0) as a function of partial pressures at several temperatures (■, 513; ○, 533; △, 553; □, 573; +, 593 K), for USY samples. The curves are calculated from Eq. (3).

positive charge, we have to assume that the interaction of two adsorbed xylene molecules necessary to form the diphenylalkane intermediate does not require that both molecules be adsorbed on Brønsted acid sites to form stable carbocations, since then the electric repulsion would make the reaction quite improbable.

Kinetic rate and adsorption constants, together with activation energies, heats of adsorption, preexponential activation factors, and entropies of adsorption have been calculated, and the influence of the zeolite composition factors can be discussed on the basis of these parameters.

TABLE 2

Kinetic Parameters and Statistical Parameters for the Best Fits to the Langmuir–Hinshelwood or Eley–Rideal Models, at 553 K

Sample	Langmuir–Hinshelwood				Eley–Rideal			
	Corr	MRD%	$k_0 \times 10^5$	K	Corr	MRD%	$k_0 \times 10^5$	K
HYD-1	0.9803	4.54	2.24	6.51	0.8758	11.44	1.92	−18.92
HYD-2	0.9694	7.37	24.50	7.23	0.9456	5.79	11.88	−21.14
HYD-3	0.9983	4.23	27.07	6.28	0.4066	12.03	13.17	52.23
HYD-4	0.9926	4.04	9.73	6.05	0.5775	15.07	12.06	−38.97
HYD-5	0.9584	7.88	2.39	5.02	0.4374	13.14	2.35	−35.13
USY-1	0.9916	2.49	14.43	5.67	0.8250	13.42	13.35	−18.37
USY-2	0.9740	5.67	18.55	4.25	0.7754	9.17	6.94	−22.70
USY-3	0.9652	8.23	16.91	3.55	0.8384	11.14	5.17	−10.06
USY-4	0.9878	4.68	3.31	2.99	0.8181	7.05	1.73	−10.40

Note. k_0 (mol/s · weight cat); K (atm $^{-1}$); MRD (mean relative deviation); Corr (correlation coefficient).

TABLE 3

Activation Energy, Adsorption Entropy, Adsorption Heat, and Preexponential Factor for the Best Fits to the Langmuir–Hinshelwood Model

Sample	Kinetic		Adsorption		Statistical values	
	$A \times 10^{-3}$	E	ΔS_{ad}	ΔH_{ad}	MRD%	Ψ (Exner)
HYD-1	414.30	119.4	−18.1	−18.6	18.8	0.21
HYD-2	250.20	95.5	−11.1	−15.2	15.3	0.20
HYD-3	457.90	107.7	−1.8	−7.4	9.7	0.16
HYD-4	447.00	113.0	−7.7	−12.5	12.4	0.25
HYD-5	240.50	116.6	−28.0	−22.9	12.8	0.20
USY-1	50.55	101.5	−3.9	−10.1	10.6	0.17
USY-2	2.01	85.1	0.5	−6.4	8.3	0.22
USY-3	2.13	85.8	−3.4	−7.7	10.9	0.09
USY-4	1.20	90.6	−15.3	−13.5	7.4	0.16

Note. A (mol/s · weight cat); E and ΔH_{ad} (kJ/mol); ΔS_{ad} (J/K · mol). Statistical values obtained for all data in each sample.

Influence of the Zeolite Al Content on the Catalytic Activity

As said above, it has been reported that the framework Al content of the zeolite (FAL) was the main parameter controlling its carboniogenic activity (*20*). However, in the last few years, some authors have shown that this framework Al cannot be the only parameter, since the presence and type of extraframework Al (EFAL) can influence the final activity and selectivity (*3*, *21*).

In the case of xylene transalkylation, if the framework Al were the only factor controlling activity then, regardless of the dealumination procedure used, only one k_0 versus Al/unit cell (u.c.) curve would be obtained. This is not the case, as can be seen in Fig. 3, where, in general, HYD samples are shown to be more active than USY. Two factors may be responsible for this. The first one could be related to a lower accessibility of the acid sites in the USY series due to the presence of a higher amount of EFAL. In order to evaluate the importance of this, transalkylation of *m*-xylene was carried out on a USY sample (27 Al/uc) in which most of the EFAL was removed without practically changing the framework Al content (24 Al/uc) by a selective treatment with NH_4F_6Si (*22*). After this, the activity did not increase, but decreased; consequently, we do not think that possible plugging due to EFAL is the main factor responsible for the lower activity of the USY series.

Recently, it has been shown (*23–26*) that due to the presence of EFAL, very strong Brønsted acid sites with hydroxyls vibrating at 3610 cm^{-1} appear, and their activity is higher than that of the high- and low-frequency classical hydroxyl groups. When

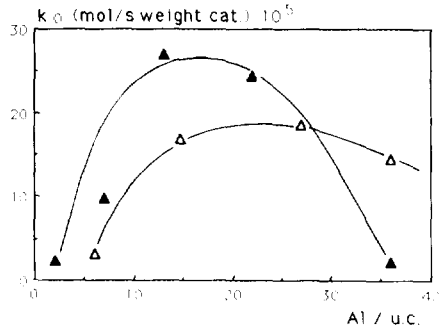


FIG. 3. Kinetic constant as a function of framework aluminum fraction in samples HYD (▲) and USY (△) at temperature of 553 K and initial partial pressure of 0.2 atm.

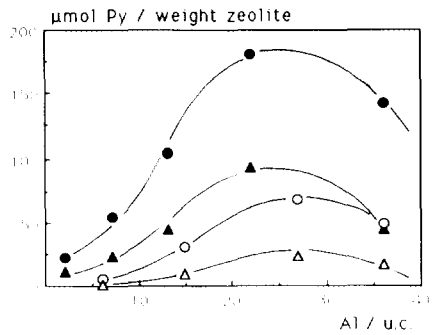


FIG. 4. Brønsted acidity of dealuminated Y zeolites as a function of framework aluminum per unit cell. In circles, pyridine retained after desorption at 623 K and vacuum (●, HYD, ○, USY). In triangles, pyridine retained after desorption at 673 K and vacuum (▲, HYD; △, USY).

the amount of these sites is plotted for the two series of dealuminated zeolites, it can be seen in Fig. 4 that a higher amount of the very strong acid sites is present in the HYD series. This, together with the fact that a smaller number of hydroxyl groups are compensated by cationic EFAL in $SiCl_4$ than in steam dealuminated samples (*24*), can explain the higher activity of the HYD with respect to USY series.

Influence of the Zeolite Al Content on the Energetic Parameters

Activation energy. The activation energies found (Table 3) indicate that the formation of the activated complex requires energies on the order of 80–119 kJ/kmol, which are in the same range as the protolytic cracking of short chain alkanes (*27*) and sensibly higher than the energies involved in the alkylation of benzene or toluene by alcohols or olefins (*28*). This would be an indication that the controlling step of the transalkylation of *m*-xylene would be the formation of the primary alkyl carbocation. It must be, however, considered that in this case this primary carbenium ion is stabilized by the delocalization of the positive charge through the aromatic ring.

It has been proposed (*29*) that when using test reactions, the activation energy of the chemical reaction step can be used as an index of the zeolite acid strength, which at the end should be related to the framework Al distribution (*30, 31*). In the case of zeolite Y, and after Beaumont and Barthomeuf's works (*1, 32, 33*), the acid strength of the remaining sites upon dealumination should increase up to a framework Si/Al of 6 and then stay constant. If this is so, the activation energy for a reaction needing strong acidities, as the one studied here, should decrease upon dealumination up to samples with a framework Si/Al ratio of 6, and then remain constant if dealumination proceeds further. This could indeed be expected if only the framework Al were responsible for the observed acidity. In our case, the evolution of the stronger acid sites, which may have a higher impact than the acid sites associated with the conventional HF and LF hydroxyls on the resultant activity, changes in the way presented in Fig. 4 and the evolution of the activation energy for *m*-xylene transalkylation is consistent with this (Fig. 5).

These results, while showing the important role of EFAL in this reaction, also indicate that the density of the acid sites strong enough to carry out a given process strongly determines the activation energy of the process as demonstrated in several kinetic studies (*34–37*). Nevertheless, special attention should be paid to the activation energy values reported in the literature, since in many cases only apparent

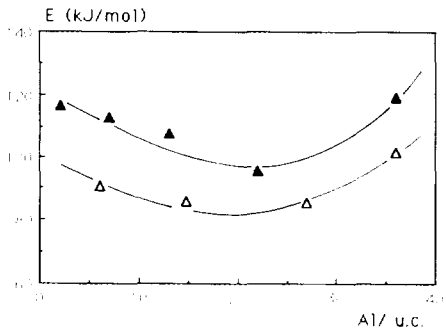


FIG. 5. Activation energy as a function of framework aluminum fraction for the dealuminates samples HYD (▲) and USY (△).

activation energies are given. In those cases, it is not infrequent to find that the apparent activation energy is much less sensible to catalyst modifications (*38–40*). This may be due to the fact that, in many cases a partial compensation between the true activation energy and the heat of adsorption occurs in a series of catalysts.

Adsorption equilibrium constant and heat of adsorption. Several authors (*41, 42*) have shown the utility of adsorption data calculated from kinetic measurements, since from these it is possible to discuss the type of mechanism, the validity of the elementary steps which made it possible to establish the kinetics of the process, surface coverage, surface heterogeneity, variations in the heat and entropy of adsorption with the surface coverage, etc. It is very rare, however, to find in the literature full kinetic studies which allow one to discuss this (*37, 43, 44*). Nevertheless, when it has been done it has always been found that catalyst modifications also produce changes in their adsorption properties. It is therefore quite surprising to find that this is systematically ignored when working on zeolites and that the changes observed on conversion or in initial rates are only related to changes in either the specific rate constant (k_0) or in the concentration of active sites [S_0]. This is even more so taking into account the important adsorption effects of the zeolites and their strong impact, especially in bimolecular reactions.

In the case of Y zeolites, there is experimental evidence from adsorption studies (*45*) that the chemical adsorption of hydrocarbons changes both qualitatively and quantitatively during dealumination. It this were so, then the adsorption equilibrium constant for *m*-xylene determined kinetically should change upon dealumination. In our case, this can be seen to occur from the values obtained at 553 K and given, as an example, in Table 2. The evolution of the adsorption equilibrium constant calculated kinetically closely matches that of the chemical adsorption of *m*-xylene reported previously (*45*) (see Fig. 6).

The heats of adsorption and entropy of adsorption on the different zeolite samples are given in Table 3. One would expect the heat of adsorption to be higher on the samples containing the highest amount of the very strong acid sites. This does not occur, but the variation of the heat of adsorption with the Al content is the contrary to that expected. This may be an indication that the adsorption constant and, therefore, the heats of adsorption calculated here not only correspond to the formation of the carbeniums (Scheme II) but also, and in a larger extension, to the chemical adsorption of *m*-xylene forming Wheland-type complexes (Scheme I). This would also explain the fact that the increment of entropy and heat of adsorption are relatively small on all catalysts.

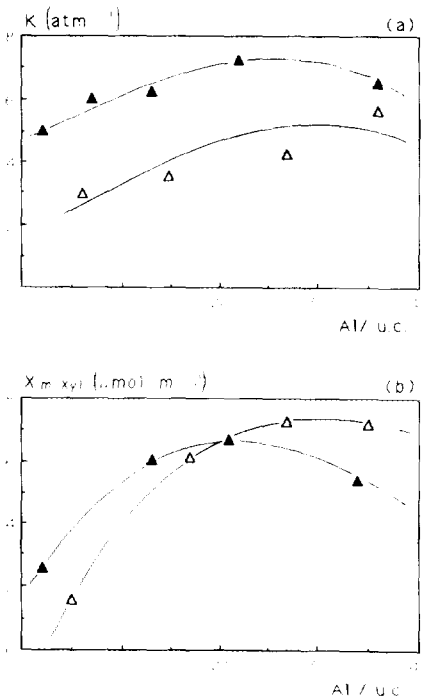


FIG. 6. (a) Adsorption equilibrium constant at 553 K and (b) *meta*-xylene adsorbed at 473 K, as a function of framework aluminum fraction for the dealuminated samples HYD (▲) and USY (△).

TABLE 4

Initial Isomerization/Transalkylation Selectivities (*I/TA*) for Sample USY-1 under Different Experimental Conditions

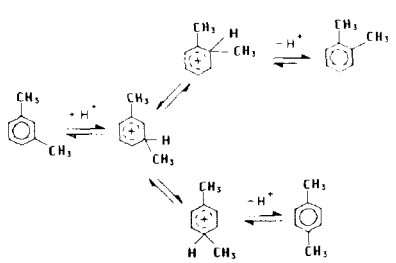
p_0 (atm)	$T(K)$	*I/TA*
0.10	553	2.34
0.20	553	2.15
0.40	553	1.71
0.60	553	1.55
0.80	553	1.60
0.20	533	2.09
0.20	573	1.47
0.20	593	1.35

Influence of the Zeolite Composition on Reaction Selectivity

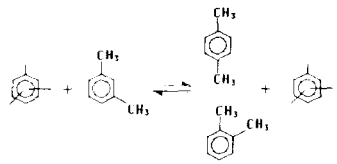
Together with the transalkylation, *m*-xylene also isomerizes to *ortho*- and *para*-xylene. It has been recently presented that in Y zeolites isomerization of xylenes can occur through a unimolecular as well as through a bimolecular mechanism similar to that for transalkylation (*48*): unimolecular isomerization via 1,2 methyl-shift (Scheme III) or bimolecular isomerization via transalkylation (Scheme IV).

When the uni- and bimolecular isomerization processes were separated kinetically (*49*), it was found that the activation energy for the unimolecular is lower than that for the bimolecular process, and this is close to the activation energy found here for transalkylation of *m*-xylene.

It was found that transalkylation needs stronger acid sites than 1,2 methyl shift



SCHEME III



SCHEME IV

isomerization (*50*). Meanwhile, 1,2 methyl shift isomerization is a first-order reaction, as has been shown above. Taking all this into account, together with the evolution of the very strong acid sites and changes in the adsorption properties (Fig. 4 and Table 3), it appears that the ratio of *m*-xylene isomerization to transalkylation to give toluene and trimethylbenzene should first decrease upon dealumination up to a framework Si/Al ratio ≈7 and then increase for further dealumination. This is indeed observed experimentally in Fig. 7.

The process variables also have a strong influence on the isomerization/transalkylation ratio. Indeed, from the kinetic study carried out here, it becomes evident that an increase in *meta*-xylene partial pressure as well as an increase in reaction temperature will cause the isomerization-to-transalkylation ratio to decrease, as observed experimentally (Table 4).

CONCLUSIONS

It has been found that the kinetics of transalkylation of *m*-xylene on dealumi-

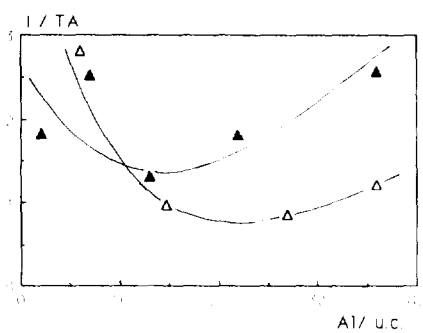


FIG. 7. Initial Isomerization/Transalkylation selectivities (*I/TA*) in function of the framework aluminum fraction for the dealuminated samples HYD (▲) and USY (△) at 553 K and 0.2 atm partial pressure.

nated Y zeolite follows a Langmuir–Hinselwood mechanism. It appears that the controlling step is the formation of the carbenium in the methyl group, which then attach, to the aromatic ring of a second *m*-xylene molecule forming a diphenylalkane carbocation.

The activity and selectivity of dealuminated Y zeolites can be related not only to classical HF and LF hydroxyl groups, but also to the presence of very strong acid sites associated with the presence of EFAL. Dealumination does not only change the number and strength of active sites, i.e., k_0 and $[S_0]$, but also the adsorption properties of the zeolites, i.e., K and ΔH_{ads}. This implies that in order to explain variations in catalytic behavior, both intrinsic activity and adsorption properties have to be considered separately.

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