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On the Compensation Effect in Acid–Base Catalyzed Reactions on Zeolites

A. CORMA,*[,1] F. LLOPIS,† J. B. MONTON,* AND S. WELLER‡

*Instituto de Tecnología Química, UPV-CSIC, Universidad Politécnica de Valencia, 46071 Valencia, Spain; †Departamento Ingeniería Química, Universidad de Valencia, Dr. Moliner 50 Burjassot, 46100 Valencia, Spain; and ‡Department of Chemical Engineering, New York University at Buffalo, Buffalo, New York

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Kinetic data for a number of acid–base catalyzed reactions carried out over a number of faujasite-type zeolites have been collected and analyzed. The nature and number of active sites has been changed by catalyst treatment and characterized, and the enthalpy and entropy of activation, activation energy, and pre-exponential factor have been determined. The results have been used to examine whether a compensation effect exists in each case and, if so, to obtain the corresponding isokinetic parameters. In addition, the results of kinetics studies reported by other authors have been analyzed in a similar way. In all zeolite-catalyzed reactions studied, a compensation effect is shown to exist. The effect is interpreted essentially as a consequence of the heterogeneity of the acidic or basic sites.

INTRODUCTION

Kinetics has been widely used to discuss reaction mechanisms, but very seldom can this tool disclose, by itself, the intimate mechanism of the reaction. This is so because kinetics is based on a "black box" methodology through which by knowing the evolution of reactants, and the products when the reaction variables are changed, one has to imagine what has occurred inside the reactor. The procedure usually involves the formulation of a hypothesis, the construction of a kinetic model, and the fitting of the experimental data to the model. This procedure, whose success is not assured even when applied to homogeneous reactions, becomes even more difficult in heterogeneous catalyzed reaction systems. Very often, more than one model, and therefore more than one hypothesis, can reproduce the experimental results. This is mainly due to limited knowledge of the catalyst surface and of the interactions between the reactants and the catalyst surface.

Fortunately, advances in physical techniques allow one *to see*, in some cases, the interaction between reactants, catalyst, and products (*1*), even if in many cases the experimental conditions are far from practical reaction conditions. Physical techniques are of great use, at least, for characterizing the active sites present on the catalysts. By preparing samples in which the nature and/or the number of the active sites are changed and measured, one may better understand the interactions of reactants with active sites. In this way it should be possible to discuss kinetic principles whose understanding is still far from complete.

Acid zeolites are catalysts whose active sites can be characterized, both in number and nature. Unfortunately, when studied as catalysts, their activity is very often calculated not from true kinetic parameters, but on the bases of conversion or, at the most, of initial rates. If full kinetic studies are carried out on a series of well characterized zeolites, one can probe deeper into the knowledge of some fundamental principles on kinetics and catalysis. One of these is the compensation effect (CE) (*2*). The CE describes a linear relation between the acti-

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[1] To whom correspondence should be addressed.

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vation energy and the logarithm of the preexponential factor, when either a series of homogeneous reactants on the same catalyst or one reaction occurring on a series of homologous catalysts is studied (*3–9*). The CE has also been called "isokinetic effect" (*10–13*), "theta rule" (*14*), or "linear free energy relation" (LFER) (*15–17*). Since its introductory description by Constable (*18*), the CE has been a source of continuous debate, sometimes even questioned as a real effect. Among the different causes suggested (*2*) to explain the CE, some authors assume that it is the result of heterogeneous energy distribution on catalyst surfaces (*19*), a linear relation between entropy and enthalpy of activation (LFER) (*20, 21*), changes in the energy levels of the transition state (*22–24*), or changes in the surface concentration of active sites with temperature (*25*).

In the present work the enthalpy and entropy of activation, the activation energy, and the preexponential factor and the isokinetic parameters have been obtained for a series of acid- and base-catalyzed reactions studied on Y zeolites, in which the nature and number of active sites has been changed and characterized. The existence of a compensation effect has then been examined. Finally, kinetic results reported by other authors have been reanalyzed and the compensation effect studied.

EXPERIMENTAL

Materials

A series of ultrastable zeolites-Y-type faujasite were prepared by dealuminating a NaY zeolite (SK-40, from Union Carbide) with framework Si/Al ratio of 2.4. The HYUS samples were made by steam calcination of partially ammonium exchanged zeolites at atmospheric pressure and 773–1023 K for 3–20 h. After steaming, they were exchanged twice with an NH_4^+ solution at 353 K over 1 h and then calcined at 823 K for 3 h. Other samples of NaY zeolite were dealuminated by $SiCl_4$ treatment (HYD) following the procedure described by Beyer and Belenikaja (*26*). The dealuminated samples were washed until no Cl^- was detected in the wash water, and then exchanged with NH_4^+ and calcined at 823 K. The physicochemical characteristics are given in Table 1.

A series of CrHNaY zeolites were prepared by repeated exchange of the sodium zeolite at 328 K and constant pH = 4.5 with an aqueous solution of chromium acetate. Details of the preparation and the analysis of this series of zeolites are given elsewhere (*27*). The degree of ion exchange of the

TABLE 1

Chemical and Structural Characteristics of the Catalyst Samples Used in the *meta*-Xylene Isomerization

Sample	Framework Si/Al ratio[a]	Al/u.c.[a]	Cryst. (%)	u.c. (Å)	(Si/Al)[b]
HYD-1	4.3	36	100	24.55	1.87
HYD-2	7.7	22	100	24.43	2.25
HYD-3	13.8	13	85	24.35	2.75
HYD-4	29.0	7	85	24.29	
HYD-5	99.0	2	85	24.25	5.99
HYUS-1	4.4	36	100	24.55	2.30
HYUS-4	31.0	6	80	24.28	2.40

[a] Al per unit cell (u.c.) calculated from Fichtner–Schmittler equation (*65*).

[b] From chemical analysis.

TABLE 2

Chemical Characteristics of the Catalyst Samples Used in *n*-Heptane Cracking

Sample	% Na^+ exchanged by		Total H^+[b]
	H^+[a]	Cr^{+3}	
CrHNaY-24	12	24	28
CrHNaY-32	13	32	34
CrHNaY-52	13	52	47
CrHNaY-58	9	58	47

[a] By direct exchange.

[b] Assuming two H^+ produced for each Cr^{+3} ion, i.e., % H^+ = % Na^+ exchange by H^+ + 2/3 Na^+ exchanged by Cr^{+3}.

TABLE 3

Chemical Characteristics of the Catalyst Samples Used in Benzaldehyde Condensation

Sample	Li	Na	K	Cs	Total[a]
LiX	353	149.5	—	—	502.5
NaX	—	472	—	—	472
KX	—	86	350	—	436
CsX	—	174.5	—	193	367.5
LiY	185	139.5	—	—	324.5
NaY	—	317	—	—	317
KY	—	30	275	—	305
CsY	—	74.3	—	200	274.3

[a] mmol per 100 g of hydrated sample.

samples is summarized in Table 2. We have assumed that for each Cr^{+3} ion three Na^+ are removed and two protons are produced.

Finally, a series of basic zeolites were prepared by exchanging the NaX and NaY zeolites by Li, K, and Cs, in a 1 *M* aqueous solution of the corresponding metal chloride, at 353 K for 1 h and using a liquid/solid ratio of 10. After that, the samples were filtered and washed free of chlorides. The chemical composition of the resultant materials is given in Table 3.

Catalyst Characterization

The chemical composition of the samples were determined by atomic absorption after dissolving the samples. The unit cell constant of the zeolites was determined by X-ray diffraction using Cu$K\alpha$ radiation and following ASTM procedure D-3942-8. The crystallinity was calculated by comparing the height of the (5,3,3) peak and considering the SK-40 as 100% crystalline.

The samples were characterized by high resolution solid state NMR spectroscopy technique. ^{29}Si and ^{27}Al magic-angle-spinning NMR monitors the different types of tetrahedral cations, depending on the neighboring atoms, as has been reviewed by Klinowski *et al.* (*28*). This technique has made it possible to establish the dependence between the amount of different class of acid sites and the framework Si/Al ratio of the zeolite.

Acidity was characterized by IR spectroscopy combined with pyridine adsorption–desorption. The zeolite powder was compressed in wafers of 10 mg cm^{-2} and mounted in a vacuum cell. All spectra were recorded at room temperature. The samples were pretreated overnight at 673 K and 1.33 mPa. For the pyridine adsorption experiments, 660 Pa of base was introduced at room temperature in the cell. The cell was outgassed in vacuum at 423 K before recording the spectrum.

The basicity of the alkaline-exchanged Y zeolites was studied by means of IR spectroscopy of the adsorbed pyrrole. Indeed, it has been shown that the shift of the infrared wavenumber of the NH stretching vibration of the pyrrole upon adsorption on zeolites, with respect to the 3410-cm^{-1} value for the liquid pyrrole, is related to the basic strength (*29*).

Catalytic Experiments

Isomerization and transalkylation of *meta*-xylene were carried out in a continuous fixed-bed glass tubular reactor. A detailed description of the system and of the analytical procedure methods have been described elsewhere (*30*). The samples HYD and HYUS series, with a diameter between 0.59 and 0.82 mm, were used for them. The reactions were studied at 493, 513, 533, 573, and 593 K reaction temperature, and the hydrocarbon partial pressure was varied between 0.08 and 0.8 atm. The contact time was changed by modifying the weight of catalyst and flow rate in order to keep the conversion low and constant in all cases.

The cracking of *n*-heptane was carried out on the CrHY zeolite samples in a continuous flow tubular reactor. A detailed description of the system and the analytical procedure methods have been described elsewhere (*31*). The experiments were carried out at atmospheric pressure, temperatures of 673, 723, and 743 K and at different catalyst to oil ratios, in the range 0.19–0.55. Pure *n*-heptane was fed at a constant space velocity in a 4-h run.

The alkaline-exchanged Y zeolites were used to catalyze the condensation of benzaldehyde with ethyl cyanoacetate, ethyl acetoacetate, and diethyl malonate in a batch reactor. An equimolecular solution of the two reactants without solvent was kept under stirring while heating up to reaction temperature. Then, 1–10 wt% of the zeolite catalysts was added and the reaction time started; details were reported elsewhere (*32*).

RESULTS AND DISCUSSION

Theoretical Bases: Relationship between the Enthalpy and Entropy of the Transition State

From the transition state theory (*33*), the rate constant for a elemental reaction is given by

$$k_r = \left(\frac{\kappa\, k_B\, T}{h_P}\right) \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-\Delta H^*}{RT}\right\}$$

$$k_r = \left(\frac{\kappa\, k_B\, T}{h_P}\right) \exp\left(\frac{-\Delta G^*}{RT}\right\}, \qquad (1)$$

where κ is the transmission coefficient (usually taken to be 1), k_B and h_P are Boltzman's and Planck's constants, respectively, T is the absolute temperature, and finally ΔG^*, ΔH^*, and ΔS^* are the increments of free energy, enthalpy, and entropy between the reactants and the transition state of the activated complex. In Eq. (1) the term $(\kappa k_B T/h_P) \cdot \exp(\Delta S^*/R)$ varies linearly with temperature, while the $\exp(-\Delta H^*/RT)$ term varies exponentially. Then, taking into account, Eq. (1) can be simplified and the classical Arrhenius equation is obtained,

$$k_r = \left[\left(\frac{\kappa\, k_B\, T}{h_P}\right) \exp\left(\frac{\Delta S^*}{R}\right)\right] \exp\left(\frac{-\Delta H^*}{RT}\right) \qquad (2)$$

or

$$k_r = A \exp\left(\frac{-E_a}{RT}\right), \qquad (3)$$

where E_a is the apparent activation energy and A is the Arrhenius preexponential factor. The expression (2) can be transformed to Eyring's equation:

$$\ln\left(\frac{k_r}{T}\right) = \ln\left(\frac{\kappa\, k_B}{h_P}\right) + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT}. \qquad (4)$$

By measurement of the kinetic rate constant at different reaction temperatures, it is possible to calculate, from Eq. (3) or (4), ΔH^*, ΔS^*, A, and E_a, and consequently to see if a correlation exists between these parameters.

It has been shown (*34*) that the correlation between the activation energy and the preexponential factor can also be written as

$$E_a = a + b \ln A \qquad (5)$$

or what it is equivalent to

$$\Delta H^* = c + d \cdot \Delta S^*, \qquad (6)$$

where a, b, c, and d are constant. Some authors (*2, 7*) related these parameters to isokinetic temperature (parameter d) and the isokinetic rate constant (parameters a and c).

Comparisons made below refer to kinetic data obtained for processes proceeding under similar conditions. All available values of $(\log A, E_a)$ within each group of related reactions were included in the linear regression analysis, and the compensation line was calculated using these formulas. The units of A are always mol g^{-1} s^{-1} and those of E_a are kJ mol^{-1}.

Compensation Effect in Catalytic Process

Isomerization and transalkylation of meta-xylene. In previous work it was shown (*35*) that xylenes are isomerized on Y zeolites through both uni- and bimolecular reactions. We have proposed a rate equation, following the Hougen–Watson methodology which takes into account both routes. The form of the equation is

$$r_0 = \frac{k_1 K_{a_1} p}{(1 + K_{a_1} p)} + \frac{k_2 (K_{a_2} p)^2}{(1 + K_{a_2} p)^2} \qquad (7)$$

where the first term relates to the unimolecular and the second term to the bimolecular mechanism, k_1 and k_2 are the rate constant for the uni- and bimolecular mechanisms, respectively, K_{a_1} and K_{a_2} are the corresponding adsorption equilibrium constants, and p is the partial pressure of *meta*-xylene.

Along with isomerization, methyl group transalkylation also occurs by a second-order reaction. We have proposed (*36*) the following rate equation for the transalkylation reaction:

$$r_0 = \frac{k_3(K_{a_3}p)^2}{(1 + K_{a_3}p)^2}, \qquad (8)$$

Here k_3 is the rate constant and K_{a_3} the adsorption equilibrium constant for the *meta*-xylene transalkylation process.

The initial rates for isomerization and transalkylation were determined at different partial pressures and temperatures (*37*); rate constants and adsorption equilibrium constants were obtained by fitting the experimental data to the rate equations. The results are summarized in Table 4.

Values for the activation energies and pre-exponential factors, calculated by Eq. (3), are plotted in Fig. 1 for the set of ultrastable Y zeolites shown in Table 1. Although there is some scatter in the points, these semilogarithmic plots indicate a reasonable linear correlation between E_a and ln A for the three reactions, i.e., there is consistency with the existence of a CE for this set of zeolites.

The enthalpy (ΔH^*) and entropy (ΔS^*) for the activated complex were calculated

TABLE 4

Kinetic and Adsorption Constants for Different Elemental Processes in the Xylene Reaction

Sample	T	Isomerization				Transalkylation	
		Unimolecular		Bimolecular		k_3	K_{a_3}
		k_1	K_{a_1}	k_2	K_{a_2}		
	533	1.65	2.64	1.13	3.84	0.85	7.58
HYD-1	553	3.38	2.01	2.38	3.32	2.24	6.51
	573	6.62	1.56	4.76	2.90	5.54	5.65
	533	14.65	2.58	8.61	3.77	11.25	8.18
HYD-2	553	27.54	2.00	16.73	3.26	24.50	7.23
	573	49.54	1.57	31.04	2.85	50.54	6.44
	533	12.39	2.78	8.32	2.65	12.84	4.26
HYD-3	553	23.38	2.16	17.28	2.29	30.91	4.01
	573	42.21	1.71	34.09	1.99	70.00	3.79
	533	6.62	2.49	5.06	2.12	3.87	6.71
HYD-4	553	13.31	1.92	11.35	1.79	9.73	6.05
	573	25.49	1.51	24.06	1.53	22.93	5.51
	533	1.63	1.08	0.82	2.02	0.92	6.05
HYD-5	553	3.69	0.79	0.69	1.65	2.39	5.02
	573	7.89	0.59	1.57	1.36	5.78	4.22
	533	6.96	4.91	2.76	9.58	6.31	6.16
HYUS-1	553	12.46	3.99	5.10	8.36	14.43	5.67
	573	21.42	3.30	9.01	7.36	31.17	5.25
	533	2.54	0.34	0.20	2.30	1.10	5.40
HYUS-4	553	5.30	0.27	0.46	1.92	2.05	4.83
	573	10.52	0.22	1.02	1.63	3.66	4.36

Note. T(K); k (mol/s.weight cat) × 10^5; K_a (l/atm).

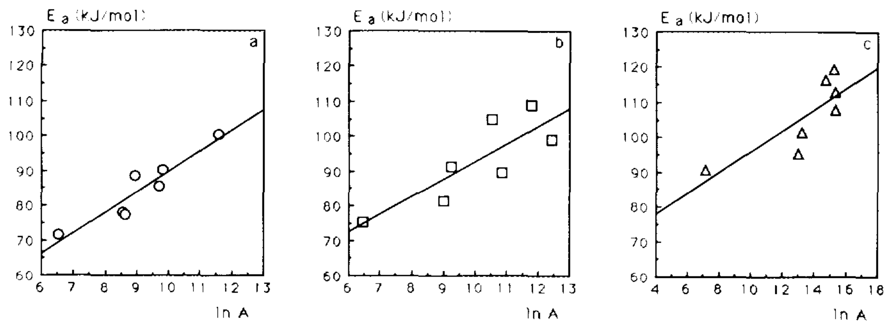

FIG. 1. Compensation effect for the elemental process in the xylene reaction over different Y zeolites (○, unimolecular isomerization; □, bimolecular isomerization; and △, bimolecular transalkylation).

from Eq. (4); these values are given in Table 5. All ΔS^* values are negative and larger, indicating that when going from reactants to the activated complex, there is a considerable restriction in the degrees of freedom. The existence of an activated complex with a high degree of ordering is consistent with a reaction mechanism in which the controlling step is the interaction of the reactant molecules with the active sites of the catalysts. The values for the increment of enthalpy when going from the reactants to the activated complex ΔH^* are in fair concordance with their homologues for activation energies.

The averaged values for *a*, *b*, *c*, and *d* parameters are shown in Table 6 for the three reactions on all catalysts studied. Values for the same quantities, but obtained by fitting the same equations to data for individual catalysts, are given in Table 7. With few exceptions, the linear correlation coefficients are high, giving credence to the existence of a CE in this system of different zeolites and three reactions.

TABLE 5

Enthalpy and Entropy of Activation Obtained for the Elemental Process in the Xylene Reaction

Sample	Isomerization				Transalkylation	
	Unimolecular		Bimolecular		ΔH^*	ΔS^*
	ΔH^*	ΔS^*	ΔH^*	ΔS^*		
HYD-1	83.7	−184.3	86.7	−181.9	114.7	−131.9
HYD-2	72.8	−186.5	76.9	−183.3	90.9	−155.0
HYD-3	73.9	−187.2	83.8	−164.9	103.2	−130.7
HYD-4	81.0	−179.3	94.4	−154.9	108.3	−131.0
HYD-5	95.6	−162.1	104.2	−160.4	112.0	−136.2
HYUS-1	65.4	−205.9	69.8	−206.2	96.8	−148.5
HYUS-4	87.5	−180.2	101.2	−171.0	72.5	−208.8

Note. ΔH^* (kJ/mol); ΔS^* (J/mol.K).

In order to explain these observations the activation energies have been plotted versus the framework Al content in Fig. 2. In other words, Fig. 2 shows the dependence of the activation energy with the potential number of acid sites. It can be seen that upon increasing the framework Si/Al ratio, the activation energy first decreases and then increases, the minimum being found at ≈22 Al/c.u. (Si/Al = 7–8).

If one considers only the framework Al and assumes that a random Al distribution exists in the dealuminated HY zeolites, one should expect that upon dealumination, while the total number of acid sites will decrease, the strength of the remaining sites will increase until framework Si/Al ratio of ≈6 is achieved. After that, all sites should be equivalent and their strength will remain constant (*38*, *39*). On this basis the activation energy should decrease upon dealumination while the acid strength of the acid sites increases and then remains constant for samples with a Si/Al ratio above 6.

TABLE 6

Compensation Effect for a Given Process on Various Catalysts

Process	Catalysts table	From Eq. (5)			From Eq. (6)		
		Corr	*a*	*b*	Corr	*c*	*d*
Unimolecular xylene isomerization	1	0.9368	30.51	5.93	0.9257	212.59	1663
Bimolecular xylene isomerization	1	0.8305	42.23	5.05	0.7923	188.10	1318
Xylene transalkylation	1	0.9256	50.94	4.03	0.9364	172.56	1126
n-Heptane cracking	2	0.9868	60.86	3.48	0.9890	124.66	1058
Condensation benzaldehyde with ethyl cianoacetate	3	0.9635	3.35	3.68	0.9632	113.20	1020

Note. Corr (linear regression coefficient) and *a*, *b*, *c* in (kJ/mol), and *d* in (K).

However, it has been shown *(40)* that in the case of USY zeolites dealuminated either by steam or, as here, by $SiCl_4$, extraframework Al exists (see Table 1). This has an indirect impact on the acid strength distribution in our samples. Octahedral Al was not detected by ^{27}Al NMR MAS, nevertheless, it is present as can be deduced from the difference of Al obtained by chemical analysis and from the unit cell size value. The existing EFAL, could be made visible by acetyl acetone impregnation *(41)*. Both the framework and extraframework composition produce acid sites of different acidities *(40)*. When the very strong acidity, calculated from the pyridinium band of the pyridine remaining adsorbed after 623 K and 673 K and 10^{-4} Torr desorption temperature, is plotted versus the zeolite framework Al content (Fig. 3b), a maximum amount of the very strong acid sites was found for the sample with 22 Al/u.c. If

TABLE 7

Compensation Effect on a Given Catalyst

Process	Sample	From Eq. (5)			From Eq. (6)		
		Corr	*a*	*b*	Corr	*c*	*d*
(a)	HYD-1	0.9989	46.42	4.78	0.9988	190.48	1328
(a)	HYD-2	0.9906	39.80	4.48	0.9922	174.43	1247
(a)	HYD-3	0.9976	41.34	4.35	0.9980	171.90	1204
(a)	HYD-4	0.9999	38.56	4.85	0.9998	184.77	1301
(a)	HYD-5	0.8764	55.94	4.14	0.8804	180.09	1149
(a)	HYUS-1	0.9922	46.08	4.19	0.9910	171.52	1167
(a)	HYUS-4	0.9231	46.17	5.10	0.9657	199.90	1623
(b)	ZXNa	0.9863	−8.63	5.83	0.9858	167.93	1622
(c)	HLaYUS	0.9865	59.96	5.83	0.9865	236.77	1616
(c)	HLaYUS-1	0.9857	47.53	5.75	0.9857	221.63	1592

Note. Process: (a) uni- and bimolecular isomerization of xylenes, transalkylation of xylenes; (b) Knoevenagel condensation of benzaldehyde with ethyl-cyanoacetate, ethyl-acetoacetate, and diethyl-malonate; and (c) *n*-heptane cracking on C2 + C5 fraction, C3 + C4 fraction, isomerization and transalkylation. Corr (linear regression coefficient) and *a*, *b*, *c* in (kJ/mol), and *d* in (K).

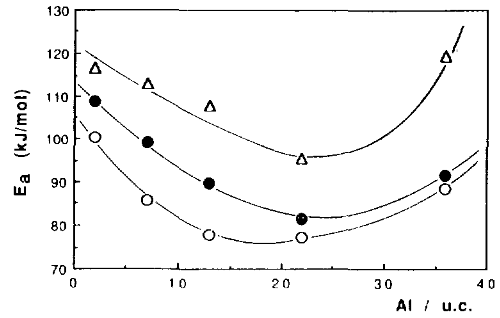

FIG. 2. Activation energy for the elemental process in the xylene reaction as a function of the aluminium T fraction in HYD samples series. (○, unimolecular isomerization; ●, bimolecular isomerization; and △, bimolecular transalkylation).

dealumination proceeds further, the amount of those sites strongly decreases, and a very good inverse correlation is then observed between the variation of the very strong acid sites (Fig. 3b) and both the activation energy (Fig. 2) and ΔH^* (Fig. 3a) for both isomerization and transalkylation of *meta*-xylene.

After this, one could explain the compensation effect on this series of zeolites by considering that a range of acid sites with different acid strength are present, each one of them needing a different activation energy for carrying out the reaction. In principle, it can be expected that the stronger the acidity, the lower the increment of enthalpy between the reactants and the activated complex will be, and also the lower will be the entropy of such a complex. Then, going from one zeolite to another, one does not expect the nature of the active sites to change, but the acid strength distribution and consequently the resultant "averaged" activation energy observed experimentally. However, since a direct correlation between the enthalpy and entropy of activation exists in the heterogeneous surface of a catalyst, a direct correlation between enthalpy and entropy of activation should be observed for the "averaged" values of enthalpy and entropy of activation obtained experimentally for the different zeolite catalysts.

n-Heptane cracking on Y zeolites. One way of introducing acidity, while controlling the equilibrium unit cell size of Y zeolites and therefore the number and strength of the acid sites, consists in introducing di- and trivalent cations by exchange. A Y zeolite was exchanged at different levels with Cr^{+3} and calcined under shallow bed conditions at 723 K. In this way a series of NaCrHY samples was prepared (Table 2). In this series of four catalysts, one expects that the samples will show acid sites of different strength and an acid strength distribution that changes with the level of exchange. A first-order kinetic equation has been used to fit the experimental data to obtain kinetics rate constants and activa-

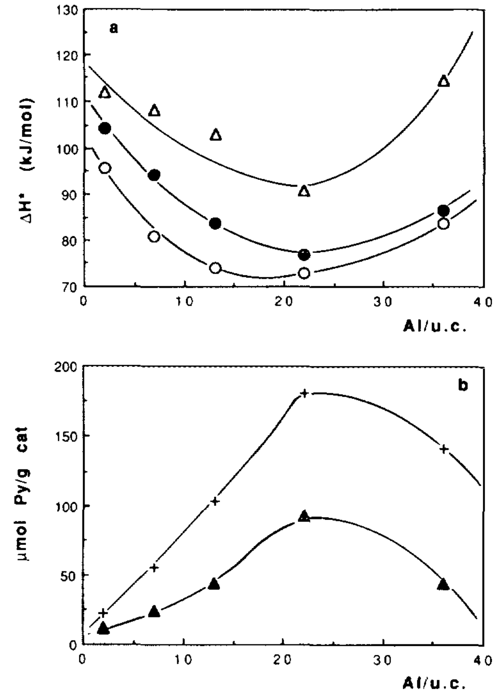

FIG. 3. Relation between the enthalpy of activation in the xylene reaction and the amount of strong acid sites, for (a) xylene isomerization (○, unimolecular and ●, bimolecular elemental process) and xylene transalkylation (△); and (b) pyridine retained after desorption at 623 K (+), 673 K (▲), and vacuum, on different Al containing in HYD samples.

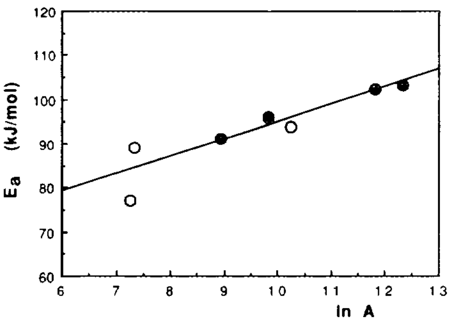

FIG. 4. Compensation effect in *n*-heptane cracking on Y zeolites with different trivalent metal exchanged (○, LaHY and ●, CrHY).

TABLE 8

Shifting in the IR Bands of Adsorbed Pyrrole for Different Zeolites

Sample	Cation	ν (N–H) Pyrrole (cm^{-1})
LiX	Li	3300
NaX	Na	3210
KX	K	3180
CsX	Cs	3160
LiY	Li	3435 (3365)
NaY	Na	3405
KY	K	3325
CsY	Cs	3280 (3390)

Note. Liquid pyrrole: NH, 3497 cm^{-1}; NH · · · N, 3410 cm^{-1}.

tion energy for the overall cracking results (*31*). Figure 4 and Table 6 show that the CE exists for *n*-heptane cracking in this series of Cr-containing zeolites.

The CE should apply to any type of zeolite in the Y series, if it represents a general principle (*42, 43*), and indeed Fig. 4 shows that samples exchanged by another trivalent ion, La^{+3} (*44*), do also fit on the same E_a vs ln A line as that determined by the CrHY samples.

Knoevenagel condensation on alkaline Y zeolite. In examining possible generalization of the compensation effect, we have correlated the activation energy and frequency factor for a completely different type of reaction: the base-catalyzed condensation of benzaldehyde with ethyl cyanoacetate in a liquid–solid reaction system. A series of alkaline X and Y zeolites were used as catalysts (Table 3). These catalysts have a heterogeneous distribution of Lewis basic sites, since different types of oxygens (O_1, O_2, O_3) are present on the zeolite (*45*). The basic strength distribution is different for each of these catalysts, as indicated by the pyrrole adsorption results (*29*) presented in Table 8. The higher the frequency shift of the adsorbed pyrrole the more shifted toward stronger basicities is the distribution of sites.

The condensation of benzaldehyde with ethyl cyanoacetate was carried out at different temperatures, and the rate constants were calculated by a second-order kinetic equation (*32*). Using these values, we obtained the activation energies and frequency factors. The results, plotted in Fig. 5, indicate that a compensation effect exists also in this series of catalysts. In addition, the CE should occur if a series of homologous reactions are carried out on a single zeolite catalyst. This has been observed for the condensation of benzaldehyde with three different condensation agents of different pK_a. In addition to ethyl cyanoacetate, which has a pK_a of 9, ethyl acetoacetate and diethyl malonate with pK_a values of 10.3 and 13.5, respectively (*32*), were chosen as reactants. Reasonably good cor-

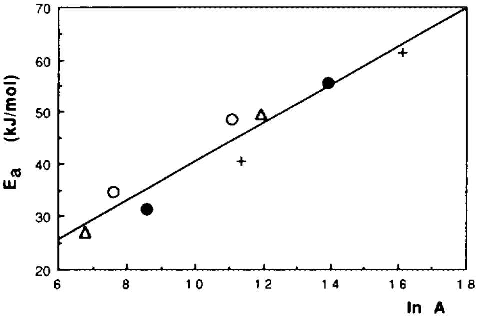

FIG. 5. Compensation effect in Knoevenagel condensation on alkaline Y zeolites (○, ZLi; △, ZNa; ●, ZK; and +, ZCs).

relation between the activation energy and the frequency factor can be deduced from the high correlation coefficients shown in Table 7.

Significance of the Fitting Parameters

An aspect which is worth discussing refers to the possibility for using the isokinetic parameters as a quantitative measure of the reactivities in series of analogous reactants. Most of the time the comparison of reaction rates for different reactants is based on the initial rates obtained at a given reaction temperature. Others use as a parameter the temperatures for which the different reactants give the same conversion *(46)*. It can be argued, however, that a more complete description of the kinetic behaviour could be achieved from the isokinetic temperature and isokinetic constant, when a compensation effect exists. Indeed, the values of these parameters define the temperature range in which these become comparable. There is, therefore, the possibility that such behaviour could be associated with the presence of a common reaction mechanism or to a common reaction intermediate (*2*).

Some authors (*2, 7*) related the parameters a or c to the rate constant at the isokinetic temperature. Values of these quantities are determined by both the activation energy and the rate of production of transition intermediates on the catalyst surface. These are closely related to the molecular geometry and the reaction mechanism. When a series of analogous compounds are studied on a catalyst, the number and characteristics of the active sites determine the value of isokinetic temperature, in such a way that low values of them are associated with inductive effects in the substrate (*47*).

Nevertheless, all of the isokinetic temperatures (parameter d in Eq. (6)) are greater than 1000 K, while all the reactions were studied at temperatures lower than 600 K. The extrapolation is substantial and, indeed, one might question the significance of any isokinetic temperature that is above the temperature where the catalysts would be stable or the reactions would even proceed as they are measured.

Compensation Effect on Other Reactions and Zeolite Catalysts

From a literature search, a series of reactions on zeolite catalysts were identified for which the kinetic parameters have been determined at different temperatures. Table 9 contains the process studied, the characteristics of the catalysts, and the literature references. The preexponential factors and activation energies given by the authors were fitted to Eq. (5), to obtain the a and b values, and the results are summarized in Table 9. We conclude from the correlation coefficients listed in Table 9 that, in general, a CE effect is operative.

Since the catalytic reactions involve adsorbed species, the surface heterogeneity of the zeolites affects the activation energies for these reactions. The global rate will be the sum of the individual rates on each type of site, each one proceeding with a different activation energy. Despite this complexity, activation energies are generally deduced with the assumption that the global rate can be described as having a "unique" activation energy. The differences in reaction rate originate in changes in the energetics and number of reactive species. Following this line of reasoning, Yoneda (*48*) has analyzed the distribution of reaction rates associated to each type of active site. His analysis is based on the assumption that in acid catalysts the reaction rate on one active site is exclusively determined by the acid strength of the site.

Experimental work which confirms this has been carried out by Li-Quin *et al.* (*54*). They prepared a series of LaY zeolite catalysts with different acidity, obtained by a progressive poisoning with Na^+. They showed that for *ortho*-xylene isomerization and cumene cracking, the higher the acidity of the catalyst, the higher the catalytic activity and the lower was the apparent activation energy. A linear correlation was

TABLE 9

Compensation Effect Obtained from Literature Data

Key	Ref.	Reactant	Catalyst	N^a	Characteristic	From Eq. (5)		
						Corr	a (kJ/mol)	b (kJ/mol)
D-1	(*50*)	Methanol	Zeolite Y	4	Acidity	0.9930	34.78	2.30
D-2	(*51*)	Ethanol (Olef)	Zeolite	17	Cation	0.9354	66.25	4.80
D-3	(*51*)	Ethanol (Ether)	Zeolite	17	Cation	0.9726	62.13	5.41
D-4	(*51*)	Butanol	Zeolite	7	Cation	0.9879	63.74	4.40
D-5	(*52*)	Octanol	Bauxite	4	Sieve	0.9537	40.07	3.30
D-6	(*52*)	Alcohol C2-C8	Bauxite	4	Alcohol	0.9540	60.21	5.55
D-7	(*53*)	Alcohol C3-C8	γ-Alumina	16	Alcohol	0.9154	18.59	4.72
C-1	(*54*)	Cumene	Zeolite Y/La	3	Acidity	0.9920	18.52	8.41
C-2	(*55*)	Cumene	Zeolite Y	5	Acidity	0.9220	40.55	3.58
C-3	(*56*)	*t*-but-Benzene	Al/SiO2	9	Al ratio	0.8877	63.35	3.87
C-4	(*57*)	*t*-but-Benzene	Clay	27	Water ratio	0.9167	54.89	3.63
HC-1	(*58*)	*n*-Pentane	Zeolite MOR	11	Acidity	0.9999	76.41	4.19
HC-2	(*59*)	*n*-Hexane	Zeolite Y/Pt	7	Pt ratio	0.9872	78.44	3.22
HC-3	(*60*)	*n*-Heptane	Zeolite Y/Ni-Mo	15	Ni/Mo ratio	0.9884	49.78	4.41
HI-1	(*58*)	*n*-Pentane	Zeolite MOR	11	Acidity	0.9999	76.41	4.19
HI-2	(*59*)	*n*-Hexane	Zeolite Y/Pt	7	Pt ratio	0.9141	52.62	5.48
I-1	(*61*)	1-Butene	Alumina/VIII Me	5	Cation	0.9735	34.31	3.91
I-2	(*62*)	*n*-Butenes	Zeolite X/Zn/Ce	8	Zn–Ce ratio	0.8877	−47.04	5.04
I-3	(*63*)	Dimethyl Butene	Zeolite X/Cu	6	Cu ratio	0.8456	70.18	3.93
I-4	(*54*)	*o*-Xylene	Zeolite Y/La	3	Acidity	0.9910	20.62	8.69
H-1	(*64*)	CO	Zeolite Y/Ru/Ni/Cu	10	Metal ratio	0.9476	73.70	4.46

Note. Key for process: (D) dehydration, (C) cracking; (HC) hydrocracking; (HI) hydroisomerization; (I) isomerization, and (H) hydrogenation.

[a] Number of catalysts or reactants used in each study.

found between the kinetic constants for the two processes and the acidity measured by Hammett indicators. Following the work of Maatman (*49*), the number of sites which are active for a given reaction depends mainly on the activation energy. Those catalytic samples with a higher acidity, to which a lower activation energy corresponds, should have a smaller density of acid sites. This can explain the results of Li-Quin *et al.* in the sense that by a continuous poisoning of sites, going from strong to weak acidity, the density of the (now) active but weak sites would increase and the apparent activation energy would also increase. It appears that the compensation effect we have found to apply in this work (see Fig. 6) is related to characteristics of the catalysts. Changes in the acidity of the active sites in the different zeolites would be responsible for the observed correlation between the activation energy and the preexponential factor.

Similar effects can be deduced on other zeolites catalysts detailed in Table 9. For

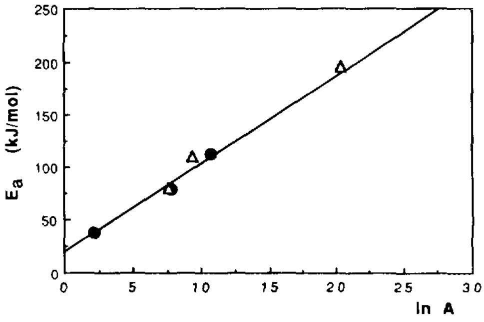

FIG. 6. Compensation effect on cumene cracking (●) and *ortho*-xylene isomerization (△) over zeolite Y exchanged with La^{+3} and Na^{+} (Ref. (*52*)).

example, C-2 and C-3 in which the acid strength distribution has been changed by modifying the framework Si/Al ratio, D-1 and C-4 by modifying the method of catalyst preparation, C-1, I-2, I-3, and H-1 by increasing the level of metal exchange, or D-2, D-3, D-4, D-5 and I-1 by changing the cation in the framework catalyst.

We have also analyzed in Table 9 catalytic processes such as hydroisomerization and hydrocracking which require bifunctional (metal plus zeolite) catalysts (HI-1, HI-2, HC-1, HC-2, and HC-3). In all cases a compensation effect has also been found. Finally, a special situation is presented in D-6 and D-7, where the catalyst is the same but the nature of the reactant was modified; in such a case a compensation effect has also been observed.

CONCLUSIONS

Kinetic parameters calculated for reactions catalyzed by zeolites can be related to such characteristics of the catalyst as number of sites and acid or base strength. Since the controlling step in the reaction is the formation of the activated complex, the distribution of acid–base strength determines the energy barrier for the reaction to occur; the number of sites is important also. Strong acid–base sites are characterized by a lower activation energy; meanwhile, the relative abundance of such sites can be related with the relative activity. However, catalysts with a low proportion of very strong acid sites will exhibit a low global reaction rate in spite of this, because the small number of these sites becomes rate-limiting. By contrast, in a catalyst with a large number of weak acid–base sites, the limiting factor becomes the high energy barrier associated with weak sites, and a low global rate will be observed.

It has been shown that a compensation effect exist in zeolite-catalyzed reactions, essentially as a consequence of their acid–base heterogeneity, which is a common feature to all catalysts studied. However, other factors such as availability of specific vibrational energy from the solid (*43*), or energy distributions to discrete reactant levels (*7*), are also common to the systems studied.

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