

Alkylation of Toluene with Propene Using Zeolite Catalysts

BRIAN D. FLOCKHART, KONG YONG LIEW,¹ AND RICHARD C. PINK

Department of Chemistry, The Queen's University, Belfast, BT9 5AG, Northern Ireland

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The catalytic activity of Y-type zeolite for the alkylation reaction of toluene with propene is strongly dependent on the degree of ion-exchange and on the calcination temperature. The activity increases as the sodium ions in Na-form Y zeolite are replaced by hydrogen ions up to at least 90% cation exchange. Optimum activity occurs at activation temperatures around 400°C when the Brønsted acidity is at a maximum. *Ortho-para* substitution always predominates, but at low activation temperatures (<400°C) the *p* isomer is preferred. This preference is reduced with increasing activation temperature, accompanied by a marked increase in the proportion of the *m* isomer. Present results indicate that the alkylation proceeds by a carbonium ion mechanism involving Brønsted acid sites on the zeolite surface. There is no correlation between the catalytic activity of the zeolite and its electron-transfer properties. The isomeric composition of the products suggests, however, that the selectivity of the catalysts is a function of their Lewis acidity. These findings, therefore, provide further evidence for the dual nature of zeolite catalysts.

INTRODUCTION

X- and Y-type zeolites exhibit high activity and versatility in alkylation capacity. Thus, rare-earth-exchanged forms of X and Y zeolites (REX, REY) and hydrogen Y zeolite (HY) are catalytically active for the alkylation of benzene and substituted benzenes with a variety of olefins, alcohols, and haloalkanes (1). A rare earth-hydrogen X zeolite has been used in the alkylation of isobutane with ethylene (2). These reactions have been postulated as proceeding via carbonium-ion-type mechanisms, the active surface sites being visualized as strongly acidic in nature and of the Brønsted character (2, 3). A study of Y zeolite as catalyst for the alkylation of toluene with methanol has shown (4) the activity of the cation-exchanged form to be in the order: REY > HY > divalent > monovalent. In the alkylation of toluene with propene, NaY zeolite was found to have negligible catalytic activity, whereas LaY and HY zeolites had high and comparable activities

(5). Changing the activation temperature from 550 to 700°C had no significant effect on the alkylation activity of either the LaY or NaY zeolite (5).

Suitably activated HY zeolites possess, in addition to the Brønsted acidity referred to above, well-marked redox properties that can promote electron-transfer reactions (6, 7). The possibility that the latter properties also play a role in alkylation reactions catalyzed by zeolites has not apparently been previously investigated. One area of particular interest in this context is the isomeric composition of the alkylaromatic products formed in these reactions. Published studies of catalyst selectivity in this field have revealed many interesting facts, but no unifying explanation. Thus, an investigation (8) of the alkylation of toluene and of ethylbenzene with ethylene demonstrated that silica-alumina (12% Al₂O₃) favoured *m* alkylation, whereas iron phosphate favoured *o* alkylation. On the other hand, alkylation of toluene with ethylene over REX zeolite followed *ortho-para* substitution (9). In the alkylation of phenol over REX or HY zeolites using a wide vari-

¹ Present address: School of Chemical Sciences, Universiti Sains Malaysia, Penang, Malaysia.

ety of alkylating agents, *ortho*-*para* orientation of substituents was generally observed, with a slight preference for *para* substitution; the *meta* isomers did not appear in significant quantity except at higher reaction temperatures or upon prolonged exposure of the reactants to the catalyst (1). An investigation (4, 10) of the alkylation reaction of toluene with methanol showed that selective formation of *p*-xylene could be achieved by the use of highly active zeolite catalysts (HY, LaY, CeY) under appropriate reaction conditions. This selectivity was attributed to the presence of strong Brønsted acid sites (4, 10). The conclusion that was drawn, however, from a study of the vapour-phase alkylation of toluene with ethylene using BF_3 -treated aluminas was that selectivity to certain isomeric ethyltoluenes depended more on reaction conditions such as the temperature than on the presence or absence of surface Brønsted acidity (11). The isomer distribution of C_8 aromatics produced from the alkylation of toluene with methanol over ZSM-5 crystals that are $<0.5 \mu\text{m}$ in size showed essentially an equilibrium distribution of the xylene product composed of 23% *ortho*, 54% *meta*, and 23% *para* at 500°C (12). When the crystal size of ZSM-5 was increased to $3 \mu\text{m}$, the product distribution altered to 18% *ortho*, 36% *meta*, and 46% *para*. When the alkylation was performed over ZSM-5 modified by treatment with certain chemical reagents, *para* selectivity as high as 97% was achieved. ZSM-5 has pore openings consisting of 10-membered oxygen rings. The rapid diffusion of *p*-xylene compared with that of *o*- and *m*-xylenes through these entry points has been suggested as accounting, in part at least, for the product selectivity of this zeolite.

In this paper the results of a study of the alkylation of toluene with propene over HY zeolite are reported, one purpose of the investigation being to see if any correlation exists between the electron-transfer activity of the catalyst and the selective formation of alkylates.

EXPERIMENTAL

Union Carbide molecular sieve catalyst SK-40, a Y-type zeolite (wt%, dry basis: Al_2O_3 , 23.5; SiO_2 , 63.5; Na_2O , 13.0) was modified as required by partial exchange of the sodium ion with ammonium ion using Lunsford's method (13). The commercial sample of silica-alumina, which contained ~13% Al_2O_3 , and the aluminium oxide-hydroxide (boehmite) have been described previously (14). The silica-alumina sample was washed in hot distilled water and dried at 120°C . Activation of all catalyst samples involved pretreatment in flowing oxygen in an electric muffle furnace for 1 hr at temperatures between 150 and 900°C , followed by cooling at 10^{-5} bar over phosphoric oxide for 30 min. The catalyst was then transferred under an atmosphere of dry nitrogen to a standard vacuum line where it was further heated for 16 hr at the same temperature as that used in the pretreatment, the pressure being 10^{-8} bar or lower.

Toluene (A.R.) was stored over active silica-alumina catalyst and filtered before use. Propene, supplied by British Oxygen Chemicals Ltd. with a minimum purity of 99.0%, was passed through a solid carbon dioxide + methanol trap before use.

The alkylation experiments were carried out in a 120 ml three-necked flask fitted with a mechanical stirrer and reflux condenser. Freshly activated catalyst, cooled to room temperature, was removed from the vacuum system and a weighed amount (~1 g) was transferred, under an atmosphere of dry nitrogen, to 100 ml toluene contained in the reaction vessel. The flask was placed in a $100 \pm 1^\circ\text{C}$ oil bath, 30 min were allowed for thermal equilibrium, and propene, at a flow rate of 100 ml min^{-1} , was then admitted to the stirred slurry. The reaction was followed by withdrawing ~1-ml samples through a sintered-glass filter at 30-min intervals, and subjecting these samples to NMR and GLC analyses.

The NMR spectra were obtained from a Varian A-60 spectrometer. A Perkin-

Elmer preparative chromatograph with a 9-ft column of Chromosorb P loaded with 10% Apiezon L and kept at 160°C, and a Griffith's gas-density-balance chromatograph using a 20-ft column of Chromosorb P loaded with 15% Apiezon L and kept at 100°C, were used for the GLC analyses. Isomeric compositions of the reaction products were determined from peak area measurements on the chromatogram.

RESULTS

Alkylation Activity of Ammonium-exchanged Zeolites

The percentage alkylation of toluene by propene, defined as the number of isopropyl groups introduced into 100 molecules of toluene, was determined by NMR spectroscopy. In most experiments the plot of percentage alkylation against time was linear when the reaction had been in progress for ~30 min; between 0 and ~30 min the plots showed some curvature, but the deviations from linearity were generally small (see, for

example, Fig. 1). Alkylation activities of the catalyst samples were therefore expressed in percentage conversion per minute per gram of catalyst. These rates are for a reaction temperature of 100°C with a flow rate for propene of 100 ml min⁻¹. For a particular catalyst sample a change in flow rate to 50 ml min⁻¹ did not alter the rate of alkylation. A change in reaction temperature from 91 to 109°C resulted in a 11% decrease in the rate when the catalyst was 90% NH₄-Y activated at 270°C.

The alkylation activity of ammonium-exchanged Y zeolite depends markedly on both the temperature of activation and the degree of sodium exchange (Fig. 2). All zeolite samples calcined below 150°C were inactive for the alkylation reaction. Optimum activity was observed with 90% NH₄-Y zeolite when the activation temperature was ~400°C, the alkylation rate being ~0.27% conversion min⁻¹ g⁻¹. For samples of the same zeolite activated at 200 and 600°C respectively, the rate was approximately one-third of this magnitude. On 80%

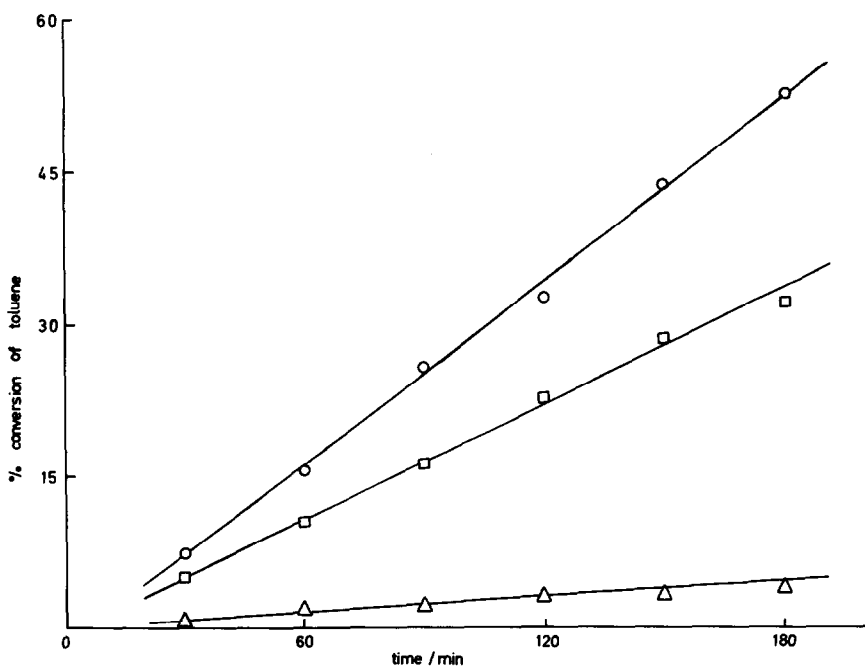


FIG. 1. Alkylation of toluene with propene over Y-type zeolite as a function of time: zeolite 90% exchanged with ammonium ion and activated at 400°C (○); 80%, 400°C (□); 34%, 325°C (△).

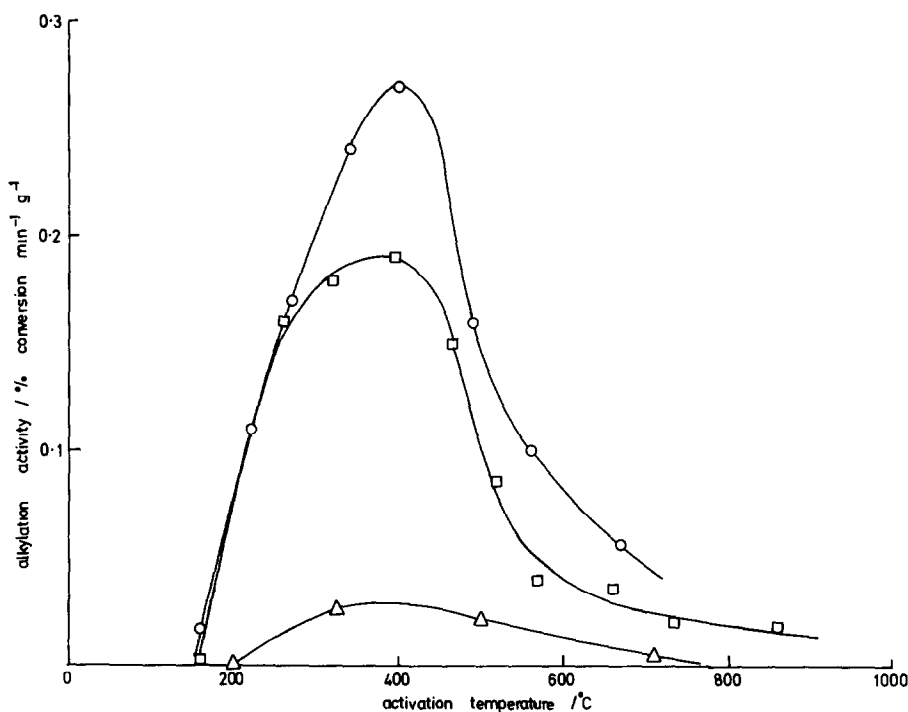


FIG. 2. Alkylation activity of Y-type zeolite exchanged with ammonium ion as a function of activation temperature: 90% exchanged (O); 80% (□); 34% (Δ).

$\text{NH}_4\text{-Y}$ zeolite activated at the optimum temperature of $\sim 400^\circ\text{C}$ the rate was 0.19% conversion $\text{min}^{-1} \text{g}^{-1}$; on 34% $\text{NH}_4\text{-Y}$ activated at the same temperature the rate was $\sim 0.03\%$ conversion $\text{min}^{-1} \text{g}^{-1}$.

Initially the only products of the alkylation reaction were the isomers of cymene identified by both NMR and GLC analyses. When the reaction had proceeded for 3 hr on 80% $\text{NH}_4\text{-Y}$ zeolite activated at 570°C , $\sim 5\%$ of the reaction product was di-isopropyl toluene. After 22 hr the distribution of the mono-, di-, and trialkylated products was in the ratio 5 : 2 : 1.

Alkylation Activity of Amorphous Silica-Alumina and Alumina

Silica-alumina ($\sim 13\% \text{Al}_2\text{O}_3$) had an alkylation activity comparable to that of the more extensively exchanged zeolite samples. With a sample activated at $\sim 500^\circ\text{C}$, the rate of alkylation was 0.14% conversion $\text{min}^{-1} \text{g}^{-1}$. Boehmite samples that had been calcined at 300, 500, and 700°C re-

spectively were catalytically inactive for the alkylation reaction.

Selectivity of the Alkylation on Ammonium-Exchanged Zeolites

Variation in the temperature of activation of 90% $\text{NH}_4\text{-Y}$ zeolite profoundly affected the orientation of the monoprolylated product. *Ortho-para* substitution always predominated, but at low activation temperatures ($< 400^\circ\text{C}$), the ratio showed a preference for *p*-cymene (Table 1). Increase in the activation temperature altered the *ortho/para* ratio in favour of the *o* isomer and also markedly increased the proportion of the *m* isomer (Table 1). Similar results were obtained with the less extensively exchanged zeolite samples. Even with the most active catalyst sample used, the isomeric composition of the product changed little with time over a 3-hr period from the commencement of the reaction. Amorphous silica-alumina ($\sim 13\% \text{Al}_2\text{O}_3$) activated at 500°C gave a product distribu-

TABLE I

Effect of Activation Temperature on the Selectivity of the Alkylation over Y zeolite 90% exchanged with Ammonium Ion

Activation temp. (°C)	Cymene isomer composition (%)		
	<i>o</i> -	<i>m</i> -	<i>p</i> -
220	36	11	53
270	35	11	54
340	40	13	47
400	42	15	43
490	49	14	37
560	50	18	32
670	52	22	26

tion of 47% *ortho*, 17% *meta*, and 36% *para*, values not greatly different from the corresponding results for 90% NH₄-Y zeolite.

Under suitable conditions alkylaromatics isomerize in the presence of oxide catalysts (3, 15). Although it seemed unlikely that an isomerization reaction was influencing present findings because of the relatively constant isomeric composition of the product with time, as a further test of this possibility neat *p*-cymene was left in contact with 90% NH₄-Y zeolite (activated at 400°C) for 20 hr at 100°C with continuous stirring of the system. No isomer other than the original was found.

Effect of Adsorbates on Alkylation Activity and Selectivity

When 80% NH₄-Y zeolite activated at 650°C was added to 100 ml toluene that contained 1.0×10^{20} molecules of perylene, the rate of alkylation was 0.045% conversion min⁻¹ g⁻¹; in the absence of perylene the rate was 0.036% conversion min⁻¹ g⁻¹. The adsorbed perylene had little effect on the selectivity, however. With perylene present the percentages of *o*-, *m*-, and *p*-cymene were 53, 17, and 30% respectively; in its absence the corresponding values were *circa* 52, 22, and 26%. Similar enhancements of catalytic activity in the pres-

ence of perylene were observed with other zeolite samples. Thus, on 90% NH₄-Y zeolite activated at 560°C the alkylation rate was 0.16% conversion min⁻¹ g⁻¹ in the presence of 1.0×10^{20} molecules of perylene, and 0.10% conversion min⁻¹ g⁻¹ in the absence of the polycyclic hydrocarbon.

In a similar experiment to those just described but substituting *p*-dimethylaminoazobenzene (1.0×10^{20} molecules) for perylene, the rate of alkylation was 0.022% conversion min⁻¹ g⁻¹ for 90% NH₄-Y zeolite activated at 490°C (0.16% conversion min⁻¹ g⁻¹ in the absence of *p*-dimethylaminoazobenzene); the percentages of *o*-, *m*- and *p*-cymene were 42, 17, and 41% respectively (49, 14, and 37% in the absence of *p*-dimethylaminoazobenzene).

Radical-Forming Activity of Ammonium-exchanged Zeolite

When toluene was added to 90% NH₄-Y zeolite activated at 400°C, the surface of the solid acquired a brownish colour that gradually deepened. After 3 hr at 100°C the sample gave a strong unresolved ESR signal with a *g* value of 2.003. Figure 3 shows the variation of the radical concentration with activation temperature of the zeolite sample. Maximum radical-forming activity was obtained when the zeolite was activated at ~620°C, whereas the alkylation activity reached its maximum value with a sample activated at ~400°C. Neither the shape of the ESR signal nor the adsorbed radical concentration were affected by the presence of propene.

DISCUSSION

Alkylation Activity

Sodium-form Y-type zeolite *x*% exchanged with ammonium ion and heated to >200°C will subsequently be referred to as *x*% HY. When 76.6% NH₄-Y zeolite was heated in air for 3 hr, temperatures in excess of 550°C were required before the ammonium ion content fell to zero (10). The samples used in the present study, how-

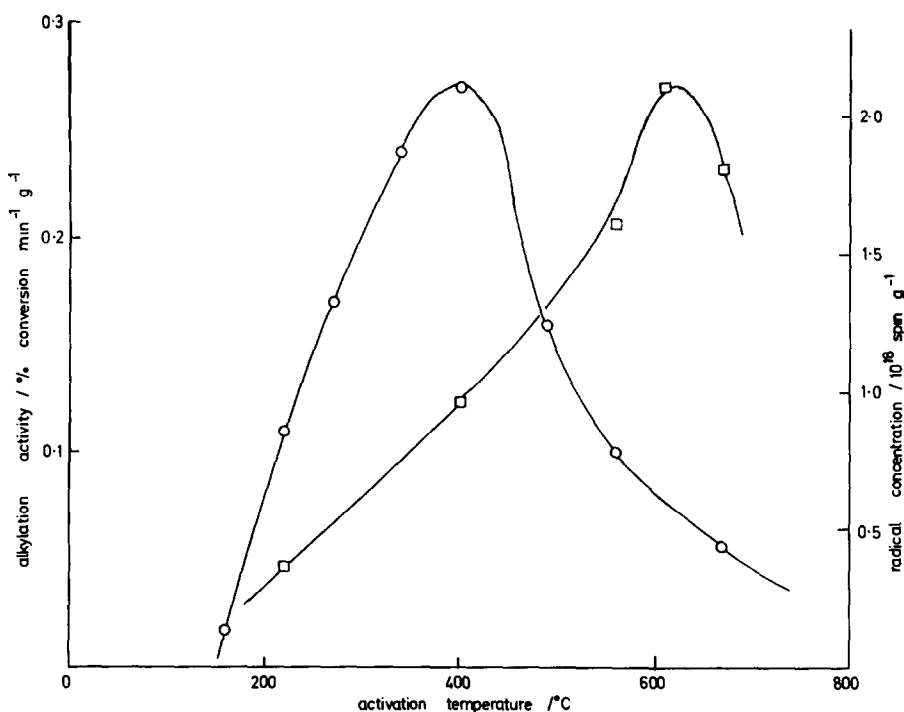


FIG. 3. Radical-forming activity of Y-type zeolite 90% exchanged with ammonium ion as a function of activation temperature with toluene as the adsorbate (\square). Alkylation activity of 90% exchanged Y zeolite as a function of activation temperature (\circ).

ever, were heated in flowing oxygen for 1 hr and then *in vacuo* for 16 hr. Consequently, complete removal of ammonia should occur at a lower calcination temperature.

Since it has already been shown that 90% HY zeolite activated at 550°C possesses high catalytic activity in the alkylation of toluene with propene (5), an important result of the present investigation is the demonstration that the alkylation ability of HY zeolite depends markedly on the activation temperature. Changing the temperature of activation was found to have no significant effect on the toluene/propene alkylation ability of LaY (5). Maxima have, however, been observed in the catalytic activity versus activation temperature plots for REX, REY, and HY zeolites when these were used as catalysts for the benzene/ethylene alkylation reaction (1). Although the maximum alkylation activities for the three samples were relatively close, the activation temperatures required to at-

tain the maxima differed markedly: 400°C (REX), 250°C (REY), 550–600°C (HY).

High catalytic activity in 80 and 90% HY for the toluene/propene alkylation reaction is confined to samples heated in the temperature range 200–600°C. Significantly, the protonic acidity of 90% HY has been shown to increase with calcination temperature up to about 325°C, to remain constant between this temperature and 500°C, and then to decline rapidly until at 800°C it is about 1/10th of its maximum value (16). Present results therefore provide support for the postulate that alkylation reactions on Y-type zeolites proceed via a carbonium-ion-type mechanism, Brønsted acidity being the origin of the alkylation activity (2, 3).

Additional evidence that Brønsted acid sites are involved in the alkylation is provided by the following findings: (a) the alkylation activity of Y-type zeolite increases with increase in the extent of sodium ion

replacement by protons (Fig. 2); (b) an adsorbed Hammett indicator (*p*-dimethylaminoazobenzene) resulted in a marked reduction in the alkylation activity of HY zeolite; (c) silica-alumina (~13% Al₂O₃) had an alkylation capacity comparable to that of Y zeolite extensively converted to the hydrogen form, whereas alumina samples calcined at various temperatures (300, 500, and 700°C) were catalytically inactive for the reaction [alumina has no strong Brønsted acidity (17)].

According to Haag (18), the rate of toluene isopropylation on REY at 110°C in the liquid phase was 3060 mmol/(hr · g catalyst) under conditions where both external gas-liquid and bulk liquid mass transfer resistances were negligible. Except for the catalyst, the present study was conducted under similar conditions, but the highest observed rate at 100°C was 0.27% conversion min⁻¹ g⁻¹, corresponding to ~150 mmol toluene reacted/(hr · g catalyst). These values differ by a factor of 20 and this could indicate the existence of some mass transfer resistances in the present study. Alternatively, a lower intrinsic activity of HY compared to REY must be assumed. Since $\text{rate}_{100^\circ\text{C}}/\text{rate}_{110^\circ\text{C}} = 3.1$ for toluene/propene alkylation over REY (18), HY would accordingly be ~60 times less active than REY.

Selectivity of the Alkylation

In the alkylation of toluene with propene over Y zeolite that is extensively in the hydrogen form *ortho-para* orientation of the substituents predominates, with a definite preference for *para* substitution when the catalyst is activated at low temperatures (~400°C) and a marked preference for *ortho* substitution at higher activation temperatures (Table 1). Over the same activation temperature range (200–700°C), the percentage of *m*-isomer in the cymene mixture doubled. The explanation for the swing toward *ortho*-orientation as the catalyst activation temperature rises above 400°C lies in the dual nature of the zeolite catalyst. At low activation temperatures

(200–400°C) the active surface sites are predominantly Brønsted acid in character and the electron-releasing methyl group in the aromatic ring of toluene ensures *ortho-para* orientation for the incoming carbonium-ion intermediate of propene that is generated by the transfer of a catalyst proton to the olefin. Although there are still many Brønsted sites on the surfaces of HY zeolites activated above 400°C, a different type of active site, which is electron-deficient, now begins to predominate. A toluene molecule adsorbed on the latter site is strongly polarized so that the electron density in the aromatic ring system decreases. Since adsorption of the molecule most likely occurs at the position *para* to the methyl group, the decrease in electron density in the ring is followed by an increase in substitution at the position *meta* to the point of adsorption leading to formation of *o*-cymene. The overall decrease in electron density in the ring also results in deactivation, with a falloff in alkylation activity as the activation temperature is further increased. The experimental findings are therefore exactly those predicted by the general theory of electrophilic aromatic substitution (19) and, in addition, provide further evidence for the dual nature of these zeolite catalysts. It should be noted that in the temperature range 500–800°C the alkylation activity due to Brønsted acidity is also declining (see previous section).

Sites with a spectrum of acceptor strengths are created on the zeolite surface as dehydroxylation proceeds. A proportion of these sites function as Lewis acid centres and are responsible for two-electron transfer processes and for the polarization of the toluene molecule that produces the swing toward *ortho*-orientation above 400°C. A smaller number of the electron-deficient sites are sufficiently powerful to induce radical formation in the adsorbed hydrocarbon molecule. This one-electron transfer activity peaks at an activation temperature of ~620°C, above which temperature the oxidizing activity of the catalyst falls off

sharply (Fig. 3). No obvious correlation therefore exists between the one-electron transfer activity of the catalyst and the activity of the catalyst for the propylation of toluene (see Fig. 3), nor between the oxidizing activity of the catalyst and the selective formation of cymene isomers on the oxide surface (see Table 1). Adsorption of perylene has, however, a significant enhancing effect on the alkylation activity of the catalyst, although only a marginal effect on its selectivity. The implication of this finding is that additional reaction sites capable of furnishing protons for carbonium-ion formation are generated on the catalyst surface. It has been established (20) that the formation of the perylene cation radical on the alumina surface is followed by further reaction leading to peroxides, quinones, etc., at room temperature. At a reaction temperature of 100°C this process is likely to occur more rapidly, and the resulting carbonaceous products may be the source of the additional protons.

From a study of CeY zeolite, it was concluded that the sites active for the generation of hydrocarbon radicals are not located in the interior of CeY, but exist on the exterior surface of the zeolite crystallites (21). No positive evidence is available from the present work that perylene molecules do not enter the supercages of HY and that the radicals result solely from reaction of the parent hydrocarbon with sites situated on the external surface of the zeolite. But the enhancement of the alkylation activity of HY zeolite by preadsorbed perylene could be interpreted as supporting this view.

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