

Alkylation Reactions over Ion-exchanged Molecular Sieve Zeolite Catalysts

Part 3.—Alkylation of Toluene and Benzene with Ethanol: Consideration of the Effects of Initial Coke Formation on *para* Selectivity

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The ethylation of toluene and benzene with ethanol at 423 K over a wide range of exchanged NaNH_4Y catalysts and also over a $\text{NH}_4\text{Y-91.5}$ sample calcined at 11 different temperatures between 523 and 875 K has been studied. Alkylation with ethanol was found not to lead to rapid catalyst deactivation or to excessive polysubstitution. The effect of such reaction variables as reaction temperature and contact time were studied in detail over an $\text{NH}_4\text{Y-87.2}$ sample. The selectivity for *m*-ethyltoluene formation remained constant at ca. 20% of the ethyltoluene product mixture irrespective of the catalyst studied, the calcination temperature used or the reaction conditions. However, the amount of the *para* isomer formed varied from 20 to 65% of the product mixture and its selectivity occurred at the expense of the *ortho* isomer. The selectivity of the catalysts was found to be a function of (i) the length of time on stream, (ii) the degree of cation exchange, (iii) calcination temperature, (iv) reaction temperature and (v) the contact time. It was found that altering the above reaction variables also varied the extent of coking of the catalysts as evidenced by the coloration changes of the catalysts. The increased selectivity for *para* formation is related to configurational diffusion of the aromatic in zeolite pores of a restricted size brought about by coke deposition. Thus *para* selectivity in these catalysts can be regulated by controlling the extent of ammonium exchange.

Primary and secondary product distribution in the methylation of toluene over zeolite catalysts has been investigated.^{1,2} High selectivity for *para* formation over cation-exchanged Y zeolites has been observed by Yashima *et al.*^{3,4} and was associated with the Bronsted acidity of the catalysts. Chen *et al.*⁵ and Kaeding *et al.*⁶ have observed high *para* selectivity over modified ZSM-5 and ZSM-11 zeolite catalysts. This was explained on the basis of an isomerization-diffusion process which promoted the selective removal of *p*-xylene from the reaction zone; however alkylation within a restricted pore size was also suggested as promoting *para* selectivity.

In the present paper a more detailed study of the *ortho/para* relationship in heterogeneous catalysis is undertaken. The effects of coking on the catalytic activity and selectivity for *para* formation are also analysed.

EXPERIMENTAL

MATERIALS

The parent zeolite was NaY [$\text{Na}_{58}(\text{AlO}_2)_{58}(\text{SiO}_2)_{134}(\text{H}_2\text{O})_{260}$] and the NH_4^+ forms of the zeolite were prepared by conventional cation-exchange procedures. For the low exchanged samples (*i.e.* < 70% exchange) ion exchange was effected by contacting 15 g of the parent NaY with the appropriate amount of NH_4Cl dissolved in 100 cm³ of deionised water. In the case of the NaNH_4Y samples of > 70% exchange, preparation was effected by repeated refluxing of 50 g of the zeolite in 250 cm³ of a 10% ammonium chloride solution over a period of three days, until the required level of exchange was achieved. The 100% exchanged NH_4Y sample

was prepared by repeated refluxing of 100 g of the zeolite in 500 cm³ of a 20% ammonium chloride solution over a period of 5 days. Between exchanges the samples were washed in hot deionised water and heated in an oven overnight at 423 K. This heat treatment provides the necessary energy of activation to accomplish a redistribution of the remaining sodium ions.⁷ This procedure was repeated until complete removal of the sodium ions was accomplished. The sodium content of the samples was determined using flame emission spectroscopy and NH₄⁺ content by elemental analysis for nitrogen. Water contents were determined using a Perkin-Elmer T. G. S. - I thermobalance operating at a heating rate of 20 K min⁻¹ and a nitrogen flow of 20 cm³ min⁻¹ was maintained over the samples. The percentage exchange of the catalysts may be inferred from the nomenclature.¹ No framework collapse could be observed before or after the activation and catalytic studies of the samples, as shown by the analysis of X-ray diffraction patterns obtained using a Jeol J.D.X. - 85 diffractometer.

The reactants benzene and toluene were of AristaR grade and were used without further purification. The AnalaR grade ethanol was further dried using the methods given by Vogel⁸ to remove all traces of water and was subsequently stored over activated sieve 4A. Ethylbenzene, *p*-ethyltoluene, *m*-ethyltoluene, *o*-ethyltoluene, 1,2-diethylbenzene, 1,3-diethylbenzene and 1,4-diethylbenzene were purchased from B. D. H. Chemicals and Fluka Ltd. Product analysis was as described previously.¹

APPARATUS AND ACTIVATION PROCEDURE

Catalytic reactions were carried out in an all-glass, fixed-bed, continuous-flow reactor operating at atmospheric pressure. Details of reactor construction and operation have been given previously.^{9,10} The catalyst were activated by slowly raising the temperature to 723 K over a period of 2 h and maintaining this temperature for a further 6 h. Oxygen at a flow rate of 120 cm³ min⁻¹ was passed over the catalyst during activation. After activation the temperature was lowered to the reaction temperature (usually 423 K) and the carrier gas changed to hydrogen at a flow rate of 120 cm³ min⁻¹.

RESULTS AND DISCUSSION

The *ortho/para* relationship in the primary product distribution and the effect of initial coking on the product selectivity were investigated in detail; such an investigation, however, would be greatly complicated or rendered impossible if isomerization, polysubstitution or very rapid catalyst deactivation were occurring. In the methylation study^{1,2} the latter two processes were present thus making an analysis of the primary product distribution difficult. Thus the main criterion for the choice of a suitable reaction was that the above three side processes were either absent or could be controlled.

From parallel experiments with a range of alkylating agents ethanol was found to be the most suitable reactant; alkylation with C₃ and C₄ alcohols was invariably found to be associated with isomerization of the products and rearrangements of the intermediate alkyl cations when the structures of the latter were suitable; the results of these studies will be dealt with in Part 4 of this series.¹¹ The ethylation of toluene and benzene with ethene was also considered as a possible test reaction and a comparison of the activity profiles for ethylation with ethene and ethanol together with the reaction conditions are shown in fig. 1; the methylation of toluene with methanol is also included for comparison. The catalyst chosen to test the suitability of the alkylating agents was NH₄Y-100 as this is the most active catalyst of the range and would be the most susceptible to deactivation and to secondary reactions of the ethyltoluenes and ethylbenzene. The activities are calculated with respect to the alkylating agent and are defined as follows

$$\text{mole \% conversion} = \frac{\text{moles of alkylated product formed}}{\text{moles of alcohol/ethylene fed}} \times 100.$$

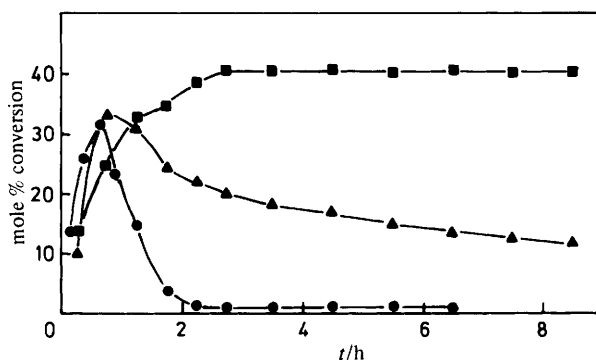


FIG. 1.—Comparison of activity profiles for alkylation of toluene over $\text{NH}_4\text{Y-100}$ with methanol at 473 K (●) with that for ethanol (■) and ethene (▲) at 423 K; ethanol:aromatic = 1:3; ethene:aromatic = 1:6; methanol:aromatic = 1:2.

At the reaction temperature of 423 K isomerization of the ethyltoluenes was considered to be negligible. High ratios of the aromatic/alkylating agent were used in order to reduce polysubstitution. The products of the ethylation reaction consisted of *p*-, *m*- and *o*-ethyltoluene and ethylbenzene. Only trace quantities of the disubstituted products of toluene or benzene were detected. It is clear from fig. 1 that deactivation occurs for alkylation with both ethene and methanol, but in the case of alkylation with ethanol the catalyst reaches a high steady-state activity. The high resistance to deactivation in the case of ethylation with ethanol as compared with ethene is due to the low partial pressure of ethene in the case of the former and to the presence of water as a side reaction product, which is known to inhibit polymerization reactions leading to catalyst deactivation.¹² A study of the dependence of the substrate selectivity on time on stream showed that it remained constant after 2 h on stream even for ethylation with ethene, where continuous deactivation occurs. The initial variation follows a profile similar to the catalytic activity profile and thus its initial variation may simply be an artefact of the presence of an induction period and not represent a change in the activity of the ethylating agent.

From these results it was concluded that the most suitable ethylating agent was ethanol. The competitive ethylation of an equimolar mixture of toluene and benzene with ethanol was also studied over all the catalysts in order to test the adherence of the ethylation reaction to the Brown selectivity relationship. In what follows the activities for the ethylation of toluene and benzene are expressed as the number of moles of aromatic converted per gram of catalyst per second. The rate of ethylation of toluene (R_T) and benzene (R_B) is calculated using the following equations

$$R_T = \frac{F_T}{W} \phi_T \quad (1)$$

$$R_B = \frac{F_B}{W} \phi_B \quad (2)$$

where F_T and F_B are the feed rates of toluene and benzene in mol s^{-1} , ϕ_T and ϕ_B are the degrees of conversion of toluene and benzene, respectively, and W is the mass of the dehydrated catalyst

$$\phi = \frac{C_o - C_i}{C_o}$$

where C_0 is the input concentration and C_i is the exit concentration. Since an equimolar mixture of toluene and benzene is used $F_T = F_B$, and consequently the relative rates are simply given as

$$\frac{R_T}{R_B} = \frac{\phi_T}{\phi_B} \quad (3)$$

Note that the calculated rate gives a measure of the average rate over the time interval used for collecting each sample but at the steady state the calculated rate will give a measure of the instantaneous activity of the catalysts.

CATALYTIC ACTIVITY OF THE CATALYSTS

Activity profiles for the ethylation of toluene and benzene over a representative range of the catalysts listed in table 1 after calcination at 723 K are presented in fig. 2. The profiles are characterized by an initial induction period with the catalytic activity remaining constant after 2 h on stream. The substrate selectivity, *i.e.* the relative rates of ethylation of toluene and benzene, is shown as a function of time on stream for just some of the catalysts studied in fig. 3 and it may be seen that it too remains constant when the overall activity of the catalysts reaches a constant value. The catalytic activity, substrate selectivity and isomer distribution after 3 h on stream are summarised in table 1.

It is evident that the selectivity for *m*-ethyltoluene formation remains constant at *ca.* 20% of the product mixture over the complete range of catalysts and it was not affected by the length of time on stream. However, the same cannot be said for the *ortho* and *para* isomers: in the low exchanged samples, $\text{NH}_4\text{Y-31.4}$ to $\text{NH}_4\text{Y-39.5}$, the *ortho* isomer accounts for *ca.* 60% of the product ethyltoluenes and remains constant at this value throughout the activity study. At higher levels of exchange the initially high selectivity for *o*-ethyltoluene formation obtains, but with increasing time on stream the selectivity for its formation decreases and there is a corresponding increase in the selectivity for *p*-ethyltoluene formation. This effect becomes progressively more pronounced as the degree of exchange increases until at 72.1% exchange the selectivity for *para* formation is higher than that for *ortho* after 2.5 h on stream and a crossover point is reached. At still higher levels of exchange this crossover point occurs at shorter times on stream until for $\text{NH}_4\text{Y-100}$ the catalyst shows *para* selectivity from the start of the activity profile. Fig. 4 shows clearly the corresponding steady-state position: the isomer distribution after 3 h on stream is plotted against the number of protons per unit cell and the crossover point between *ortho* and *para* selectivity is striking. The adherence of the ethylation results to the Brown selectivity relationship² after 3 h on stream is shown in the final column of table 1. A plot of $\log P_i^{\text{Me}}$ as a function of S_f showed considerable scatter from the predicted straight line. This is due mainly to the large variations in the selectivity for *para* isomer formation. However, it is also clear that the product distribution does not vary according to the predictions of the Brown selectivity relationship; thus the increased selectivity for *para* formation is not accompanied by a drop in the selectivity for *meta* or a corresponding increase in the substrate selectivity (column 4, table 1).

At this point it is instructive to compare the results of the present study with those found in the literature for homogeneous catalysis; some literature data are summarised in table 2. It is observed that the substrate and positional selectivity vary for different homogeneous systems. The variations in positional selectivity are caused mainly by difficulties in the analysis of the products, especially for the *ortho* isomer,¹³ and by the presence of isomerization.¹⁴ Even so it is clear that homogeneous ethylation reactions are characterised by relatively high *ortho/para* ratios and by a *meta*

TABLE 1.—COMPETITIVE ETHYLATION OF TOLUENE AND BENZENE WITH ETHANOL AT STEADY-STATE ACTIVITY OVER A WIDE RANGE OF NaNH_4Y ZEOLITES AT 423 K

sample	$\text{H}^+/\text{u.c.}$	rate/ 10^{-8} $\text{mol g}^{-1} \text{s}^{-1}$	relative rate k_T/k_B	ethyltoluene composition (mole %)				partial rate factors				$\log P_T^{\text{Me}}$	$\log M_T^{\text{Me}}$	S_T
				<i>para</i>	<i>meta</i>	<i>ortho</i>	P_T^{Me}	M_T^{Me}	O_T^{Me}	$\log P_T^{\text{Me}}$	$\log M_T^{\text{Me}}$			
$\text{NH}_4\text{Y-31.4}$	18.2	0.90	3.2	18.3	20.8	60.9	3.51	1.99	5.84	0.54	0.24	1.80		
$\text{NH}_4\text{Y-35.5}$	20.6	3.33	2.93	19.3	20.2	60.5	3.40	1.75	5.28	0.53	0.28	2.12		
$\text{NH}_4\text{Y-39.5}$	22.9	3.74	3.07	19.0	20.7	60.3	3.51	1.91	5.95	0.54	0.26	1.95		
$\text{NH}_4\text{Y-43.6}$	25.3	5.14	2.55	21.1	20.8	58.1	3.25	1.60	4.44	0.51	0.31	2.50		
$\text{NH}_4\text{Y-46.4}$	26.9	5.71	2.45	23.4	21.3	55.3	3.46	1.57	4.06	0.54	0.34	2.74		
$\text{NH}_4\text{Y-48.1}$	27.9	6.24	2.19	25.0	21.1	53.9	3.29	1.39	3.54	0.52	0.37	3.62		
$\text{NH}_4\text{Y-60.3}$	35.0	6.30	2.00	30.5	22.6	46.9	3.71	1.38	2.81	0.57	0.43	4.07		
$\text{NH}_4\text{Y-72.1}$	41.8	8.81	2.11	40.6	22.4	37.0	5.18	1.43	2.34	0.71	0.56	4.61		
$\text{NH}_4\text{Y-78.4}$	45.5	9.96	2.05	44.5	22.1	33.4	5.48	1.36	2.05	0.74	0.60	5.5		
$\text{NH}_4\text{Y-87.2}$	50.6	11.57	2.08	50.6	21.5	27.9	6.34	1.35	1.74	0.80	0.67	6.17		
$\text{NH}_4\text{Y-91.5}$	53.1	14.20	2.29	54.7	20.7	24.6	7.51	1.42	1.69	0.87	0.72	5.72		
$\text{NH}_4\text{Y-93.3}$	54.1	18.90	2.94	58.6	20.1	21.1	10.38	1.78	1.88	1.01	0.76	4.08		
$\text{NH}_4\text{Y-98.3}$	57.0	21.59	2.67	59.6	20.5	19.9	9.57	1.65	1.59	0.98	0.76	4.5		
$\text{NH}_4\text{Y-100}$	58.0	25.92	2.65	63.9	19.7	16.4	10.19	1.57	1.30	1.00	0.81	5.12		

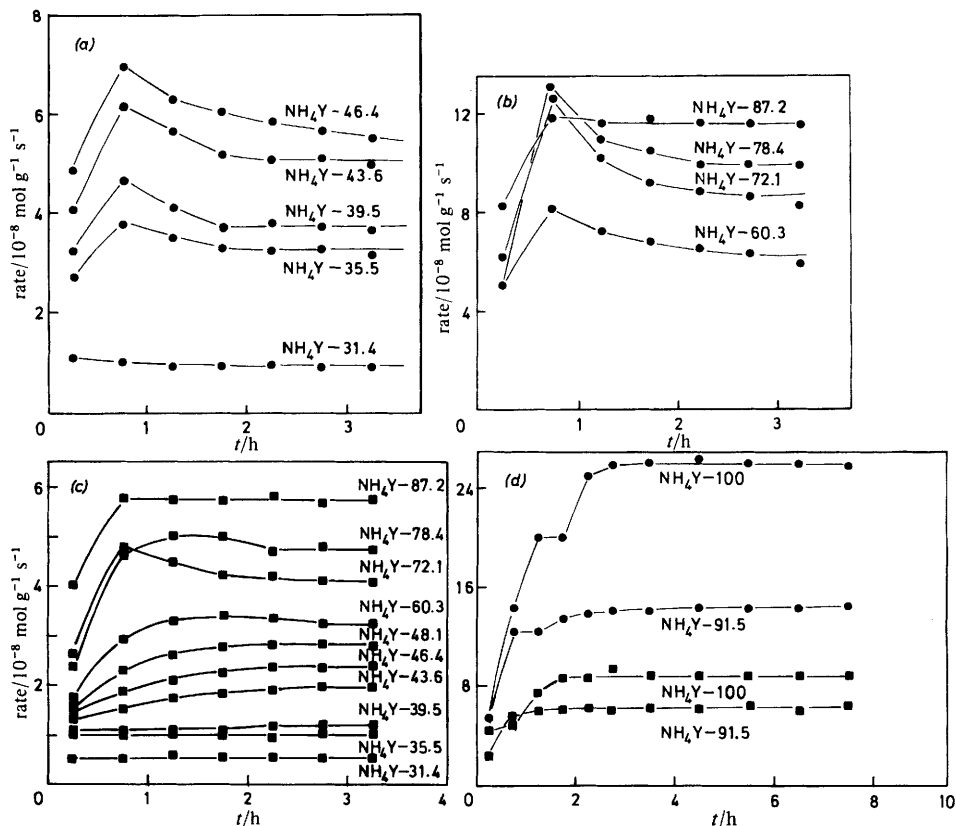


FIG. 2.—(a) and (b) Rate of competitive ethylation of toluene at 423 K as a function of time on stream over a range of ammonium-exchanged Y zeolite catalysts of increasing acidity; toluene: benzene: ethanol = 3:3:1; $W/F = 31.4 \text{ g (mol h}^{-1}\text{)}^{-1}$. (c) Rate of competitive ethylation of benzene at 423 K as a function of time on stream over a range of ammonium Y zeolite catalysts of increasing acidity; toluene: benzene: ethanol = 3:3:1; $W/F = 31.4 \text{ g (mol h}^{-1}\text{)}^{-1}$. (d) Rate of competitive ethylation of toluene (●) and benzene (■) at 423 K as a function of time on stream over $\text{NH}_4\text{Y-91.5}$ and $\text{NH}_4\text{Y-100}$; toluene: benzene: ethanol = 3:3:1; $W/F = 31.4 \text{ g (mol h}^{-1}\text{)}^{-1}$.

distribution of ca. 20%; although the *meta* distribution corresponds closely with that obtained in the present study for a wide range of zeolite catalysts it is evident from the results of this section that a very real difference exists between homogeneous catalysis and the present heterogeneous systems with respect to the positional selectivity especially in the highly acidic catalysts.

EFFECT OF CALCINATION TEMPERATURE ON THE PRODUCT DISTRIBUTION

The effect of calcination temperature on the catalytic activity, the substrate and positional selectivity was studied in detail over $\text{NH}_4\text{Y-91.4}$ for 11 different calcination temperatures between 523 and 873 K. Again the catalytic activity, substrate and positional selectivity reached a constant value after 2 h on stream. The results for 3 h on stream are summarised in table 3. The catalytic activity as a function of calcination temperature is shown in fig. 5; the shape of the activity profile is seen to be very similar to the effect of calcination temperature on the Bronsted acidity as measured by pyridine adsorption.¹⁶ This strongly supports the conclusion that the Bronsted acidity is the origin of the catalytic activity. The ethyltoluene distribution as a function of

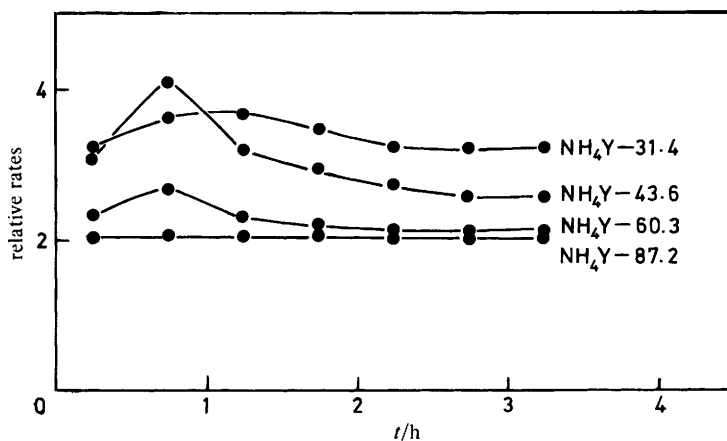


FIG. 3.—Relative rates of ethylation of toluene and benzene at 423 K over a range of ammonium-exchanged Y zeolite catalysts which were calcined at 723 K.

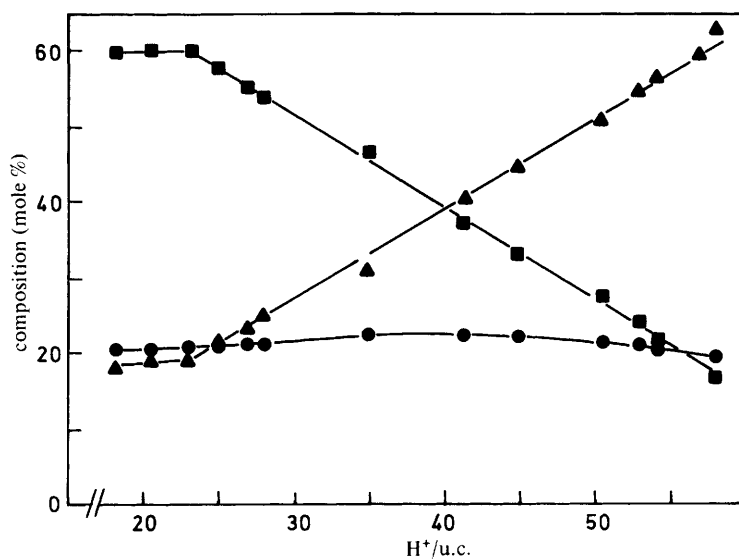


FIG. 4.—Steady-state activity at 423 K showing the variation of ethyltoluene composition as a function of the number of protons per unit cell. ■, *ortho*; ▲, *para*; ●, *meta*; toluene:benzene:ethanol = 3:3:1.

time on stream was studied in detail for a range of calcination temperatures and it was found that on progressing from 423 to 673 K the isomer distribution varied with time on stream in exactly the same way as it did on changing from low exchanged NH_4Y zeolites to the higher exchanged samples (fig. 5); however, for calcination temperatures above 773 K the opposite trend was observed (fig. 6).

Thus the selectivity of the catalysts for *p*-ethyltoluene formation after 3 h on stream, *c.f.* table 3 and fig. 6, increases in going from a calcination temperature of 523–673 K, remains constant up to 773 K and decreases again up to 873 K. It is thus evident that the selectivity for *p*-ethyltoluene formation follows a profile identical to the catalytic activity profiles of the catalysts shown in fig. 5. Conversely, the selectivity for *o*-ethyltoluene varies in the opposite sense to the *para* isomer (see fig. 6) with the *meta*

isomer remaining essentially constant at *ca.* 20% of the product mixture except at the lower calcination temperatures where it tends to be less. At first sight then it would seem that these phenomena are only directly related to the Bronsted acidity, but as shown later other factors are also involved.

TABLE 2.—FRIEDEL-CRAFTS ETHYLATION OF TOLUENE AND BENZENE

catalyst/alkyl halide	substrate selectivity, k_T/k_B	ethyltoluene composition (mole %)		
		<i>para</i>	<i>meta</i>	<i>ortho</i>
BF ₃ /C ₂ H ₅ F ^a	2.7-0.6	24-32	23-29	44-49
AlBr ₃ /C ₂ H ₅ Br ^b	2.6	41.0	21.0	38.0
— ^c	—	34.0	18.0	48.0

^a Ref. (14); ^b ref. (15); ^c ref. (13).

EFFECT OF REACTION TEMPERATURE, SPACE VELOCITY AND CATALYST MASS ON THE SELECTIVITY OF *p*-ETHYLTOLUENE FORMATION OVER NH₄Y-87.2

Since the selectivity for *o*- or *p*-ethyltoluene formation could not be rationalised in terms of the activity of the ethyl cation a more detailed examination of the effects of the reaction conditions was undertaken. The catalyst studied in this instance was NH₄Y-87.2, since it was in this exchange range of the NH₄Y samples that the biggest variation in the selectivity for *o*- and *p*-ethyltoluene with time on stream occurred. Only the ethylation of toluene with ethanol was studied. The effect of reaction temperature on both the activity and selectivity after 3 h on stream (where they reached constant values) can be gauged from the data in table 4 and from fig. 7(a). It is clear that the selectivity for *para* formation increases with temperature accompanied by a corresponding drop in the selectivity for *ortho* formation, with the selectivity for *meta* remaining constant; the effect of reciprocal space velocity and catalyst mass on the steady-state activity and selectivity is shown in fig. 7(b) and (c), respectively; thus increasing the value of any one of these parameters increases both the steady-state catalytic activity and the selectivity for *para* formation at the steady state. We have further observed that increasing the magnitude of these variables also leads to correspondingly longer and more pronounced induction periods both in the catalytic activity and in the time needed to reach a steady-state isomer distribution. Both induction periods (*i.e.* for catalytic activity and product distribution) were approximately the same and the longer the induction period the higher the *para* selectivity.

CORRELATION OF *p*-ETHYLTOLUENE SELECTIVITY WITH COKING OF THE CATALYSTS

Even though deactivation was not observed in the ethylation reaction with ethanol, nevertheless the more active samples changed colour in the course of the reaction. The colour change, or darkening of the catalysts, seems to be associated with increasing *para* selectivity and increasing acidity. Thus the low exchanged NH₄Y catalysts, which were *ortho* selective throughout the activity profile, remained white in colour. However, the higher exchanged NH₄Y catalysts underwent increasing darkening passing from white, through yellow, to light brown, and then to dark brown in colour. This darkening of the catalysts follows closely the activity of the samples and the increased selectivity for *para* formation. Thus in the case of NH₄Y-91.5 calcined at

TABLE 3.—COMPETITIVE ETHYLATION OF TOLUENE AND BENZENE WITH ETHANOL OVER $\text{NH}_4\text{Y-91.5}$ CALCINED AT DIFFERENT TEMPERATURES

calcination temp./K	rate/ 10^{-8} $\text{mol g}^{-1} \text{s}^{-1}$	relative rates, k_T/k_B	ethyltoluene composition (mole %)				partial rate		$\log \frac{P_f^{\text{Me}}}{M_f^{\text{Me}}}$	$\frac{\log P_f^{\text{Me}}}{\log M_f^{\text{Me}}}$
			<i>para</i>	<i>meta</i>	<i>ortho</i>	M_f^{Me}	P_f^{Me}	$\log P_f^{\text{Me}}$		
523	3.75	3.70	19.7	15.0	65.3	1.66	4.37	0.64	0.42	2.91
548	4.95	3.36	22.6	15.7	61.7	1.58	4.56	0.66	0.46	3.29
585	7.15	2.42	30.4	21.7	47.9	1.58	4.43	0.64	0.44	3.2
623	9.10	1.28	40.4	21.1	38.5	1.44	5.53	0.74	0.58	4.67
673	14.40	2.55	54.4	20.9	24.7	1.60	8.32	0.92	0.71	4.60
723	14.20	2.29	54.7	20.7	24.6	1.42	7.51	0.87	0.72	5.72
773	14.15	2.80	55.5	21.1	23.4	1.77	9.32	0.97	0.72	3.91
793	11.55	2.33	50.2	21.3	27.5	1.49	7.02	0.84	0.67	4.89
823	8.75	2.10	44.9	21.9	33.2	1.38	5.67	0.75	0.61	5.38
848	4.90	2.25	30.4	21.3	48.3	1.44	4.11	0.61	0.45	3.86
873	2.75	2.62	26.2	20.4	53.4	1.60	4.11	0.61	0.41	3.01

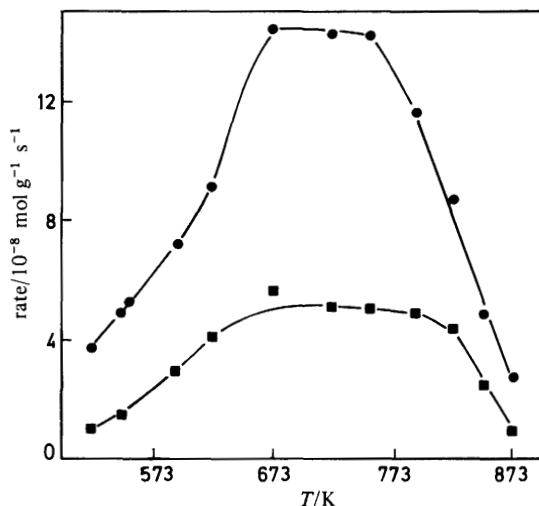


FIG. 5.—Steady-state rates of ethylation of toluene (●) and benzene (■) at 423 K over $\text{NH}_4\text{Y-91.5}$ calcined at several temperatures; toluene:benzene:ethanol = 3:3:1; $W/F = 31.4 \text{ g (mol h}^{-1}\text{)}^{-1}$.

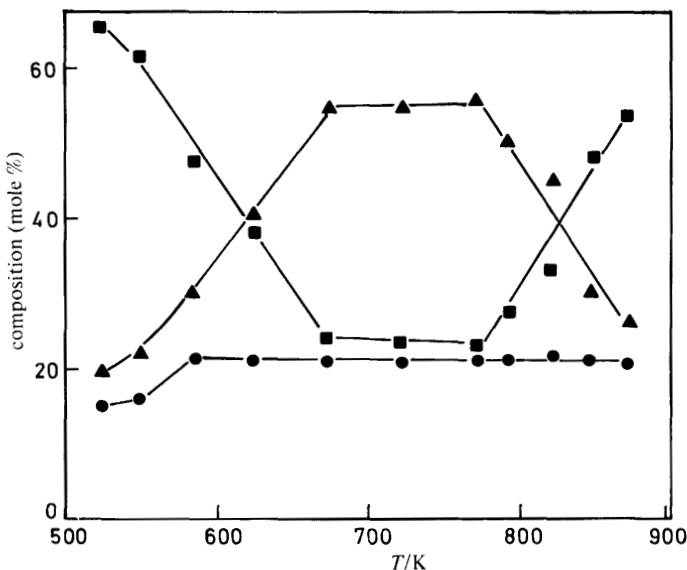


FIG. 6.—Composition of ethyltoluene isomer mixture after 3 h on stream at 423 K over $\text{NH}_4\text{Y-91.5}$ calcined at several temperatures; ■, *ortho*; ●, *meta*; ▲, *para*.

different temperatures, the catalysts remained white or slightly grey when ethylation was studied after calcination at 523 or 873 K and were *ortho* selective but turned brown when ethylation was studied after calcination at 673 to 773 K and were *para* selective. Also when $\text{NH}_4\text{Y-87.2}$ was studied at lower contact times (*i.e.* under conditions of high space velocity or small mass of catalyst) the catalyst bed remained white and the catalyst was *ortho* selective. However, as the contact times increased the catalyst bed became increasingly coloured until at the higher contact times studied the bed was deep brown in colour and was *para* selective.

It was further noted that the discoloration of the catalyst pellets was not uniform: pellets at the top of the reactor were only slightly coloured whereas the catalyst pellets at the bottom of the reactor were the most coloured or coked. This effect was investigated in the case of catalyst $\text{NH}_4\text{Y-87.2}$ where the mass of catalyst was varied between 0.5 and 4.0 g. When 0.5 g was used the catalyst bed remained white and was *ortho* selective. On increasing the mass of catalyst from 1.0 to 4.0 g the lower regions of the catalysts bed became progressively darker in colour while the observed selectivity for *para* formation progressively increased, *cf.* fig. 7(c). Note that a linear

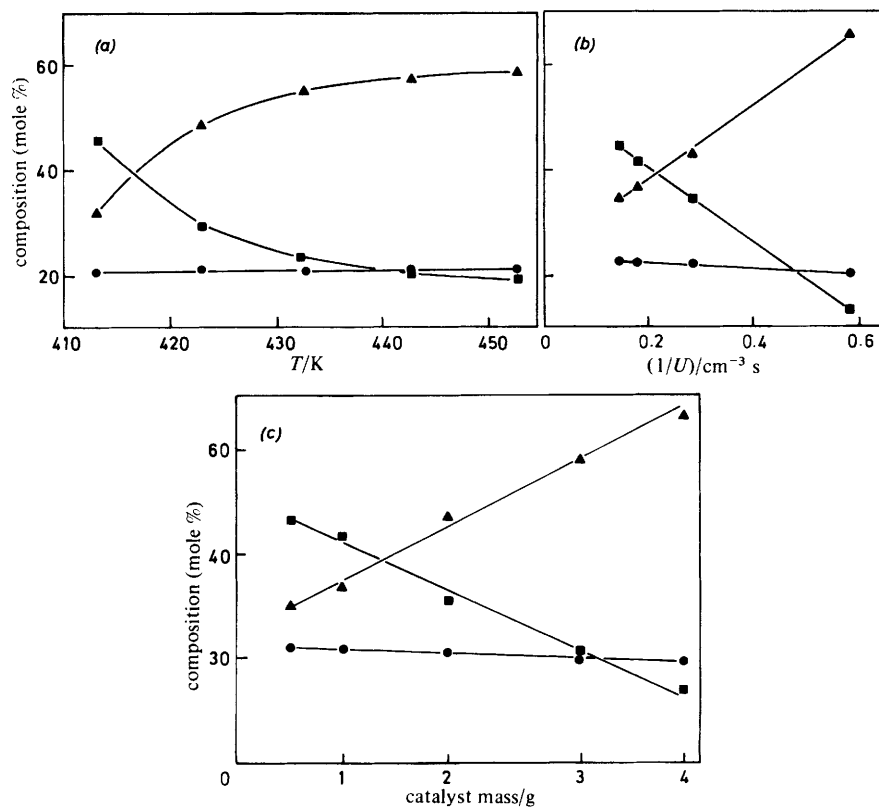


FIG. 7.—(a) Composition of ethyltoluene isomer mixture after 3 h on stream over $\text{NH}_4\text{Y-87.2}$ as a function of the reaction temperature; ■, *ortho*; ●, *meta*; ▲, *para*; toluene:ethanol = 6:1; calcination temperature = 723 K; $W/F = 34.0 \text{ g} (\text{mol h}^{-1})^{-1}$. (b) Composition of ethyltoluene isomer mixture after 3 h on stream at 423 K over $\text{NH}_4\text{Y-87.2}$ as a function of the reciprocal space velocity; ■, *ortho*; ●, *meta*; ▲, *para*; toluene:ethanol = 3:1; calcination temperature = 723 K. (c) Composition of ethyltoluene isomer mixture after 3 h on stream at 423 K over $\text{NH}_4\text{Y-87.2}$ as a function of catalyst mass. ■, *ortho*; ●, *meta*; ▲, *para*; toluene:ethanol = 4:1; calcination temperature = 723 K; $F = 6.02 \times 10^{-2} \text{ mol h}^{-1}$.

relationship also exists between the ethyltoluene composition with respect to the *ortho* or *para* isomers and the depth of the catalyst bed. It is now clear that a very definite link exists between the increased selectivity of the catalysts for *para* formation and the deposition of carbonaceous material in the course of the reaction, as evidenced by the observed coloration of the catalyst pellets; the long induction times for the more active catalysts might then be due to loss of the ethylating agent in the coke-forming reactions before these reactions have ceased and the catalyst has reached a steady-state activity; this point is referred to below. It is thus logical that those catalysts with the

most extensive induction periods (or coking) should be the most *para* selective, as indeed we have observed. The association of acidity with the build-up of carbonaceous material in the catalyst pores would thus explain why a seemingly non-related set of reaction parameters such as reaction temperature, contact time and intrinsic activity (Bronsted acidity) should dramatically change the selectivity for *para* formation. Increasing the magnitude of any one of the above reaction variables will not only increase the activity of the catalyst but will also increase the extent of coke formation, as evidenced by the change in colour of the catalysts. It also explains why the selectivity for *para* formation increases with time on stream. Although a carbon analysis of the spent catalysts did show an increasing carbon content with deepening catalyst colour it was not possible to establish a relationship with *para* selectivity owing to the relatively small differences between the coke levels of the samples.

TABLE 4.—RATE OF ETHYLATION AND COMPOSITION OF ETHYLTOLUENES AFTER 3 h ON STREAM FOR NH₄Y-87.2

<i>T</i> /K	rate/10 ⁻⁸ mol g ⁻¹ s ⁻¹	ethyltoluene composition (mole %)		
		<i>para</i>	<i>meta</i>	<i>ortho</i>
413	6.17	33.1	21.0	45.9
423	10.69	48.7	21.4	29.9
433	15.64	55.3	20.9	23.8
443	21.54	57.3	21.5	21.2
453	33.78	58.9	21.4	19.7

When ethylation was carried out over the partially deactivated NiY and Ni, SnY catalysts (using samples over which the methylation study with methanol had already been carried out, see Part I) it was noted that changing the reaction conditions such as temperature and space velocity did not lead to further deactivation and had little or no effect on the positional selectivity. This latter observation indicates that variations of such reaction variables as contact time and temperatures do not in themselves bring about the change in positional selectivity.

Plots of conversion against the reciprocal space velocity showed that the reactor was operating in the differential mode and that in the activity range studied the degree of conversion gives a direct measure of the rate of reaction. For the case of a differential flow reactor the change in concentration and, therefore, the degree of conversion (ϕ) of the reactant in question (toluene) must be kept small enough so that the rate per gram of catalyst (γ_m) can be considered as a constant. When this is the case a linear relationship is observed between (γ_R) and ϕ , *i.e.*

$$\gamma_R = \gamma_m M = UC_o\phi \quad (4)$$

where M is the mass of catalyst sample in g, U is the space velocity of reactants plus carrier gas in cm³ s⁻¹ and C_o is the input concentration in mol cm⁻³. Writing eqn (4) in the following form

$$\phi = \left(\frac{\gamma_m}{C_o}\right) M \left(\frac{1}{U}\right) \quad (5)$$

one can readily see that changing U while keeping all the other parameters constant should give a straight line for a plot of ϕ against $1/U$ and the plot should have a zero intercept; similarly varying only M should also give a straight line for a plot of ϕ

against M which again should pass through the origin. The space velocity was altered by varying both the feed rate of the reactants and the carrier gas such that the molar ratio of hydrogen to hydrocarbon remained constant, *i.e.* C_0 was kept constant. We obtained the required linear relationships with zero intercept at the origin for the above plots, showing that a mass balance occurs for the aromatic fraction at the steady state. This means that none of the ethyltoluene products are irreversibly adsorbed on the catalyst surface and that no further alkylation to form polysubstituted products, which are not detected in the product mixture, is occurring. This is very important as the occurrence of either of the above two processes (irreversible adsorption or further alkylation) would lead to an apparent change in the selectivity of the catalysts. The absence of the above two processes is further suggested by the relative constancy of the *meta* fraction irrespective of the reaction conditions used. A further consequence of the linearity of these plots is that the value of γ_m stays constant over the activity range studied even though the selectivity for *para* formation varies dramatically. The constancy of γ_m means that the deposition of carbonaceous material is only minor and does not directly eliminate the active sites, or block access to them, or introduce large diffusional effects; this conclusion is also supported by the shapes of the activity profiles.

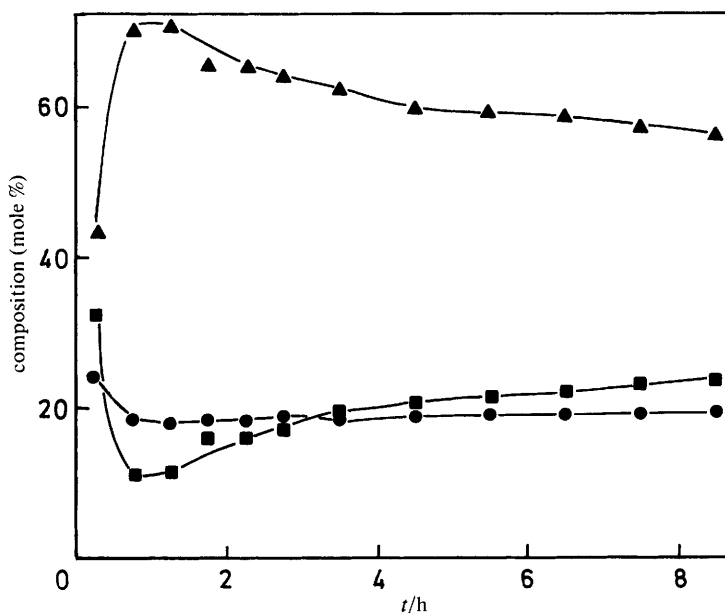


FIG. 8.—Composition of ethyltoluene isomer mixture as a function of time on stream over $\text{NH}_4\text{Y-100}$ at 423 K; ■, *ortho*; ●, *meta*; ▲, *para*; toluene:benzene:ethylene = 1.5:1.5:1.

It is interesting to compare the effect of time on stream on the product distribution for ethylation with ethanol (fig. 5) with that for ethylation with ethene over $\text{NH}_4\text{Y-100}$, fig. 8, where catalyst deactivation, as already noted (fig. 1), has occurred; it is a striking fact that where deactivation of the catalysts occurs the selectivity for *ortho* formation starts to increase again (fig. 8) with a corresponding drop in the selectivity for *para* formation. Over the partially deactivated NiY and Ni, SnY catalysts the reaction was found¹ to be *ortho* selective; for the latter catalysts the formation of carbonaceous materials has become even more serious with the permanent blockage of part or all

of the internal pore structure and the consequent localisation of the alkylation reaction towards the pore mouths. This also explains why in the methylation of toluene with methanol a very definite increased selectivity of *p*-xylene formation was observed at the beginning of the activity profiles,¹ especially for the more-acidic LaY and NH₄Y catalysts: thus at the beginning of the activity profile most of the methylation reaction was occurring in the internal pore structure where only moderate coking had occurred; however, after deactivation the reaction was localised on the external surface or pore mouths so that the selectivity for *para* formation dropped and became very similar to that occurring in homogeneous catalysis or on solids with no three-dimensional small pore structure, e.g. Nafion H. This effect is considered in greater depth in the next section.

ORIGIN OF *para* SELECTIVITY AND THE CONCEPT OF CONFIGURATIONAL DIFFUSION IN ZEOLITES OF RESTRICTED PORE SIZES

In homogeneous alkylation the random motions of the aromatic and the alkylating agent bring about the initial interaction between the two species. The probability of the ethylating agent interacting with the *ortho*, *meta* and *para* positions of an aromatic such as toluene are in the ratio of 2:2:1, assuming that the methyl group does not introduce any steric effect. After the initial interaction the orientated τ -complex is formed followed by the formation of a 6-complex, with the rate of formation of the latter species determining the rate of ethylation and the orientation. However, in the confined space of the zeolite internal pore structure the initial interaction of the aromatic with the ethylating agent does not occur as a result of the random motions of both species. Instead the aromatic encounters the adsorbed carbonium ion as a result of its normal diffusional motion through the zeolite pore structure. However, zeolite diffusion is in the extremity of Knudsen region, i.e. in the configurational regime,¹⁷ which implies that the configuration of the organic species, among other factors, influences zeolite diffusion. It is proposed that in samples which contain low levels of coke diffusion becomes very sensitive to the configuration adopted by the aromatic owing to the reduced space within the zeolite pores, and the aromatic (toluene in the present instance) approaches the adsorbed carbonium ion with the *para* position foremost and consequently preferred substitution occurs at this position. Even though the configurational diffusion of the aromatic is being influenced by the reduced space within the pore structure it is not affecting the rate of reaction, as was shown by the constancy of γ_m ; only the orientation is changed. This then explains why the selectivity for *para* formation occurs almost solely at the expense of the *ortho* isomer since it is the position farthest away from the methyl group which will be most affected by the orientating effect. Also, since the *ortho* and *para* positions are activated to the same extent, the orientating effect does not greatly affect the rate of reaction.

Applying the above conclusions to the range of NH₄Y samples of the present study, it is suggested that in the less acidic samples the aromatic approaches the adsorbed ethyl cation in a fairly random configuration so that the two electron-dense *ortho* positions are preferentially alkylated. There may, however also be some orientating effect favouring *ortho* substitution as the amount of *ortho* formed does tend to be higher than in homogeneous catalysis: evidence for such an effect was found from heats of immersion¹ and from infrared studies of adsorbed aromatics on these catalysts, the results of which will be published elsewhere. In the more active samples containing small levels of coke the preferred configuration of attack is with the electron-dense *para* position directed towards the surface carbonium ion. These changes in positional selectivity are also reflected in small changes in the substrate selectivity, as can be seen on a close examination of table 1. The *ortho* selective catalysts show high substrate

selectivity as the electron-dense *ortho* positions are being preferentially alkylated. In the intermediate case where attack on the *ortho* or *meta* positions is not preferred, the substrate selectivity decreases and a slight increase in the selectivity for *meta* formation is obtained. Again where the electron-dense *para* positions are preferentially directed towards the adsorbed ethyl cation the substrate selectivity again increases.

Thus the selectivity for *para* formation is directly related to the relative shape and size of the aromatic with respect to the internal pore structure of the zeolite. The larger the aromatic or the smaller the internal pore structure, the more selective the catalyst will be towards *para* substitution. This is also demonstrated in the ethylation of ethylbenzene with ethanol over NH₄Y-87.2: the results are summarised in table 5. It is clearly seen that increasing the size of the aromatic has the effect of increasing the selectivity for *para* formation to such an extent that none of the *ortho* isomer is formed.

TABLE 5.—COMPOSITION OF DIETHYLBENZENE OBTAINED FROM ETHYLATION OF ETHYLBENZENE OVER NH₄Y-87.2 AT DIFFERENT TEMPERATURES

T/K	rate ^a /10 ⁻⁸ mol g ⁻¹ s ⁻¹	diethyltoluene composition (mole %)		
		<i>para</i>	<i>meta</i>	<i>ortho</i>
423	23.28	78.5	21.5	—
453	53.28	87.2	12.8	—
thermodynamic distribution at 300 K		28.0	69.0	3.0

^a Data taken after 3 h on stream. Ethylbenzene:ethanol = 6:1.

CONCLUSION

The selectivity of ammonium Y zeolite catalysts in the ethylation of toluene is a function of (i) the length of time on stream, (ii) the degree of proton exchange, (iii) the calcination temperature, (iv) the reaction temperature and (v) the contact time. Increasing any of these reaction parameters leads to an increased yield of *para*-ethyltoluene at the expense of the *ortho* isomer; this increased selectivity is related to configurational diffusion of the aromatic in zeolite pores of a restricted size brought about by carbon overlayer formation.

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