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Alkylation Reactions over Ion-exchanged Molecular Sieve Zeolite Catalysts

Part 1.—Alkylation of Toluene with Methanol: Consideration of the Effects of Reaction Parameters on Catalyst Deactivation and the Extent of Polysubstitution

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The alkylation of toluene with methanol under non-isomerizing conditions has been studied over a range of ion-exchanged zeolite catalysts. Rapid deactivation with increasing time on stream was observed in the case of LaY and NH_4Y catalysts, whereas a NiY and a range of Ni,SnY samples manifested a high steady-state activity; the catalytic activity at the steady state could be related to the chemical composition of these latter samples. Catalyst deactivation was always associated with the formation of polysubstituted products. From a detailed study of the systems at the steady state it was concluded that (i) methylation of toluene is always associated with the formation of tri- or tetra-methylbenzenes to a greater or lesser extent over the partially deactivated catalysts; (ii) the origin of the polymethylated products is a weakly adsorbed *o*-xylene species; (iii) the selectivity towards polysubstitution varies with time on stream. This results from a change in the strength of interaction between the xylenes and the catalyst surface as shown by studies of the heats of immersion of the catalysts.

Zeolite catalysts have proved to be one of the most rewarding areas of catalytic research in recent years. This is because these silica–aluminas with their three-dimensional crystalline lattices can be readily subjected to relatively clear modifications of their structures and chemical compositions allowing complex investigations of their catalytic and sorption properties. Of the many different types of reactions studied over these catalysts, electrophilic aromatic substitution has received considerable attention over the past 15 years. The most studied reaction of this type has been alkylation of the aromatics toluene and benzene with various alkylating agents. These include ethylene,[1-5] propylene,[4,6-8] cyclohexene,[9] hex-1-ene,[2] dec-1-ene,[2] ethyl chloride,[2] ethanol[2,10] and methanol.[2,11-15] Early on in the studies of alkylation reactions over zeolite catalysts the close similarity between heterogeneous and homogeneous alkylation systems was recognised. This was evidenced by the similarities in the structures of the product alkylaromatics and the similar patterns of both substrate and positional selectivity, indicating that the reaction mechanism in both cases involved an electrophilic attack on the electron-rich aromatic ring by a carbonium-ion-type intermediate:[16] thus the alkylation of toluene has been found to be *ortho/para* orientating and the rate of alkylation of toluene is greater than that of benzene. The heterogeneous alkylation of toluene with methanol over zeolites, however, is a reaction which has not been studied extensively. This is because methanol is a poor alkylating agent and also because the catalysts undergo rapid deactivation due to coke formation.[2] The reaction can be complicated further by the isomerization of the primary alkylated products and by further methylation forming the tri- and tetra-methylbenzenes. Allen *et al.*[17] found in a comprehensive study of the homogeneous methylation of toluene, using a wide variety of methylating agents and Friedel–Crafts catalysts, that isomerization always accompanied alkylation.

The alkylation of toluene with methanol has great potential industrially because of the ready availability of the reactants and the importance of *p*-xylene in the production of terephthalic acid for use in the synthesis of polyester fibres. The present paper concentrates on methylation, mainly on Y zeolite catalyst systems incorporating tin, in an effort to reduce deactivation and to increase the steady-state activity; previous work on various aspects of deactivation is summarised in ref. (18)-(22). Other papers in the present series will deal with primary product selectivity in alkylation, alkylation with other alcohols, the effect of zeolite structure and carbon overlayers in ethylation and spectroscopic analysis of the nature of the reaction intermediates and active sites.

EXPERIMENTAL

MATERIALS

The parent zeolite was NaY [Na_{58} $(AlO_2)_{58}$ $(SiO_2)_{134}$ $(H_2O)_{260}$] and the cationic and ammonium forms were prepared by conventional cation-exchange procedures using aqueous solutions of their chloride salts. Except for sample 5 (*cf.* table 1) the preparation of the Ni,SnY catalysts was achieved by initially preparing a tin sample (NaDMTY) by ion exchanging the parent sodium Y with a 0.1 mol dm^{-3} solution of dimethyl tin dichloride. Since the dimethyl tin dichloride solution was found to be highly acidic, the pH of the solution was adjusted to 4.5 using sodium hydroxide solution so as to prevent aluminium extraction and destruction of the zeolite structure. This sample was then further exchanged for 12 h with the appropriate quantities of Ni using 100 cm^3 exchange solution to give the Ni,Sn combination. The quantities of materials used in the exchange procedure are given in table 1. In the case of the LaY and NH_4Y samples the sodium content was determined by flame emission spectrophotometry. For the NiY and Ni,SnY samples the tin content was determined by polarography,[23] whereas the nickel and sodium contents were determined by atomic absorption and flame emission spectrophotometry, respectively. The composition of the catalysts is given in table 2. Retention of crystallinity by the catalysts after both activation and catalysis was verified by X-ray diffraction.

The organic reagents toluene and methanol were AristaR grade (> 99.9% purity) and were used without further purification.

ANALYSIS

Product analysis was carried out using a Pye Unicam G.C.V. chromatograph employing a flame ionisation detector. The chromatograph was used in conjunction with a Pye Unicam DP 88 computing integrator. The products of reaction were identified by comparison with the retention times of known standards purchased from B.D.H. chemicals and Fluka Ltd. The products were separated on columns of 5% Bentone and 5% di-isodecylphthalate on Chromosorb W. The column temperature was normally 343 K and the nitrogen carrier gas flow rate was 30 cm^3 min^{-1}. Product samples were collected after time intervals of 0.25 or 0.5 h until steady-state activity was reached and at hourly periods thereafter. Consequently pre-steady-state

TABLE 1.—PREPARATION OF Ni,SnY SAMPLES FROM NaDMTY

catalyst	mass of sample	mass of metal salt
6	15 g of NaDMTY	2.4295 g of $NiCl_2 \cdot 6H_2O$
7	15 g of NaDMTY	1.8222 g of $NiCl_2 \cdot 6H_2O$
8	15 g of NaDMTY	1.2148 g of $NiCl_2 \cdot 6H_2O$
9	15 g of NaDMTY	0.6074 g of $NiCl_2 \cdot 6H_2O$
10	15 g of NaY	1.6095 g of $NiCl_2 \cdot 6H_2O$
5	10 g of NaY	1.6197 g of $NiCl_2 \cdot 6H_2O$ +0.7408 g Me_2SnCl_2

TABLE 2.—COMPOSITION OF THE CATALYSTS

(*a*) Catalysts not containing tin

catalyst	M^{n+}/u.c.	water content (weight %)
NH_4Y-100[a]	58.0	21.22
LaY-88.9	17.2	24.90
NiY-27.4 (catalyst 10)[b]	6.7	26.40

[a] The notation MY-*x* denotes *x*% exchange of sodium by M^{n+}. [b] This sample also contained 2.5 H^+.

(*b*) Catalysts containing tin

catalyst	Ni^{2+}/u.c.	Sn^{n+}/u.c.	Na^+/u.c.	water content (weight %)
5	7.0	1.2	30.2	26.80
6	7.9	3.2	26.9	26.08
7	6.4	4.5	29.1	25.84
8	5.1	6.4	29.0	24.60
9	3.0	7.1	35.9	23.77

analyses are integral in nature whereas those performed after the steady state was reached reflect the true instantaneous catalytic activity.

APPARATUS AND ACTIVATION PROCEDURE

Catalytic reactions were carried out in an all-glass, fixed-bed, continuous-flow reactor operating at atmospheric pressure. The catalysts were pelletized without binder using a pressure of 4000 kg cm^{-2}, sieved and then particles of 1700-1500 μm were selected for use. The mass of hydrated catalyst sample (W) used was 2.0 g and it was diluted with an equal volume of anti-bumping granules. Details of the reactor construction and operation have been given previously.[24]

Activation procedures were adopted so as to generate the maximum number of Bronsted acid sites for the NH_4Y[2, 25] and LaY[2, 26] samples. This is because in alkylation reactions it is generally accepted that the origin of the catalytic activity is the Bronsted acidity. The NH_4Y samples were calcined in oxygen at a flow rate of 120 cm^3 min^{-1} at 723 K for 6 h. Elemental analysis for nitrogen after this pretreatment did not detect the presence of this gas in the activated catalysts and therefore they were considered to be completely in the hydrogen form. The LaY sample was activated by calcination in oxygen at a flow rate of 120 cm^3 min^{-1} for 3 h at 573 K. The NiY and Ni,SnY catalysts were activated by reduction of the nickel ions in gaseous hydrogen thus generating Bronsted acidity; these catalysts were then treated in flowing hydrogen at a flow rate of 120 cm^3 min^{-1} for 6 h at 723 K. The chemistry of the reduction process has been studied extensively;[27] it is unlikely that tin is reduced by this hydrogen treatment since previous Mossbauer studies[23] of a SnY and a Ni,SnY sample treated in hydrogen as described above did not show the presence of tin metal.

RESULTS AND DISCUSSION

CATALYTIC ACTIVITY OF THE CATALYSTS

The methylation of toluene with methanol was studied over all the catalysts listed in table 2 and typical activity profiles as a function of time on stream are presented in fig. 1 (*a*)-(*c*). In all cases hydrogen was used as a carrier gas at a flow rate of 120 cm^3 min^{-1} and the hydrocarbon feed rate was 5.87 cm^3 h^{-1}, thus giving a contact time between the reactants and catalyst of *ca.* 0.5 s. The severity of the alkylating conditions varied with the activity of the catalysts: this was arranged so as to study the reaction at reasonably low conversion levels, to reduce polysubstitution of the primary alkylated products and to eliminate isomerization of the alkylated products. The activity was reduced by increasing the toluene to methanol ratio for the more active NH_4Y and LaY catalysts and by reducing the reaction temperature. In parallel experiments it was established that isomerization of the product xylenes was absent under the reaction conditions of this paper.

The catalytic activity is expressed as the moles of product formed or toluene converted with respect to moles of toluene fed. The mole % conversion is defined as

$$\text{mole \% conversion} = \frac{\sum_{j=1}^{j=n} x_j}{\sum_{j=1}^{j=n} x_j + x_T} \times 100 \qquad (1)$$

where x_j is the mole fraction of a given methylated product of toluene in the aromatic product mixture, x_T is the mole fraction of unreacted toluene in the aromatic product mixture and n is the number of alkylated products of toluene. Since the reactor was operating under differential conditions the rate of methylation may be calculated from the equation

$$R = \frac{F}{W}\frac{\phi}{100}$$

where F is the feed rate of toluene in mol s^{-1}, ϕ is the % conversion and W is the catalyst mass in g.

The products of the methylation reaction consisted of *p*-, *m*- and *o*-xylene, 1,2,4-trimethylbenzene (1,2,4-TMB or pseudocumene), 1,2,3-trimethylbenzene (1,2,3-TMB or hemimellitene) and 1,2,4,5-tetramethylbenzene (1,2,4,5-tetra-MB or durene). Trace quantities of benzene and ethylbenzene were also observed in the product mixture at the beginning of the reaction for all the catalysts studied; however, after the first hour on stream these products were no longer observed. Under more severe reaction conditions the symmetrical 1,3,5-trimethylbenzene (1,3,5-TMB or mesitylene) was formed; however, under the reaction conditions under which the activity profiles of fig. 1 were obtained this product was not formed.

An examination of the shapes of the activity profiles shows that (i) they are characterised by the presence of an induction period and (ii) all the catalysts undergo deactivation. The extent of deactivation varied, being greatest (and similar) for the LaY and NH_4Y [fig. 1 (*c*)] catalysts, where the activity dropped off to such an extent that these catalysts were practically inactive after 3.0 h on stream. For the NiY and Ni,SnY catalysts the activity remains essentially constant after 4 h on stream [fig. 1 (*a*) and (*b*)], with the steady-state activity being quite high with respect to the initial activity. This continuous changing of the rate of reaction with time on stream makes the comparison of the activities of different catalysts a very delicate matter. It also makes an examination of the effects of such reaction parameters as space velocity, temperature and mole ratio of toluene to methanol on the rate of reaction and the distribution of the products very difficult. Changing the value of any one of the above reaction parameters may also affect the extent of coke formation and subsequent catalyst deactivation and selectivity; thus it can be anticipated that an observed effect on the degree of conversion of changing a given reaction variable may be the result

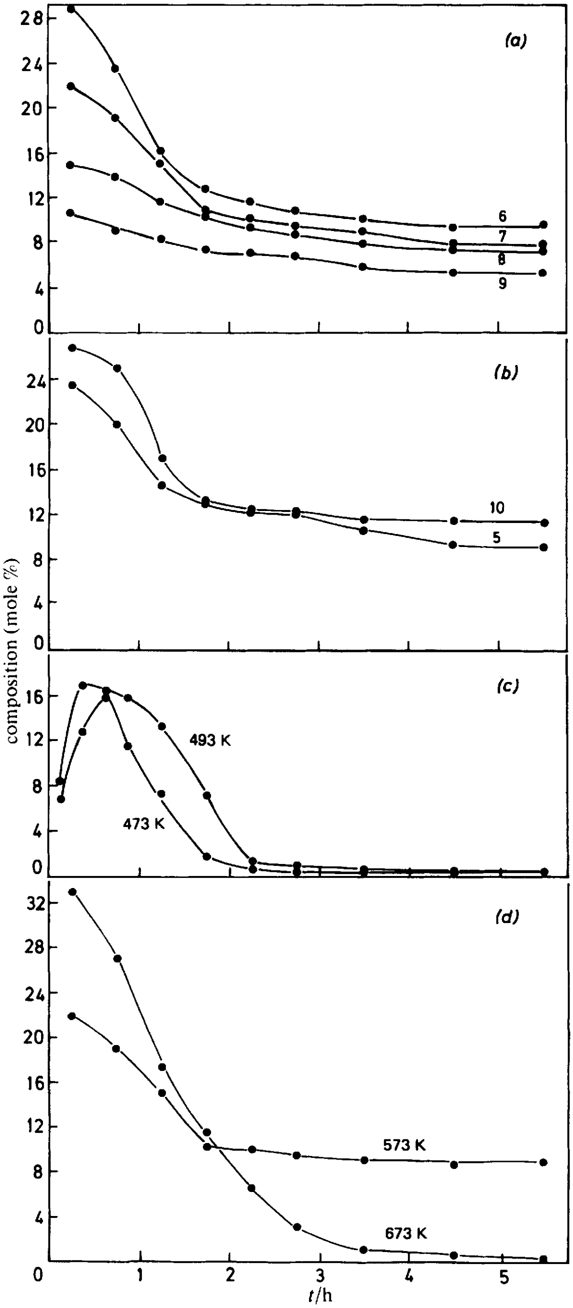
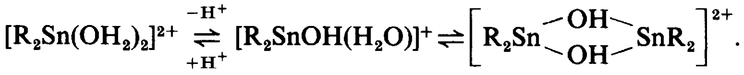


FIG. 1.—Catalytic activity [as defined in eqn (1)] as a function of time on stream for the methylation of toluene over (*a*) Ni,SnY catalysts 6, 7, 8 and 9 under the reaction conditions $T = 573$ K; toluene:MeOH = 1:2; feed rate $W/F = 21.3$ g (mol $h^{-1})^{-1}$; (*b*) catalysts 5 and 10, same reaction conditions; (*c*) NH_4Y-100 under the reaction conditions toluene:MeOH = 2:1; $W/F = 28.8$ g(mmol $h^{-1})^{-1}$; (*d*) Ni,SnY catalyst 7 under the reaction conditions toluene: MeOH = 1:2; $W/F = 21.3$ g (mol $h^{-1})^{-1}$.

of the effect of a number of factors other than the independent variable under study. The presence of an induction period and the integral sampling technique used also mean that the activity cannot be extrapolated back to zero time on stream. Due to these difficulties it was decided to concentrate on the NiY and Ni, SnY samples after they had reached their steady-state activity. Note that increasing the reaction temperature to 673 K even for the Ni,SnY catalysts leads to complete deactivation, as shown in fig. 1 (*d*) for catalyst 7. Consequently in the following sections where the effects of space velocity, mole ratio of toluene to methanol in the reactant feed and changing the reaction temperature are investigated, the studies will be confined to the NiY and Ni,SnY catalysts at or below 573 K.

RELATION OF CATALYTIC ACTIVITY OVER NiY AND THE Ni, SnY SAMPLES TO THE DEGREE OF CATION EXCHANGE AND CATALYST COMPOSITION

As many of the results described in the present paper apply to the deactivated NiY and Ni, SnY catalysts it is important to examine whether or not the catalytic activity at the steady state can be related to the chemical composition of the catalysts. It has been suggested by many workers that coke deposited on the catalyst surface may be responsible for the catalytic activity, especially in the case of silica–alumina catalysts;[28, 29] since the present reaction system shows very high coke-forming tendencies this possibility cannot be completely discounted. However, it was found that the steady-state activity (*i.e.* the activity after 5.0 h on stream for both the non-regenerated and regenerated catalysts) was directly related to the number of exchanged positions occupied by sodium or tin, as shown in fig. 2. Here 'regenerated catalysts' refers to samples of the catalysts listed in table 2(*b*), which were subjected to several catalysis and regeneration cycles in oxygen at 723 K followed by reduction in hydrogen at 723 K, the results of which will be published separately. In the present analysis it is assumed that the tin is singly charged and this assumption is consistent with the hydrolysis reactions occurring in the ion-exchanged tin solutions



$$[R_2Sn(OH_2)_2]^{2+} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} [R_2SnOH(H_2O)]^+ \rightleftharpoons \left[R_2Sn\begin{smallmatrix}OH\\OH\end{smallmatrix}SnR_2\right]^{2+}.$$

Increasing the pH will shift the equilibrium towards the singly-charged tin species. Even if the charge on both tin and nickel is assumed to be 2+, the total number of positive charges contributed by tin, nickel and sodium does not add up to 58, *cf.* table 2(*b*); the missing positive charges are probably contributed by protons exchanged from solution, though aluminium extraction cannot be completely ruled out. Because of this complication in the chemical analysis of the samples the number of exchanged cation positions will be based on the residual sodium and tin content, *i.e.* $(58-R)$ where $R = (Na^+ + Sn^{n+})/u.c.$, and it is this quantity which is plotted on the abscissa of fig. 2(*a*) and (*b*). Note also that fig. 2(*b*) can be extrapolated back to the origin indicating that the ion-exchange procedure and not coke deposition is responsible for the catalytic activity. The pure NaY was found to be catalytically inactive. In fig. 2(*c*) and (*d*) it is shown that a linear relationship also exists between the catalytic activity and the number of nickel ions per unit cell. Note also that the points that define the linear part of the plot in fig. 2(*a*) are taken solely from the data for the Ni,SnY samples and that the NiY sample falls completely off the plot with a catalytic activity value much higher than predicted by the range of Ni,SnY samples. However, in the case of fig. 2(*d*) the catalytic activity for NiY does fall within experimental error on the plot showing that the fraction of the catalytic activity introduced by the exchange of nickel ions and their subsequent reduction is independent of the presence or absence of tin. This is in agreement with the Mössbauer studies,[23] which showed that under the reduction conditions used tin is not reduced, and therefore eliminates the possibility of alloy formation between tin and nickel. The effect of tin exchange on both the catalytic activity and the extent of deactivation then seems to be only related to the extent of proton exchange resulting from hydrolysis of the dimethyltin exchange solutions. In the case of regenerated catalysts note also that the plot cuts the abscissa at 2 Ni^{2+} per unit cell, suggesting that the reduced catalytic activity is due not only to dehydroxylation but also to incomplete re-reduction of the nickel ions in the low-exchange samples. This is probably due to the fact that after the oxygen treatment the nickel ions have migrated into the inaccessible S_I positions where reduction is very difficult.

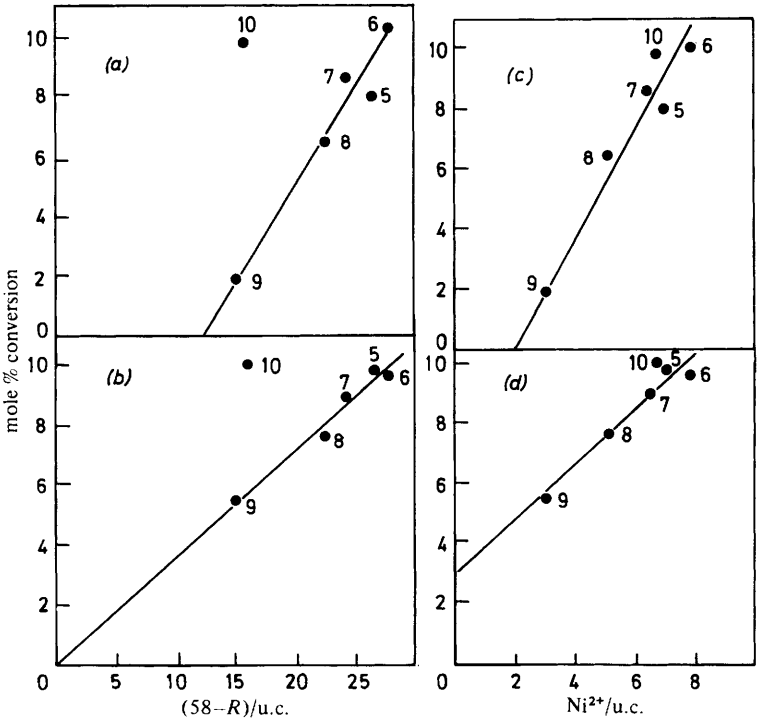


FIG. 2.—Steady-state methylation activity (5 h on stream) as a function of the number of exchanged cation positions for (*a*) the regenerated catalysts, (*b*) the non-regenerated catalysts and as a function of the number of nickel ions per unit cell for (*c*) the regenerated catalysts and (*d*) the non-regenerated catalysts.

It is thus felt that tin does not have any direct bearing on the catalytic stability of these catalysts, with the extent of deactivation being related only to the intrinsic activity or Bronsted acidity of the catalysts. This is because both the methylation reaction and coke formation arises from the Bronsted acidity of the catalysts, and fig. 2 clearly shows that the presence of tin has no direct effect on the catalytic activity. Increasing the reaction temperature also accelerates both types of reaction, as shown in fig. 1(*d*). Other points arise: the catalysts may be stabilized to some extent by the presence of nickel metal and the use of hydrogen atmosphere, which may lead to the hydrogenation of coke precursors; reduced activity of the Ni, SnY samples may have some origin in partial aluminium extraction in the preparation of the parent DMTY sample.

EFFECT OF SPACE VELOCITY, MOLE RATIO OF TOLUENE TO METHANOL AND TEMPERATURE ON THE ACTIVITY AND PRODUCT DISTRIBUTION

The effect of these parameters were studied in detail over a sample of catalyst 10, (NiYD), which had already reached its steady-state activity (and consequently was partially deactivated) in the alkylation reaction; the reaction conditions and experimental results are summarized in table 3(*a*)-(*c*), where U is defined as the flow rate of reactants and carrier gas at the reaction temperature. It is clear that the polymethylated products make up quite a high fraction of the product composition. This is the case even where extremely mild reaction conditions are used and the degree of conversion of toluene is very low. The mole % *meta* isomer in the products remains constant at 14-16% and the % *para* varies to a small extent between 25 and 33%. However, the biggest variation in going from one set of reaction conditions to another occurs for *o*-xylene and the polymethylated products. This is clearly seen if we compare rows 1 and 4 of table 3(*b*): the mole % *o*-xylene decreases by 19% in going from a toluene:MeOH ratio of 6.0-0.5 while the trimethyl and tetramethyl products increases by 16%. This would suggest that *o*-xylene is the xylene which is primarily aklylated to give the polymethylated products. In the final column of each table the sum of the mole % conversion to *o*-xylene and the polymethylated products is given and it is seen that these always add up to a fairly constant value of 55-60%, irrespective of the reaction conditions.

VARIATION OF THE PRODUCT DISTRIBUTION WITH TIME ON STREAM

Activity profiles for the NiY and Ni,SnY samples, both regenerated and non-regenerated, were found to be very similar. The mole % conversion to the various alkylated products of toluene over all the catalysts was studied in detail. Conversion to the *p*- and *m*-xylenes followed roughly the same profile as the overall activity of the catalyst [fig. 1(*a*)], whereas in contrast the activity profile for the conversion to the *o*-xylene or the polymethylated products did not. Initially there is high selectivity for *o*-xylene formation with low amounts of the polymethylated products being formed, but with increasing times on stream a rapid drop in the selectivity for *o*-xylene formation occurs accompanied by an equally rapid rise in the selectivity for the polymethylated products. When the sum of the mole % conversion to *o*-xylene and the polymethylated products was plotted against time on stream, an activity profile which was similar to the total activity of the catalyst [fig. 1(*a*)] and the activity for *p*- and *m*-xylene formation was obtained. This again suggests that the polymethylated products arise from further methylation of *o*-xylene and that the selectivity towards further aklylation changes with time on stream, reaching a constant value after 1.5 h. If this is indeed the case then a plot of mole % composition against time on stream should be constant after 1.5 h on stream for *p*-xylene, *m*-xylene and for the sum of the *o*-xylene and polymethylated products present. This will be true if the initial selectivity of the catalysts for the formation of the three xylenes does not change with time on stream; this latter point is very important and should be noted. In fact, this is found to be very nearly the case, as shown in fig. 3. As expected the *o*-xylene and polymethylbenzenes initially vary substantially with time on stream, but the sum of the *o*-xylene and polymethylated products remains constant; a slight deviation does occur for the initial times on stream and this arises due to a slight variation in the selectivity for *p*-xylene formation, a phenomenon which was consistently observed to a greater or lesser extent for all the other catalysts and which will be discussed later. The selectivity for *m*-xylene formation remains remarkably constant at *ca.* 14% of the product mixture. Similar results to those shown in fig. 3 were observed for NiY, NH_4Y

TABLE 3.—STEADY-STATE ACTIVITY AND PRODUCT COMPOSITION FOR THE METHYLATION OF TOLUENE WITH METHANOL OVER NiYD FOR SEVERAL SPACE VELOCITIES, MOLE RATIOS AND REACTION TEMPERATURES

		product composition (mole %)							
U/cm^3 s^{-1}	mole % conversion	p-xylene	m-xylene	o-xylene	1,2,4-TMB	1,2,3-TMB	1,2,4,5-tetra-MB	poly-MB	poly-MB+ o-xylene
				(a) T = 573 K; toluene:MeOH = 2:1					
2.35	6.41	33.5	14.4	29.6	14.3	2.6	5.6	22.5	52.1
4.85	4.87	29.9	14.6	32.4	13.3	4.1	5.7	23.1	55.5
9.85	2.92	25.3	15.1	36.6	12.7	4.8	5.5	23.0	59.6
mole ratio toluene:MeOH					(b) T = 573 K				
6.0	1 93	25.7	15.4	48.1	7.5	3.3	—	10.8	58.9
4.0	2.76	26.8	15.2	43.1	9.8	4.0	1.1	14.9	58.0
2.0	4.87	29.9	14.6	32.4	13.3	4.1	5.7	23.1	55.5
0.5	10.04	29.0	15.6	28.8	17.7	4.0	5.9	27.6	56.4
T/K				(c) toluene:MeOH = 2:1					
523	1.1	26.3	15.2	44.2	8.6	4.3	1.4	14.3	58.5
548	2.9	26.8	15.1	34.9	12.0	4.7	6.5	23.3	58.1
573	4.97	29.9	14.6	32.4	13.3	4.1	5.7	23.1	55.5

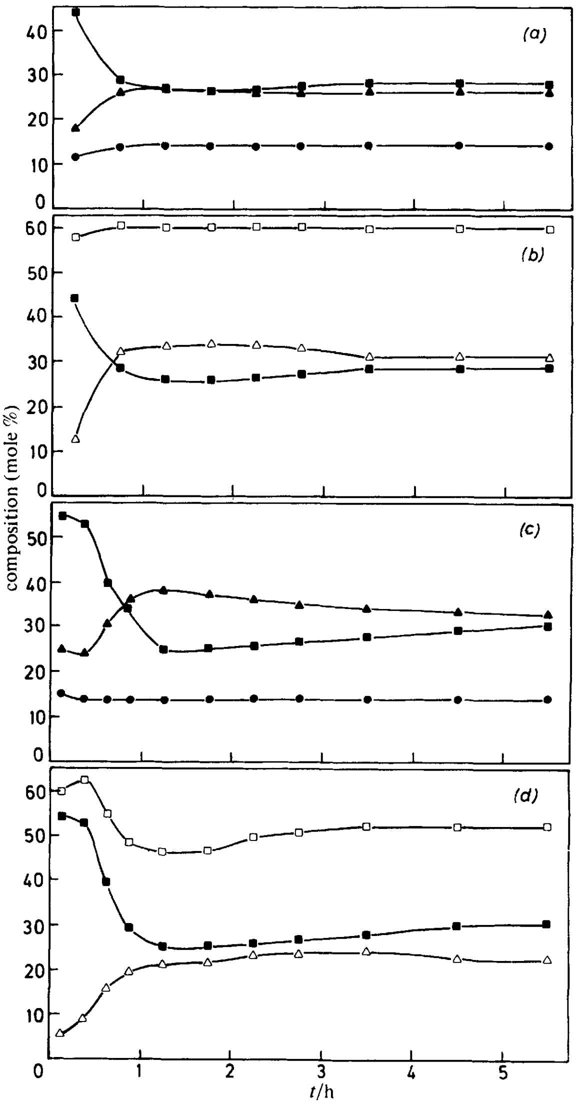


FIG. 3.—Composition of methylated product mixture as a function of time on stream at 573 K. ▲, *p*-xylene; ●, *m*-xylene; ■, *o*-xylene; □, *o*-xylene+poly-MB; △, poly-MB. (*a*) and (*b*) Ni,SnY catalyst 9; toluene:MeOH = 1:2; $W/F = 21.3$ g (mol $h^{-1})^{-1}$. (*c*) and (*d*) Ni,SnY catalyst 10; toluene:MeOH = 2:1; $W/F = 28.8$ g (mol $h^{-1})^{-1}$.

and Ni,SnY, which represent catalysts of widely different composition. Although these catalysts have widely different activity profiles, fig. 1 (*b*) and (*c*), nevertheless in all cases the selectivity for *m*-xylene formation remains remarkably constant at 14% and the *o*-xylene and the polymethylated products show the same mirror image relationship as observed for catalyst 9. However, the sum of the mole % composition of these latter two products does not reach a constant value until after some time on stream: this is due to relatively large variations in the selectivity for *p*-xylene formation at the beginning of the activity profiles. The reason for the variation in the selectivity for *p*-xylene formation with time on stream will not be dealt with here but is the subject of another paper in this series. For the present it is the origin of the polymethylbenzenes which will be considered more fully.

The relationship between the *o*-xylene and the polymethylbenzenes can be further seen from the results of a wide temperature study, between 473 and 723 K, conducted for the range of catalysts. The results for catalyst 7 are presented in fig. 4(*a*) and (*b*); similar results were found for all the other samples. The data points of the ordinate represent the average selectivity over the first hour on stream. The selectivity for *p*- and *m*-xylene formation only varies moderately with temperature over the catalyst, with the increase in the formation of the *m*-xylene at the higher temperature evidently owing to isomerization. As the reaction conditions become more vigorous at high reaction temperatures the mole fraction of the *o*-xylene in the products drops rapidly [fig. 4(*b*)] accompanied by a corresponding increase in the polysubstituted products: this, of course, would be in complete accord with a greater degree of methylation of *o*-xylene to the polymethyl products at higher reaction temperatures.

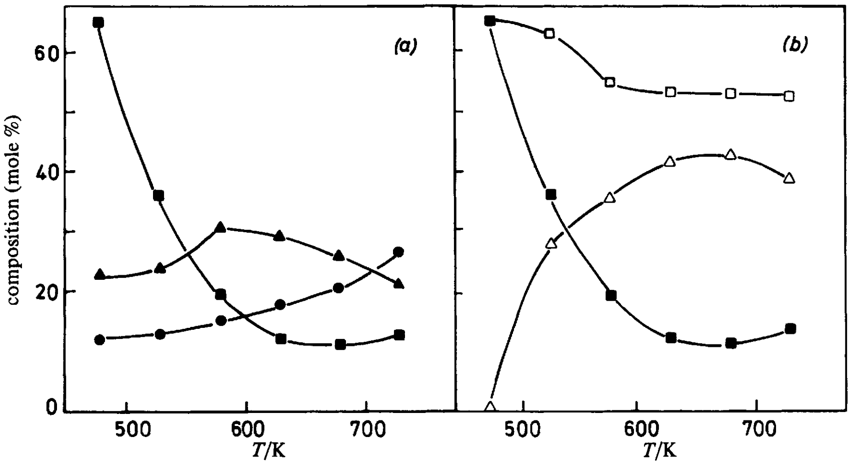


FIG. 4.—Composition of methylated product mixture as a function of reaction temperature over catalyst 7. ▲, *p*-xylene; ●, *m*-xylene; ■, *o*-xylene; □, *o*-xylene+poly-MB; △, poly-MB. Conditions: toluene:MeOH = 1:2; $W/F = 21.3$ g (mol $h^{-1})^{-1}$.

METHYLATION OF THE XYLENES

In order to prove conclusively that the polymethylbenzenes are formed by further methylation of *o*-xylene a competitive methylation of the three xylenes was undertaken over a sample of catalyst 10 (NiYD) which had reached its steady-state activity in the methylation of toluene. The steady-state results for the competitive methylation of an aromatic feed consisting of 24.0 mole % *p*-xylene, 13.3 mole % *m*-xylene and 62.7 mole % *o*-xylene are given in table 4(*a*); this reactant mixture corresponds with the xylene distribution that would be expected if no further methylation of the xylenes occurred. The reactant mixture was diluted with n-hexane so as to reduce the partial pressures of the xylene over the catalyst to values which would be expected under reaction conditions. The catalytically inert n-hexane was also used as an internal standard to check that a mass balance for the aromatic fraction was maintained and this was in fact found to be the case. The results of table 4(*a*) clearly show that only *o*-xylene is further alkylated, with the mole fraction of the *p*- and *m*-xylenes in the total aromatic fraction being the same as in the reactant mixture. When competitive

TABLE 4.—COMPETITIVE METHYLATION OF MIXTURES OF *o*-, *m*- AND *p*-XYLENE IN n-HEXANE OVER NiYD AT 573 K

mole % conversion	total aromatic composition of product mixture (mole %)					
	p-xylene	*m*-xylene	*o*-xylene	1,2,4-TMB	1,2,3-TMB	1,2,4,5-tetra-MB
(*a*) n-hexane:aromatic:MeOH = 62:12:24; aromatic composition: 24 mole % *p*-, 13.3 mole % *m*- and 62.7 mole % *o*-xylene						
14.7	23.5	13.2	48.6	11.4	1.9	1.4
(*b*) n-hexane:aromatic:MeOH = 62:12:24; aromatic composition: equimolar in *o*-, *m*- and *p*-xylene						
13.4	32.1	30.0	24.4	10.4	1.4	1.6

methylation of an equimolar mixture of the three xylenes was investigated, *o*-xylene was again methylated to form the polymethyl products but the other xylenes were also methylated to some extent, as shown in table 4(*b*). Methylation reactions of each of the xylenes were also studied and representative results are given in table 5: methylation of *p*-xylene gives only 1,2,4-trimethylbenzene and durene, which are the expected products of this reaction; on the other hand, methylation of *m*-xylene gives all three trimethylbenzenes and durene; *o*-xylene gives 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene and durene, which are the products found in the competitive methylation studies of the three xylene isomers and in the methylation studies of toluene. Note that the ratio 1,2,4-isomer + durene to the 1,2,3-isomer is roughly the same as that which occurs in the competitive methylation studies, *cf.* table 4(*a*) and (*b*), and is also close to that for most of the catalysts at the steady-state activity. Note that the activity for separate methylation of *p*- and *m*-xylene is substantial (*ca.* 14%) in comparison with that for *o*-xylene (*ca.* 22%), indicating that methylation of these isomers can occur over these catalysts also.

HEATS OF IMMERSION OF HY-100, NaY AND NiYD IN *o*-, *m*- AND *p*-XYLENE

In order to gain an insight into why *o*-xylene is preferentially methylated and also why the selectivity towards polymethylation changes with time on stream or ageing of the catalyst, the strength of interaction between the xylenes and the catalyst surface was probed using the heat of immersion technique; other work[30-32] from these laboratories has shown that analysis of heats of immersion of solids in a particular liquid can yield information on comparative strengths of adsorption and on cation accessibility. The catalysts studied were HY-100, NaY and NiYD samples partially deactivated after methylation of toluene at 573 K. The heats of immersion are presented in table 6. Also shown are some of the physical properties of the xylenes which can make important contributions to the heats and the activities for the separate methylation of the three xylenes over NiYD. In the case of NaY and HY-100 it is clear that the heats of immersion decrease in the order *o*-xylene $\gg$ *m*-xylene $>$ *p*-xylene. Since the heats of liquefaction, the polarizabilities and the molecular volumes of the three xylenes are similar, it is clear that this order can be readily explained by the increase in the dipole–electrostatic-field interaction energy term in going from *p*-xylene to *o*-xylene. However, in the case of NiYD the heats of immersion for the three xylenes are greatly reduced in comparison with HY-100 or NaY and the order of the heats

TABLE 5.—METHYLATION OF *p*-, *m*- AND *o*-XYLENE WITH METHANOL OVER NiHY

n-hexane:aromatic:MeOH = 72:4:24; $T = 573$ K

xylene isomer in feed	steady-state mole % conversion	total aromatic composition of product mixture (mole %)						
		p-xylene	*m*-xylene	*o*-xylene	1,2,4-TMB	1,2,3-TMB	1,3,5-TMB	1,2,4,5-tetra-MB
p	14.0	86.0	—	—	9.9	—	—	4.1
m	13.4	—	86.6	—	9.2	1.3	1.1	1.8
o	22.9	—	—	77.1	14.8	2.6	—	5.5

TABLE 6.—HEATS OF IMMERSION (ΔH_D) OF HY-100, NaY AND NiYD IN *p*-, *m*- AND *o*-XYLENE

					heats of immersion/J g^{-1}			catalytic activity of NiYD
adsorbate	α/nm^3	ΔH_L^{298} /kJ mol^{-1}	V_m/nm^3	μ/D	NaY	HY-100	NiYD	(mole % conversion)
p-xylene	0.014 24	43.37	0.2052	0.02	243	295	179	14.0
m-xylene	0.014 21	42.65	0.2043	0.30	251	299	181	13.4
o-xylene	0.014 16	43.43	0.2008	0.45	272	330	146	22.9

α = molecular polarizability; ΔH_L^{298} = molar heat of liquefaction at 298 K; V_m = molecular volume calculated from density at 298 K; μ = dipole moment.

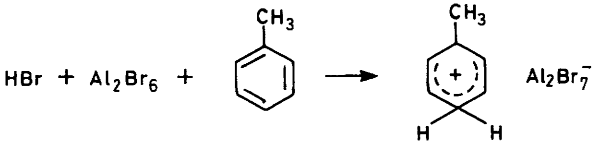
is completely changed. The heats for *p*-and *m*-xylene are about the same, as were the rates of methylation of the two isomers over the NiYD catalyst; the heat for *o*-xylene is appreciably less but the rate of methylation of this isomer is much greater than for the other two. Thus it is evident that the interaction between the surface of NiYD and *o*-xylene is less than for *p*- or *m*-xylene and, further, that the rate of methylation of the xylenes seems to correlate well with a weak interaction between the xylene and the surface. At the beginning of the activity profiles, where catalysis is occurring over a relatively fresh non-coked catalyst, very few polysubstituted products of toluene are formed and the three xylenes undergo strong specific interaction with the catalyst surface; in the partially deactivated catalyst, however, the interaction with the surface is much less and the more weakly adsorbed *o*-xylene is further methylated. The reduced heats over the deactivated catalyst may be due to a number of factors including partial blockage of the internal pore structure, reduction of the electrostatic field strengths due to the presence of coke and the deposition of a layer of coke on sites such as sodium ions which undergo strong specific interaction with the absorbate molecules. It would seem that the interaction of the xylenes with the deactivated catalyst is non-specific in nature, as occurs for the adsorption of molecules such as ethylene, ethane, propylene and propane on graphitized carbon black.[33, 34] If this is also the case for the three xylenes, then the heats should be greatly reduced in comparison with those for a fresh catalyst and should tend towards the same value, which is what is observed. The reduction in the heat for *o*-xylene may also be due to an added unfavourable orientation between the dipole moment of the *o*-xylene and the local electrostatic field within the zeolite. It is thus evident that formation of polymethylbenzene occurs through the intermediary of a weakly adsorbed *o*-xylene species, *i.e.*

$$\text{toluene} \rightarrow o\text{-xylene (ads)} \rightarrow \text{poly-MB}.$$

The fact that the extent of polysubstitution is independent of the contact time with the catalyst surface, as shown in table 3 (*a*) column 9, shows that *o*-xylene, once formed, is further methylated without being initially desorbed from the catalyst surface.

The conclusion that it is a weakly adsorbed species that is alkylated is consistent with a Rideal-type mechanism proposed by Venuto *et al.*[16] for heterogeneous aromatic substitution. It was proposed that the adsorbed carbonium ion attacks a gaseous or weakly adsorbed aromatic species in the rate-determining step. Alkylation of a strongly adsorbed species was not suggested as such a species would be positively charged as a result of π-electron transfer to the adsorption site. Such an adsorbed aromatic would not be attacked by another positively charged species due to the presence of coulombic repulsion.

Note that further methylation of the xylenes does not occur in homogeneous catalysis, *e.g.* when toluene is methylated[35] using $CH_3Br/AlBr_3$ in excess aromatics. This result is unexpected as the presence of alkyl groups attached to the aromatic ring should lead to an increase in the susceptibility toward electrophilic attack in the order benzene < toluene < xylene, and consequently large amounts of polysubstituted products should be formed. However, it was noted that the more basic xylenes were deactivated toward further methylation by reaction with the product HBr/Al_2Br_6 to form a positively charged complex, as shown in scheme 1.



SCHEME 1

In the case of aromatics adsorbed on zeolites a comparable reaction leading to deactivation of the aromatic ring would be strong specific interaction with a hydroxyl group or metal cation, as discussed earlier. If the xylenes were not deactivated as in scheme 1, the xylene most susceptible to further methylation would be *m*-xylene.[36] It is thus evident that in the catalytic alkylation of xylenes in heterogeneous systems the strength of adsorption is a critical factor in determining whether alkylation will occur or not.

CONCLUSION

From the results presented in this paper it may be concluded that in the alkylation of toluene with methanol over zeolite catalysts under non-isomerizing conditions, polymethylation always occurs. Catalyst deactivation is associated with the formation of the secondary polysubstituted products, the selectivity of formation of which depends on the strength of adsorption of the primary products. It is shown conclusively that the origin of the secondary products is a weakly adsorbed *o*-xylene species. The selectivity of formation of the primary products will be examined in Part 2.[37]

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(PAPER 1/1833)