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Combined Catalytic and Infrared Study of the Modification of H-ZSM-5 with Selected Poisons to Give High *p*-Xylene Selectivity

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The methylation of toluene with methanol has been compared over unmodified Zeolite HZSM-5 and over HZSM-5 samples that were partially or fully poisoned with preadsorbed quinoline or trimethylphosphite (TMP). The hydroxyl stretching region of the HZSM-5 zeolites was examined using infrared spectroscopy. Application of this technique to unmodified HZSM-5 showed that exposure to D_2O vapor caused deuteration of both the internal hydroxyls (3605 cm^{-1}) and the external hydroxyls (3740 cm^{-1}). Quinoline was shown to react with only the external hydroxyls whereas TMP reacted with and poisoned both the internal and external hydroxyls when adsorbed at room temperature. Desorption of quinoline was accompanied by dehydroxylation. Studies with a continuous-flow microcatalytic reactor demonstrated that HZSM-5 samples modified by preadsorption with quinoline or TMP prior to measurement of the activity profiles for alkylation exhibited diminished catalytic activity relative to unmodified HZSM-5 samples. However, they showed increased selectivity toward xylenes and toward *p*-xylene in particular. High *para* selectivity is attributed to the selective poisoning of the surface hydroxyls. TMP was found to be the more efficient poisoning agent and yielded the higher *para* selectivity, which is explicable in terms of more effective reaction with the surface hydroxyls.

INTRODUCTION

Alkylation reactions over ion-exchanged zeolites have received considerable attention in recent years (*1*). Foremost among the various types of alkylation reactions studied has been the methylation of toluene with methanol in an attempt to produce a product mixture rich in *p*-xylene (*2–5*). Interest in this selective conversion arises from the ready availability of methanol and toluene, and the importance of *p*-xylene in the synthesis of polyester fibers.

The mechanism of the methylation and ethylation of toluene and benzene has been thoroughly studied over the faujasite-type zeolites under nonisomerizing conditions (*6*). Both reactions were in general found to obey a linear free energy relationship (*7*) originally developed by Stock and Brown (*8*) for electrophilic aromatic substitution in homogeneous systems. Deviations from the rule, as manifested in higher than expected *para* selectivity, were however observed in moderately deactivated catalysts where small levels of coke were deposited (*9, 10*). The increased *para* selectivity was explained as arising from alkylation in a restricted pore structure where diffusional effects became important. In the more restricted pore structure of HZSM-5 configurational diffusion, coupled with isomerization at or near the surface, predominate in determining the product xylene distribution. High *para* selectivity in these catalysts has been achieved by treating the catalysts with a range of poisons such as polymers (*4*), phosphorus (*4*), and boron (*4*) compounds. These are considered to have the effect of poisoning the surface sites and/or reducing the internal pore dimensions, thus favoring the rapid and selective diffusion of *p*-xylene to the surface.

The origin of the catalytic activity for alkylation over zeolite catalysts is their Brønsted acidity which is in the form of surface hydroxyls (*11, 12*). In the case of HZSM-5 two types of hydroxyl arise (*11*)

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exhibiting two distinct bands in the ir spectrum. A band at 3605 cm^{-1} is associated with hydroxyls occurring in the internal pore structure at the channel intersections. This hydroxyl gives rise to strong Brønsted acidity (*13*) and is in general associated with the catalytic activity of HZSM-5, in particular with the shape-selective activity. A further hydroxyl band occurs at 3720–3740 cm^{-1}, and is due to surface hydroxyls or possibly silica impurities. This latter hydroxyl is associated with weak Brønsted acidity (*13*) and is not associated with shape-selective catalysis, but may give rise to extensive isomerization of the product xylene molecules after diffusion to the surface.

To date very little direct spectroscopic evidence exists on the location and nature of the interaction between HZSM-5 and poisons that are known to promote high *para* selectivity. The main object of the present study is to obtain such evidence and to clarify the interplay between the surface and internal sites in promoting high *para* selectivity.

EXPERIMENTAL

Materials. NH_4ZSM-5 was prepared by replacing the sodium ions of a NaZSM-5 sample (Si/Al ratio = 18.0 crystallite size 0.2–1.0 μm, obtained by courtesy of E. Derouane) with ammonium ions using a 1.0 *M* solution of NH_4NO_3. After ion exchange the catalyst was thoroughly washed with hot deionized water and dried overnight in a vacuum oven at 403 K. Sodium analysis of the exchange solution gave the formula $Na_{0.4}(NH_4)_{4.6}ZSM$-5. Both methanol and toluene were Analar grade and were used without further purification in the catalytic studies. Quinoline and trimethylphosphite (TMP) were Analar grade and were further dried using activated molecular sieve 5 Å before use.

APPARATUS AND PROCEDURE

Catalytic studies. Catalytic runs were carried out in a continuous flow microcatalytic reactor operating at atmospheric pressure. A diagram of the apparatus is shown in Fig. 1. Fifty milligrams of catalyst were employed and the catalyst was activated at 773 K for 4.0 h in a flow of O_2 at a flow rate of 40.0 ml per minute. Activation under these conditions converts the NH_4ZSM-5 to the active hydrogen form. After activation the carrier gas was changed to nitrogen. Toluene and methanol were supplied by passing nitrogen (20.0 ml/min) through toluene and methanol saturators maintained at 295 and 250 K, respectively, giving toluene and methanol partial pressures of 23.1 and 6.2 Torr, respectively. Catalyst poisoning with quinoline and trimethylphosphite (TMP) was carried out by closing taps t_1 and t_2 thus isolating the reactor and then injecting the poison through a septum at the top of the reactor using an accurately calibrated microsyringe. In all the poisoning experiments the vapor of the poison was allowed to contact the catalyst for 20 min at 633 K and was then flushed with N_2 for a further 20 min at 633 K before the reaction was initiated or before heating to the reaction temperature.

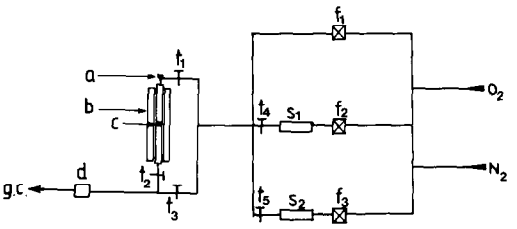

FIG. 1. Schematic representation of microcatalytic flow reactor used in the alkylation studies over HZSM-5 samples: a = injection port; b = furnace; c = catalyst bed; d = sampling valve with 0.5-ml sample loop; S_1 = methanol saturator; S_2 = toluene saturator; f_1, f_2, and f_3 = precision needle valves; t_1–t_5 = helium leak-tested taps.

Product analysis was carried out using a Pye Unicam G.L.C. equipped with a F.I.D. detector. The products were separated on a column containing 5% Bentone + 5% diisodecylphthalate supported on Chromosorb W. The column temperature was set at 353 K and the nitrogen flow rate through the column was 20.0 ml per minute. Under the alkylation conditions used the synthesis re-

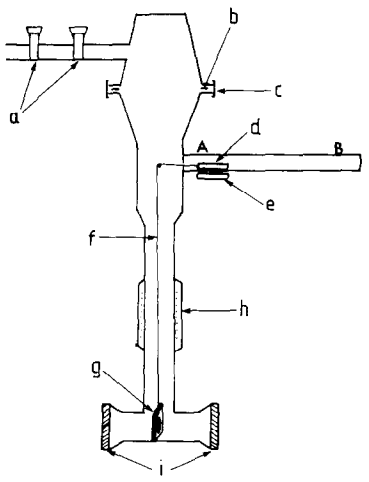

FIG. 2. Schematic representation of vacuum infrared cell used for the infrared studies; a = high-vacuum Teflon taps; b = rubber O-ring; c = Rotulex clip 64/40; d = internal magnet (m_1); e = external magnet (m_2); f = brass chain; g = nickel disk holder; h = heated zone, i = NaCl plates.

action from methanol to give light hydrocarbons or aromatics was found not to be significant (especially over the poisoned catalyst) and no attempt was made to separate and quantify this side reaction. The degree of conversion to the aromatic products was calculated with respect to the feed toluene.

Infrared studies were carried out in a portable high-vacuum ir cell equipped with a heating section as shown in Fig. 2. Dynamic vacua of 2×10^{-5} Torr could be achieved and the samples were initially activated at 673 K for 4.0 h before poisoning. Self-supporting disks were prepared for the ir studies by compressing 10.0 mg of sample at a pressure of 7.0 tons for 2 min. The disk holder was connected via a light chain to a magnet (m_1) as shown in Fig. 2. By sliding magnet m_1 between the points A and B using magnet m_2 the sample could be positioned in the center of the furnace during activation or between the two NaCl plates at the bottom of the cell when running spectra. After activation at 673 K the temperature was lowered to the required value and quinoline, TMP, and D_2O were contacted with the zeolite sample at their room-temperature vapor pressures.

RESULTS

Infrared studies. A typical ir spectrum in the hydroxyl stretching region is shown in Fig. 3 for the ZSM-5 sample outgassed at 673 K for 4 h. The spectrum is characterized by an intense band at 3605 cm^{-1} and a weak shoulder at 3740 cm^{-1}. Upon exposure to D_2O vapor at 473 K for 20 min, partial deuteration occurred with the appearance of two peaks at 2670 and 2740 cm^{-1} and with a corresponding reduction in the intensity of the peaks in the OH hydroxyl stretching regions. The peak at 2670 cm^{-1} resulted from deuteration of the more highly acidic hydroxyl located at the channel intersections whereas the peak at 2740 cm^{-1} was due to deuteration of the less acidic surface hydroxyl. Longer exposure to D_2O, as is shown in Fig. 3, resulted in more extensive deuteration, but the peak at 2740 cm^{-1} is relatively less pronounced than in the previous spectrum.

In Figs. 4b and c the effects of contacting the activated HZSM-5 with quinoline at room temperature and at 473 K are shown. Quinoline adsorption may be seen not to

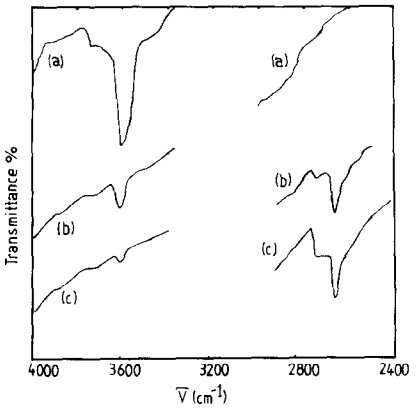

FIG. 3. Effect of D_2O adsorption upon the infrared spectrum of HZSM-5 in the hydroxyl stretching region: (a) as prepared from NH_4ZSM-5 by prior high-temperature oxidation at 773 K and outgassing for 4.0 h; (b) as for (a) but following contact of D_2O (P_{D_2O} = 17 Torr) with sample for 20.0 min at 473 K followed by low-temperature outgassing for 1.0 h at 473 K; (c) as for (b) but with longer contact of D_2O with sample (4.0 h at 473 K) and longer low-temperature outgassing (473 K for 3.0 h).

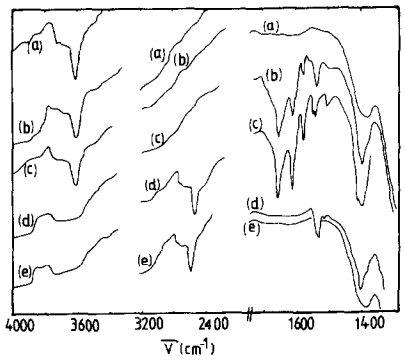

FIG. 4. Infrared spectra of HZSM-5 prepared as for Fig. 3a but then subjected to quinoline adsorption at room temperature or 473 K followed by outgassing at 473 K; (a) as prepared from NH_4ZSM-5 by oxidation at 773 K and outgassing for 4 h; (b) as for (a) but following exposure to quinoline (P_Q = 0.1 Torr) at room temperature for 1 h, followed by outgassing at 473 K for 2 h; (c) as for (b) but with quinoline adsorbed at 473 K for 1 h followed by outgassing at 473 K for 2 h; (d) as for (c) but with subsequent exposure to D_2O (P_{D_2O} = 17 Torr) for 4 h at 473 K followed by 4 h outgassing at 473 K; (e) sample treated as in 4(d) except that it was outgassed at 673 K before deuteration.

reduce appreciably the intensity of the low frequency hydroxyl band at 3605 cm^{-1}. A number of sharp peaks occur in the wavenumber range 1700–1350 cm^{-1} and these can be attributed to the ring stretching and/or bending modes of the adsorbed quinoline molecule (*14*). Quinoline adsorption at 473 K followed by deuteration (also at 473 K) gives spectrum 4d. The expected peak at 2670 cm^{-1} is clearly seen but the shoulder at 2740 cm^{-1} is notably absent when compared with spectrum 3c. This latter negative effect upon deuteration of a sample previously contacted with quinoline was found to be completely reproducible. After deuteration it was also evident that the intensities of the quinoline peaks were reduced somewhat. Outgassing at 673 K after quinoline adsorption and subsequent deuteration at 473 K was found to give a spectrum (Fig. 4e) in which all the quinoline peaks were absent, as also was the shoulder at 2740 cm^{-1}.

Effects of TMP adsorption on the hydroxyl stretching region are shown in Figs. 5a to c. Adsorption at room temperature led to elimination of the hydroxyl peaks at 3605 cm^{-1} and to the appearance of a number of peaks not previously present. The two peaks at 2960 and 2860 cm^{-1} are probably due to the antisymmetric and symmetric stretching modes, respectively, of the CH_3 groups of TMP whereas the peak at 1457 cm^{-1} is probably due to an antisymmetric bending vibration of the CH_3 group. The assignment of the peak at 1378 cm^{-1} is uncertain. Adsorption at 633 K followed by outgassing at 723 K also resulted in elimination of the hydroxyl frequency at 3605 cm^{-1}, but the peaks due to the methyl groups were also absent, indicating that demethylation of the TMP had occurred, or that the TMP itself had been desorbed from the surface with an accompanying dehydroxylation of the surface.

Catalytic studies. The activity of HZSM-5 for the methylation of toluene was studied at 793 and 893 K. At 793 K the reaction was studied over a period of 7.0 h; the activity after 5 min (taken as a measure of the initial activity) and the activity and product distribution after 7 h are presented in Table 1. The initial activity and product distribution at both temperatures were quite similar. However, catalyst deactivation occurred much more rapidly at 893 K, as shown by the much lower activity after 7.0 h for reaction at this temperature in comparison to

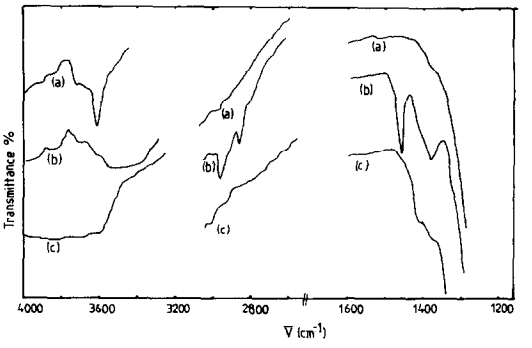

FIG. 5. Infrared spectra of HZSM-5 before and after trimethylphosphite (TMP) adsorption at room temperature and 633 K; (a) HZSM-5 as prepared from NH_4ZSM-5 by outgassing at 673 K for 4.0 h, (b) TMP adsorbed at room temperature for 1 hr, outgassed at room temperature for 2.5 h, (c) TMP adsorbed at 633 K for 20 min, and then outgassed at 723 K for 1 h.

TABLE 1

Catalytic Activity and Product Distribution after 5 and 420 min on stream. Methanol : Toluene = 1 : 3.72, F/W = 3.28 grams of reactants delivered per hour per gram of catalyst Reaction Temp. = 793 and 893 K

Poison	Reaction temp. (K)	Time on stream (min)	Mole % conversion	Mole % xylenes	Xylene composition			Mole % ethyl-toluenes	Ethyltoluene comp.			Mole % TMB	Trimethylbenzene (TMB) composition		
					para	*meta*	*ortho*		*para*	*meta*	*ortho*		1,2,3-TMB	1,2,4-TMB	1,3,5-TMB
None	793	5.0	53.0	89.0	45	40	15	4.0	55	41	4	7.0	16	66	18
None	793	420.0	50.0	73.0	59	26	16.0	2.0	77	21	2	25.0	1	96	3
None	893	5.0	55.0	88.0	40	40	20	0.6	62	31	7	11.4	15	73	12
None	893	420.0	21.0	78.0	82	10	8	0.7	86	12	2	21.3	—	96	4
Quinoline 20.0 μl	793	5.0	28.0	93.0	85	9	6	1.0	92	8.0	—	6.0	—	94	6

the activity at 793 K. In both cases the selectivity for *p*-xylene, *p*-ethyltoluene, and 1,2,4-trimethylbenzene formation increased dramatically with catalyst aging, the effect being most dramatic for methylation at 893 K where the greatest level of deactivation occurred.

Poisoning the catalyst with 20 μl of quinoline at 633 K for 20 min before the reaction was initiated had the effect of also promoting high para selectivity as shown in Table 1. It was further found that poisoning with greater quantities of quinoline or poisoning for longer periods of time did not give higher *para* selectivity or reduce the activity further, so that 20.0 μl of quinoline represented the maximum poisoning effect of this poison under the present conditions. Comparisons of the xylene distribution obtained for disproportionation, alkylation, and synthesis reactions are shown in Table 2 before and after poisoning with quinoline. It may be observed that the xylene distribution over the unpoisoned catalyst was relatively independent of the reaction route used to produce them.

Poisoning with TMP had an effect initially similar to quinoline, i.e., lower catalytic activity coupled with higher *para* selectivity. However, no limiting effect similar to that achieved with 20 μl of quinoline was observed. This is shown clearly in Fig. 6, where the effect of using larger

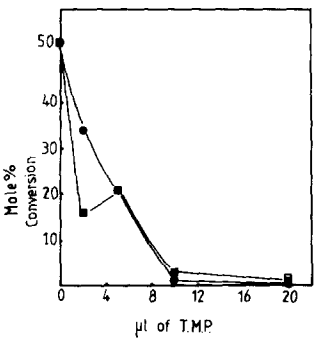

FIG. 6. Effect of contacting HZSM-5 with trimethylphosphite (TMP) on the catalytic activity at 793 K; catalytic activity at 793 K vs μl of TMP used. Poisoning carried out at 633 K for 20 min. Methanol : toluene = 1 : 3.7; ● = activity after 5 min; ■ = activity after 420 min.

TABLE 2

Xylene Distribution Resulting from Disproportionation, Synthesis, and Methylation over a Nonpoisoned and a Poisoned HZSM-5 Catalyst. Methanol : Toluene = 1 : 3.7, Reaction Temp. = 793 K, Catalyst Poisoned at 633 K for 20 min

Poison	Type of reaction	Reaction temp. (K)	Time on stream (min)	Mole % conversion	Mole % xylenes	Xylene composition (%)		
						para	*meta*	*ortho*
None	Disproportionation	793	5.0	4.2	98	36	48	16
None	Synthesis	793	5.0	37.0	76	41	46	13
None	Methylation	793	5.0	55.0	79	47	41	12
Quinoline (10 μl)	Disproportionation	793	5.0	1.0	100	89	7	4
Quinoline (10 μl)	Synthesis	793	5.0	20.0	91	89	7	4
Quinoline (10 μl)	Methylation	793	5.0	23.0	84	87	7	6

pulses of poison on the catalytic activity is shown and it is clear that, after exposure to 20 μl, activity was almost completely eliminated. Increasing the pulse size of poison at small exposures up to 5.0 μl led to a dramatic increase in the *para* selectivity after which the selectivity reached a fairly constant value as is shown in Fig. 7. Other than an initial variation, the selectivity for overall xylene formation was not greatly altered by increased TMP poisoning as shown in Fig. 8.

Poisoning was also carried out on catalyst samples that had previously been contacted with the reactant mixture at 793 K for 1 h. The temperature was lowered to 633 K in the presence of the reactants and the reactor subsequently flushed with N_2 at 633 K for varying lengths of time before poisoning with 20 μl of TMP. The effect of such a treatment on the catalytic activity after 5 min and 7 h on stream is shown on plots (a) and (b) of Fig. 9. After completion of the activity study at 793 K the temperature was raised to 893 K and the sensitivities of activity and product distribution to duration of flushing prior to poisoning were again measured. Subsequent activities after 1 h on stream at 893 K are presented on plot (c) of Fig. 9. It is clear from plots (a) and (b) that flushing of the reactor for increasing lengths of time at 633 K before poisoning, had the effect of reducing the subsequent activity. Poisoning resulted in high xylene and *para* selectivity as shown in Figs. 10 and 11. However, neither the xylene nor *para* selectivity were greatly affected by the time of flushing with N_2 even though the catalytic activity was changed quite substantially.

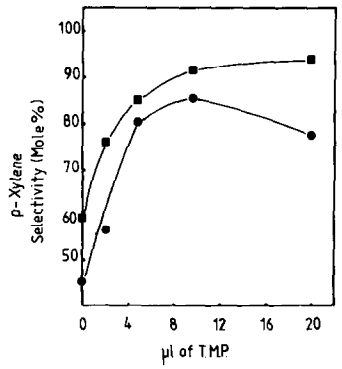

FIG. 7. Effect of trimethylphosphite (TMP) poisoning on the *p*-xylene selectivity of HZSM-5; selectivity within the xylenes for *p*-xylene formation at 793 K vs microliters of TMP used. ● = Selectivity after 5 min; ■ = selectivity after 420 min.

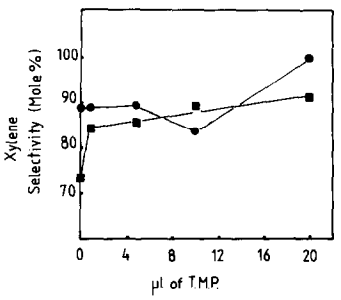

FIG. 8. Effect of trimethylphosphite poisoning on the total xylene selectivity of HZSM-5; total xylene selectivity at 793 K vs μl of TMP used. ● = Selectivity after 5 min; ■ = selectivity after 420 min.

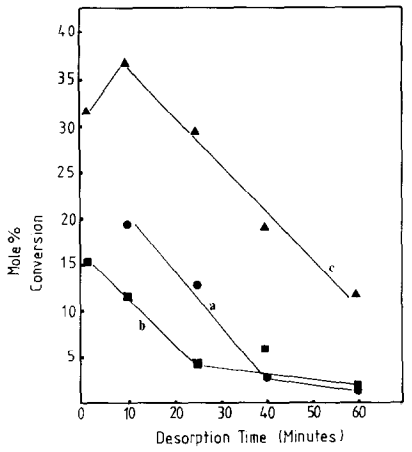

FIG. 9. Catalytic activity of HZSM-5 as a function of the length of time of desorption of reactants and products prior to poisoning with trimethylphosphite at 633 K; methanol : toluene = 1 : 3.7. ● = Activity after 5 min, T = 793 K; ■ = activity after 420 min, T = 793 K; ▲ = activity after 60 min, T = 893 K.

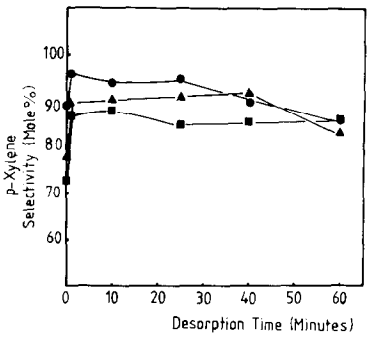

FIG. 10. Total xylene selectivity of HZSM-5 at 793 and 893 K as a function of the length of time of desorption of the reactants and products prior to poisoning of HZSM-5 with trimethylphosphite at 633 K; ● = selectivity after 5 min, T = 793 K; ■ = selectivity after 420 min, T = 793 K; ▲ = selectivity after 60 min, T = 893 K.

DISCUSSION

Contact of the HZSM-5 sample with D_2O led to deuteration of both hydroxyls as shown in Fig. 3, and clearly indicated their acidic nature. Deuteration can be considered to occur as a result of the following equilibria occurring at the surface:

$$ZOH \rightleftharpoons ZO^- + H^+$$

$$D_2O \rightleftharpoons DO^- + D^+$$

$$ZO^- + D^+ \rightleftharpoons ZOD$$

It is evident that the peak at 2740 cm^{-1} resulting from deuteration of the external hydroxyl is more evident in the partially deuterated sample. This probably arises as the hydroxyls on the external surface will be the first to come into contact with the D_2O and thus will tend to be deuterated more rapidly than internal hydroxyls, even though the latter are more acidic.

Adsorption of quinoline as shown in Fig. 4 does not remove the low frequency hydroxyl at 3605 cm^{-1} suggesting that quinoline does not penetrate the pore structure of HZSM-5, and thus only reacts with the acidic hydroxyls on the external surface or at the pore mouths. This is further supported by the observation that upon subsequent deuteration of the quinoline-treated sample, the shoulder at 2740 cm^{-1} arising from deuteration of the external hydroxyls was notably absent. Upon outgassing the quinoline-treated sample at 673 K followed by deuteration at 473 K, it was clear that the quinoline peaks were completely removed, suggesting that the base had been desorbed from the surface. However, the

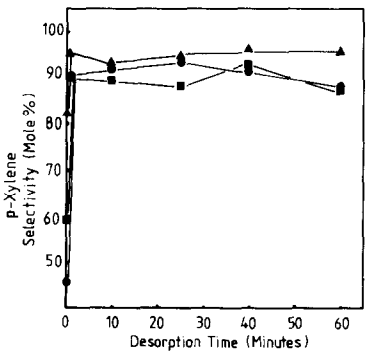

FIG. 11. p-Xylene selectivity within the xylenes at 793 and 893 K as a function of the length of time of desorption of reactants and products prior to poisoning HZSM-5 with trimethylphosphite at 633 K; ● = selectivity after 5 min, T = 793 K; ■ = selectivity after 420 min, T = 793 K; ▲ = selectivity after 60.0 min, T = 893 K.

shoulder at 2740 cm^{-1} did not reappear in the spectrum indicating that desorption at 673 K was accompanied by dehydroxylation. In the NaHY zeolites, it has previously been observed by Jacobs and Uytterhoeven (*15*) that the desorption of the base pyridine was accompanied by extensive dehydroxylation. This point is of special relevance to the present catalytic studies, since at the lower temperatures quinoline adsorbed at the external surface, and pore mouths may be physically blocking the movement of reactants and products in and out of the pore structure. In fact initial studies of the present system showed that the quinoline-poisoned sample was practically inactive at 633 K in contrast to the non-poisoned catalyst. However, at 793 K where quinoline had desorbed from the surface it showed considerable activity as shown in Table 1.

In contrast to quinoline, the ir results for TMP adsorption show that it readily penetrates the pore structure as illustrated by the spectra in Fig. 5. Interaction with the hydroxyls probably occurs as a result of the reaction:

$$P(OCH_3)_3 + ZOH \rightarrow Z\text{–}O\text{–}P(OCH_3)_2 + CH_3OH$$

Following outgassing at 673 K the peaks due to the methyl groups disappeared but the hydroxyl group did not reappear in the ir spectrum. This suggests that the $-P(OCH_3)_2$ species desorb from the surface with accompanying dehydroxylation, or alternatively that only demethylation occurred, and that the remaining phosphorus groups in the surface were not detected in the ir spectra.

Catalytic studies. From Table 1 it is evident that at 793 K very little deactivation occurred in the methylation reaction over the 7-h period studied. However, over the same time period the product selectivity did change quite substantially with the catalyst becoming more *para*-selective not only for *p*-xylene and *p*-ethyltoluene but also within the trimethylbenzenes (TMB) where the selectivity for the 1,2,4-trimethylbenzene increased. These changes in selectivity can be explained as arising from partial poisoning of the surface sites (with resultant reductions in isomerization of products reaching the surface) and preservation of the more shape-selective catalysis of the internal pore structure. The reduction in activity may also be contributed to by pore mouth blockage due to coke deposition on the surface. The increased selectivity observed for the trimethylbenzenes (cf. Table 1) with catalyst aging has also been found over the Y-zeolites (*6*), where it was shown that coking had the effect of reducing the strength of adsorption of the xylenes thus favoring polysubstitution. A similar explanation probably also applies here. Alkylation at 893 K gave rise to more rapid deactivation and, as expected, to higher *para* selectivity. Treatment of the catalyst with 20 μl of quinoline led to reduced activity (53.0 to 28% conversion), but to much greater *para* selectivity, the *p*-xylene now accounting for 79% of the total product mixture. This observation is again consistent with the internal hydroxyls being the sites responsible for high *para* selectivity. Indeed the ir results of Fig. 4 clearly showed that quinoline selectivity poisoned only the surface sites.

The effect of poisoning with TMP was much more extensive than that for quinoline, the activity being progressively reduced to zero with increasing pulse size of that poison. This observation is again consistent with the ir studies which showed that TMP could penetrate the pore structure and react with the hydroxyls at the channel intersections. The *para* selectivity was higher than that for poisoning with quinoline, suggesting that TMP was more efficient in poisoning the hydroxyls at the surface or near the pore mouths. Figure 9 shows that poisoning the catalyst with 20.0 μl of TMP after prior contact with the reactants has the effect of substantially diminishing the poisoning efficiency of TMP.

This may readily be explained by postulating that after short flushing times with N_2 the reactants and products only desorb from the surface sites, thereby exposing them to poisoning. Conversely the internal sites remain protected from poisoning by the presence of the reactants and the products of the methylation reaction. Flushing for longer periods of time led to exposure of the internal sites and allowed subsequent poisoning by TMP accompanied by the expected loss in activity. In a separate series of studies the efficiency of toluene and methanol were compared in protecting the internal sites from poisoning with TMP. It was found that methanol was by far the more efficient, which would be consistent with its expected stronger interaction with the hydroxyls. The loss in catalytic activity after flushing periods of greater than 2 min was not accompanied by any change in *p*-xylene selectivity, as shown clearly in Fig. 11. This suggests that the promotion of *para* selectivity by TMP was confined to the removal of surface hydroxyls and that any restriction of the internal pore opening due to the presence of phosphorus groups did not play an important role. Differences here observed between quinoline and TMP as poisons then arise rather from more efficient poisoning of the surface sites in the case of TMP.

From the comparison of the xylene distribution resulting from alkylation, disproportionation, and synthesis over the nonpoisoned and poisoned catalyst (cf. Table 2), it is evident that the distribution is relatively independent of the reaction. This was initially rather surprising, considering the different mechanisms involved in producing the separate xylenes from alkylation (*6, 8*), disproportionation (*4*), and synthesis from methanol (*16*). However, it may be understood if a process common to the three reactions, but unrelated to the detailed mechanisms of the different reactions, predominates in controlling the product distribution. This would be consistent with the conclusion of other workers that the xylene selectivity is determined by (i) the relative rates of diffusion of the three xylenes to the surface and by (ii) any subsequent isomerization that occurs there. This is also supported by an observation in the present work that over the poisoned catalysts the selectivity for *p*-ethyltoluene was always greater than that of *p*-xylene, as would be expected from the larger molecular dimensions of *p*-ethyltoluene and its resultant higher sensitivity to diffusional effects.

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