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The Kinetics of the Vapor-Phase Ammoxidation of Xylene Isomers over a Vanadium Catalyst

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The kinetics of the vapor-phase ammoxidation of xylene isomers over a vanadium oxide catalyst was studied in a flow system. The reaction-rate data obtained for each xylene were then correlated with the rate equations based upon the Langmuir-Hinshelwood mechanism; this correlation suggested that each xylene reacted by a parallel consecutive reaction scheme in which tolunitrile was involved as an intermediate. The order of the relative ease of reaction was : para >meta≒ortho. The ratio of the specific rate constant of xylenes, k_X, to that of tolunitriles, k_M, was 6 for meta and para isomers and 4 for the ortho isomer at 400°C; this ratio decreased with an increase in the reaction temperature. The order of relative ratios for the direct formation of dicyanobenzenes from xylenes was ortho>meta>para, while that for the direct formation of carbon oxides and hydrogen cyanide was ortho≒meta>para. The ratio of the specific rate constant for the formation of dicyanobenzenes from tolunitriles, k_2, to k_M decreased with an increase in the ratio of k_X to k_M. These results seem to result from the adsorptivities of xylenes and tolunitriles on the catalyst surface.

The kinetic study of the vapor-phase ammoxidation of *m*-xylene has been discussed in a previous paper.[1] The rate equations based upon the Langmuir-Hinshelwood mechanism for the parallel consecutive reaction scheme provided a satisfactory interpretation of the experimental data. However, few kinetic data for other xylenes have been presented.[2,3]

The present study is an attempt to develop greater insight into the reaction processes which take place on the catalyst surface.

Experimental

Experimental Apparatus and Procedures. The apparatus and procedure were similar to those employed in the previous paper,[1] but the product-collecting section consisted of air-cooling, water-cooling, and dry ice-cooling traps. The reaction products in the traps were dissolved out in methanol, and both the dicyanobenzenes and phthalimide were analyzed spectrophotometrically. Tolunitriles and unreacted xylenes in the methanol solution were determined by gas-liquid chromatography. A column of 30 wt% dioctyl phthalate on Chromosorb W was used for xylenes and tolunitriles, and a column of 10 wt% Benton-34 on Chromosorb W for mixed xylenes.

Materials. The *o*-xylene and the *p*-xylene were obtained from the Tokyo Kasei Co. and were 99% pure. The *o*-tolunitrile was also obtained from the Tokyo Kasei Co. and was purified by distillation; bp 93°C at 20 mmHg.

The catalyst was one employed in the previous work.

Results and Treatment of Data

The results of the catalytic ammoxidation of *o*-, *m*- and *p*-xylenes over a vanadium oxide catalyst are shown in Table 1.

These rate data were correlated by the treatment which was used in the previous work for *m*-xylene. The relationship obtained by this treatment are shown in Figs. 1 to 9.

In the ammoxidation of *o*-xylene, phthalimide was formed with phthalonitrile. The formation of phthalimide was not always parallel to the formation of phthalonitrile, as Fig. 10 shows, but the rate of the formation of both phthalimide and

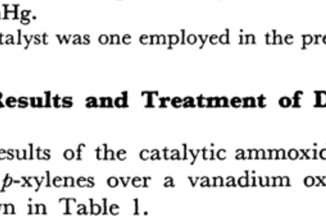

Fig. 1. Zero order plot of *p*-xylene disappearance at various initial concentration of *p*-xylene at 400°C.
P_{XO}: ○, 0.015 atm; △, 0.020 atm

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[1] M. Ito and K. Sano, This Bulletin, **40**, 1307 (1967).
[2] D. J. Hadley, *Chem. & Ind.*, **1961**, 238.
[3] A. Uchida, Y. Asaoka and S. Matsuda, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **68**, 300 (1965).

TABLE 1. RATE DATA FOR THE AMMOXIDATION OF *o*-, *m*- AND *p*-XYLENE AT 400°C

Catalyst volume	8 cc
Concentration of xylene	0.88—2.5%
Concentration of ammonia	8%
Concentration of air	Residue

Feed rate of xylene mmol/hr		Space velocity hr^{-1}	P_{XO} atm	Q_X	Conversion to DCB[1]	TN[2]	PI[3]	CO_2	HCN
p-Xylene	5.91	1100	0.015	0.748	0.142	0.542		0.047	0.017
p-Xylene	8.08	1500	0.015	0.485	0.072	0.371		0.033	0.009
p-Xylene	5.08	710	0.020	0.818	0.169	0.570		0.061	0.018
m-Xylene	3.00	550	0.015	0.957	0.355	0.390		0.164	0.048
m-Xylene	5.08	710	0.020	0.552	0.143	0.313		0.076	0.020
m-Xylene	8.08	900	0.025	0.333	0.082	0.196		0.044	0.011
o-Xylene	3.44	1100	0.0088	0.670	0.149	0.324	0.103	0.072	0.022
o-Xylene	5.05	1400	0.010	0.524	0.113	0.276	0.063	0.054	0.018
o-Xylene	3.44	730	0.0132	0.776	0.131	0.352	0.177	0.095	0.021
o-Xylene	2.95	580	0.0144	0.869	0.161	0.354	0.220	0.108	0.026
o-Xylene	3.44	640	0.015	0.702	0.115	0.330	0.153	0.080	0.024
o-Xylene	4.26	800	0.015	0.650	0.111	0.309	0.143	0.069	0.019
o-Xylene	7.21	1350	0.015	0.374	0.074	0.200	0.053	0.036	0.011
o-Xylene	5.05	920	0.0153	0.498	0.093	0.249	0.095	0.045	0.015
o-Xylene	5.05	690	0.0204	0.540	0.086	0.257	0.117	0.064	0.015
o-Xylene	6.39	730	0.0244	0.390	0.067	0.201	0.077	0.036	0.009

[1] Dicyanobenzene [2] Tolunitrile [3] Phthalimide

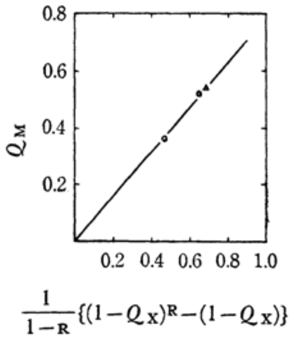

Fig. 2. Relationship between Q_M and Q_X (*p*-xylene). R is one-sixth.

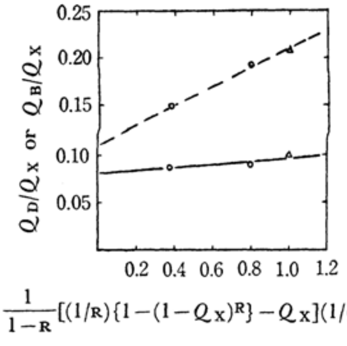

Fig. 3. Relationship between Q_D (or Q_B) and Q_X (*p*-xylene). R is one-sixth.
Broken line: Ratio of Q_D to Q_X
Solid line: Rate of Q_B to Q_X

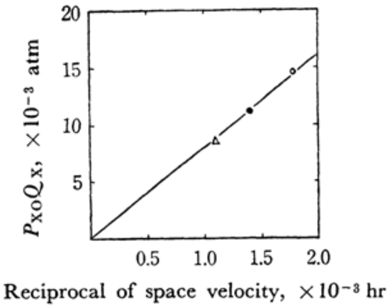

Fig. 4. Zero order plot of *m*-xylene disappearance at various initial concentration of *m*-xylene at 400°C.
P_{XO}: ○ 0.015 atm ● 0.020 atm
△ 0.025 atm

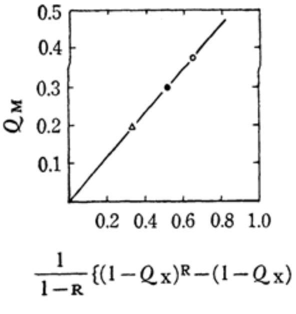

Fig. 5. Relationship between Q_M and Q_X (*m*-xylene). R is one-sixth.

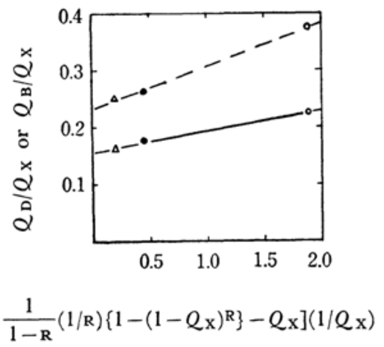

Fig. 6. Relationship between Q_D (or Q_B) and Q_X (*m*-xylene). R is one-sixth.
Broken line: Ratio of Q_D to Q_X
Solid line: Ratio of Q_B to Q_X

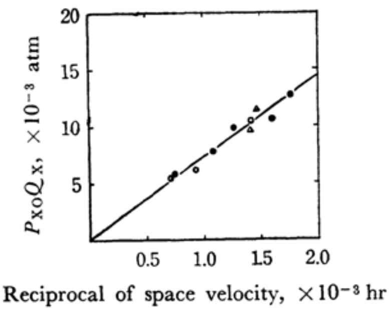

Fig. 7. Zero order plot of *o*-xylene disappearance at various initial concentration of *o*-xylene at 400°C.
P_{XO}: ○ 0.0088—0.0132 atm
● 0.0144—0.0153 atm
△ 0.0204—0.0244 atm

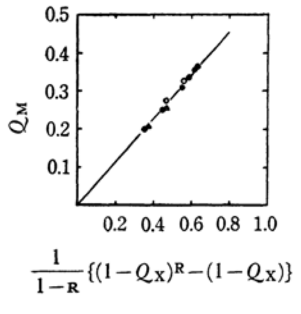

Fig. 8. Relationship between Q_M and Q_X (*o*-xylene). R is one-fourth.

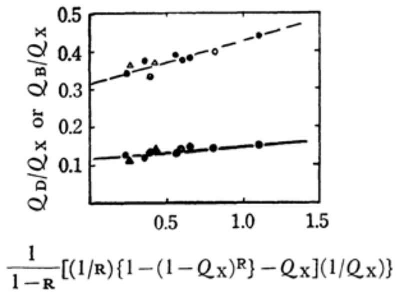

Fig. 9. Relationship between Q_D (or Q_B) and Q_X (*o*-xylene). R is one-fourth.
Broken line: Ratio of Q_D to Q_X
Solid line: Ratio of Q_B to Q_X

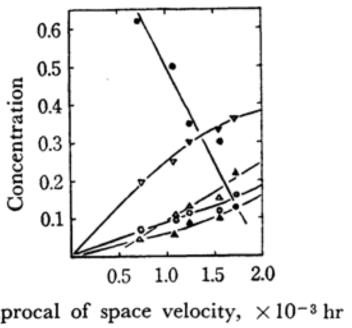

Fig. 10. Ammoxidation of *o*-xylene at 400°C.
Concentration of *o*-xylene 1.44—1.53%
Concentration of ammonia 8%
● Unconverted xylene ▽ *o*-Tolunitrile
○ Phthalonitrile △ Phthalimide
▲ Carbon oxides and hydrogen cyanide

phthalonitrile was similar to that of isophthalonitrile or terephthalonitrile in the ammoxidation of *m*- or *p*-xylene. It was, therefore, assumed that the sum of phthalimide and phthalonitrile corresponded to the quantity of isophthalonitrile or terephthalonitrile. Further details on the ammoxidation of *o*-xylene will be reported in a separate paper.

A good linear relationship is obtained in each figure. These results indicate that this reaction kinetics is adaptable for the ammoxidation of each xylene. The values of the specific rate constant for each reaction path, obtained from Figs. 1 to 9, are listed in Table 2. It is found that the rates of reaction of each path are remarkably affected by the kind of xylene. The rate data in Table 2

TABLE 2. RATE CONSTANTS FOR AMMOXIDATION OF XYLENE ISOMERS AT 400°C

	k_XRT_0 atm/hr	k_X/k_M	k_1/k_X	k_3/k_X	k_5/k_X	k_2/k_M	k_4/k_M
o-Xylene	7.2	4	0.56	0.12	0.32	0.77	0.23
m-Xylene	7.8	6	0.59	0.16	0.24	0.74	0.26
p-Xylene	11.7	6	0.79	0.08	0.12	0.87	0.13

Table 3. Rate data for ammoxidation of *o*- and *m*-tolunitrile at 400°C

Catalyst volume 8 cc
Concentration of ammonia 8%

	P_{MO} atm	Space velocity hr^{-1}	Q_M	Conversion to			Selectivity	
				DCB*	PI	CO_2, HCN	DCB, PI	CO_2, HCN
o-Tolunitrile	0.015	980	0.655	0.260	0.332	0.063	0.904	0.096
o-Tolunitrile	0.010	1480	0.632	0.280	0.291	0.062	0.902	0.098
m-Tolunitrile	0.015	980	0.980	0.890		0.090	0.908	0.092
m-Tolunitrile	0.010	1480	0.984	0.853		0.090	0.904	0.096
m-Tolunitrile	0.0061	1480	1.000	0.878		0.122	0.878	0.122

* Dicyanobenzene

Table 4. Rate data for ammoxidation of *p*-xylene at 380°C

Catalyst volume 8 cc
Concentration of *p*-xylene 0.737—2.5%
Concentration of ammonia 8%

Feed rate of *p*-xylene mmol/hr	Space velocity hr^{-1}	P_{XO} atm	Q_X	Conversion to			
				TPN*1	*p*-TN*2	CO_2	HCN
3.00	1130	0.00737	0.975	0.287	0.603	0.057	0.022
5.08	1450	0.00983	0.550	0.081	0.400	0.026	0.009
3.00	550	0.015	0.985	0.331	0.521	0.083	0.019
4.28	800	0.015	0.675	0.120	0.464	0.038	0.011
5.08	950	0.015	0.577	0.089	0.408	0.023	0.009
5.91	1100	0.015	0.502	0.077	0.382	0.026	0.007
7.19	1340	0.015	0.401	0.045	0.302	0.019	0.007
8.08	1500	0.015	0.335	0.040	0.233	0.015	0.006
7.19	1000	0.020	0.392	0.049	0.265	0.018	0.006
8.08	1130	0.020	0.314	0.039	0.224	0.016	0.004
8.08	900	0.025	0.336	0.045	0.250	0.020	0.006

*1 Terephthalonitrile *2 *p*-Tolunitrile

Table 5. Effect of reaction temperature for rate constants

	Reaction temp., °C	k_X/k_M	k_1/k_X	k_3/k_X	k_5/k_X	k_2/k_M	k_4/k_M
m-Xylene	400	6	0.59	0.16	0.24	0.74	0.26
m-Xylene	420	4	0.55	0.20	0.25	0.81	0.19
p-Xylene	380	8	0.80	0.06	0.11	0.84	0.16
p-Xylene	400	6	0.79	0.08	0.12	0.87	0.13

also indicate that the apparent rate of the reaction of *o*-tolunitrile, which is an intermediate in the ammoxidation of *o*-xylene, is more rapid than that of *m*-tolunitrile.

In order to compare the ammoxidation of each tolunitrile with its reactivities, each tolunitrile was then ammoxidized under conditions similar to those used for the ammoxidation of xylenes. The results are listed in Table 3. These results indicate that the rate of the reaction of *m*-tolunitrile in the absence of xylene is considerably faster than that of *o*-tolunitrile. The order of reaction for *o*-tolunitrile was also found to be nearly zero with respect to the concentration of *o*-tolunitrile, while the rate of the reaction of *m*-tolunitrile was pseudo-first order with respect to the concentration of *m*-tolunitrile. The selectivities for the formation of dicyanobenzenes and phthalimide from tolunitriles were also higher than those in the presence of xylenes.

The values of the specific rate constant at various reaction temperatures, obtained from Tables 2 and 4 in this paper and from Table 7 in the previous paper, are listed in Table 5. The linear relationships in Figs. 11, 12, and 13 for the rate data in Table 4 indicate that this reaction kinetics is adaptable for the ammoxidation of *p*-xylene at 380°C. It is found that the ratios of k_X to k_M,

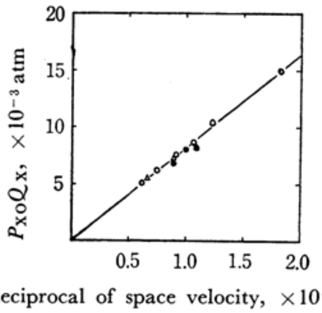

Fig. 11. Zero order plot of *p*-xylene disappearance at various initial concentration of *p*-xylene at 380°C.

P_{XO}: △ 0.00737—0.00983 atm
○ 0.015 atm
● 0.020—0.025 atm

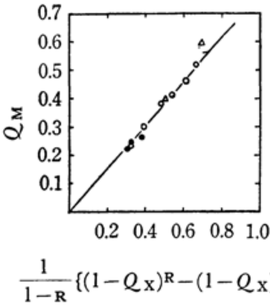

Fig. 12. Relationship between Q_M and Q_X (*p*-xylene) at 380°C.
R is one-eighth

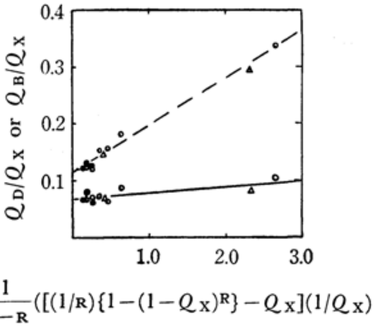

Fig. 13. Relationship between Q_D (or Q_B) and Q_X (*p*-xylene) at 380°C.
R is one-eighth
Broken line: Ratio of Q_D to Q_X
Solid line: Ratio of Q_B to Q_X

of k_3 to k_X, and of k_2 to k_M are affected by the reaction temperature.

As has been described in the previous paper, the rates of reaction in the ammoxidation of xylene were remarkably affected by the adsorption of xylene. In order to observe the interaction in the reaction of mixed xylenes, the ammoxidation of a mixture of *m*- and *p*-xylenes was carried out. The results, shown in Table 6, indicate that the rate of the reaction of *p*-xylene is faster than that of *m*-xylene.

If it is assumed that the catalytic sites which participate in the adsorption of xylenes are the same for both *m*- and *p*-xylenes, the rates of the reaction of *m*- and *p*-xylenes in the ammoxidation of the mixture of *m*- and *p*-xylenes can be represented by Eqs. (1) and (2) respectively, on the basis of the Langmuir-Hinshelwood mechanism:

$$-\mathrm{d}C_m/\mathrm{d}(V/F) = \frac{k_m K_m P_m}{K_m P_m + K_p P_p} \tag{1}$$

$$-\mathrm{d}C_p/\mathrm{d}(V/F) = \frac{k_p K_p P_p}{K_m P_m + K_p P_p} \tag{2}$$

where C_m and C_p are the concentrations of *m*- and *p*-xylene respectively, mol cc⁻¹; k_m and k_p are the specific rate constants of reaction of *m*- and *p*-xylene respectively, mol cc^{-1} hr^{-1}; K_m and K_p are the adsorption equilibrium constants for *m*- and *p*-xylene respectively, atm^{-1}; P_m and P_p are the partial pressure of *m*- and *p*-xylene respectively, atm. These equations are recast into Eq. (3) by dividing:

$$\mathrm{d}C_m/\mathrm{d}C_p = k_m K_m P_m / k_p K_p P_p \tag{3}$$

TABLE 6. RATE DATA FOR AMMOXIDATION OF MIXED XYLENES AT 400°C

Catalyst volume	8 cc
Concentration of xylene	2%
Concentration of ammonia	8%

Feed rate of xylene mmol/hr	Content of *p*-xylene	Space velocity hr⁻¹	Conversion of		
			Xylene	*m*-Xylene	*p*-Xylene
5.08	0.00	710	0.552		
7.19	0.25	1000	0.459	0.390	0.659
7.19	0.50	1000	0.513	0.354	0.674
8.08	0.50	1130	0.378	0.279	0.477
5.08	0.50	710	0.629	0.490	0.768
7.19	0.75	1000	0.559	0.376	0.620
5.08	1.00	710	0.818		

Using Eqs. (5) and (6) in the previous paper, Eq. (3) becomes:

$$\mathrm{d}Q_m/\mathrm{d}Q_p = k_m K_m P_m / k_p K_p P_p \tag{4}$$

where Q_m and Q_p are the conversions of *m*- and *p*-xylene respectively, mol mol^{-1}. By integrating Eq. (4), the following relationship is obtained:

$$\log \frac{1}{1-Q_p} = \frac{k_p K_p}{k_m K_m} \log \frac{1}{1-Q_m} \tag{5}$$

Figure 14 was obtained by using the experimental data given in Table 6. It can be seen that a reasonable fit of the data is obtained. The ratio of $k_p K_p$ to $k_m K_m$ was 2.1, calculated from the slope in Fig. 14. The ratio of K_p to K_m is, therefore, 1.4, since the ratio of k_p to k_m is 1.5, as was shown in Table 2. It can be seen that there is no difference in the strength of the two xylenes on the catalyst surface.

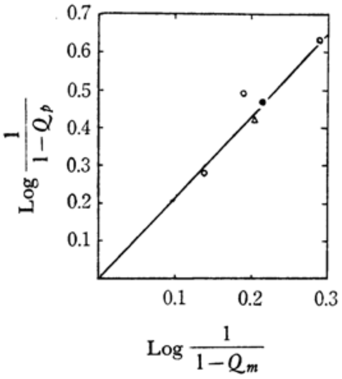

Fig. 14. Relationship between Q_m and Q_p at 400°C.
Content of *p*-xylene: ● 25%
○ 50%
△ 75%

Discussion

In view of the results described above, the kinetic model based upon the Langmuir-Hinshelwood mechanism provides a satisfactory interpretation of the ammoxidation of each xylene. This suggests that the reaction rates and selectivities for the ammoxidation of each xylene are dependent upon the adsorptivities and reactivities of related reactants.

As is shown in Table 2, the great differences in the kinetics for each xylene are in the relative ratios for the direct formation of dicyanobenzenes from xylenes and for the formation of tolunitriles from xylenes, that is, k_5/k_X and k_1/k_X. The order of the ratio of k_5 to k_X was ortho>meta>para, while the order of the ratio of k_1 to k_X was the opposite. Taking account of the steric effect, these results suggest that the adsorption of xylene on the catalyst surface takes place predominantly by way of the methyl groups. The ratio of k_5 to k_X, therefore, appears to show the degree to which two methyl groups of xylene adsorb simultaneously on the catalyst surface. A similar suggestion was made by Rafikov.[4]

The order of the relative ease of reaction was: para>meta≒ortho. A similar result was obtained by Matsuda[3] (meta≒para>ortho). It is assumed, according to the proposed kinetics, that the over-all rate of reaction is proportional to the quantity of xylene adsorbed on the catalyst surface. Taking account of the steric effect on the adsorption described above, it may be suggested that the quantity of xylene adsorbed on the catalyst surface increases with an increace in the ratio of k_1 to k_X, since the adsorption sites on the catalyst surface are saturated by methyl groups of xylenes. From the results in Table 2, the reactivities of the methyl group for each xylene seem, therefore, to be nearly equal.

The ratios of k_X to k_M were identical for the meta and para isomers, but that for the ortho isomer was smaller. This indicates that the specific reaction rate of *o*-tolunitrile, k_M, is larger than that of *m*-tolunitrile, since the specific rate constants of both *m*- and *o*-xylenes, k_X, are nearly equal. The rate of the reaction of tolunitrile in the absence of xylene is represented by the following equation, given in the previous paper:

$$r_M = k_M' K_M P_M/(1 + K_M P_M) \tag{6}$$

Since the order of reaction for *o*-tolunitrile was found to be nearly zero with respect to the concentration of *o*-tolunitrile, it may be suggested that the adsorption equilibrium constant for *o*-tolunitrile, K_M, is considerably larger than that for *m*-tolunitrile. In the presence of xylene, the rate of the reaction of tolunitrile can be represented by Eq. (7):

$$r_M = k_M' K_M P_M / K_X P_X = k_M P_M / P_X \tag{7}$$

It seems, then, that the larger specific rate constant of *o*-tolunitrile, k_M, is ascribed to the larger adsorption equilibrium constant for *o*-tolunitrile, K_M.

The ratio of k_X to k_M for both *m*- and *p*-xylene decreased with an increase in the reaction temperature. This indicates that the temperature dependency of k_M is greater than that of k_X. The activation energy for the k_X and k_M'' for the meta isomer are 43.7 and 31.2 kcal/mol respectively. k_M'' is also nearly equal to $k_M' K_M$ at low tolunitrile concentrations. From Eq. (7), the greater temperature dependency of k_M may be ascribed to the greater temperature dependency of K_X, that is, the greater heat of adsorption of xylenes.

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[4] S. R. Rafikov, B. V. Suvorov, A. A. Sabirova, V. A. Svetasheva, A. D. Kagarlitskii and B. A. Zhubanov, *Izv. Akad. Nauk Kaz. SSSR., Ser. Khim.*, **1962**, No. 1, 67.

The order of the relative ratio for the direct formation of carbon oxides and hydrogen cyanide from xylene, k_2/k_X, was ortho$\fallingdotseq$meta$>$para, while the order of the ratio of k_1 to k_X was the opposite. The ratio of k_3 to k_X also increased with an increase in the reaction temperature, while the temperature dependency of the ratio of k_1 to k_X was the opposite. Taking account of the relative strength of adsorption for *m*- and *p*-xylene, K_p/K_m, it seems that these results may be ascribed to the decrease in the adsorption type of xylene, which leads to the formation of carbon oxides and hydrogen cyanide, under which conditions the ratio of k_1 to k_X increases.

As Table 3 shows, the higher selectivities for the formation of dicyanobenzenes and phthalimide from tolunitriles were obtained in the absence of xylenes. The ratio of k_2 to k_M also increased with an increase in the reaction temperature, as is shown in Table 5, while the temperature dependency of k_X/k_M was the opposite of that of k_2/k_M. This suggests that the ratio of k_2 to k_M decreases with an increase in the depression of the rate of the reaction of tolunitriles by xylenes. It seems that these results may be ascribed to the promotion of the degradation reaction of tolunitrile, which occurs either in the gas phase homogeneously or on the catalyst surface by way of the Rideal mechanism, in which tolunitrile in the gas phase reacts with lattice oxygens of catalyst, inhibiting the adsorption of tolunitrile.

Since the temperature dependencies of k_3/k_X and k_4/k_M, both of which participate in the selectivity for dicyanobenzene, are opposite, the over-all selectivity for dicyanobenzenes seems to be independent of the reaction temperature. Indeed, the selectivity for dicyanobenzene has been reported not to be affected by the reaction temperature under optimum conditions.(2)

The fact that the adsorption equilibrium constants for *m*- and *p*-xylenes are nearly identical suggests that the ammoxidation of a mixture of *m*- and *p*-xylenes proceeds smoothly under conditions similar to those for *m*-xylene and that the selectivity of each toward dicyanobenzenes is the same as that of the individual xylene. Indeed, it has also been reported that the yield for each dicyanobenzene in the ammoxidation of mixed xylenes over a vanadium-oxide catalyst supported on alumina is the same as that in the absence of the other.(2)

The interpretations of the kinetics of xylene isomers, especially with regard to selectivities, will be confirmed by further studies carried out over mixed catalysts.

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