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The Kinetics of the Vapor-Phase Ammoxidation of *m*-Xylene over Mixed Vanadium Catalysts

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The kinetics of the vapor-phase ammoxidation of *m*-xylene over a chromium-vanadium catalyst and an antimony-vanadium catalyst, in which the atomic ratio of chromium or antimony to vanadium was unity, was studied in a flow system and compared with that over a vanadium catalyst. The reaction-rate data obtained were then correlated with the reaction kinetic model proposed for a vanadium catalyst. There was no great difference in the reaction rates of *m*-xylene over the various catalysts. The ratios of the specific rate constant of *m*-xylene to that of *m*-tolunitrile, k_X/k_M, for both mixed vanadium catalysts were considerably smaller than that for a vanadium catalyst. The relative ratio for the formation of *m*-tolunitrile from *m*-xylene, k_1/k_X, was nearly equal for a vanadium catalyst and a chromium-vanadium catalyst, but it was larger for an antimony-vanadium catalyst. The order of the relative ratio for the direct formation of carbon oxides and hydrogen cyanide from *m*-xylene was: vanadium catalyst > chromium-vanadium catalyst > antimony-vanadium catalyst. The order of the selectivity for the formation of isophthalonitrile from *m*-tolunitrile on these catalysts was similar to the order of k_X/k_M. It seems that those results may be ascribed to the weaker adsorptivity for *m*-xylene on mixed vanadium catalysts.

The kinetic study of the vapor-phase ammoxidation of *m*-xylene over a vanadium catalyst showed that the rate and the selectivity of this reaction were affected by the adsorptivity and the reactivity of related reactants.[1,2] The yield for isophthalonitrile in the ammoxidation of *m*-xylene was reported to be improved by the use of mixed vanadium catalysts, especilly the chromium-vanadium catalyst[3] and the antimoy-vanadium catalyst. A basic study of the ammoxidation of *m*-xylene over mixed vanadium catalysts was, therefore, of interest in order to gain a better understanding of the reaction processes which take place on the catalyst surface.

The present study is an attempt to clarify the reaction kinetics and the mechanism of the ammoxidation of *m*-xylene over mixed vanadium catalysts.

Experimental

Experimental Apparatus and Procedure. The apparatus and procedure were similar to those employed in a previous work.[2]

Material. *m*-Xylene and *m*-tolunitrile were the same as were employed in a previous work.[1]

Catalyst. The chromium-vanadium catalyst was prepared by impregnating an alundum carrier (27 g) with a solution which contained vanadyl oxalate and chromic oxalate, obtained from vanadium pentoxide (1.6 g) and chromic acid (1.8 g) respectively. After drying, the impregnated carrier was calcinated in air at 550°C for 4 hr.

The antimony-vanadium catalyst was prepared by impregnating an alundum carrier (27 g) with a solution which contained vanadyl oxalate and antimonyl tartarate, obtained from vanadium pentoxide (1.2 g) and antimony trioxde (1.9 g) respectively. After drying, the impregnated carrier was calcinated in air at 450°C for 4 hr.

Each calcinated catalyst was aged for 2 days before use. The surface areas of these catalysts were 0.76 m^2/g for the chromium-vanadium catalyst and 0.55 m^2/g for the antimony-vanadium catalyst after reaction.

Results and Treatment of Data

The results of the catalytic ammoxidation of *m*-xylene over a chromium-vanadium catalyst and an antimony-vanadium catalyst are shown in Tables 1 and 2.

These rate data were correlated by the treatment proposed in a previous work for *m*-xylene over a vanadium catalyst.[1] The relationships obtained by this treatment are shown in Figs. 1 to 6.

A good linear relationship was obtained in each figure except Fig. 4, in which the linear relationship held to only about a 65 per cent reaction. These results indicate that the reaction kinetics over a vanadium catalyst is adaptable for the ammoxidation of *m*-xylene over these mixed vanadium catalysts when the conversion of *m*-xylene is not very high. The values of the specific rate constant for each reaction path, obtained

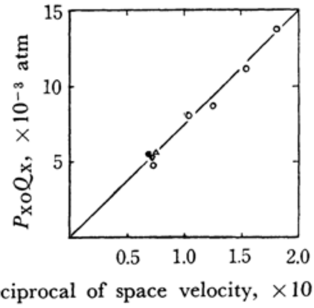

Fig. 1. Zero order plot of *m*-xylene disappearance at various initial concentration of *m*-xylene over a chromium-vanadium catalyst at 400°C.
P_{XO}*: ▽ 0.006 atm ● 0.010 atm
○ 0.015 atm △ 0.020 atm

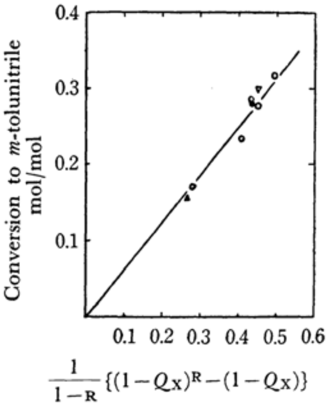

Fig. 2. Relationship between Q_M and Q_X over a chromium-vanadium catalyst.
R is ½.

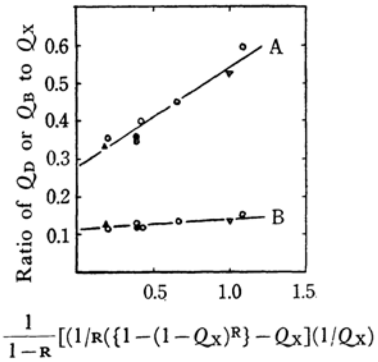

Fig. 3. Relationship between Q_D or Q_B and Q_X over a chromium-vanadium catalyst.
A: Ratio of Q_D to Q_X
B: Ratio of Q_B to Q_X

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[1] M. Ito and K. Sano, This Bulletin, **40**, 1307 (1967).
[2] M. Ito and K. Sano, *ibid.*, **40**, 1315 (1967).
[3] D. J. Hadley, *Chem. & Ind.*, **1961**, 238.

* The nomenclature is the same as that described in our previous paper.[1,2]

TABLE 1. RATE DATA FOR THE AMMOXIDATION OF *m*-XYLENE OVER A CHROMIUM-VANADIUM CATALYST AT 400°C

Catalyst volume	8 cc
Concentration of *m*-xylene	0.6—2.0%
Concentration of ammonia	8%

Feed rate of *m*-xylene mmol/hr	Space velocity hr^{-1}	P_{XO} atm	Q_X	Conversion to			
				IPN	TN	CO_2	HCN
2.91	540	0.015	0.913	0.542	0.232	0.106	0.033
3.44	640	0.015	0.742	0.326	0.316	0.078	0.022
4.26	800	0.015	0.580	0.232	0.278	0.052	0.015
5.08	950	0.015	0.544	0.189	0.285	0.054	0.016
7.21	1350	0.015	0.319	0.113	0.168	0.029	0.009
9.36	1310	0.020	0.290	0.096	0.157	0.029	0.008
5.08	1420	0.010	0.546	0.190	0.286	0.054	0.016
2.91	1350	0.006	0.889	0.465	0.302	0.091	0.031

TABLE 2. RATE DATA FOR THE AMMOXIDATION OF *m*-XYLENE OVER AN ANTIMONY-VANADIUM CATALYST AT 400°C

Catalyst volume	8 cc
Concentration of *m*-xylene	1.0—2.0%
Concentration of ammonia	8%

Feed rate of *m*-xylene mmol/hr	Space velocity hr^{-1}	P_{XO} atm	Q_X	Conversion to			
				IPN	TN	CO_2	HCN
3.44	640	0.015	0.898	0.548	0.214	0.100	0.036
3.44	640	0.015	0.877	0.506	0.228	0.107	0.036
4.28	800	0.015	0.768	0.398	0.262	0.081	0.027
4.28	800	0.015	0.764	0.383	0.265	0.088	0.027
5.08	950	0.015	0.639	0.262	0.306	0.052	0.019
5.08	950	0.015	0.678	0.290	0.292	0.071	0.025
6.35	1190	0.015	0.603	0.239	0.278	0.067	0.019
7.19	1340	0.015	0.470	0.172	0.236	0.048	0.014
5.08	1420	0.010	0.720	0.304	0.306	0.081	0.029
9.36	1310	0.020	0.393	0.125	0.231	0.027	0.010

TABLE 3. RATE CONSTANTS FOR THE AMMOXIDATION OF *m*-XYLENE OVER MIXED VANADIUM CATALYSTS AT 400°C

Kind of catalyst	$k_X R T_O$ atom/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
Vanadium	7.8	6	0.59	0.16	0.23	0.74	0.26
Chromium-Vanadium	7.3	2	0.61	0.11	0.29	0.82	0.18
Antimony-Vanadium	9.7	1.2	0.72	0.08	0.20	0.83	0.17

TABLE 4. RATE DATA FOR THE AMMOXIDATION OF *m*-TOLUNITRILE OVER MIXED VANADIUM CATALYSTS AT 400°C

Catalyst volume	8 cc
Concentration of *m*-tolunitrile	1.5%
Concentration of ammonia	8.0%
Space velocity	980 hr^{-1}

Kind of catalyst	Conversion of *m*-tolunitrile	Conversion to			Selectivity for IPN
		IPN	CO_2	HCN	
Vanadium	0.980	0.890	0.074	0.016	0.90
Chromium-Vanadium	0.909	0.855	0.045	0.009	0.94
Antimony-Vanadium	0.836	0.790	0.036	0.010	0.94

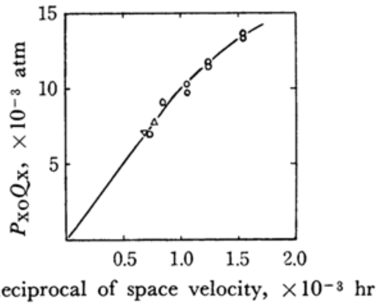

Fig. 4. Zero order plot of *m*-xylene disappearance at various initial concentration of *m*-xylene over an antimony-vanadium catalyst at 400°C.
R_{XO}; △ 0.010 atm ○ 0.015 atm
△ 0.020 atm

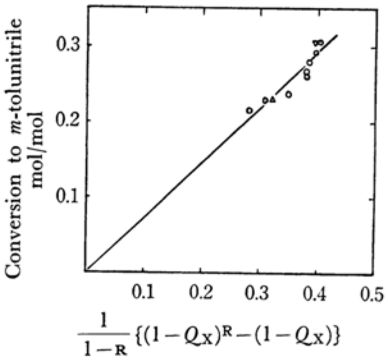

Fig. 5. Relationship between Q_M and Q_X over an antimony-vanadium catalyst.
R is 1/1.2.

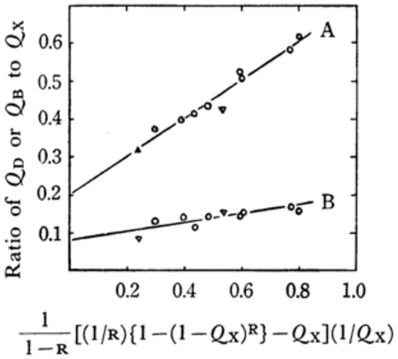

Fig. 6. Relationship between Q_D or Q_B and Q_X over an antimony-vanadium catalyst.
R is 1/1.2.
A: Ratio of Q_D to Q_X
B: Ratio of Q_B to Q_X

from Figs. 1 to 6, are listed in Table 3, along with the results for a vanadium catalyst.$^{2)}$ It is found that the reaction rates of each path are remarkably affected by the kind of catalyst. The rate data in Table 3 also indicate that the apparent rate of the reaction of *m*-tolunitrile in the presence of *m*-xylene over these mixed vanadium catalysts is considerably faster than that over a vanadium catalyst.

In order to compare it with the reactivity of *m*-tolunitrile over the vanadium catalyst and the mixed vanadium catalysts, the ammoxidation of *m*-tolunitrile over these catalysts was then carried out under conditions similar to those used for the ammoxidation of *m*-xylene. The results, listed in Table 4, indicate that the rate of the reaction of *m*-tolunitrile in the absence of *m*-xylene over mixed vanadium catalysts is rather slower than that over a vanadium catalyst.

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 *m*-xylene over these mixed vanadium catalysts.

The rates of the reaction of *m*-xylene over each mixed vanadium catalyst are nearly independent of the concentration of *m*-xylene under the given conditions. This fact suggests that the reaction proceeds by way of the saturated adsorption of the *m*-xylene on the catalyst surface. At a higher conversion of *m*-xylene, the zero-order plot of *m*-xylene disappearance came to deviate from the rate data for an antimony-vanadium catalyst, as is shown in Fig. 4. At a low initial concentration of *m*-xylene, a good fit of the rate to the zero-order plot was, however, shown at a higher conversion of *m*-xylene. Moreover, the ratio of the specific rate constant of *m*-xylene to that of *m*-tolunitrile, k_X/k_M, for an antimony-vanadium catalyst was smaller than that for other catalysts. These results suggest that the inhibition of the adsorption of *m*-xylene by *m*-tolunitrile can not be ignored for the rate of reaction of *m*-xylene over an antimony-vanadium catalysy at a higher concentration of *m*-tolunitrile, though the adsorption of *m*-xylene is so strong that it can be regarded as a saturated adsorption.

There was no great difference in the reaction rates of *m*-xylene over the various catalyst, as is shown in Table 3. Taking account of the surface area of each catalyst and the ratio of k_1 to k_X, which appears to show the degree of adsorption taking place by way of the single methyl group of *m*-xylene, the catalytic activity for the methyl group of *m*-xylene seemed to be about the same for each catalyst.

The greatest difference in the kinetics over each catalyst is the ratio of k_X to k_M. The ratios of k_X to k_M for both mixed vanadium catalysts were very much smaller than that for a vanadium catalyst. On the other hand, the ratios of the reaction rate of *m*-xylene to that of *m*-tolunitrile in the absence of *m*-xylene, r_X/r_M', for mixed vanadium catalysts were rather larger than that for a vanadium catalyst under similar conditions. These ratios can be represented by Eqs. (1) and (2):[1,2]

$$k_X/k_M' = k_X K_X/k_M' K_M \quad (1)$$

$$r_X/r_M' \propto k_X/k_M' K_M \quad (2)$$

Thus, it seems that the smaller ratio of k_X to k_M for mixed vanadium catalysts may be ascribed to the smaller adsorption equilibrium constant for *m*-xylene, K_X. This interpretation is confirmed by the fact that the zero-order plot of *m*-xylene disappearance over an antimony-vanadium catalyst came to deviate from the rate data at a higher conversion of *m*-xylene, as Fig. 4 shows.

The relative ratio of the formation of *m*-tolunitrile from *m*-xylene, k_1/k_X, was nearly equal for a vanadium catalyst and a chromium-vanadium catalyst, but it was larger for an antimony-vanadium catalyst. Taking account of the weaker adsorptivity for *m*-xylene on an antimony-vanadium catalyst and the reactivity of antimony oxide, which is inactive in this reaction, it seems that the increase in the ratio of k_1 to k_X, which appears to show the increase in the degree of single-methyl-group adsorption for *m*-xylene, may be ascribed to the strength of adsorption and the surface structure of an antimony-vanadium catalyst.

The order of the relative ratio for the direct formation of carbon oxides and hydrogen cyanide from *m*-xylene, k_3/k_X, was vanadium catalyst > chromium-vanadium catalyst > antimony-vanadium catalyst. This order agreed with that of k_X/k_M, too. This finding suggests that the strong adsorption sites of catalysts in which the adsorbed xylene leads to the formation of carbon oxides and hydrogen cyanide are less for mixed vanadium catalysts than for a vanadium catalyst.

The selectivity for the formation of isophthalonitrile from *m*-tolunitrile, k_2/k_M, for mixed vanadium catalysts was higher than that for a vanadium catalyst. This tendency was opposite to the ratio of k_X to k_M. In the absence of *m*-xylene, a higher selectivity was obtained for all catalysts, as is shown in Table 4. As has been described in a previous paper,[2] this result confirms the interpretation according to which the ratio of k_2 to k_M decreases with an increase in the depression of the rate of the reaction of *m*-tolunitrile by *m*-xylene.

The reaction kinetics was similar in the two mixed vanadium catalysts, as has been described above, though the properties of the added metal oxides in mixed vanadium catalysts were different; for example, chromium oxide was active in this reaction, while antimony oxide was inactive. A basic study of the physical properties of these mixed vanadium catalysts is, therefore, of interest in advancing the general knowledge of heterogeneous catalysis. This subject will be discussed in a separate paper.

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