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Reaction Mechanism of Ammoxidation of Toluene

I. Kinetic Studies of Reaction Steps by Pulse and Flow Techniques

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It was found in the pulse technique that toluene was adsorbed on V_2O_5/Al_2O_3 and V_2O_5 catalysts, and subsequent injection of ammonia gave benzonitrile. The adsorbed species was stable particularly on the V_2O_5/Al_2O_3. The catalyst activity was easily recovered by injection of molecular oxygen. The reaction mechanism of ammoxidation of toluene was therefore proposed as consisting of three elementary steps: (i) oxidative adsorption of toluene, accompanied with abstraction of hydrogens in the side chain; (ii) reaction of the adsorbed species with ammonia; (iii) reoxidation of catalyst by oxygen. Based on the mechanism, rate constants and concentration of active sites were measured by the pulse technique. The mechanism was confirmed also by a usual kinetic analysis in the flow technique, and kinetic constants were obtained consistent with the pulse technique.

INTRODUCTION

Ammoxidation has been well known as the synthesis process of nitriles from hydrocarbons, such as acrylonitrile and benzonitrile from propylene and toluene, respectively. In particular, much work has been reported on the mechanism and kinetics of ammoxidation of propylene (*1*). It is believed that propylene forms an adsorbed allyl intermediate in an initial step, and it is subsequently dehydrogenated to react with ammonia on Bi–Mo and U–Sb mixed oxide catalysts, etc.

As for the synthesis of benzonitrile, several patents have been issued in the past, envisaging the use of mixed oxides consisting of vanadium, molybdenum, and chromium (*2*). Most of these oxides were supported on alumina which was calcined at a high temperature (about 1000°C). On the other hand, some plausible ideas were proposed about the reaction mechanism. According to the study of Hadley (*3*), toluene was oxidized to benzoic acid, followed by the reaction with ammonia to form benzonitrile, since toluene was oxidized to benzoic acid preferably to benzaldehyde in the absence of ammonia. Ogata *et al.* (*4*) also had a similar conclusion about the reaction step, because benzoic acid gave benzonitrile quantitatively by the reaction with ammonia. On the other hand, Saito and Ohta (*5*) suspected that benzonitrile was produced via benzaldehyde as an intermediate compound. These previous workers have tried to understand the reaction mechanism from the viewpoint of the intermediate compound. However, it is also necessary to have an insight into active sites on which the reaction takes place and the interaction of substances oxidized with active sites.

The purpose of this communication is then to show the reaction mechanism of

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ammoxidation of toluene in detail, based on the consideration mentioned above. Kinetic study will be shown by the pulse and the flow techniques.

NOMENCLATURE

A	frequency factor (cm^3/sec)
Am	concentration of adsorbed species (mol/g-cat)
C	concentration in gas phase (mol/g-cat)
C_0	concentration of pulse sample in gas phase (mol/g-cat)
F	flow rate of carrier gas (cm^3/sec)
h	Planck constant (erg sec)
k	rate constant (g-cat/mol sec)
k_B	Boltzmann constant (erg/°K)
q	concentration of available active sites (mol/g-cat)
q_0	total concentration of active sites (mol/g-cat)
q^*	concentration of produced benzonitrile (mol/g-cat)
t	time (sec)
t_0	pulse width (sec)
T	reaction temperature (°K)
u	linear velocity of carrier gas (cm/sec)
v	reaction rate (mol/g-cat sec)
W	catalyst weight (g-cat)
x	distance down catalyst bed (cm)
ϵ	void fraction in the catalyst bed ($=1$) (cm^3/g-cat)
Ω	pulse size ($= C_0 t_0 F/\epsilon$) (mol)
θ	contact time ($= W\epsilon/F$) (sec)
( )	concentration in gas phase (mol/cm^3)

EXPERIMENTAL METHODS

Procedure

The ammoxidation of toluene was carried out by the pulse and the flow techniques. In the pulse technique, toluene and ammonia were alternately injected into the reactor which was made of 6 mm o.d. Pyrex glass, installed in the electric furnace, and the products were analyzed simultaneously by FID gas chromatograph. The carrier gas N_2 was deoxidized through a reduced Cu–Zn catalyst bed at 300°C, and dehydrated with a silica gel column. In the flow technique, toluene, ammonia, and oxygen were mixed and flowed into the reactor. Trapped liquid products and gaseous components were analyzed by gas chromatograph under the following condition; a 50 cm silica gel column and a 1.5 m molecular sieve column for CO_2 and O_2, N_2, and CO at room temperature, and a 2 m silicone DC 550 on Celite 545 column at 200°C for toluene and benzonitrile. Ammonia was analyzed by titration.

Catalyst

Catalyst V_2O_5/Al_2O_3 was prepared by wetting the support θ-Al_2O_3, obtained by precalcinating Al_2O_3 (Sumitomo Alumina, KAT-6) at 1000°C for 24 hr, with an aqueous solution of ammonium metavanadate, and adding oxalic acid at 100°C until the solution became pale-blue, to give 5% by weight V_2O_5 in the final sample. Subsequently, it was dried and calcined at 400°C for 3 hr in an air stream. Unsupported V_2O_5 catalyst was also prepared from aqueous ammonium metavanadate solution in a similar way. In an X-ray diffraction pattern of V_2O_5 used in a flow reaction, V_2O_4 only was observable. Such reduced catalysts were used also in the pulse technique in order to allow the surface state to be coincided with that in the flow technique. Surface areas by BET method were 33.6 m^2/g in V_2O_5/Al_2O_3 and 1.8 m^2/g in V_2O_5.

RESULTS

Pulse Reaction on V_2O_5/Al_2O_3 and V_2O_5

Toluene and ammonia were repeatedly injected on V_2O_5/Al_2O_3 and V_2O_5 catalysts at 370°C using pulse reaction apparatus. It was found that benzonitrile was formed at the ammonia pulse rather than at the toluene pulse, as shown in Fig. 1. Particularly on V_2O_5, benzonitrile was formed only

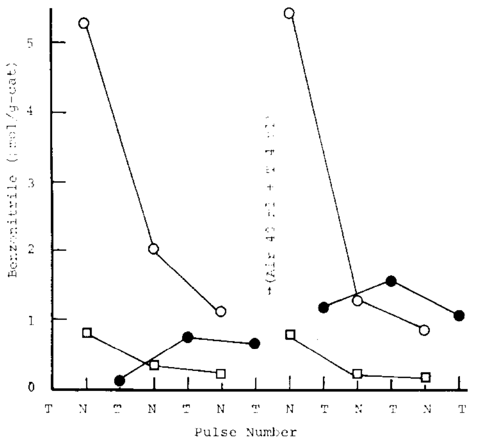

FIG. 1. Benzonitrile formation with repeated injections of toluene (2 μl) and ammonia (10 ml) pulses on V_2O_5/Al_2O_3 (○ ●) and V_2O_5 (□) at 370°C.

at the ammonia pulse. The formation of benzonitrile at the ammonia pulse on V_2O_5/Al_2O_3 was conspicuous on the fresh or oxidized catalyst. The activity decreased with pulse number, but easily recovered by the injection of oxygen. These findings show that an adsorbed intermediate from toluene reacts with ammonia to form benzonitrile.

Then, the stability of the adsorbed intermediate was examined. The amount of benzonitrile produced was measured by varying the time from toluene pulse until ammonia pulse. Ten milliliters of air were injected to reoxidize the catalyst surface before the adsorption of toluene. As shown in Fig. 2, the benzonitrile obtained at the ammonia pulse on V_2O_5/Al_2O_3 was nearly independent of the interval between toluene and ammonia pulses. About 90% of the adsorbed intermediate remained on the surface even 70 min after the adsorption of toluene, and formed benzonitrile by the injection of ammonia. This informs us of the stability of the intermediate adsorbed on V_2O_5/Al_2O_3. On the other hand, the nitrile formation on V_2O_5 decreased with the lapse of time from the toluene pulse until the ammonia pulse. Although the carrier gas which passed through the V_2O_5 bed was trapped at 77°K for about 30 min after the adsorption of toluene, no hydrocarbons were detected by FID gas chromatograph. This suggests that the decrease of benzonitrile formation was not ascribable to the desorption of the adsorbed intermediate. It seemed therefore that the adsorbed intermediate was converted to

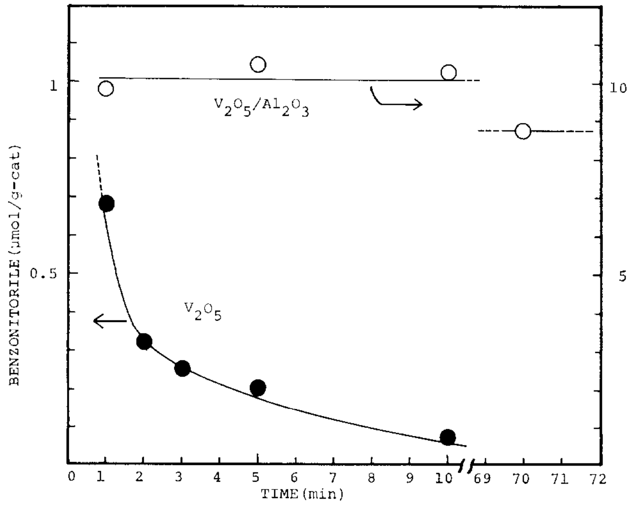

FIG. 2. Variation in the obtained benzonitrile at the ammonia pulse with the time from toluene pulse until ammonia pulse on V_2O_5 (●) and V_2O_5/Al_2O_3 (○).

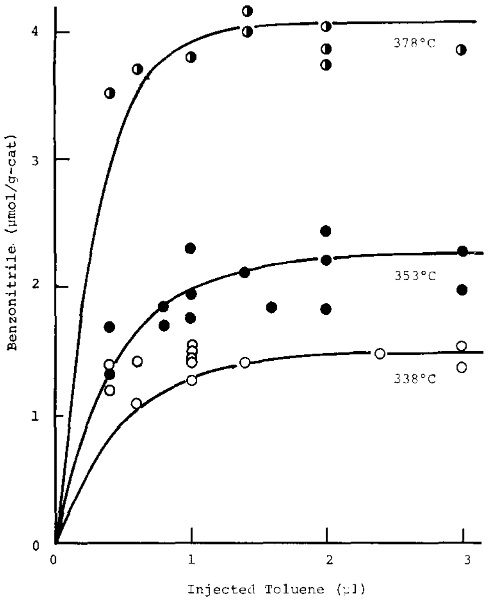

FIG. 3. Plots of produced benzonitrile against injected toluene at 338°C (○), 353°C (●), and 378°C (◑). 10 ml of ammonia were injected to form benzonitrile.

carbon oxides by surface oxygen. As a whole, the adsorbed intermediate is stable on the V_2O_5/Al_2O_3, but easily removed from the V_2O_5 catalyst as carbon oxides and water. Such a stability of the intermediate on the V_2O_5/Al_2O_3 allows us to carry out a kinetic measurement described below.

Measurements of Rate Constants by Pulse Technique

On the basis of above findings, ammoxidation of toluene can be divided into three elementary steps: (i) oxidative adsorption of toluene; (ii) reaction of adsorbed intermediate with ammonia; (iii) reoxidation of the catalyst by oxygen, i.e.,

$$\text{toluene} + (\text{O}) \xrightarrow{k_1} (\text{T}), \tag{1}$$

$$(\text{T}) + NH_3 \xrightarrow{k_2} \text{benzonitrile} + (\ ), \tag{2}$$

$$(\ ) + O_2 \xrightarrow{k_3} (\text{O}), \tag{3}$$

where (O) and ( ) denote the active site and the vacant reduced site, and (T) means the adsorbed intermediate.

Assuming first order kinetics for the concentrations of gas component and surface site, the rate equation in the pulse reaction is

$$-\frac{dq}{dt} = kqC. \tag{4}$$

If a rectangular pulse with concentration C_0 and width t_0 is injected and C_0 is essentially constant, Eq. (4) becomes Eq. (5) under the condition: $q = q_0$ at $t = 0$; $q = q'$ at $t = t_0$,

$$\ln (q_0/q') = kC_0t_0. \tag{5}$$

If a sufficient amount of ammonia is injected after adsorption of toluene, all the adsorbed toluene should be converted to benzonitrile. The concentration of benzonitrile (q^*) thus obtained corresponds to the decrease in concentration of surface site associated with the pulse reaction,

$$q^* = q_0 - q'. \tag{6}$$

By substituting this into Eq. (5), we get,

$$\ln \frac{q_0}{q_0 - q^*} = \frac{k_1\Omega\epsilon}{F}. \tag{7}$$

The total concentration of active site q_0 can be estimated from the saturated concentration of benzonitrile, and the plot of $\ln (q_0/q_0 - q^*)$ against $\Omega\epsilon/F$ gives the rate constant k_1. In a similar way, the rate constant k_2 is obtained by the relationship between injected ammonia and produced benzonitrile at the surface saturated with adsorbed intermediate.

Figures 3 and 4 show the relations of concentration of formed benzonitrile with amounts of injected toluene and ammonia at various temperatures. The solid lines in Figs. 3 and 4 represent the theoretical curve on the basis of Eq. (7). The concentration of benzonitrile produced was saturated at 2 μl of toluene and 3 ml of ammonia. Consequently, the injection of 10 ml of ammonia after adsorption of toluene in Fig. 3 was enough to convert all of the adsorbed intermediate into benzonitrile, and satisfy the condition necessary to derive the equations. Similarly, the catalyst surface was saturated with adsorbed toluene at the injection of 10 μl of toluene in Fig. 4, which allowed us to measure q_0 and k_2 on the basis of Eq. (7). The total concentration of active site q_0, k_1, and k_2 were calculated as described above, and shown in Figs. 5 and 6, respectively. The values of q_0 by both the measurements were in good agreement, as shown in Fig. 6.

On the other hand, the rate constant k_3 was measured from the adsorption of gaseous oxygen by the pulse method. Because the amount of adsorbed oxygen was given by the conversion of injected oxygen, experiments were carried out in a high conversion level. In such a case, rate equations are written in a following,

$$\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial x} + \frac{\partial q}{\partial t} = 0, \tag{8}$$

$$\frac{\partial q}{\partial t} = k_3(q_0 - q)C. \tag{9}$$

In the initial,

$$C = 0, \quad \text{and} \quad q = 0 \quad \text{at } t = 0, \tag{10}$$

and at the boundary

$$\begin{aligned} C &= C_0 \quad \text{at } x = 0, \\ q &= 0 \quad \text{at } x = ut. \end{aligned} \tag{11}$$

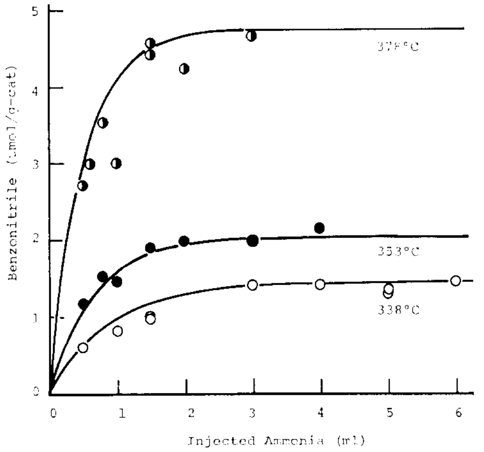

FIG. 4. Plots of produced benzonitrile against injected ammonia at 338°C (○), 353°C (●), and 378°C (◑). Ammonia was injected into the surface fulfilled with the reaction intermediate by the injection of toluene 10 μl.

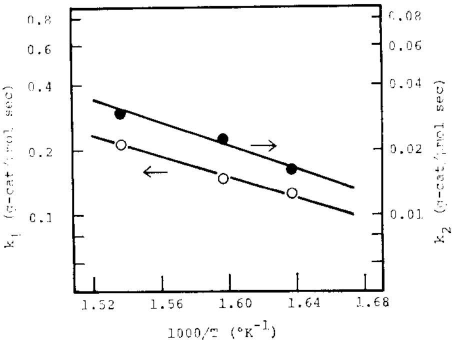

FIG. 5. Arrhenius plots of k_1 and k_2.

By solving Eqs. (8) and (9) under the condition of Eqs. (10) and (11), we get Eq. (12) about the profile of the gaseous concentration at the outlet (*6*),

$$C = \frac{C_0}{1 + \beta \exp(-k_3C_0t)}, \tag{12}$$

$$\beta = -1 + \exp(k_3q_0x/u). \tag{13}$$

Because the pulse width is kept a constant at the outlet, the average concentration of gaseous component $\bar{C}$ is then given by

$$\begin{aligned} \bar{C} &= \frac{1}{t}\int_0^{t_0} C dt \\ &= C_0\left\{1 - \frac{1}{k_3C_0t_0}\right. \\ &\quad \left.\times \ln\frac{1+\beta}{1+\beta\exp(-k_3C_0t_0)}\right\}. \end{aligned} \tag{14}$$

Finally, the concentration of adsorbed oxygen Am is drawn as

$$\begin{aligned} \mathrm{Am} &= \frac{(C_0 - \bar{C})t_0F}{W\epsilon} \\ &= \frac{1}{k_3\theta}\ln\frac{1+\beta}{1+\beta\exp(-\delta\Omega)}, \end{aligned} \tag{15}$$

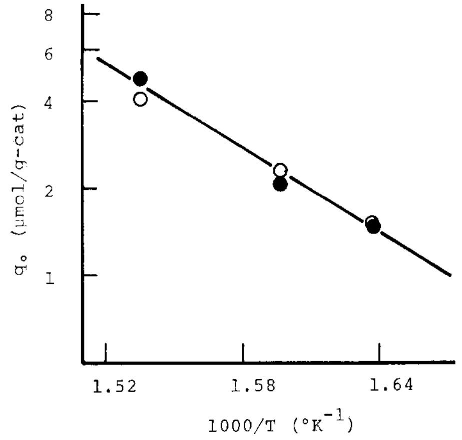

FIG. 6. Temperature dependence of q_0 derived from the adsorption of toluene (○) and the reaction with ammonia (●).

where

$$\theta = W\epsilon/F, \quad \delta = k_3\theta/W. \tag{16}$$

The relationship of the concentration of adsorbed oxygen with the inlet volume is shown in Fig. 7. The surface sites were saturated with the adsorbed oxygen at 6 ml of air injected, and the total concentration of active sites q_0 was estimated from the saturated concentration of adsorbed oxygen, because Am was equal to q_0 at infinite Ω. The rate constant k_3 was calculated from a set of Am and Ω by the nonlinear least squares method (7), and the theoretical relation on Eq. (15) is shown by the solid line in Fig. 7. At 363°C, k_3 and q_0 were 0.071 g-cat/μmol sec and 43.4 μmol/g-cat, respectively.

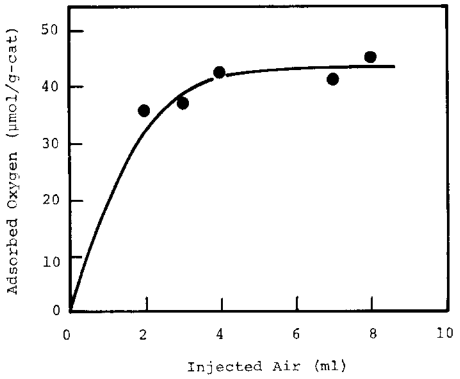

FIG. 7. Plots of adsorbed oxygen against injected air at 363°C.

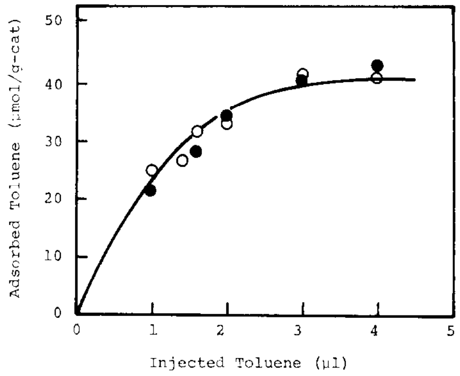

FIG. 8. Plots of adsorbed toluene against injected toluene at 363°C (●) and 338°C (○).

The adsorbed amount of toluene may be also measured from the adsorption of toluene by the pulse method, and the rate constant of toluene adsorption may be calculated as described above. Figure 8 shows the result of the adsorption of toluene by the pulse method. The total concentration of active sites was estimated from the saturated concentration of toluene adsorbed, and the rate constant; k'_1, was calculated to be 0.095 and 0.084 g-cat/μmol sec at 338 and 363°C, respectively, and q_0 was consistent with that of oxygen adsorption, but above 10 times as much as that estimated from the benzonitrile formation. This suggests the existence of sites which are available for the oxidative adsorption of toluene, but inactive for the nitrile formation. It follows that only a small part of active sites contributes to the ammoxidation. In fact, the oxygen pulse gave carbon oxides, even after the ammonia pulse did not produce benzonitrile.

Kinetic Measurement by the Flow Technique

An attempt to confirm the reaction mechanism described above was tried by a usual kinetic analysis in the flow technique. Kinetic measurement by the flow technique revealed that reciprocal plots of the rate of nitrile formation with concentrations of toluene, ammonia, and oxygen were expressed by straight lines, as shown in Fig. 9. It follows that the rate equation for the flow technique was given as

$$\frac{q_0}{v} = \frac{1}{k_1\epsilon[\phi - \mathrm{CH_3}]} + \frac{1}{k_2\epsilon[\mathrm{NH_3}]} + \frac{1}{k_3\epsilon[\mathrm{O_2}]} + \frac{1}{k_4}. \quad (17)$$

The rate equation in Eq. (17) may suggest that the reaction mechanism mentioned above should be modified about the reoxidation of the catalyst by oxygen. The corresponding step seems to be modified as

$$(\ ) + \mathrm{O_2} \xrightarrow{k_3} (\mathrm{O_2}^*), \quad (18)$$

$$(\mathrm{O_2}^*) \xrightarrow{k_4} (\mathrm{O}). \quad (19)$$

It is considered that molecular oxygen is adsorbed, followed by an activation to an appropriate form available for the reaction. Reciprocal plots in Fig. 9 made it possible to calculate k_1q_0, k_2q_0, k_3q_0, and k_4q_0 from slopes and intercepts. In the flow technique, however, it was impossible to determine k and q_0 separately. In order to compare between kinetic constants in pulse and flow techniques, the value of k_2 was assumed to be independent of measurement methods, and k_1, k_3, k_4, and q_0 in the flow technique were calculated. The comparison was made between rate constants and concentrations of active sites in Table 1. The values of k_1 were in good agreement, but active sites in the flow technique were about three times as much as those in the pulse technique. Such a high concentration in the flow technique may be connected with the repeated activation of sites owing to the presence of oxygen in the gas phase. The values of k_3 were not consistent at all, because the constant k_3 in the pulse technique was measured from the total adsorption of oxygen, and influenced by the adsorption of oxygen available for the combustion as well as for the ammoxidation, while that of the flow technique was purely derived from the nitrile formation. Consequently, it can be said that the mechanism described above is valid not only in the pulse technique but also the flow technique.

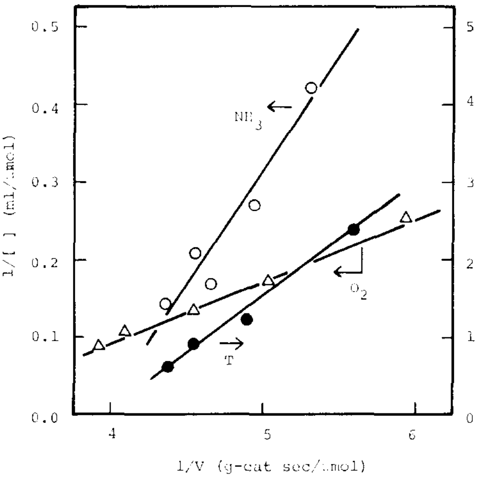

FIG. 9. Reciprocal plots of rate of benzonitrile formation at 363°C with concentrations of $\mathrm{NH_3}$ (○), toluene (●), and oxygen (△) in the flow technique.

TABLE 1

Comparison between Kinetic Constants in the Flow and Pulse Techniques at 363°C

		Flow	Pulse	Activation[a] energy (kcal/mol)
$k\left(\frac{\text{g-cat}}{\mu\text{mol sec}}\right)$	k_1	0.149	0.174	10.6
	k_2	0.0252	0.0252	11.7
	k_3	0.0071	0.071	
(sec^{-1})	k_4	0.0448	—	
$q_0\left(\frac{\mu\text{mol}}{\text{g-cat}}\right)$		9.05	3.00	19.7

[a] Obtained by the measurement in the pulse technique.

DISCUSSION

Kinetic measurements here described may suggest that the proposed mechanism is very plausible, because the concentration of active site and rate constant for each step can be obtained with reasonable agreement by both the pulse and flow techniques. The constants k_1 and k_2 were derived purely from the rate of nitrile formation, and gave the basis for the comparison between the pulse and flow reactions. The concentration of active sites simultaneously obtained by the pulse technique was influenced by the reaction temperature. As stated above, only one tenth of sites contributes to the nitrile formation. It seems that adsorbed intermediates on other sites do not form benzonitrile by the reaction of ammonia. Selectivity of active sites may be changed with increase of reaction temperature, which increases active sites. The difficulty in measurement of constant k_3 by the pulse technique is also due to the existence of such a dual type of active sites. The adsorption of oxygen on sites inactive for the ammoxidation, which may be preferred over the reoxidation of available sites for the ammoxidation, is included in the reoxidation of catalyst by the pulse technique. The constant term k_4 was necessary for the analysis of the rates in the flow technique. Because it was of the zeroth order for concentration of gaseous oxygen, the activation or the reaction of adsorbed species on the surface seems to be regarded as the corresponding step. A possible step may be the activation of adsorbed oxygen, e.g., $O_2^- \rightarrow O^{2-}$, as was previously discussed on the problem about active oxygen species adsorbed on V_2O_5/SiO_2 by Yoshida *et al.* (*8*).

The rate constant in the pulse technique can be obtained for each active site, and the frequency factor which does not include the terms of concentrations of active sites can be easily calculated. It follows that kinetic measurements by the pulse technique allows us to discuss the reaction mechanism on the theory of absolute reaction rate (*9*). Based on the activated complex theory, the frequency factor in the adsorption of toluene A can be written as

$$A = \frac{k_B T}{h} \frac{f_\ddagger}{F_g f_s},$$

where A was experimentally obtained as 1.6×10^{-15} (cm^3/sec), and F_g was estimated to be about 10^{31}, because it consisted of terms $f_t f_r f_v / V$:

$$\log (f_r/V) = \log (2\pi m k_B/h^2)^{\frac{3}{2}} = 27.466;$$
$$\log f_r \simeq 3.4; \quad \log f_v \simeq 0.$$

At least it can be said that $f_\ddagger$ has the order of 10^3. Consequently, it is considered that the activated complex in the adsorption step of toluene is in a half-mobile state on the surface. As for the reaction of adsorbed intermediate with ammonia, similar arguments could be applied. The observed frequency factor A was 7.9×10^{-16} (cm^3/sec), and other terms may be assumed as $\log (f_t/V) = 26.4$ and $\log f_r \simeq 0.15$. $f_\ddagger$ may be then evaluated as having the order of 10^{-2}. Taking into consideration some experimental errors, it may be suggested that the activated complex of ammonia is in an immobile state. Furthermore, the so-called turnover number in the flow technique was about 1.4 min^{-1} at 363°C.

It is considered that the stability of the adsorbed intermediate of toluene is worth noting. As was clearly shown in a preceding description, the intermediate is not physically adsorbed, but chemically bonded with the surface sites. The adsorption of toluene may initially take place by abstraction of hydrogen of the side chain. Probably, dehydrogenated toluene is adsorbed in a state of benzyl intermediate because it is stabilized by a gain in delocalization energy. This is well supported by the conception of π-allyl intermediate in the oxidation of propylene. Although the side chain of toluene may be further oxidized to some extent, it is now difficult to describe the structure of the stable adsorbed intermediate. Identification of the real structure of the species will be presented in the next part of this series (*10*).

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