Ammoxidation of Xylenes on V_2O_5/Al_2O_3 Catalyst

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Ammoxidation of xylene isomers on V_2O_5/Al_2O_3 catalyst was investigated by pulse and infrared studies in order to understand the reaction mechanism. It was found by the pulse technique that tolunitrile, dicyanobenzene, and benzonitrile were produced by the reaction of adsorbed intermediate with ammonia. An infrared study of adsorbed species identified the precursors of these compounds as methyl- or cyanobenzoate ions adsorbed on Al_2O_3. Xylene was oxidized on V_2O_5 and then stabilized on Al_2O_3 as the methylbenzoate ion, thus forming tolunitrile by the reaction with ammonia. Tolunitrile was further oxidized to cyanobenzoate ion, and subsequently produced dicyanobenzene. Such a substituted benzoate ion was not as stable as the benzoate ion, and the substituent was attacked by the surface oxygen of the neighboring V_2O_5 and made to enter combustion or to dealkylation. The benzoate ion formed thus produced simply benzonitrile. *p*-Xylene formed mostly tolunitrile, *o*-xylene was most easily dissociated into benzonitrile, and as a result dicyanobenzene was obtained from *m*-xylene in the highest selectivity.

INTRODUCTION

Ammoxidation has been used in the chemical industry to produce the materials for synthetic fibers or fine-chemical products such as drugs or dye. The process is carried out under comparatively mild conditions and the industrial performance necessarily requires a high selectivity. In order to heighten the reaction selectivity, care should be paid to the reduction of by-products, including carbon oxides and other dissociation products. For example, the synthesis of acrylonitrile is accompanied by the formation of CO, CO_2, CH_3CN, and HCN, and these by-products are primarily responsible for the decrease of selectivity into acrylonitrile. In a more complex molecule, obviously, there are various kinds of routes by which nitriles are formed.

In our previous investigations of toluene ammoxidation (*1–3*), the adsorbed benzoate ion was stabilized on Al_2O_3, and subsequently it formed benzonitrile by the reaction with ammonia. In this paper, ammoxidation of xylenes is investigated as an example of the reaction of larger molecules. It was previously reported that tolunitrile, dicyanobenzene, and benzonitrile were formed from *o*-, *m*-, and *p*-xylenes, and rates of nitrile formation were treated kinetically by Ito and Sano (*4*). Furthermore, the formation of phthalimide, in particular from *o*-xylene, was discussed by Saito and Ohta (*5*), and Ogata and Sakanishi (*6*). The present study investigates these reactions by pulse and infrared studies in terms of the adsorbed intermediate and its interaction with surface sites. The purpose of this study is to clarify the real structure of the adsorbed intermediate and to learn the mechanism of the reaction.

EXPERIMENTAL METHOD

The ammoxidation of *o*-, *m*-, and *p*-xylenes was carried out by the pulse technique. Air, xylene, and ammonia were repeatedly injected into the reactor, which was made of 6-mm-o.d. Pyrex glass, and installed in the electric furnace; the products were analyzed simultaneously by a gas chromatograph. Liquid products were analyzed by the use of Silicone DC 550 supported on a Celite column at 200°C. The carrier gas, He, was deoxidized through a reduced Cu–Zn catalyst bed at 300°C and dehydrated with a silica gel column.

Infrared spectra were recorded on a Jasco IR-G spectrometer in the region 4000–1000 cm^{-1} using the ir *in situ* cell connected with a vacuum line. Evacuation and adsorption were performed in an upper furnace section, and their spectra were taken in a lower section at room temperature. Products were trapped in the sidearm, cooled at −196°C, and analyzed by a gas chromatograph.

The V$_2$O$_5$ supported on Al$_2$O$_3$ catalyst used here was prepared by the method previously described (*1*). θ-Al$_2$O$_3$, obtained by the calcination of Sumitomo Alumina KAT-6 at 1000°C for 22 hr, was used as a support of the catalyst for the pulse reaction. In the infrared study, Alon G was also used as a support in order to heighten the transmittance.

RESULTS

Pulse Reaction

Air, xylene isomers, and ammonia pulses were consecutively injected into a V$_2$O$_5$/Al$_2$O$_3$ catalyst at 400°C. Separate experimental runs were performed in order to learn the distribution of gas and liquid products, because they were not analyzed simultaneously. At the first injection of xylenes, nearly all of them were either converted to products or irreversibly held by the catalyst. A material balance as low as 35% in the initial condition, which could indicate the strong adsorption of xylenes, was enhanced with number of pulse, and the reaction attained the steady state over the third pulse of xylene. The distribution of the products from xylene isomers measured at the steady state is shown in Table 1. Injection of xylene gave a small amount of benzene, toluene, and tolualdehyde, as well as combustion products. Aromatic nitriles, i.e., benzonitrile and corresponding tolunitrile and dicyanobenzene (phthalonitrile, isophthalonitrile, and terephthalonitrile from *o*-, *m*-, and *p*-xylenes, respectively), were obtained at the ammonia pulse only. This finding shows clearly that nitriles are produced through adsorbed xylene as a stable intermediate. *p*-Xylene formed *p*-tolunitrile in the highest selectivity. *o*-Xylene mostly gave benzonitrile as the dissociation product. Among these isomers, the highest amount of dicyanobenzene was obtained from *m*-xylene. Throughout this

TABLE 1

Distribution of the Products from *o*-, *m*-, and *p*-Xylenes in the Pulse Reaction[a]

Pulse	Concentration (μmol/g)									Material balance[b] (%)
	ϕ–CN	NC–ϕ–CH$_3$	NC–ϕ–CN	ϕ–H	ϕ–CH$_3$	ϕ–CHO	CO$_2$/8	CO/8	H$_3$C–ϕ–CH$_3$ unreacted	
p-Xylene				Trace	0.034	Trace	0.68	0.031	21.0	82.0
NH$_3$	0.45	4.75	0.93							
Air							5.60	1.25		
m-Xylene				Trace	0.029	Trace	0.73	0.029	22.2	75.7
NH$_3$	0.38	2.37	1.55							
Air							6.00	1.25		
o-Xylene				0.041	0.030	Trace	1.43	0.027	22.2	77.5
NH$_3$	4.38	0.21	0.10							
Air							5.60	1.25		

[a] Xylene (2 μl), NH$_3$ (10 ml), and air (5 ml) were subsequently injected into 400 mg of V$_2$O$_5$/Al$_2$O$_3$ catalyst at 400°C. The interval from xylene to ammonia was kept constant, 15 min.
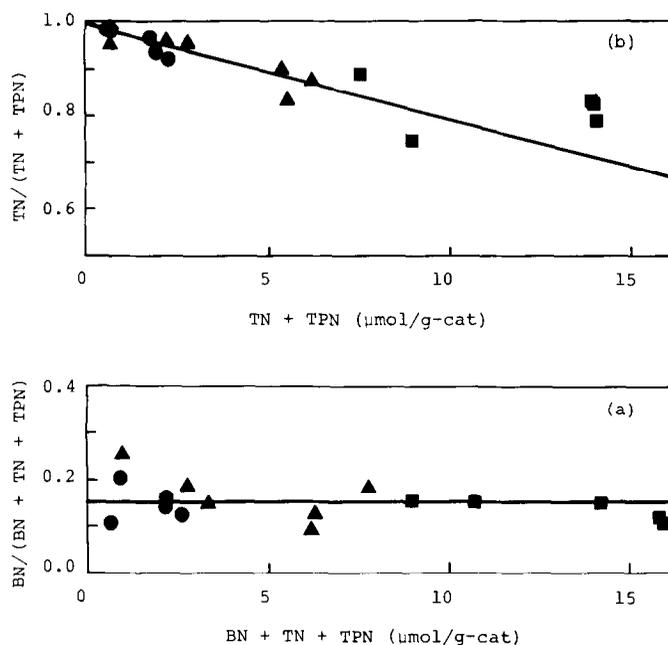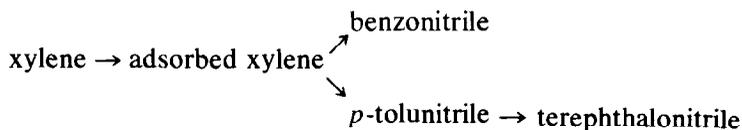[b] Based on injected xylenes.

FIG. 1. Dependence of reaction selectivity on the amount of formation in the ammoxidation of p-xylene over 150 (●), 400 (▲), and 750 mg (■) of the V_2O_5/Al_2O_3 catalyst: (a) selectivity of benzonitrile against the amount of nitriles, benzonitrile (BN), tolunitrile (TN), and terephthalonitrile (TPN); (b) selectivity of tolunitrile against the amount of tolunitrile and terephthalonitrile.

experiment, phthalimide was not found. An air pulse burned the adsorbed xylene into carbon oxides, and could oxidize the surface to repeat the reaction. Total conversion of xylene was nearly the same regardless of these isomers.

The distribution of benzonitrile, p-tolunitrile, and terephthalonitrile produced at the ammonia pulse was measured by varying the pulse size of ammonia and the catalyst weight. As shown in Fig. 1a, the selectivity into benzonitrile, expressed as the ratio of benzonitrile to the sum of nitriles, was independent of the total amount of nitriles. On the other hand, the production of other nitriles, p-tolunitrile and terephthalonitrile, was dependent on the sum of these nitriles. The selectivity into p-tolunitrile could be extrapolated to 100% with a decrease in the sum of p-tolunitrile and terephthalonitrile, as shown in Fig. 1b. Consequently, benzonitrile was formed independently via the adsorbed intermediate, while p-tolunitrile and terephthalonitrile were formed in a consecutive path, i.e.,

$$\text{xylene} \rightarrow \text{adsorbed xylene} \begin{array}{c} \nearrow \text{benzonitrile} \\ \searrow \\ p\text{-tolunitrile} \rightarrow \text{terephthalonitrile} \end{array}$$

STABILITY OF ADSORBED INTERMEDIATE

The amount of the produced nitriles was measured by varying the time from the xylene pulse until the ammonia pulse. As the time passed, p-tolunitrile and terephtha-

lonitrile from the p-xylene decreased, while benzonitrile increased (Fig. 2). Likewise, o-tolunitrile and phthalonitrile from the o-xylene decreased, and benzonitrile markedly increased, as the time from the o-xylene pulse until the ammonia pulse elapsed (Fig. 3). This suggests that at least two kinds of species are adsorbed and that the species capable of forming tolunitrile and dicyanobenzene changes into another species relating to benzonitrile during the adsorption. However, these productions did not completely compensate each other; the total sum of nitriles from the p-xylene decreased, while that from the o-xylene increased.

On the other hand, injection of ammonia after the adsorption of tolunitrile over V_2O_5/Al_2O_3 catalyst gave dicyanobenzene and benzonitrile. Also the product distribution from o- and p-tolunitriles was measured by varying the interval between the adsorption of tolunitrile and the injection of ammonia (Fig. 4). As with xylene isomers,

the decrease of dicyanobenzene and, conversely, the increase of benzonitrile were observed. The total sum of the nitriles, however, decreased from the time of the tolunitrile pulse to that of the ammonia pulse.

As previously shown in toluene ammoxidation (1), such decreases in the production of tolunitrile and dicyanobenzene from xylene and tolunitrile are based on the conversion of adsorbed xylene into carbon oxides and/or another adsorbed species relevant to benzonitrile. Except for the case of o-xylene, adsorbed species mainly enter combustion rather than dealkylation, thus decreasing the nitrile formation, because the total amount of obtained nitriles decreases as the time elapses.

The decay of tolunitrile and dicyanobenzene was quantitatively analyzed by applying the first-order kinetic equation about the concentration of surface species. The amount of nitriles, tolunitrile, and dicyanobenzene (N) was assumed to decrease with
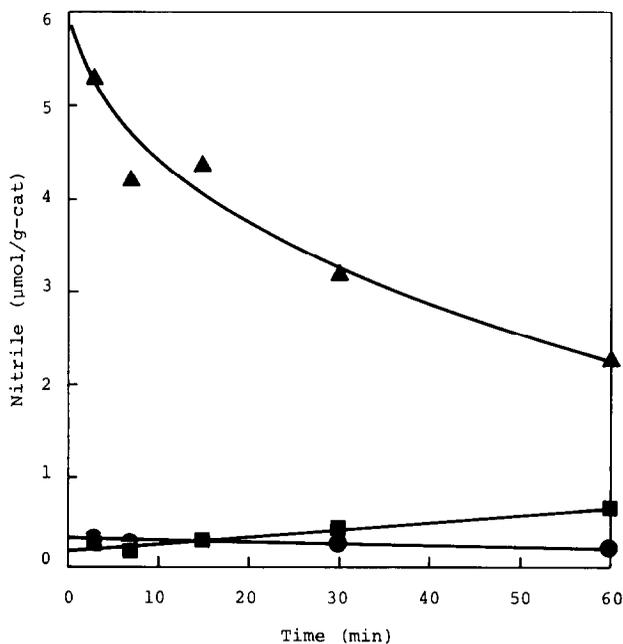

FIG. 2. Variation of tolunitrile (▲), terephthalonitrile (●), and benzonitrile (■) produced at injection of ammonia with time elapsed from p-xylene pulse till ammonia pulse.
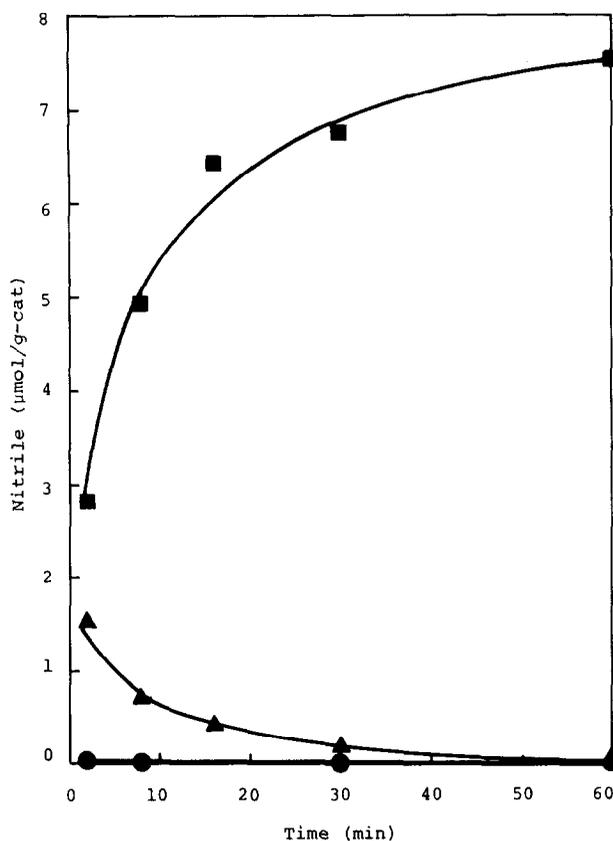
FIG. 3. Variation of tolunitrile (▲), phthalonitrile (●), and benzonitrile (■) produced at injection of ammonia with time elapsed from o-xylene pulse till ammonia pulse.

the time (t) in the equation,

$$N = N_0 \exp(-kt),$$

where N_0 denotes the initial value of formed nitriles, and k is the rate constant.

As shown in Table 2, it was found that the value of k of the *ortho* compounds was greater than that of the *para* compounds. In other words, *ortho* adsorbed species were more easily converted into carbon oxides than *para* adsorbed species. Furthermore, the adsorbed species from xylenes were decreased slightly faster than those from tolunitriles.

The initial values of formed nitriles and k were measured also in the case of p-xylene on unsupported V_2O_5, as shown in Table 2. The value of k on V_2O_5 was exceedingly higher than those on V_2O_5 supported on

Al_2O_3. Nitriles were hardly formed on V_2O_5 15 min or more after adsorption of xylene. This suggests that the reaction intermediate on V_2O_5/Al_2O_3 is not stabilized on V_2O_5, but on Al_2O_3, as in the toluene ammoxidation (*1, 2*)

TABLE 2

Variation of Concentration of Adsorbed Intermediate

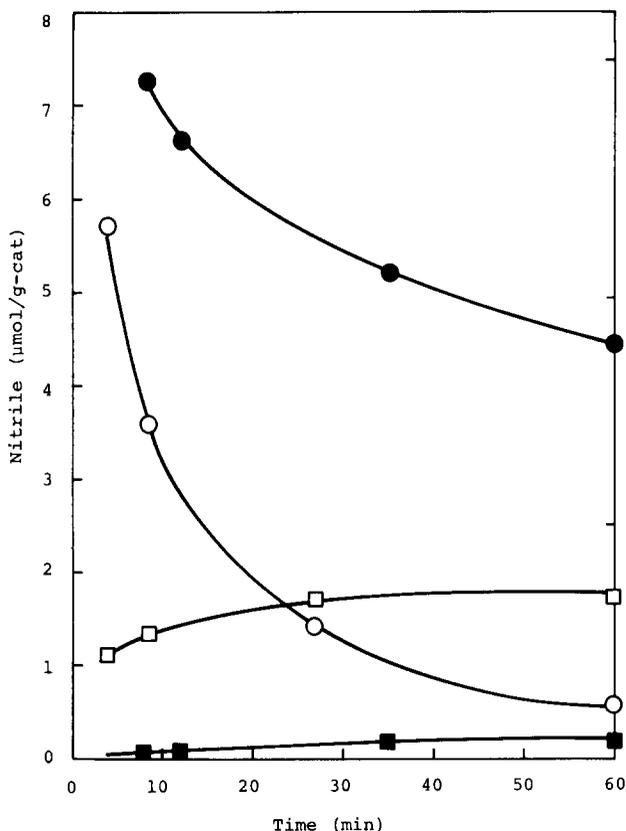| Adsorbate	Adsorbent	Initial value of formed nitriles (μmol/g-cat)	k (10^{-3} min^{-1})
p-Xylene	V_2O_5/Al_2O_3	5.36	12.8
o-Xylene	V_2O_5/Al_2O_3	1.30	49.0
p-Tolunitrile	V_2O_5/Al_2O_3	30.1	9.1
o-Tolunitrile	V_2O_5/Al_2O_3	5.34	39.3
p-Xylene	V_2O_5	0.168	135.3
Toluene	V_2O_5/Al_2O_3	15.3	2.2

FIG. 4. Variation of terephthalonitrile (●) and benzonitrile (■) from p-tolunitrile and of phtha-
lonitrile (○) and benzonitrile (□) with time elapsed from o-tolunitrile pulse till ammonia pulse.

INFRARED SPECTRA OF ADSORBED
MOLECULES

p-Xylene, p-Tolualdehyde, and Deuterated p-Xylene

An infrared study was made to identify the real structure of molecules adsorbed during the ammoxidation. The spectrum observed in the adsorption of p-xylene at 400°C on evacuated V_2O_5/Al_2O_3 is shown in Fig. 5b. On the other hand, Fig. 6b shows the spectrum obtained when p-tolualdehyde was adsorbed on Al_2O_3 at 400°C. These are in good agreement and were identified as the methylbenzoate ion; details of the identification are given in Table 3. Carboxylate ion, methyl group, C=C, and C—H bonds attached to the benzene ring were clearly observable. Absorptions at 2966, 2907, and 1260 cm^{-1} were due to the

contamination of silicone grease. The adsorbed species were then contacted with ammonia, followed by evacuation at 400°C. The intensities of the spectra were decreased as shown in Figs. 5c and 6c. In Fig. 5c, the 2250-cm^{-1} band ascribable to the C≡N stretching vibration in conjugated molecules was also observed, which suggested the formation of aromatic nitrile in the adsorbed layer. Because benzonitrile is not physically adsorbed at this temperature, this absorption band of the cyano group may be due to cyanobenzoate ion. Simultaneously, the products formed by the contact with ammonia were trapped in the sidearm cooled at liquid nitrogen temperature. As shown in Table 4, tolunitrile, terephthalonitrile, and benzonitrile were found in the trapped product. On the other hand, in the adsorption of p-tolualdehyde
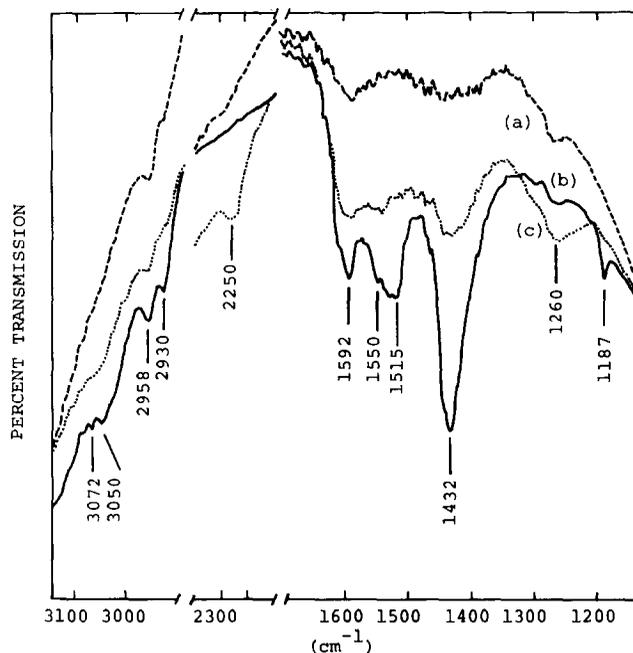
Fig. 5. Infrared spectra of p-xylene adsorbed on V_2O_5/Al_2O_3: (a) evacuated at 400°C for 2 hr; (b) after adsorption of p-xylene (10 Torr) at 400°C for 10 min in the presence of oxygen (0.1 Torr), followed by evacuation at 400°C; (c) after contact with ammonia (about 50 Torr) at 400°C, followed by evacuation at 400°C.

TABLE 3

Observed Frequencies of p-Xylene and Deuterated p-Xylene Adsorbed on V_2O_5/Al_2O_3 and p-Tolualdehyde Adsorbed on $Al_2O_3{}^a$

p-Xylene adsorbed on V_2O_5/Al_2O_3	p-Tolualdehyde adsorbed on Al_2O_3	Deuterated p-xylene adsorbed on V_2O_5/Al_2O_3	Assignment[b]
3072	3072	2287	ν(CH), ω(CD)
3050	3032	2275	ω(CH), ω(CD)
	3020		ν(CH)
2958	2956		$\nu_{asym}(CH_3)$
2930	2927		$\omega_{sym}(CH_3)$
	2870		$2\delta_{asym}(CH_3)$
1592	1600	1572	ω(C═C)
1550	1550	1530	$\nu_{asym}(COO^-)$
1515	1515	1470	ν(C═C)
1432	1440	1415	$\nu_{sym}(COO^-)$
		1390	ν(C═C)
	1295		δ(CH)
1187	1185		δ(CH)

^{a} Wavenumber in cm^{-1}.

^{b} Symbols used: ν, stretching; δ, deformation; asym, asymmetric; sym, symmetric; CH and C═C, C—H and C═C bonds in the benzene ring, respectively; CH_3 and COO^-, methyl and carboxylate groups in the side chain, respectively,

on Al_2O_3, tolunitrile and a small amount of benzonitrile were detected. Therefore, the adsorbed methylbenzoate ion on V_2O_5/Al_2O_3 reacts with ammonia to give tolunitrile, terephthalonitrile, and benzonitrile.

Furthermore, a similar adsorption study was carried out using deuterated p-xylene,

TABLE 4

Distribution of the Products Trapped in ir *in situ* Cell^a

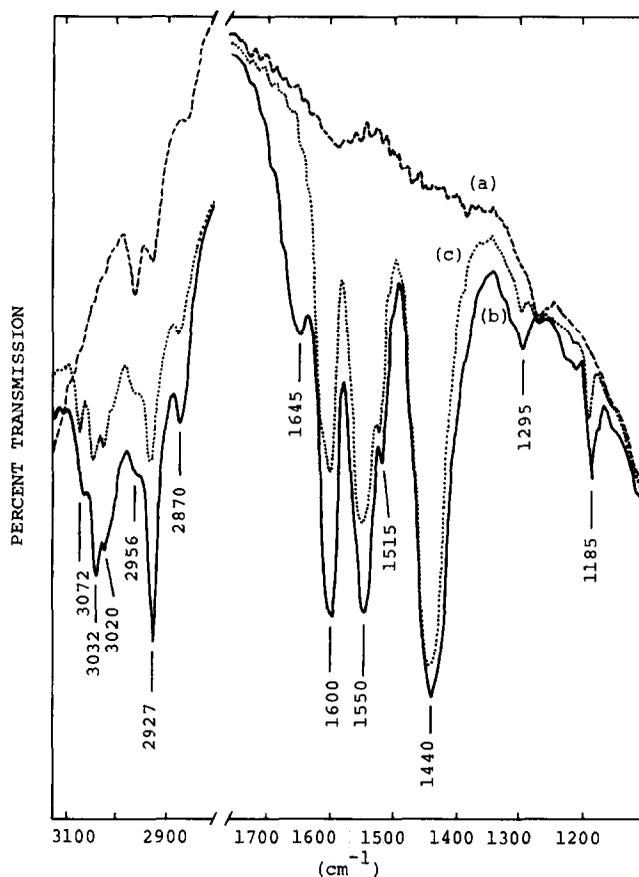| Reactant	Adsorbent	Benzo-nitrile	Tolu-nitrile	Dicyano benzene
p-Xylene	V_2O_5/Al_2O_3	0.46	1.0	0.86
p-Tolualdehyde	Al_2O_3	0.17	1.0	0.0
Deuterated-p-xylene	V_2O_5/Al_2O_3	0.91	1.0	0.23
o-Tolualdehyde	Al_2O_3	0.031	1.0	0.0
o-Xylene	V_2O_5/Al_2O_3	1.0	0.36	0.0

^{a} The compound of maximum production is taken as unity.

FIG. 6. Infrared spectra of p-tolualdehyde adsorbed on Al_2O_3: (a) evacuated at 400°C for 1 hr; (b) after adsorption of p-tolualdehyde (0.5 Torr) for 15 min, followed by evacuation at 400°C; (c) after contact with ammonia (about 50 Torr) at 400°C, followed by evacuation at 400°C.

with $C_5D_4(CD_3)_2$ as adsorbate. Adsorption of D–p-xylene on V_2O_5/Al_2O_3 revealed the spectrum shown in Fig. 7b, in which the C–D bond in the benzene ring was clearly observed. Simultaneously, the O–D bond appeared at 2700 cm^{-1}, which suggested the abstraction of hydrogens in the side chain by surface oxygen. As shown in Table 3, the absorption bands of C=C bonds shifted down by 20–35 cm^{-1} due to the increase of molecular weight. This can be compared to the normal methylbenzoate ion. The 1432-cm^{-1} band of normal methyl-benzoate ion split into two absorptions at 1415 and 1390 cm^{-1} in the adsorption spectrum of D–p-xylene. Because the asymmetric stretching vibration of the carboxylate ion at 1550 cm^{-1} shifted down by 20

cm^{-1}, the 1415-cm^{-1} band of deuterated methylbenzoate ion can be attributed to another vibration of the carboxylate ion. The absorption at 1390 cm^{-1}, therefore, may be due to the stretching vibration of the C=C double bond. Accordingly, these vibrations of the carboxylate ion and the C=C bond may overlap at 1432 cm^{-1} in the normal methylbenzoate ion.

Introduction of ammonia brought about a decrease of spectrum intensity, and liquid products, tolunitrile, benzonitrile, and terephthalonitrile were collected in the cooled trap (Table 4). Simultaneously, it was found that the OD band which appeared in the adsorption of D–p-xylene disappeared in the reaction with ammonia. This fact indicates that the formation of
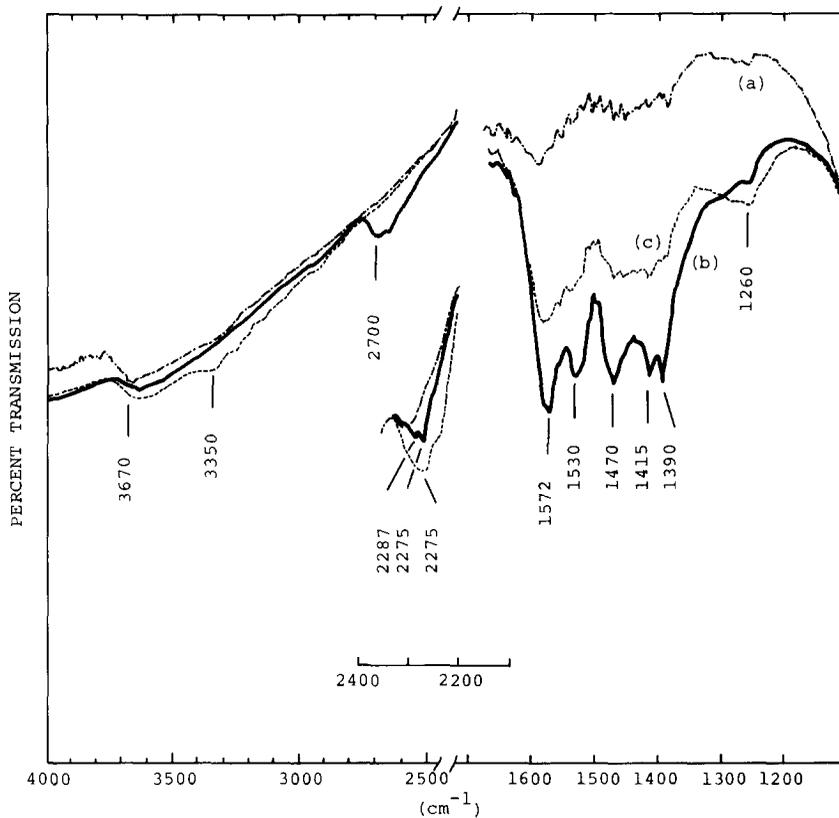
Fig. 7. Infrared spectra of p-deuteroxylene (CD$_3$C$_6$D$_4$CD$_3$) adsorbed on V$_2$O$_5$/Al$_2$O$_3$: (a) evacuated at 400°C for 1 hr; (b) after adsorption of p-deuteroxylene (7 Torr) at 400°C for 10 min in the presence of oxygen (0.1 Torr), followed by evacuation at 400°C; (c) after contact with ammonia (about 50 Torr) at 400°C, followed by evacuation at 400°C.

nitriles is accompanied by the consumption of surface hydroxyls. Also in this case, the absorption of the cyano group in the conjugated molecules was observed at 2275 cm^{-1} in Fig. 7c, probably due to the adsorbed cyanobenzoate ion.

o-Xylene, o-Tolualdehyde, and Benzaldehyde

Adsorption of o-xylene on V$_2$O$_5$/Al$_2$O$_3$ at 400°C for 5 min followed by evacuation at room temperature revealed the spectrum shown in Fig. 8b. This was identical to the spectrum observed when o-tolualdehyde was adsorbed on Al$_2$O$_3$, as shown in Table 5. As with p-methylbenzoate ion, methyl group, carboxylate ion, C=C, and C—H bonds in the benzene ring were observed. When ammonia was contacted with ad-

sorbed o-tolualdehyde on Al$_2$O$_3$, o-tolunitrile and a trace of benzonitrile were formed (Table 4). These observed spectra were therefore identified as o-methylbenzoate ion.

The o-methylbenzoate ion adsorbed on V$_2$O$_5$/Al$_2$O$_3$ was further evacuated at 400°C for 1 hr, thus resulting in a change of the spectrum as shown in Fig. 8c. The absorption bands at 2975, 2950, and 2930 cm^{-1} contributing to the methyl group disappeared, and the absorptions of the carboxyl group at 1545 and 1420 cm^{-1} were shifted to 1560 and 1436 cm^{-1}, respectively. The spectrum thus obtained was in good agreement with that of the benzoate ion on Al$_2$O$_3$ (2). Liquid products obtained by the contact of ammonia with such an adsorbed species contained more benzonitrile than
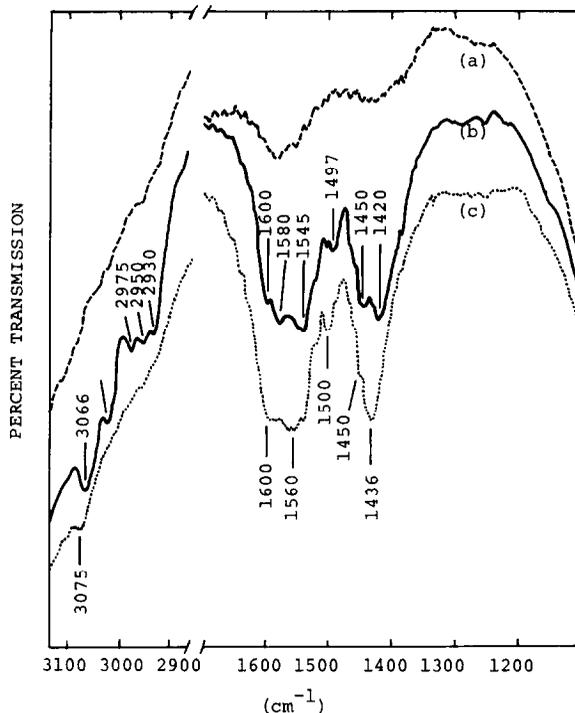
FIG. 8. Infrared spectra of o-xylene adsorbed on V_2O_5/Al_2O_3: (a) evacuated at 400°C for 2 hr; (b) after adsorption of o-xylene (10 Torr) at 400°C for 5 min in the presence of oxygen (0.1 Torr), followed by evacuation at room temperature; (c) after evacuation at 400°C for 1 hr.

tolunitrile. Therefore, adsorbed o-methyl-benzoate ion was turned into benzoate ion by allowing it to stand at 400°C. This agrees well with the finding that the production of benzonitrile increases with the lapse of time from the xylene pulse till the ammonia pulse.

m-Xylene, m-Tolualdehyde, and m-Tolunitrile

Identification of adsorbed species has also been performed using m-xylene and related compounds. The absorption bands in which m-xylene and m-tolunitrile were adsorbed on V_2O_5/Al_2O_3, and m-tolualde-hyde was adsorbed on Al_2O_3, are listed in Table 6. As shown in the table, methyl group, carboxylate ion, C=C, and C—H bonds were observed in these spectra. It was therefore concluded that m-xylene on V_2O_5/Al_2O_3 and m-tolualdehyde on Al_2O_3 were both stabilized as the m-methylben-zoate ion. On the other hand, the spectrum

of m-tolunitrile adsorbed on V_2O_5/Al_2O_3 contained a sharp absorption of the cyano group at 2260 cm^{-1}; it was therefore identified as the m-cyanobenzoate ion.

DISCUSSION

Infrared study has revealed that ad-sorbed xylene is, in the first place, stabi-lized on V_2O_5/Al_2O_3 as the methylbenzoate ion. Because it is not stable on V_2O_5 and because the same adsorbed species is found on Al_2O_3, obviously, the methylben-zoate ion is adsorbed on the surface of Al_2O_3. On the other hand, oxidation occurs only on V_2O_5 so that the intermediate com-pound formed on V_2O_5 migrates to the sur-face of Al_2O_3. As understood from a trace of tolualdehyde in the pulse reaction, it is thought that xylene is converted into tolualdehyde on V_2O_5 and then the latter migrates to Al_2O_3, through a gas phase, to be stabilized as the methylbenzoate ion, in

TABLE 5

Observed Frequencies of o-Xylene Adsorbed on V_2O_5/Al_2O_3 and of o-Tolualdehyde and Benzaldehyde Adsorbed on Al_2O_3[a]

o-Xylene adsorbed on V_2O_5/Al_2O_3[b]	o-Tolualdehyde adsorbed on Al_2O_3	o-Xylene adsorbed on V_2O_5/Al_2O_3[c]	Benzaldehyde adsorbed on Al_2O_3	Assignment[d]
3066	3054	3075	3065	$\nu(CH)$
3025	3020		3035	$\nu(CH)$
2975	2966			$\nu_{asym}(CH_3)$
2950				$\nu_{asym}(CH_3)$
2930	2925			$\nu_{sym}(CH_3)$
1600	1608	1600	1600	$\nu(C=C)$
1580	1583			$\nu(C=C)$
1545	1545	1560	1550	$\nu_{asym}(COO^-)$
1497	1493	1550	1550	$\nu(C=C)$
1450	1450	1450	1455	$\nu(C=C)$
1420	1422	1436	1435	$\nu_{sym}(CCO^-)$
	1385			$\delta(CH)$
	1290			$\delta(CH)$
	1163		1180	$\delta(CH)$

[a] Wavenumber in cm^{-1}.
[b] Evacuated at room temperature.
[c] Evacuated at 400°C.
[d] Symbols defined in Table 3.

a way similar to that of the toluene ammoxidation described in our former study (3). As shown above, the reaction of ammonia with the o- or p-methylbenzoate ion on Al_2O_3 gave the corresponding tolunitrile.

TABLE 6

Observed Frequencies of m-Xylene and m-Tolunitrile Adsorbed on V_2O_5/Al_2O_3 and of m-Tolualdehyde on Al_2O_3[a]

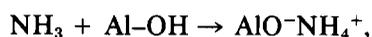| m-Xylene adsorbed on V_2O_5/Al_2O_3	m-Tolualdehyde adsorbed on Al_2O_3	m-Tolunitrile adsorbed on V_2O_5/Al_2O_3	Assignment[b]
3060	3056	3060	$\nu(CH)$
	3031		$\nu(CH)$
	2957		$\nu_{asym}(CH_3)$
	2929		$\nu_{sym}(CH_3)$
	2875		$2\delta_{asym}(CH_3)$
	2743		$2\delta_{sym}(CH_3)$
		2260	$\nu(C\equiv N)$
1592	1599	1592	$\nu(C=C)$
1550	1558	1550	$\nu_{asym}(COO^-)$
1488	1492		$\nu(C=C)$
1450	1450	1432	$\nu(C=C)$
1415	1414	1410	$\nu_{sym}(COO^-)$

[a] Wavenumber in cm^{-1}.
[b] Symbols defined in Table 3.

Also on V_2O_5/Al_2O_3, it was found that the formation of tolunitrile was accompanied by the decrease of spectrum intensity of the methylbenzoate ion. Furthermore, the distribution of products obtained in an ir in situ cell in the cases of o- and p-xylenes was analogous to that of the pulse reaction. Consequently, the methylbenzoate ion on Al_2O_3 can be regarded as the reaction intermediate to form tolunitrile in the ammoxidation of xylene on the V_2O_5/Al_2O_3 catalyst.
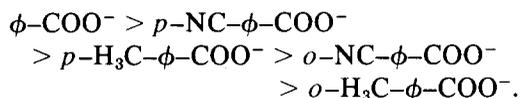
Dicyanobenzene is formed in a consecutive path via tolunitrile, as surmised from the dependence of the reaction selectivity on the production amount. In the adsorbed layer, the cyano group in conjugated molecules is detected after the reaction with ammonia. Adsorption of m-tolunitrile revealed the adsorbed cyanobenzoate ion in the ir spectrum. Probably, the cyanobenzoate ion stabilized on Al_2O_3 forms dicyanobenzene in the reaction with ammonia.

As mentioned above, the reaction of ad-

sorbed species with ammonia takes place on Al_2O_3. The behavior of surface hydroxyls implies the interaction of Al_2O_3 with hydrocarbon and ammonia. In our previous paper (2), the ammonium ion, NH_4^+, is proposed as the reacting species of ammonia on the basis of the variation of concentration of surface hydroxyl. The use of a deuterated compound, D–p-xylene, enables us to deduce the detailed mechanism of this reaction. As described above, the OD band appeared in the adsorption of D–p-xylene, and disappeared in the reaction with ammonia. Consequently, the mechanism proposed in the ammoxidation of toluene to elucidate the adsorbed state of ammonia may be valid also in this case. Namely, ammonia reacts with Al–OH to form the ammonium ion, NH_4^+, thus readily converting carboxylate to nitriles, i.e.,

$$NH_3 + Al\text{--}OH \rightarrow AlO^-NH_4^+,$$

$$Al\text{--}O^-NH_4^+ + R\text{--}COOAl \rightarrow$$
$$R\text{--}CN + H_2O + 2Al\text{--}OH.$$

The adsorbed intermediate of xylene, the methylbenzoate ion, is not as stable as the benzoate ion, as understood from the comparison between these decay constants. Also the cyanobenzoate ion is gradually converted into the combustion products, as well as the benzoate ion. The stability of adsorbed species is ordered in this sequence according to the values of k;

$$\phi\text{--}COO^- > p\text{--}NC\text{--}\phi\text{--}COO^-$$
$$> p\text{--}H_3C\text{--}\phi\text{--}COO^- > o\text{--}NC\text{--}\phi\text{--}COO^-$$
$$> o\text{--}H_3C\text{--}\phi\text{--}COO^-.$$

The side chain other than the carboxylate ion is weakened by the attack of surface oxygen. Al_2O_3 does not have the ability to dissociate the adsorbed species, as mentioned above. In fact, the distribution of the trapped products in the ir cell obtained by the adsorption of tolualdehyde on Al_2O_3 showed that only a little amount of benzonitrile was obtained as the dissociation product. It seems that the carboxylate ion is

stabilized without further oxidation, because it is attached to aluminum oxide of low oxidation activity. In other words, methyl and cyano groups of substituted benzoate ions are attacked by the surface oxygen of neighboring vanadium oxide to form the benzoate ion or carbon oxides. The stability of $para$ compounds relative to $ortho$ compounds is easily elucidated by the steric requirement of this combustion mechanism. Obviously, the methyl or cyano group placed $para$ to the carboxylate ion takes a position away from the surface so that it is not easily attacked. Likewise, dicyanobenzene was not readily obtained from p-xylene, because the methyl group situated $para$ to the carboxylate ion is mostly difficult to oxidize. As a result, dicyanobenzene was formed from m-xylene at the highest selectivity. It can be thus considered that the reaction selectivity is determined by such a steric location of the substituent group which is the target in the direct attack by surface oxygen.

Among these adsorbed species, the o-methylbenzoate ion was easily converted into the adsorbed benzoate ion, thus preferentially forming benzonitrile as a result of the reaction with ammonia. The increase of the total amount of nitriles may be based on the difference in the rates of nitrile formation. The formation of benzonitrile from the adsorbed benzoate ion is faster than that of tolunitrile or dicyanobenzene, and the increase in the concentration of the benzoate ion in place of the methylbenzoate ion brings about the increase of the total sum of nitriles. However, other adsorbed species, if attacked by surface oxygen, are converted to carbon oxides rather than benzoate ion.

A consecutive mechanism for production of tolunitrile and dicyanobenzene is consistent with the proposals by Ito and Sano (4) and Ogata and Sakanishi (6) on the basis of kinetic study. They proposed that dicyanobenzene was also produced directly from xylene. In view of this, dicarboxylate ion ($^-OOC\text{--}\phi\text{--}COO^-$), which attached to

the surface of Al_2O_3 through both terminals, must be considered. However, such an adsorbed species was not found, and the direct path of the formation of dicyanobenzene may be disregarded. Selectivity of tolunitrile and dicyanobenzene from o-, m-, and p-xylenes in the continuous-flow method by Ito and Sano (4) is approximately identical with ours in the pulse technique. Therefore, the mechanism proposed here may be applied also to the flow reaction.

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