

Ammoxidation of Toluene over $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{ZrO}_2\text{-SiO}_2$, and $\text{TiO}_2\text{-SiO}_2$

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Activities of $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{ZrO}_2\text{-SiO}_2$, and $\text{TiO}_2\text{-SiO}_2$ catalysts were very weak or nothing at all in the initial state, but increased greatly within the course of the reaction. Such an increase of the activity was also observed by the treatment by oxidation of other hydrocarbons, and in addition the activity was diminished by the burning of carbon by air. It was found by ESR that the activity was correlated well with the concentration of carbon radical. The surface of treated $\text{SiO}_2\text{-Al}_2\text{O}_3$ was covered with carbonaceous material that showed absorption bands belonging to carbonyl or carboxyl group in the ir spectrum. The pulse method revealed that benzonitrile was given off by the reaction of the adsorbed intermediate from toluene with ammonia. The intermediate was fully stable on Al_2O_3 , ZrO_2 , and TiO_2 , but not on activated carbon and fresh $\text{SiO}_2\text{-Al}_2\text{O}_3$. The activity of activated carbon for the ammoxidation was confirmed. These findings suggest that the activity of these catalysts is bi-functional; toluene is oxidized on carbon surface oxides, followed by stabilization as adsorbed benzoate ion to produce benzonitrile on Al_2O_3 , ZrO_2 , and TiO_2 .

INTRODUCTION

In our previous papers (1-3), ammoxidation of toluene on $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ was investigated to clarify the reaction mechanism. The ammoxidation of toluene is initiated with oxidation of the side chain to form benzaldehyde on V_2O_5 . The intermediate compound benzaldehyde migrates to the surface of Al_2O_3 through the gas phase to be stabilized as the benzoate ion, followed by the reaction with ammonia to form benzonitrile. Reduced sites are then reoxidized by oxygen.

The available activity of Al_2O_3 for oxidative dehydrogenation of ethylbenzene has already been reported by Alkhozov *et al.* (4). As described below, preliminary experiments have found that $\text{ZrO}_2\text{-SiO}_2$ and $\text{TiO}_2\text{-SiO}_2$ catalysts are active in forming benzonitrile as a result of ammoxidation. In a past patent for the ammoxidation of toluene (5), $\text{SiO}_2\text{-Al}_2\text{O}_3$ was also described to be active. The catalytic activity of such solid acid catalysts with low oxidation power for the oxidation reaction is of major interest.

The purpose of this study is, then, to

make clear the reaction mechanism and active sites on typical solid acids, $\text{SiO}_2\text{-Al}_2\text{O}_3$ and $\text{ZrO}_2\text{-SiO}_2$, and on $\text{TiO}_2\text{-SiO}_2$ the acidity of which was observed by Tanabe *et al.* (6). The roles of constituent oxides will be investigated by ESR, ir, and the pulse method.

EXPERIMENTAL METHODS

Eight kinds of catalysts were used in this study. Silica-alumina that contained 15% by weight Al_2O_3 was supplied by Nikki Chemical Co., Ltd. (N631 (L)) and calcined at 500°C for 2 hr. BET surface area of obtained $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst was 447 m^2/g . A $\text{TiO}_2\text{-SiO}_2$ catalyst was prepared by impregnation of TiCl_4 solved in ethanol with silica gel (Dokai Chemical, Pore Dia S-70A). After vaporization at 80°C, this was treated with 4 N NH_4OH to remove Cl^- ion, followed by washing with water until the pH equaled 7, and then calcinating at 500°C for 3 hr by air. The final sample of $\text{TiO}_2\text{-SiO}_2$ had the surface area of 250 m^2/g . A $\text{ZrO}_2\text{-SiO}_2$ catalyst was also prepared in a similar way from $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$. Titania and zirconia were supported on SiO_2 with atomic ratio (Ti or Zr/Si) of 1 : 10. ZrO_2 was sup-

ported on SiO_2 as mentioned above, or silica gel which was obtained by the hydrolysis of silica sol (Shokubai Kasei), and these were shown as $\text{ZrO}_2\text{-SiO}_2$ (1) and $\text{ZrO}_2\text{-SiO}_2$ (2) of which BET surface areas were 266 and 140 m^2/g , respectively. The impurity of silica gel and $\text{SiO}_2\text{-Al}_2\text{O}_3$ which were commercially supplied was mainly iron below 0.05 wt%. The impurity level of chlorine in $\text{TiO}_2\text{-SiO}_2$ and $\text{ZrO}_2\text{-SiO}_2$ (1) was checked by the fluorescent X-ray method, and found to be less than 0.1 wt%.

The unsupported oxides of which they consist were prepared in the following way. Al_2O_3 was obtained by the calcinating of Sumitomo Activated Alumina KHD at 1000 or 400°C for 22 hr. TiO_2 was prepared by calcinating at 450°C for 3 hr of $\text{Ti}(\text{OH})_4$ precipitated from TiCl_4 , dropwise dissolved in water at 80°C. ZrO_2 was prepared by thermal decomposition of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ at 500°C for 4 hr. Activated carbon was supplied from Takeda Chemical Industry, Ltd.

(HGE-538), and used without further pretreatment.

The equipment used in the pulse and the flow techniques have been previously described in detail (1). An infrared spectrum of $\text{SiO}_2\text{-Al}_2\text{O}_3$ was recorded on a Jasco IR-G spectrophotometer. The fresh or treated samples of $\text{SiO}_2\text{-Al}_2\text{O}_3$ were mixed with KBr, and compressed into disks. ESR spectrum of $\text{SiO}_2\text{-Al}_2\text{O}_3$ was measured by a JEOL ME-1X type spectrometer (X-band). g -Value of the spectrum was determined as compared with the Mn^{2+} impurity in MgO .

RESULTS

Catalytic Activity of $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{ZrO}_2\text{-SiO}_2$, and $\text{TiO}_2\text{-SiO}_2$

The catalytic activity increased gradually with the time-on-stream, and reached the stationary state about 1 hr after the initiation of the reaction. Once the activity was stabilized, its deactivation was not observed significantly. Figure 1 shows the

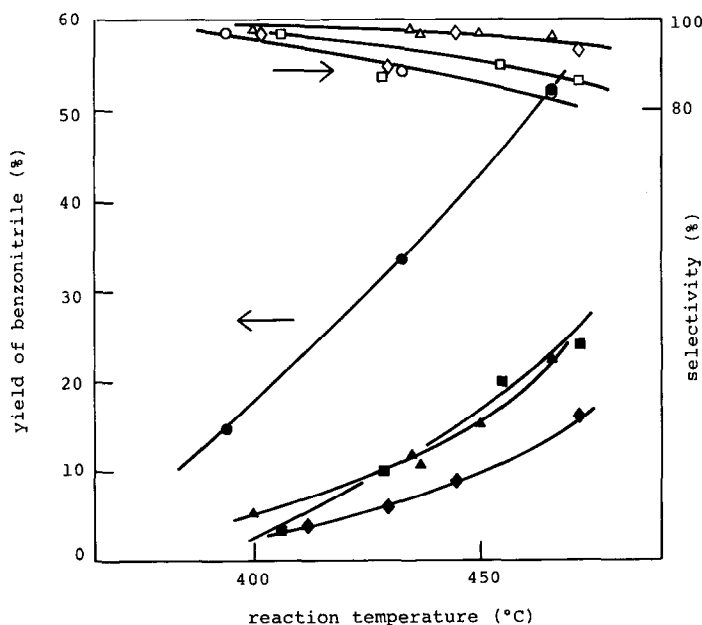


FIG. 1. Yield and selectivity of benzonitrile formation on $\text{SiO}_2\text{-Al}_2\text{O}_3$ (● ○), $\text{TiO}_2\text{-SiO}_2$ (▲ △), $\text{ZrO}_2\text{-SiO}_2$ (1) (◆ ◇), and $\text{ZrO}_2\text{-SiO}_2$ (2) (■ □) under the reaction condition: total flow rate, 220 ml/min; catalyst weight, 1.0 g; composition of gases, toluene: O_2 : NH_3 : N_2 = 0.0340:0.15:0.21:0.61. Yield and selectivity are defined: yield, (benzonitrile)/(benzonitrile + CO_x + toluene) \times 100; selectivity, (benzonitrile)/(benzonitrile + CO_x) \times 100.

yield and selectivity of benzonitrile in the stationary state of the flow reaction in the temperature range of 390–470°C. By-products, CO and CO₂ were very low compared to the formation of benzonitrile, and the ammoxidation over these catalysts proceeded in a high selectivity. Among these catalysts, the SiO₂–Al₂O₃ catalyst had the highest activity. It is remarkable that such typical solid acid catalysts as SiO₂–Al₂O₃ and ZrO₂–SiO₂ are active in the ammoxidation reaction.

The pulse technique has been applied to these catalysts, and it revealed that benzonitrile was formed by the reaction of the stable adsorbed intermediate of toluene with ammonia on these catalysts also. The saturated amount of the intermediate on the catalysts used in a flow reaction was then measured by means of the pulse technique. Repeated injections of toluene pulse cause the surface to be covered with the adsorbed intermediate. After confirming the elution of all the injected toluene, ammonia pulses are injected to form benzonitrile until benzonitrile is not detected. The sum of the formed benzonitrile corresponds to the concentration of saturated adsorbed intermediate on the surface. As shown in Table 1, four pulses of toluene were needed to make the surface saturated with the adsorbed intermediate. The amount of benzonitrile was the highest in the first injection of ammonia pulse, and gradually decreased with the number of pulses. Fi-

nally, it was very low after more than four pulses. As understood from the comparison of the amount of saturated adsorbed intermediate with the yield of benzonitrile in the flow reaction, the greater concentration of saturated adsorbed intermediate the catalyst possessed, the greater amount of benzonitrile it formed in the flow reaction.

If saturated amount of adsorbed intermediate corresponds to number of active site, one can estimate the catalytic activities from the viewpoint of turnover frequency (TOF). The TOF for the ammoxidation of toluene at 400°C which were calculated based on this method were 0.35, 0.16, 0.14, and 0.08 KS⁻¹ over SiO₂–Al₂O₃, TiO₂–SiO₂, ZrO₂–SiO₂ (1), and ZrO₂–SiO₂ (2), respectively. These are smaller than 1.0 KS⁻¹ on V₂O₅/Al₂O₃, a typical catalyst in the ammoxidation with 3.03 μmol/g of saturated adsorbed intermediate.

The activities of the catalysts used in this communication increased with the course of the flow reaction, as mentioned above. The comparison of catalytic activity in the fresh state to that in the aged state was made by the pulse technique, and is shown in Table 2. First of all, an air pulse was injected to oxidize the surface, and each shot of toluene and ammonia pulses was injected to produce benzonitrile. It was found that the benzonitrile formation on the aged catalyst markedly exceeded that of the fresh one for all the catalysts. The silica-alumina catalyst had no activity in the

TABLE 1
Saturated Adsorbed Intermediate (10⁻⁸ mol/g)^a

Catalyst	Pulse number ^b	Benzonitrile formed at NH ₃ pulse			Saturated adsorbed intermediate
		First	Second	Third	
SiO ₂ –Al ₂ O ₃	10	25.7	1.55	0.78	28.9
ZrO ₂ –SiO ₂ (1)	4	9.28	0.71	0.35	10.3
ZrO ₂ –SiO ₂ (2)	4	16.1	0.36	0.13	16.9
TiO ₂ –SiO ₂	4	17.6	0.0		17.6

^a Pulse sizes of toluene and ammonia, 0.4 μl and 5 ml, respectively; catalyst amount, 1 g.

^b Number of toluene pulse required for the saturation with adsorbed intermediate.

TABLE 2
Increase of Activity by Aging of Catalysts

Catalyst	Benzonitrile formed in the pulse reaction ^a (10 ⁻⁸ mol/g)	
	Fresh	Aged
SiO ₂ -Al ₂ O ₃	0.0	11.0
ZrO ₂ -SiO ₂ (1)	0.17	11.1
ZrO ₂ -SiO ₂ (2)	0.18	12.0
TiO ₂ -SiO ₂	4.9	7.2

^a By NH₃ pulse (5 ml) over the catalyst (1 g) after toluene (0.4 μl) was injected.

initial state at all. A little activity of the ZrO₂-SiO₂ catalyst was inherently active in some degree, but increased by being used in the flow reaction.

Such an increase of the catalyst activity during the flow reaction was investigated in more detail by using the SiO₂-Al₂O₃ that was the most typical and active in this study. The SiO₂-Al₂O₃ was treated for 3 hr at about 400°C by the oxidation reaction of various reactants, i.e., NH₃, toluene, propylene, butane, and 1-butene, and subjected to the pulse reaction. After oxidation of the surface by air pulse, toluene and ammonia pulses were individually injected to give benzonitrile. The influence of oxy-

gen mixed with toluene and ammonia pulses on the benzonitrile formation was also investigated. As clearly shown in Table 3, the activity for benzonitrile formation appeared in the oxidation of hydrocarbons, but was not found in the initial state or on the catalyst treated with the oxidation of ammonia. Simultaneously, the color of the SiO₂-Al₂O₃ catalyst became black after the oxidation of hydrocarbons. Reoxidation by the flowing of oxygen at 500°C for 3 hr diminished the catalyst activity, and additionally the white color of the SiO₂-Al₂O₃ was recovered. These results allowed us to suspect that the appearance of the catalyst activity may be based on the deposit of carbonaceous material on the surface. Furthermore, the mixing of oxygen with toluene pulse increased the formation of benzonitrile, but not so much in the case of ammonia in all of the samples. This suggests that oxygen is required for the proceeding of the reaction only on the adsorption step of toluene.

Stability of Adsorbed Intermediate on Constituent Oxides

Roles of constituent oxides have been examined by the use of them individually. Toluene was not oxidized by the injection

TABLE 3
Benzonitrile Formed in the Pulse Reaction on Treated SiO₂-Al₂O₃ at 418°C (10⁻⁸ mol/g)

Pulse reaction ^c	Fresh	Treated in the oxidation of						
		NH ₃	C ₇ H ₈ ^a	Reoxidn ^b	C ₇ H ₈	C ₃ H ₆	C ₄ H ₁₀	C ₄ H ₈
O → T → N	0.0	Trace	11.0	0.05	6.04	7.64	1.49	3.97
O → T + O → N	0.52	0.56	38.8	0.58	21.3	27.3	4.10	11.9
O → T → N + O	Trace	0.03	16.2	0.08	6.69	8.88	—	—
radical number (× 10 ¹⁸ /g)	0.0	—	9.97	—	—	6.19	4.94	16.7

^a Ammoxidation of toluene.

^b Reoxidation in O₂:N₂ = 2:1 at 500°C for 3 hr after ammoxidation of toluene.

^c Made by subsequent injection of air (O) (5 ml), toluene (T) (0.4 μl), and ammonia (N) (5 ml) pulses over the catalyst (1.0 g). The flow rate of nitrogen carrier was 50 ml/min. Influences of air pulse mixing (T + O, N + O) were also examined.

of toluene on Al_2O_3 , ZrO_2 , and TiO_2 , while benzaldehyde was adsorbed on them and gave benzonitrile by subsequent ammonia pulse. On activated carbon, and $\text{SiO}_2\text{-Al}_2\text{O}_3$ which was treated under the actual condition of toluene ammoxidation, however, benzonitrile was obtained by injections of toluene pulse followed by ammonia pulse. Then, the reaction intermediate of toluene on $\text{SiO}_2\text{-Al}_2\text{O}_3$ (treated) and activated carbon or benzaldehyde on Al_2O_3 , ZrO_2 , TiO_2 , and $\text{SiO}_2\text{-Al}_2\text{O}_3$ (fresh) was allowed to be adsorbed and subsequently to react with ammonia injected at different intervals between the toluene or benzaldehyde pulse and the ammonia pulse.

As shown in Fig. 2, the formation of benzonitrile decreased or kept nearly constant. Such a decay curve can be analyzed in terms of the stability of the reaction intermediate, as previously reported (3). The initial value of formed benzonitrile and rate constant k were calculated by the least-squares method using the equation for the concentration of reaction intermediate

$$T = T_0 \exp(-kt),$$

where T_0 denotes the initial concentration of reaction intermediate.

The small value of k on Al_2O_3 , ZrO_2 , and TiO_2 (Table 4) indicates a high stability of the reaction intermediate, whereas the large value of k on carbon suggests the conversion of the intermediate into other products. Because no dissociation product or desorbed benzaldehyde is detected when eluted gas from the carbon bed is trapped at liquid nitrogen temperature, the decay of benzonitrile formation is due to the combustion of reaction intermediate with the attack of active surface oxygen.

As shown in Table 4, the initial value of formed benzonitrile per surface area on the fresh $\text{SiO}_2\text{-Al}_2\text{O}_3$ was only about 4% of that on Al_2O_3 . This is much smaller than had been expected from the content of Al_2O_3 in the $\text{SiO}_2\text{-Al}_2\text{O}_3$. Furthermore, the intermediate on the fresh $\text{SiO}_2\text{-Al}_2\text{O}_3$ was unstable, as understood from the value of k . Because the activity of $\text{SiO}_2\text{-Al}_2\text{O}_3$ in the combustion is negligible, the adsorbed intermediate may be converted into carbonaceous material on the surface. In fact, the color of the $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst became black after the

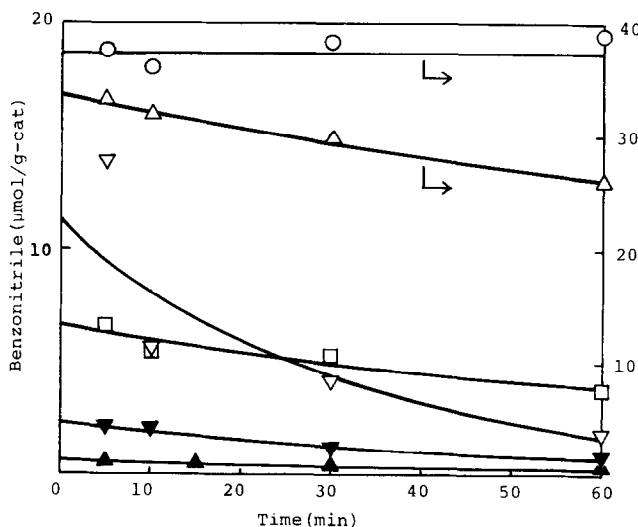


FIG. 2. Variation of benzonitrile formation at the ammonia pulse with the time required from the toluene pulse until the ammonia pulse. Reaction intermediate is adsorbed from benzaldehyde on ZrO_2 (○), Al_2O_3 (1000) (△), TiO_2 (□), and activated carbon (▽), or from toluene on activated carbon (▼) and treated $\text{SiO}_2\text{-Al}_2\text{O}_3$ (▲).

TABLE 4
Variation of Concentration of Adsorbed Intermediate^a

Catalyst	Adsorbate	Initial value of formed benzonitrile		<i>k</i> (10 ⁻³ min ⁻¹)	Surface area (m ² /g)
		(μmol/g)	(μmol/m ²)		
Al ₂ O ₃ (400) ^b	Benzaldehyde	137	0.81	0	169
Al ₂ O ₃ (1000) ^b	Benzaldehyde	33.7	1.02	4.4	33
ZrO ₂	Benzaldehyde	37.0	1.25	0	30
TiO ₂	Benzaldehyde	6.57	1.93	9.0	3.4
Activated carbon	Benzaldehyde	11.2	0.0092	31.1	1220
Activated carbon	Toluene	2.35	0.0019	19.5	1220
SiO ₂ -Al ₂ O ₃ (fresh)	Benzaldehyde	15.3	0.0342	29.8	447
SiO ₂ -Al ₂ O ₃ ^c (treated)	Toluene	0.526	—	5.1	—

^a Reaction was made by toluene (2 μl) and NH₃ (10 ml) over the catalyst (400 mg) at 400°C. Air pulse (5 ml) was used for the oxidation of the catalyst.

^b Obtained by calcination at 400 or 1000°C.

^c Treated in ammoxidation of toluene.

pulse reaction, as mentioned above. On the other hand, the adsorbed intermediate on treated SiO₂-Al₂O₃ was stable in a similar degree to that on Al₂O₃.

ESR and *ir* Spectra of SiO₂-Al₂O₃

ESR of the treated SiO₂-Al₂O₃ showed a sharp singlet having the line width of 3.6 G at *g* value of 2.001. No spectrum was observed in the fresh state of SiO₂-Al₂O₃. This sharp singlet could be identified as the carbon radical that deposited on the surface (7-9). The number of carbon radicals on variously treated SiO₂-Al₂O₃ also was measured as shown in Table 3. It was found that the most carbon radical was formed by the oxidation with 1-butene.

The SiO₂-Al₂O₃ was treated by the oxidation of toluene at 500°C for various times, and the number of carbon radicals and the amount of benzonitrile formed in the pulse technique were measured, as shown in Fig. 3. The catalyst activity increased with the course of the reaction, and also with the increase of the carbon radical.

IR spectra of the catalysts were recorded

to determine the phenomena occurring on the surface. As shown in Fig. 4, new bands at 1760 and 1460 cm⁻¹ appeared on the catalyst treated by toluene oxidation. The absorption at 1620 cm⁻¹ was identified as water adsorbed on the surface. Reoxidation of the catalyst by the flowing of a mixture of oxygen and nitrogen removed these absorptions at 1760 and 1460 cm⁻¹. Therefore, these could be regarded as the adsorbed species relevant to the carbonaceous deposit as observed in the ESR measurement. Direct observation of the surface of activated carbon by an infrared study confirmed the existence of surface oxides having the functional groups such as carbonyl, carboxyl, or hydroxyl, and it was reported that these were observed in the region from 1750 to 1400 cm⁻¹ (6). It is sure, therefore, that the bands observed at 1760 and 1460 cm⁻¹ are due to the surface oxides formed during oxidation reaction. Probably, the absorption at 1760 cm⁻¹ is due to carbonyl or carboxyl groups on the surface, and, on the other hand, the absorption at 1460 cm⁻¹ is identified as the stretch-

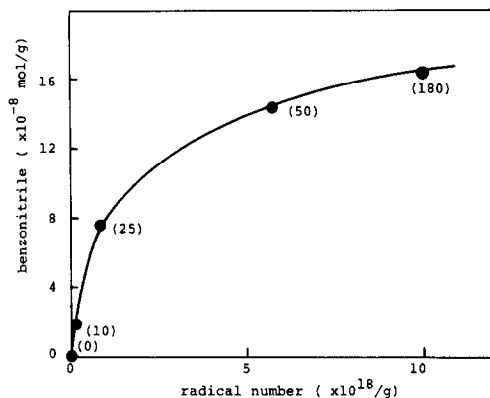


FIG. 3. Relationship of the amount of saturated adsorbed intermediate to the number of carbon radicals on $\text{SiO}_2\text{-Al}_2\text{O}_3$. The treatment time is shown in minutes in parentheses.

ing vibration of C-H bond or carboxyl groups.

DISCUSSION

The increase of activity on these catalysts, particularly on $\text{SiO}_2\text{-Al}_2\text{O}_3$, with the course of reaction is of interest in understanding the whole nature of the catalytic activity. As mentioned above, Al_2O_3 does not possess the oxidizing activity necessary for the toluene oxidation. Furthermore,

SiO_2 does not take part in the oxidation of toluene nor the adsorption of the reaction intermediate, as previously reported (2). The cause of the oxidation activity should therefore be sought in the activation of surface oxygen. In other words, available oxidized sites appeared when they were used in the oxidation reaction.

As shown above, the catalytic activity for ammoxidation of toluene appeared because of the oxidation of every hydrocarbon. The $\text{SiO}_2\text{-Al}_2\text{O}_3$ treated by toluene oxidation possessed the surface oxides like carbonyl or carboxyl groups, as shown in the infrared spectra, and the concentration of formed carbon radical had an intimate relation with the catalyst activity. According to Poole *et al.* (8), the number of unpaired spins in the coke on the treated $\text{SiO}_2\text{-Al}_2\text{O}_3$ increased linearly with the carbon concentration. A similar conclusion was drawn in the study on the coke formation on Al_2O_3 made by Berger and Roth (9). It is well known that carbon radicals are produced by the degassing of CO and CO_2 (11), and decreased by the irreversible adsorption of oxygen at 400°C (10). Therefore, the carbonaceous material having

>C=O or -COOH deposited on the sur-

face can be regarded as oxidized sites available for the oxidation of toluene.

Peculiar oxidation activity of the carbonyl group was previously reported in the oxidative dehydrogenation of ethylbenzene on polynaphthoquinone by Iwasawa *et al.* (12). Alkhozov *et al.* (4) discussed the activity of carbonaceous material on Al_2O_3 for the styrene synthesis on the basis of a similar idea. The oxidation activity of activated carbon was confirmed also in this study. The activity of activated carbon is, however, too active to make the intermediate fully stabilized. In view of this, it is difficult to suppose that carbonaceous material plays a role as adsorption sites as well as oxidation active sites. The high stability of the intermediate on the treated $\text{SiO}_2\text{-}$

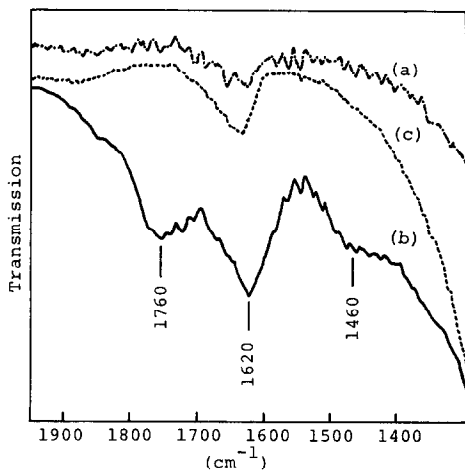


FIG. 4. IR spectra of the $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalysts which were untreated (a), treated by oxidation of toluene (b), and reoxidized by the flowing of oxygen and nitrogen at 500°C (c).

Al_2O_3 , as suspected from the low value of k , suggests that constituent Al_2O_3 is available for adsorption sites. Consequently, the activity of treated $\text{SiO}_2\text{-Al}_2\text{O}_3$ is considered to consist of oxidation activity of carbon and adsorption property of Al_2O_3 , as found in the $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ (3). If the surface of $\text{SiO}_2\text{-Al}_2\text{O}_3$ is fully saturated with the carbonaceous material, the catalytic activity should be based only on carbon. In such a case, the reaction intermediate is unstable and readily converted to carbon oxides. In the present case, however, it is considered that the catalyst is not fully covered with the carbonaceous material, and the uncovered sites of Al_2O_3 are available for the adsorption. Benzonitrile formed on activated carbon was eluted in the chromatogram that possessed a peak width at half peak height of about four times as much as that on Al_2O_3 . This was probably caused by the adsorbability of carbon. Such a broad chromatogram was not observed on the treated $\text{SiO}_2\text{-Al}_2\text{O}_3$. This observation is in agreement with the above consideration of the roles of constituent Al_2O_3 of $\text{SiO}_2\text{-Al}_2\text{O}_3$.

As shown above, the initial value of formed benzonitrile on fresh $\text{SiO}_2\text{-Al}_2\text{O}_3$ was only about one-third as much as expected from pure Al_2O_3 . Therefore, the acid sites of $\text{SiO}_2\text{-Al}_2\text{O}_3$ are not available for accommodating the reaction intermediate. On such an acid site as $\text{SiO}_2\text{-Al}_2\text{O}_3$, the reaction intermediate is subjected to cracking, thus forming carbonaceous material available for the ammoxidation. Because the carbonaceous material is removed by burning of catalyst with oxygen at 500°C , a small portion of them may be converted into carbon oxides even during the ammoxidation reaction. However, the rebuild of

this species is relatively easy to occur at the surface, thus obtaining the steady state of the reaction.

The $\text{ZrO}_2\text{-SiO}_2$ and $\text{TiO}_2\text{-SiO}_2$ catalysts may also have an activity similar to those of $\text{SiO}_2\text{-Al}_2\text{O}_3$. The stability of intermediate on ZrO_2 and TiO_2 was shown by the use of benzaldehyde as adsorbate. Carbonaceous material would be formed as the oxidizing active sites during the oxidation reaction. However, titania has some ability for ammoxidation of toluene in its initial state. It is, therefore, considered that the oxidation activity of carbonaceous surface oxide was added to that of TiO_2 . Acid sites on these catalysts may be used for forming carbonaceous material thereon, as on $\text{SiO}_2\text{-Al}_2\text{O}_3$.

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