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Reaction Mechanism of Ammoxidation of Toluene

IV. Oxidation State of Vanadium Oxide and Its Reactivity for Toluene Oxidation

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In order to determine the mechanism of the ammoxidation of toluene, vanadium oxide supported on Al_2O_3 during the ammoxidation has been characterized by the titrimetric method, ESR, and the temperature-programmed reoxidation. Vanadium oxide was severely reduced during the reaction, and in the state almost equivalent to V_2O_4. The oxidation state was influenced profoundly by the atmospheric condition because of the thin layer of vanadium oxide on Al_2O_3. Furthermore, the adsorbed hydrocarbon material on the surface of vanadium oxide inhibited the reoxidation, stabilizing the severely reduced surface. Pulse experiments on the definite oxidation state of vanadium revealed that only benzaldehyde could be formed significantly on the V_2O_4 catalyst. Therefore, the first step of the ammoxidation of toluene could be deduced to be the formation of benzaldehyde on V_2O_4.

INTRODUCTION

The reaction mechanism of the ammoxidation of toluene on V_2O_5/Al_2O_3 catalyst has been previously investigated by the authors. Reaction steps have been measured kinetically by pulse and flow methods (*1*), and the stable adsorbed intermediate is determined by infrared study to be benzoate ion on Al_2O_3 (*2*). The bifunctional activity of this catalyst which consists of the oxidation activity of V_2O_5 and the dehydration property of Al_2O_3 is stressed (*3*). On the basis of these previous studies, one may envisage the mechanism to some extent, although it includes complex different steps. However, we still have some problems about the active sites of vanadium oxide and alumina and how they actually contribute to the ammoxidation of toluene. One would ascertain a more detailed mechanism by understanding the active sites and their relation with reaction steps. In the present study, the oxidation state of vanadium oxide and its activity for toluene oxidation which can be regarded as the first step of the ammoxidation will be reported upon.

As observed in many oxidation reactions, metal oxides as catalysts are reduced more or less due to activities and atmospheric condition. Vanadium oxide is also known to be reduced in the reaction since the study by Simard *et al.* (*4*), and this problem is still investigated with new tools (*5*). One could predict the different activity and selectivity when the catalyst was reduced to a definite or an intermediate oxidation state. It is therefore of interest to determine the oxidation state of vanadium during the reaction and its activity for toluene oxidation.

EXPERIMENTAL METHOD

Preparation of V_2O_5 and V_2O_5/θ-Al_2O_3 containing 5 wt% V_2O_5 has been described in a previous paper (*1*).

In order to determine the oxidation state of vanadium during the ammoxidation, the supported catalyst was used in the reaction for 4 hr, followed by quenching in the helium stream. Reactions have been per-

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formed at 400°C with 1.0 g of catalyst, and by flowing 76 ml/min of gas mixture consisting of oxygen (0.32 atm), ammonia (0.22 atm), toluene (0.046 atm), and nitrogen as a balance. The quenched sample was used for the determination of the oxidation state of vanadium by titration, ESR, and temperature-programmed reoxidation (TPRO).

The degree of reduction was determined manganometrically after dissolving the samples in a small amount of H_2SO_4 (1 : 1) solution. Basically, reduced ions are oxidized to V^{5+} by the $KMnO_4$ (0.1 *N*) solution. As has been already indicated (*6*), however, the simple manganometrical titration cannot differentiate between V^{4+} and V^{3+}. We tried to distinguish them by the method mentioned below.

Assuming that the reduced sample contains V^{5+}, V^{4+}, and V^{3+}, the titration amount of $KMnO_4$ can be described as

$$T_1 = V^{4+} + 2V^{3+},$$

where V^{4+} and V^{3+} denote the amount of V^{4+} and V^{3+} ions, respectively. The solution thus obtained which contained only V^{5+} ions is used for the subsequent titration by the use of iron(II) ammonium sulfate. Because the V^{5+} ions are reduced to V^{4+} ions in this titration, the titration amount (T_2) is shown as

$$T_2 = V^{5+} + V^{4+} + V^{3+}.$$

On the other hand, the amount of V^{5+} ions inherently present in the reduced sample can be measured independently by the titration with iron(II) ammonium sulfate by using another solution,

$$T_3 = V^{5+}.$$

These procedures are, therefore, enough to calculate amounts of each ion.

TPRO involves raising the temperature at a linear rate of 10°C/min as the mixture of helium and oxygen (O_2, 5.15 vol%) is swept through the reactor, and the consumption of oxygen is continuously monitored with a pair of thermal conductivity detectors. Product H_2O was trapped at −78°C after emerging from the reactor. The amount of O_2 required for the reoxidation was measured as compared with the intensity of injected oxygen. Reduced vanadium oxides were prepared by using 600 Torr of H_2 at 500°C in the quartz microbalance vessel, and the degree of reduction of the catalyst was measured by the decrease in weight. On the other hand, supported vanadium oxides were reduced by flowing a mixture of H_2 and He (H_2, 6.21 vol%) at 480°C in the TPRO reactor.

ESR of the supported catalyst was measured at room temperature with a JEOL-ME-1X spectrometer (X band). The *g* value was determined as compared with the Mn^{2+} impurity in MgO.

The pulse technique was performed with a conventional apparatus. Helium was deoxygenated just before entering the reactor with a SiO_2 column at liquid nitrogen temperature. The DEGS-and-H_3PO_4-on-silan-treated-Chromosorb column was used at 100°C up to 220°C in the temperature-programmed mode, which enabled us to separate the compounds of high boiling points. Toluene (0.4 μl) was injected into the catalyst bed at 400°C. Reduced samples of vanadium oxide with average oxidation state, V_2O_4 and $V_2O_{4.3}$, were prepared with 600 Torr of H_2 at 500°C to adjust the composition gravimetrically.

The infrared spectrum of vanadium oxide was measured with an emissionless infrared diffuse reflectance spectrometer (Japan Spectroscopic Co., EDR-31) (*18*) at ambient temperature by the use of 5 wt% of oxide mixed with KBr.

RESULTS

Chemical Measurements of Oxidation States

Concentrations of vanadium oxides having different oxidation states were determined by the titrimetric method for the V_2O_5/Al_2O_3 catalyst, fresh or quenched after the reaction. The fresh sample of the V_2O_5/Al_2O_3 catalyst contained V_2O_5, except for 2.2 wt% of V_2O_4 (Table 1).

TABLE 1

Oxidation State of Vanadium Oxide Supported on Al_2O_3

	Loaded (wt%)			Average oxidation state
	V_2O_5	V_2O_4	V_2O_3	
Fresh	4.92	0.12	—	$V_2O_{4.98}$
Used	0.37	4.43	0.27	$V_2O_{4.02}$

On the other hand, the quenched V_2O_5/Al_2O_3 catalyst was reduced significantly. Eighty-seven percent vanadium existed as V_2O_4 with small amounts of V_2O_3 and V_2O_5 in the quenched sample.

Average oxidation states were calculated to be $V_2O_{4.98}$ and $V_2O_{4.02}$ for fresh and used vanadium catalysts, respectively. It was concluded that vanadium oxide was available for the reaction in the state nearly equivalent to V_2O_4.

ESR Measurement

The ESR spectrum was measured on fresh, quenched, and reoxidized samples of V_2O_5/Al_2O_3 catalyst. As was previously observed (7), the V_2O_5/Al_2O_3, even when fully oxidized, provided the ESR signal due to the V^{4+} ion which was characteristic of the hyperfine structure (hfs) of vanadium (Fig. 1). On the contrary, the quenched one had the signal with fairly high intensity, including another kind of V^{4+} signal which was broad in linewidth and unobservable in the fresh catalyst. It has been previously reported (7) that there are two kinds of V^{4+} species detectable by ESR; one sharp signal with the hfs is due to the dissolved V^{4+} ion in the alumina matrix, and another broad

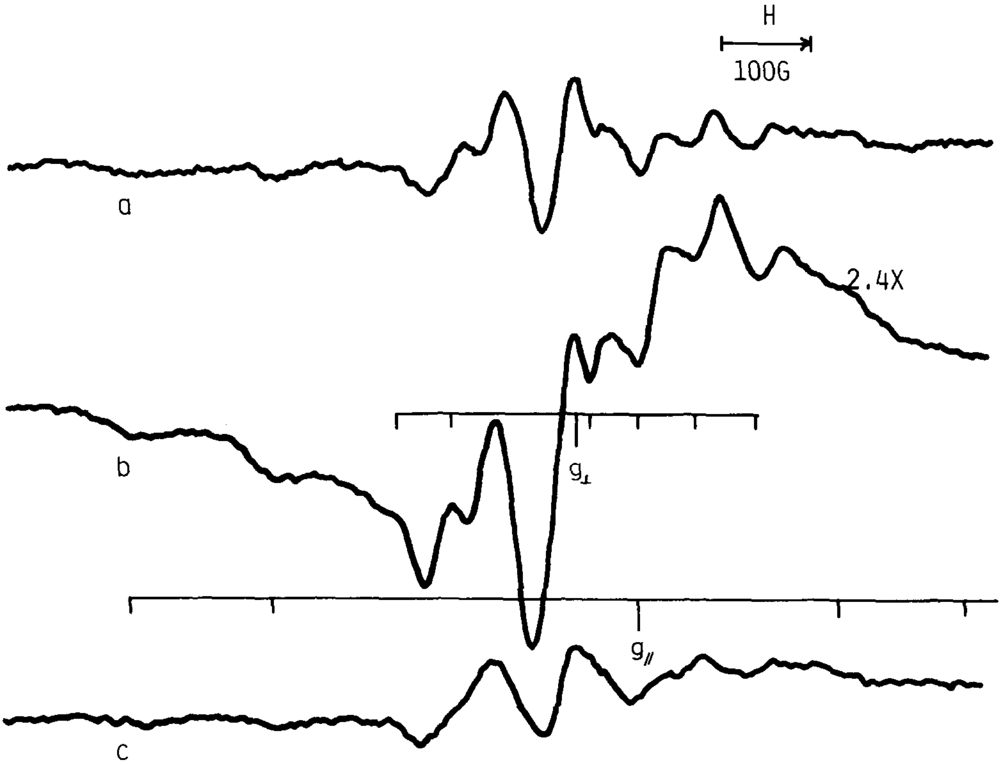

FIG. 1. ESR spectra of supported vanadium oxide, fresh (a), quenched (b), and reoxidized (c). The g values of hyperfine structure were 1.989 ($g_\perp$) and 1.935 ($g_\parallel$).

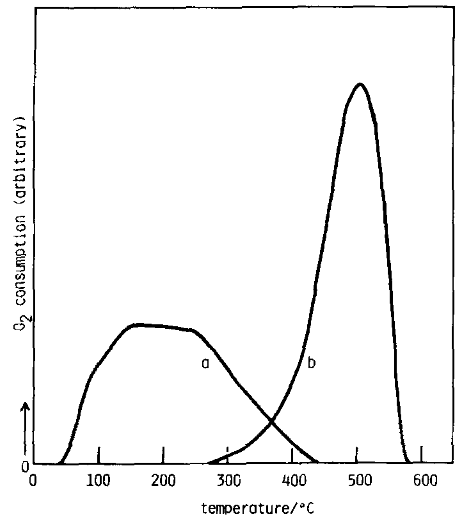

FIG. 2. TPRO curves of $V_2O_{4.16}/Al_2O_3$ (a) and $V_2O_{4.00}$ (b) reduced by hydrogen.

signal can be attributed to a V^{4+} agglomerate at the surface. The present study therefore could also detect these species of V^{4+} ion. Both of them were increased by the reaction, as observed by the comparison between fresh and quenched samples. Reoxidation of the reduced catalyst by the TPRO which will be mentioned in the following section reduced the intensity of the ESR signal and recovered its initial condition.

The signal intensities on used and reoxidized samples calculated by the double integration were 14.3 and 1.1 times as much as that of the fresh catalyst. The relative intensity of the V^{4+} signal on the used catalyst was much lower than that estimated by the titration method, because the latter showed that the V^{4+} ion concentration in the used catalyst was 35 times as much as that in the fresh one.

TPRO

First, the TPRO experiment was applied to supported and unsupported vanadium oxides which had been reduced by hydrogen (*8*, *9*). As shown in Figs. 2a and b, the supported vanadium oxide was more readily reoxidized than the unsupported vanadium oxide; the reoxidation of the former catalyst began at 50°C and finished at 430°C, while in the latter case it took place slowly at 290°C, and finished rapidly at 580°C. Oxidation states as surmised from the consumption of oxygen were $V_2O_{4.16}/Al_2O_3$ for the supported catalyst, and $V_2O_{4.00}$ for the unsupported catalyst. The latter was in agreement with the chemical composition $V_2O_{3.93}$ as determined by weight loss upon reduction. This rationalized the method for evaluating oxidation states of reduced samples in the TPRO experiment. It was noticeable, therefore, that these catalysts were characterized as having quite different profiles of reoxidation in spite of nearly the same degree of reduction.

The TPRO of the supported catalyst used in the reaction was then measured to be compared with that of hydrogen-reduced catalyst. As shown in Fig. 3a, gas evolved from the quenched catalyst predominantly at temperatures above 350°C. It is likely that carbon dioxide was formed by the com-

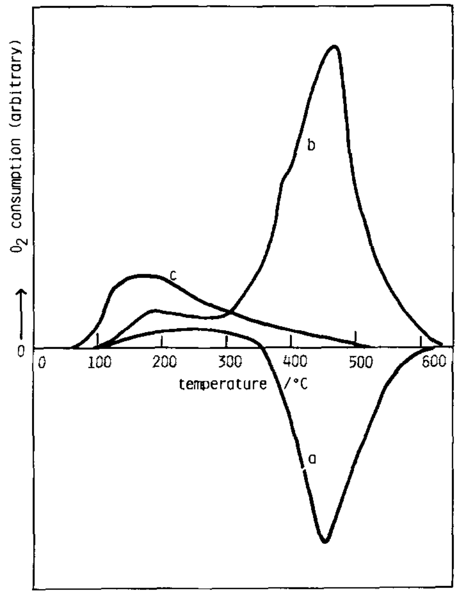

FIG. 3. TPRO curves of supported vanadium oxide catalyst, quenched (a, b) and reduced by hydrogen after the reoxidation (c). Evolved gas was detected (a), but trapped (b) with a SiO_2 column. Average oxidation state (c) was $V_2O_{4.40}$.

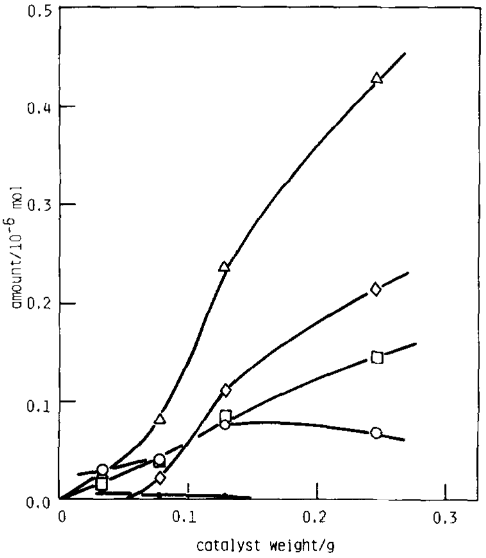

FIG. 4. Oxidation of toluene on V_2O_5 with pulse method: benzoic acid (△); maleic anhydride (◇); anthraquinone (□); benzaldehyde (○); bibenzyl (●).

bustion of adsorbed hydrocarbon, because a silica gel trap at −78°C could remove the influence of gas evolution completely, and the TPRO pattern for oxygen consumption was obtained as in Fig. 3b. It consisted of the combination of two kinds of reoxidation peaks with the peak maxima located at both ca. 200 and 470°C. Consumption of oxygen at low temperature, however, corresponded to only 19% of the amount required for the oxidation of catalyst, which was due to the average oxidation state being determined to be $V_2O_{4.02}$ by the titrimetric method. The remaining reduced sites, therefore, should be reoxidized at temperatures above 350°C. The amount of oxygen required for the complete oxidation of catalyst corresponded to about 50% of the oxygen consumption peak at high temperatures. In other words, the high-temperature peak included not only the reoxidation of reduced catalyst but also the combustion of adsorbed hydrocarbon in a 1 : 1 ratio.

The reoxidized sample was again reduced by flowing hydrogen and subjected to the TPRO experiment in Fig. 3c. The TPRO pattern thus obtained was approximately the same as that in the H_2-reduced sample of the virgin catalyst, but completely different from that of the quenched catalyst. It was observed, therefore, that the quenched catalyst was not easily reoxidized as compared with that of the hydrogen-reduced one. One can suspect that the quenched sample had different properties from the H_2-reduced catalyst in view of the reoxidation.

Pulse Reaction on V_2O_5 and V_2O_4

Reactivities of V_2O_5 and V_2O_4 for the oxidation of toluene were measured by the pulse method. In order to obtain the reaction profiles of vanadium oxide only, unsupported oxide was used, because aluminum oxide could adsorb benzaldehyde and benzoic acid.

Since reactivity of V_2O_5 varied only a little with number of toluene pulse, the activities during the first to the fourth pulse numbers were averaged. Products included benzoic acid, maleic anhydride, and benzaldehyde as well as dimeric compounds such as anthraquinone and bibenzyl (diphenyl-

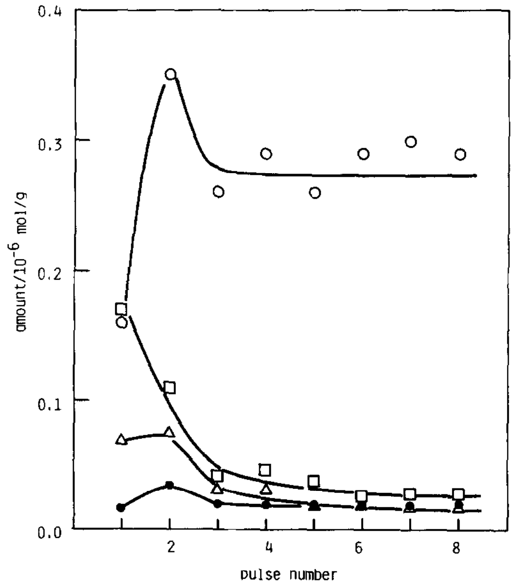

FIG. 5. Oxidation of toluene on V_2O_4 (0.16 g) with pulse method: benzaldehyde (○); anthraquinone (□); *trans*-stilbene (△); bibenzyl (●).

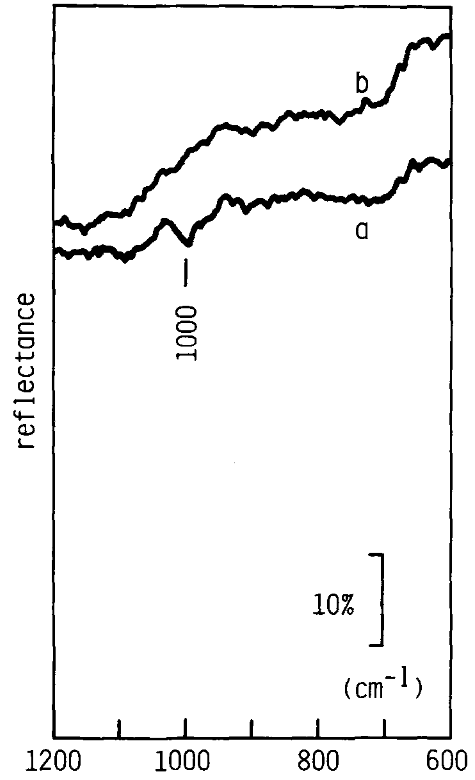

FIG. 6. Infrared spectrum of V_2O_4 before (a) and after (b) the pulse reaction in Fig. 5.

ethane). A small amount of *trans*-stilbene was also formed, although the amount was not determined because its chromatogram could not be separated from that of benzoic acid. Dependence of the activity on the catalyst weight was obtained as shown in Fig. 4. Benzoic acid was primarily formed under this condition. The amount of benzaldehyde had the maximum value against the catalyst weight. Therefore, the consecutive reaction of benzaldehyde to benzoic acid and maleic anhydride could be indicated, although direct formations of these compounds were not necessarily neglected. In fact, the injection of benzaldehyde on V_2O_5 yielded benzoic acid and maleic anhydride. The obtained product and possible reaction step were, therefore, in agreement with the previous study on V_2O_5 (*10*). The formation of anthraquinone from toluene was, however, greater than expected in the previous study, since the latter stated that a small fraction of yellow-needle crystal of anthraquinone was obtained as a by-product of toluene oxidation. It will be reported later whether only the pulse experiment on the fresh V_2O_5 results in the increase or decrease of anthraquinone.

In the case of V_2O_4 in Fig. 5, the catalyst activity was unstable in the initial condition, but attained its stabilized state after the third pulse of toluene. Activity on the V_2O_4 was small compared with that on the V_2O_5. Benzaldehyde was primarily formed with benzoic acid not being formed at all. Small amounts of by-products were also formed especially in the first and second pulses.

A supplementary result about the oxidation state of vanadium oxide was obtained by the infrared spectrum in Fig. 6; because the $V^{5+}{=}O$ species could be observed at 1000 cm^{-1} only before the pulse reaction, the change of catalytic activity in the initial condition may arise from the reduction of the V^{5+} ion in the impurity level. Therefore, it was found from the stationary activity that benzaldehyde was the significant product on the V_2O_4 catalyst.

Because some investigators (*4*, *11*) claimed that the $V_2O_{4.33}$ was an active form in the catalytic oxidation of hydrocarbons, the reduced catalyst of average oxidation state $V_2O_{4.3}$ was used for the pulse reaction to be compared with cases of V_2O_5 and V_2O_4. As shown in Fig. 7, the activity of the $V_2O_{4.3}$ fluctuated greatly, and its degree of conversion into various products was in general similar to that on V_2O_4. A small amount of benzoic acid was obtained also on the $V_2O_{4.3}$ catalyst.

DISCUSSION

Working State of Vanadium Oxide in the Ammoxidation

Chemical measurement of vanadium on the supported catalyst indicated that the catalyst was severely reduced and in a state almost equivalent to V_2O_4. On the other

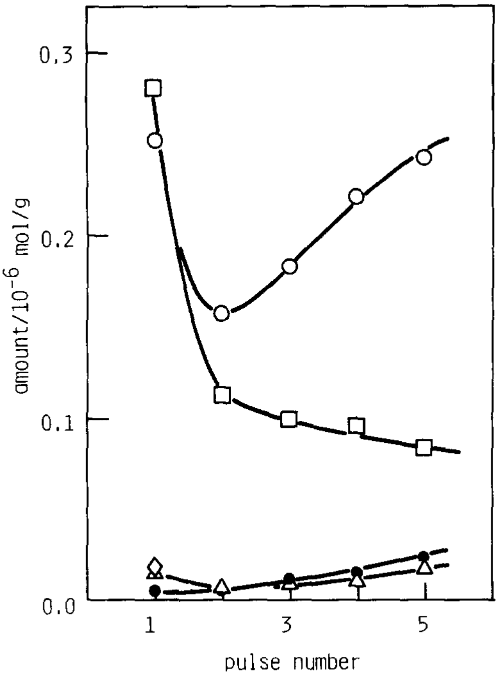

FIG. 7. Oxidation of toluene on $V_2O_{4.3}$ (0.16 g) with pulse method: benzaldehyde (○); anthraquinone (□); *trans*-stilbene (△); bibenzyl (●); benzoic acid (◇).

hand, a pulse experiment in the definite oxidation state of vanadium oxide has shown that benzaldehyde is the significant product as a result of toluene oxidation on V_2O_4. One can therefore conclude that the oxidation of toluene into benzaldehyde takes place on the V^{4+} species, which can be regarded as the first step of the ammoxidation of toluene in the supported vanadium catalyst.

As previously indicated, the vanadium oxide is very easily reduced during oxidation of hydrocarbons (*4*). It seems that the oxidizing condition could be obtained by a large excess in the amount of oxygen, since Andersson and Lundin (*12*) observed in the ammoxidation of 3-picoline that the reduced catalyst was gradually oxidized under the condition of air to 3-picoline mole ratio, 240. In addition, ammonia also could influence the surface condition as a reductant (*13*). As observed in the TPRO experiment, toluene affects the surface oxidation state in a manner different from hydrogen. It is thought that toluene not only reduces the vanadium oxide but also retards the reoxidation. Adsorbed material on the surface of vanadium oxide probably covers the surface to retard the reoxidation. The influence of benzoate ion adsorbed on the aluminum oxide which was detected by infrared study (*2*) has not been understood yet.

The TPRO experiment proved the difference in properties of V_2O_5 and V_2O_5/Al_2O_3 in view of reduction and reoxidation. Supported vanadium is more easily reduced and reoxidized than the unsupported vanadium oxide. No evidence of the interaction of vanadium oxide with the support can be indicated, because the interaction is usually associated with a shift of temperature to higher degree due to its low mobility of oxide (*14*). Therefore, the structural difference between them is a good basis for understanding the behaviors. The vanadium oxide may be widely spread at the surface of alumina, thus forming the relatively thin layer of vanadium oxide. Diffusion of oxygen in the bulk of oxide, which frequently determines the rate of the reduction–reoxidation process, proceeds readily in such a thin lamella of oxide (*15*).

It is an interesting fact that the quenched sample provides a different TPRO pattern from the hydrogen-reduced one. The degree of reduction is fairly high in all cases studied, and almost all sites of vanadium oxide must be used for the reduction and reoxidation; selective reduction of an active site by hydrogen or toluene and ammonia could be possibly neglected. Most plausibly, the adsorbed hydrocarbon may retard the reoxidation of the used catalyst. It is thought that reduced sites incorporating adsorbed material cannot be reoxidized easily until these are free from the adsorbed one which could be removed by the combustion. Not only the atmospheric condition but also the structural characteristic of vanadium oxide on the aluminum oxide make the surface oxidation state severely reduced.

At least two kinds of V^{4+} species were observed in this study. These could be identified as isolated species and cluster compounds on the basis of the linewidth of the spectrum from which one can deduce the condition of oxide on the support (*7, 16*). The V_2O_5/Al_2O_3 catalyst concerned with here has the fairly well dispersed state of the oxide, since it is characteristic of the sharp hfs of the occluded V^{4+} ion.

By comparison of ESR and chemical measurements of V^{4+}, it was determined that smaller amounts of V^{4+} ion could be detected by ESR. There is a recent paper claiming that the manganometrical titration affords the extent of the reduction expressed as $V^{4+} + 2V^{3+}$, while all of the V^{4+} should be measured by the ESR spectrum, with the difference corresponding to the amount of V^{3+} (*6*). However, the present method of titration could distinguish the V^{4+}, as well as the V^{3+}, and the V^{4+} detectable by ESR, in the reduced state, was clearly less than that determined by the titration. It is possible that some of the V^{4+} sites interacted with each other to be inactive in ESR measurements.

Oxidation of Toluene on Vanadium Oxides

As for the selectivity in the oxidation of toluene, it was found that benzaldehyde was the significant product on the reduced vanadium oxides such as V_2O_4 and $V_2O_{4.3}$. Although the average oxidation state cannot be directly connected with the active *surface* sites, it seems that fairly high oxidation states are required for the production of benzoic acid. Thus, one can deduce that benzaldehyde which is formed on the V^{4+} site is the intermediate compound in forming benzonitrile in the ammoxidation of toluene. In other words, the first step of the ammoxidation is, probably, initiated by the oxidation of toluene into benzaldehyde on the V_2O_4 on the aluminum oxide. As far as the present study is concerned, the argument for the reaction mechanism regarding benzoic acid as the intermediate (*17*) needs further justification. Detailed study on the reaction of benzaldehyde on the aluminum oxide surface as well as the characterization of the active site is now in progress.

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