Reaction Mechanism of Ammoxidation of Toluene

III. Bifunctional Activity of V_2O_5 Supported on Al_2O_3 Catalyst

In previous papers (*1, 2*), the reaction mechanism of ammoxidation of toluene into benzonitrile on V_2O_5 supported on Al_2O_3 was investigated by kinetic and infrared studies. First, toluene is oxidized to be stabilized on the surface as the benzoate ion. Subsequently, the adsorbed benzoate ion reacts with ammonia to form benzonitrile. The reduced sites are then reoxidized by oxygen to repeat the reaction. Oxidation of toluene certainly takes place on the surface of V_2O_5, because the oxidation activity of Al_2O_3 is negligibly small. On the other hand, the benzoate ion acting as the reaction intermediate is stabilized on Al_2O_3, but not on V_2O_5, because the intermediate adsorbed on V_2O_5 is accessible to the attack of surface oxygen, and readily removed as carbon oxides. Adsorption of benzaldehyde on Al_2O_3 revealed the ir spectrum of benzoate ion, which rapidly went into benzonitrile by the reaction with ammonia. This fact shows that alumina takes a role of converting the adsorbed carboxylate ion into nitrile. In other words, the V_2O_5 supported on Al_2O_3 catalyst has a bifunctional activity, i.e., the oxidation power of V_2O_5 and the dehydration property of Al_2O_3. In this communication, we comment on how the intermediate product of toluene migrates from the surface of V_2O_5 to Al_2O_3. In addition, availability of Al_2O_3 as an oxidation catalyst will be discussed in terms of the reactivity of the adsorbed benzoate ion with ammonia.

The equipment of the pulse technique has been previously described in detail (*1*). Alumina that were obtained by calcination of Al_2O_3 (Sumitomo KHD) at various temperatures for 22 hr, V_2O_5, and V_2O_5 supported on Al_2O_3 (*1*) were used in this paper.

Assuming first-order kinetics for the concentration of intermediate (*T*), because that of surface oxygen is able to be regarded as being invariable, the decrease of concentration of the intermediate with the lapse of time (*t*) is described as

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

where T_o is the concentration of intermediate in the initial state and k denotes the rate constant. Such a variation of concentration of reaction intermediate brings about the decay of formed benzonitrile within the interval from the toluene pulse to the ammonia pulse, and the initial value of formed benzonitrile and k were calculated from the decay curve by the least-squares method. Table 1 shows these constants obtained from experiments in which ammonia was injected on V_2O_5 supported on Al_2O_3, V_2O_5–Al_2O_3 mixture, and V_2O_5 at different intervals from the toluene pulse, and on Al_2O_3 with adsorbed benzaldehyde. The small value of k for V_2O_5 supported on Al_2O_3 is similar to that for Al_2O_3, which suggests the existence of the adsorbed intermediate on Al_2O_3 in the V_2O_5 supported on Al_2O_3. On the other hand, the value of k for V_2O_5 is about 40 times as much as that for V_2O_5 supported on Al_2O_3, and therefore the reaction intermediate is clearly unstable on V_2O_5 as compared to Al_2O_3. In the case of V_2O_5–Al_2O_3 mixture, which is prepared only by mechanically mixing V_2O_5 and Al_2O_3 (1 : 2) by weight with a spatula, the reaction intermediate is stabilized to produce benzonitrile by the injection of ammonia even about 1 hr after the adsorption of toluene. The benzonitrile formed 10 min after the toluene pulse is based on the activity of mixed Al_2O_3, because hardly any

472

TABLE 1

Variation of Concentration of Adsorbed Intermediate

Catalyst[a]	Adsorbate	Initial value of formed Benzonitrile (μmol/g)	k (10^{-3} min^{-1})
V_2O_5 supported on Al_2O_3	Toluene	15.3	5.6
V_2O_5–Al_2O_3 mixture	Toluene	2.80[b]	10.0
V_2O_5	Toluene	0.608	223.0
Al_2O_3	Benzaldehyde	33.7	4.4

[a] Al_2O_3 calcined at 1000°C was used.
[b] Amount per gram Al_2O_3.

benzonitrile is formed on V_2O_5 10 min after the adsorption of the intermediate. In fact, the value of k in such an experiment on the V_2O_5–Al_2O_3 mixture is analogous to that for Al_2O_3 or V_2O_5 supported on Al_2O_3. Therefore, the bifunctional activity is found only by mixing of V_2O_5 with Al_2O_3. This is indicative of the migration of an intermediate product from V_2O_5 to Al_2O_3 through the gas phase. Because benzaldehyde is oxidized into benzonitrile via the adsorbed benzoate ion on Al_2O_3, like toluene on V_2O_5 supported on Al_2O_3, the migrating intermediate product may be benzaldehyde (2). This fact suggests that the intermediate compound benzaldehyde can migrate from the surface of V_2O_5 to Al_2O_3 through the gas phase also on V_2O_5 supported on Al_2O_3.

As is easily understood from the discussion, alumina is not merely a support of V_2O_5, but has a vital role in the ammoxidation as an oxidation catalyst. The reaction of benzaldehyde and ammonia thereon is accompanied by a loss of oxygen, but the constant activity is kept by the injection of air. Oxygen is desorbed as water, and the sites are easily reoxidized by gaseous oxygen. Patents for this process (3) stated that alumina calcined at high temperature (about 1000°C) was available as a support. However, the reason why such an alumina of relatively small surface area is particularly useful in this reaction has not been indicated so far. After benzaldehyde was adsorbed on three kinds of alumina which

were calcined at 400, 1000, and 1200°C, ammonia pulses were repeatedly injected to form benzonitrile. As shown in Fig. 1, benzonitrile formation decreased sharply with the number of ammonia pulses on Al_2O_3 (1000 and 1200°C). On the other hand, the benzonitrile formation on Al_2O_3 (400°C) had the maximum value with respect to the number of pulses, and gradually decreased at more than three pulses. However, such a maximum profile of nitrile formation was not observed by using a quarter amount of alumina and a double amount of injected ammonia. Therefore, ammonia injected at the initial stage is adsorbed on acid sites inactive for the ammoxidation which suppresses the desired reaction. If the adsorbed benzoate ion is reacted with ammonia in a static equipment, the decay of the adsorbed species will be expressed as a first-order kinetic equation; $T = T_0 \exp(-\kappa\tau)$, where T_0 is the initial concentration of adsorbed benzoate ion, and κ and τ denote the rate constant and the contact time, respectively. Because such a decrease of concentration is proportional to the profile as shown in Fig. 1 in a pulse technique, specific values of the rate constants are obtained by plotting the logarithm of the amount of benzonitrile against the number of pulses. The rate constants in arbitrary units are 1.0, 2.5 and 3.4 on Al_2O_3 calcined at 400, 1000, and 1200°C, respectively. Consequently, the rate of Al_2O_3 (400°C) is much slower than
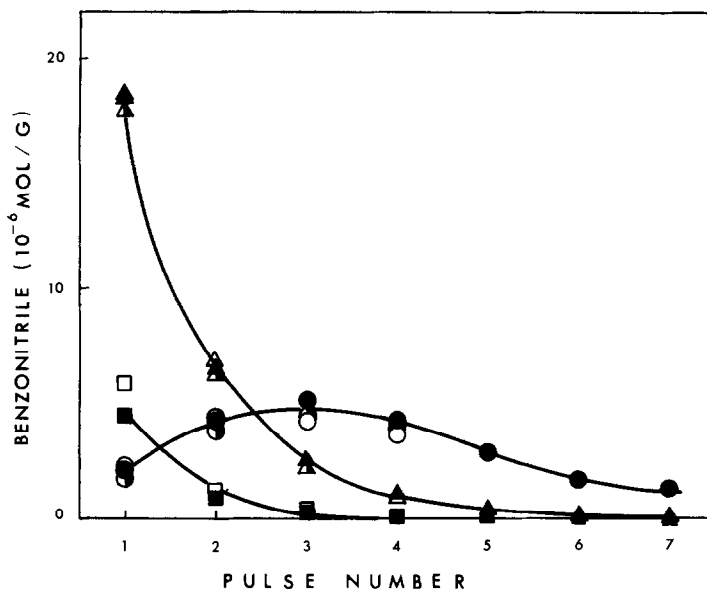
FIG. 1. The variation of benzonitrile formation with repeated injection of NH_3 on Al_2O_3 which had been calcined at 400 (O) , 1000 ($\triangle$) , and 1200°C ($\square$) , and allowed to adsorb the benzoate ion by injection of 2 μl of benzaldehyde. The same experimental runs were performed three times: first (O$\triangle\square$) , second (◑▲◲) , and third (●▲■).

others; this may be the reason why such an alumina is ineffective in spite of high surface area. Calcination at a higher temperature above 1000°C results in a decrease in active sites, and so the alumina calcined at 1000°C is the most effective in this reaction. There is a report about the appearance of maximum acidity of Al_2O_3 which is calcined at 450°C (4). We may be able to correlate this property of Al_2O_3 (about 400°C) with a small affinity for the benzoate intermediate or a strong adsorption of ammonia, thus affording a slow rate of benzonitrile formation.

REFERENCES

1. Murakami, Y., Niwa, M., Hattori, T., Osawa, S., Igushi, I., and Ando H., *J. Catal.* **49**, 83 (1977).
2. Niwa, M., Ando, H., and Murakami, Y., *J. Catal.* **49**, 92 (1977).
3. U.S. Patent, 2,499,055 (1950).
4. Tanabe, K., "Solid Acids and Bases: Their Catalytic Properties," p. 46. Kodansha, Tokyo, 1970.

YUICHI MURAKAMI
HIROSHI ANDO
MIKI NIWA

Department of Synthetic Chemistry
Faculty of Engineering, Nagoya University
Furo-cho, Chikusa-ku, Nagoya 464, Japan