JOURNAL OF CATALYSIS 49, 92–96 (1977)

Reaction Mechanism of Ammoxidation of Toluene

II. Identification of Reaction Intermediate Adsorbed on V_2O_5/Al_2O_3 by Infrared Spectroscopy

Miki Niwa, Hiroshi Ando, and Yuichi Murakami

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

Received February 2, 1977; revised May 4, 1977

Adsorption of toluene at 400°C on evacuated V_2O_5/Al_2O_3 revealed the spectrum of the benzoate ion, and the absorbance was decreased by the contact with NH_3. Simultaneously, benzonitrile was detected in the trapped liquid products by gas chromatograph. Such behavior of the benzoate ion was in good agreement with that of the adsorbed intermediate in the ammoxidation of toluene previously reported. The benzoate ion appeared also in the adsorption of benzaldehyde on Al_2O_3, and furthermore gave benzonitrile by the contact with ammonia. No spectrum was however observable on V_2O_5, V_2O_5/SiO_2, and SiO_2. It can be considered that the oxidative adsorption of toluene may occur on V_2O_5, but the benzoate ion is stabilized on the surface of Al_2O_3, followed by the production of benzonitrile. The reaction scheme is proposed as

$$\text{Ph-CH}_3 + (\text{O}^{2-}) \rightarrow (\text{Ph-COO}^-) + (\text{OH}^-), \tag{1}$$

$$(\text{OH}^-) + \text{NH}_3 \rightarrow (\text{NH}^+{}_4) + (\text{O}^{2-}), \tag{2}$$

$$(\text{Ph-COO}^-) + (\text{NH}^+{}_4) \rightarrow \text{Ph-CN} + \text{H}_2\text{O}. \tag{3}$$

INTRODUCTION

The surface intermediate has been recently detected from various viewpoints with the aid of powerful tools such as ir, esr, and XPS. In particular, ir spectroscopy may be regarded as the most widespread technique available for the observation of catalyst or adsorbed species. However, findings from ir spectra should be correlated with the kinetic features of the reaction by some appropriate methods. From such a point of view, the identification of adsorbed species during the ammoxidation of toluene by ir spectroscopy may be very useful to clarify the reaction mechanism, because the stable adsorbed toluene is on the surface, and verified to be the reaction intermediate not only in the pulse technique but also in the flow technique (*1*).

The π-allyl species adsorbed on ZnO (Kadox) in the propylene oxidation was observed by Dent and Kokes (*2*), and concurrent studies have dealt with the same problem (*3, 4*). However, it seems to be difficult to measure the reaction intermediate on a selective catalyst such as Bi_2O_3–MoO_3.

In this paper, the adsorbed species from toluene dealt with in Part I (*1*) are identified by ir spectroscopy, and the mechanism and active sites are discussed in more detail.

EXPERIMENTAL METHODS

Samples used here were V_2O_5/Al_2O_3, Al_2O_3, V_2O_5/SiO_2, SiO_2, and V_2O_5. To heighten the transmittance, Alon G and Cab-O-Sil were used as Al_2O_3 and SiO_2, respectively, and V_2O_5 was supported on

ISSN 0021-9517

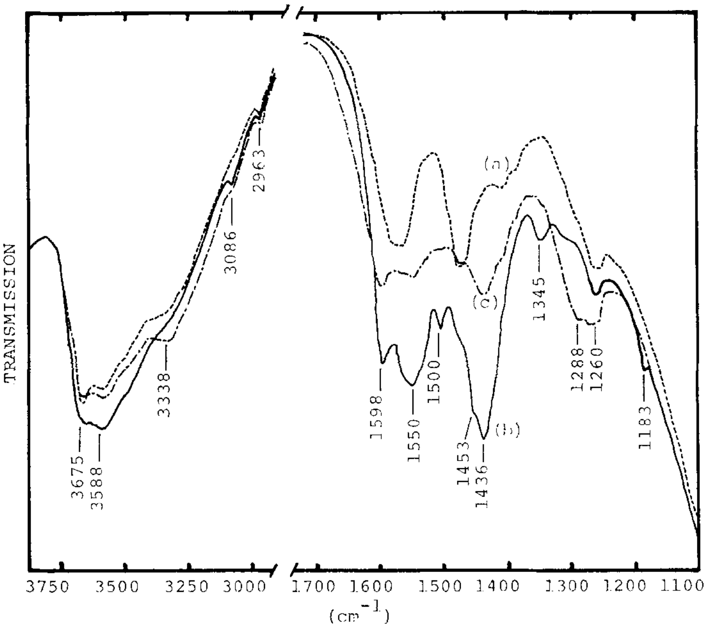

FIG. 1. Infrared spectra of toluene adsorbed on V_2O_5/Al_2O_3: (a) evacuated V_2O_5/Al_2O_3; (b) after adsorption of toluene, followed by evacuation; (c) after contact of ammonia, followed by evacuation.

them in the method previously described (*1*). Vanadium oxide supported on θ-Al_2O_3, the oxide catalyst used in Part I (*1*) was also available for the measurement of ir spectra. Samples (80 mg) were compressed under a pressure of 3–4 ton/cm^2 to form a round pellet of 20 mm in diameter.

Spectra were recorded on a Jasco IR-G spectrometer in the region 4000–1300 cm^{-1}. The spectral slit width was 1.25 mm. The ir cell was made of a Pyrex glass, and constructed to maintain the furnace part up to 450°C. The pellet holder of Pyrex glass was hanging in the cell by a platinum wire. Evacuation or adsorption was performed in an upper furnace part, and then the pellet was lowered to expose ir beam at room temperature. Liquid products were trapped in the side arm cooled at −196°C, and analyzed by gas chromatograph.

Toluene and benzaldehyde were purified by vacuum-distillation. Ammonia was used without further purification.

RESULTS

The adsorption of hydroxyl groups on the evacuated V_2O_5/Al_2O_3 was observed around 3500 cm^{-1}, as shown in Fig. 1a. The absorbance was decreased by the vacuum-evacuation, but was hardly varied after it was evacuated for 2 hr. Toluene was adsorbed on a sufficiently evacuated sample at 400°C for 5 min, followed by evacuation at 400°C for 15 min. The spectrum thus obtained (Fig. 1b) showed clearly the bands at 1550 and 1436 cm^{-1} which were ascribed to the assymmetric and symmetric stretching vibrations of carboxylate ion, and furthermore the absorptions of C=C and C–H stretching vibrations in the benzene ring were found at 1598, 1500, and 1453 cm^{-1} and 3086 cm^{-1}, respectively. This spectrum was therefore identified as an adsorbed benzoate ion, Ph–COO$^-$, and substantially the same as that reported by Kuiper *et al.* (*5*) in the adsorption of benzaldehyde on Al_2O_3. Besides these ad-

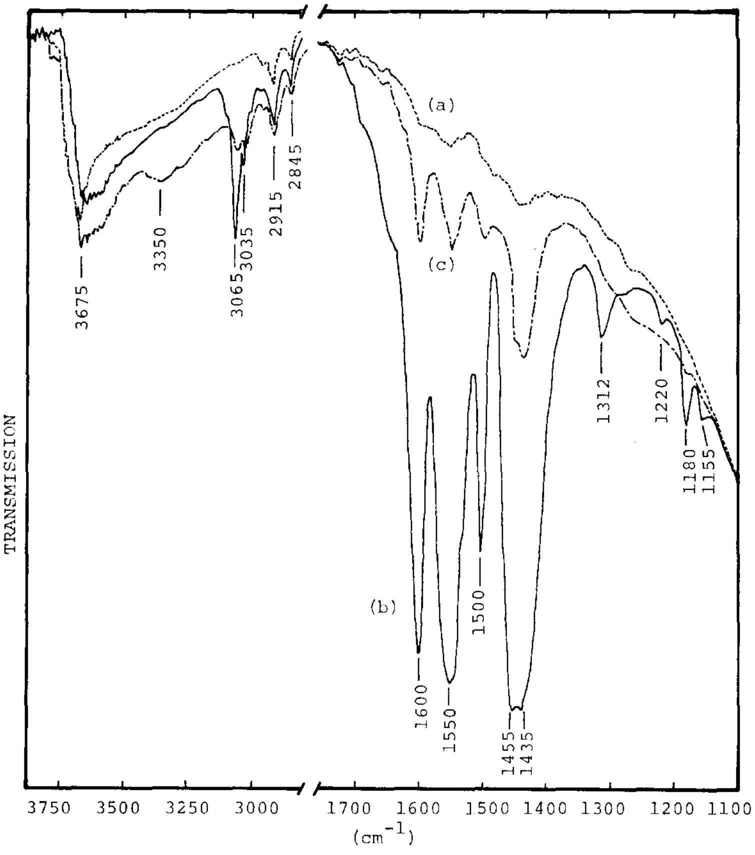

FIG. 2. Infrared spectra of benzaldehyde adsorbed on Al_2O_3: (a) evacuated Al_2O_3; (b) after adsorption of benzaldehyde, followed by evacuation; (c) after contact of ammonia, followed by evacuation.

sorption bands, dust spectra which were observable in the silicone grease were also found at 2963, 1410, and 1260 cm^{-1}. However, a small absorption at 1345 cm^{-1} is still unknown. The absorption ascribable to carbonyls seemed to be observed at 1310 cm^{-1}, but the intensity was very small. Its intensity was slightly increased by the adsorption of toluene at 400°C, followed by the evacuation at room temperature. It may probably be ascribable to a small amount of benzaldehyde physically adsorbed.

Ammonia was then introduced into *in situ* cell to be contacted with the adsorbed benzoate ion at 400°C, and after 10 min the liquid products were trapped at liquid nitrogen temperature, followed by evacuation at 400°C for 15 min. As shown in Fig. 1c, the absorbance of the adsorbed benzoate ion was decreased by such a contact with ammonia. According to Lambert–Beer's equation, it seemed that about 50% of the adsorbed benzoate ion was removed from the surface. In the spectrum, absorptions of adsorbed NH_3 were found at 3338 and 1288 cm^{-1}, which were ascribed to stretching and deformation vibrations, respectively (*6*). The spectrum obtained by the evacuation at room temperature after the reaction with ammonia contained an absorption at 2225 cm^{-1} which was due to a cyano group attached to alkylbenzenes, probably benzonitrile physically adsorbed. In the simultaneously trapped products, furthermore, only benzonitrile was found by gas chromatograph. In conclusion, it was found that benzonitrile was formed by the reaction between the adsorbed benzoate ion and gaseous ammonia.

In Part I (*1*), pulse technique showed that benzonitrile was obtained from an adsorbed intermediate of toluene by the injection of ammonia. Behavior of the intermediate agreed well with that of the benzoate ion found here using ir spectroscopy. It can therefore be said that the adsorbed intermediate of toluene relevant to benzonitrile formation is identified as the benzoate ion.

As mentioned above, Kuiper *et al.* (*5*) have previously reported the spectrum of the benzoate ion on Al_2O_3 in the adsorption of benzaldehyde. Ammonia was allowed to contact the benzoate ion adsorbed on Al_2O_3. Figure 2b shows the spectrum of benzoate ion adsorbed on Al_2O_3, in which benzaldehyde was adsorbed at 400°C, followed by evacuation at 400°C. This was nearly the same to that of the benzoate ion on V_2O_5/Al_2O_3, but included the absorption of benzaldehyde physically adsorbed at 1310 cm^{-1}. By the introduction of ammonia, the intensity of benzoate ion decreased and benzonitrile was detected in the trapped products. Consequently, the adsorbed benzoate ion gives benzonitrile not only on V_2O_5/Al_2O_3 but also on Al_2O_3.

Toluene on V_2O_5/SiO_2 and benzaldehyde on SiO_2 were examined to be compared with the results mentioned above. However, no spectrum of adsorbed species was obtained except for a little portion of physically adsorbed aldehyde on SiO_2. Furthermore, the detection of adsorbed species on V_2O_5 was very difficult. This is in good agreement with the observation that the reaction intermediate on V_2O_5 is not so stable as that on V_2O_5/Al_2O_3, as shown in Part I (*1*).

DISCUSSION

As clearly shown in a preceding description, the benzoate ion is adsorbed on the V_2O_5/Al_2O_3, and gives benzonitrile by the reaction of ammonia. The adsorbed intermediate found by the pulse technique is therefore identified as the benzoate ion. It is worth noting that the benzoate ion adsorbed on V_2O_5/Al_2O_3 is substantially the same to that on Al_2O_3 from the standpoint of the ir spectrum as well as the reaction profile with ammonia. This allows us to surmise that the benzoate ion on V_2O_5/Al_2O_3 is adsorbed on the surface of Al_2O_3. Such a consideration about the role of alumina surface is supported by the fact that the detection of adsorbed intermediate on V_2O_5 and V_2O_5/SiO_2 is very difficult. It may be considered that the reaction intermediate adsorbed on V_2O_5 and V_2O_5/SiO_2 is unstable and easily removed from the surface as carbon oxides and water, unlike that on V_2O_5/Al_2O_3 (*1*). In other words, Al_2O_3 is essential to form the stable intermediate as the adsorbent, as far as oxides used here are concerned. From such a point of view, Al_2O_3 is not merely a support of V_2O_5 but has an important role in the ammoxidation of toluene. It may be said that such a property of the alumina that makes the reaction intermediate stable on the surface contributes high reaction selectivity of V_2O_5/Al_2O_3 catalyst in the ammoxidation of toluene.

On the other hand, V_2O_5 acts as the oxidizing reagent of toluene, because toluene is oxidized on V_2O_5/Al_2O_3 and V_2O_5 but not on Al_2O_3. Therefore, the activity of V_2O_5/Al_2O_3 is constituted of dual functional activity, i.e., oxidizing activity of V_2O_5 and adsorbing property of Al_2O_3. It may be considered that toluene is oxidized on the surface of V_2O_5, followed by translation to be stabilized on the surface of Al_2O_3. Such a consideration may be supported by the suspicion on the activated complex theory that the activated complex of toluene is in a half-mobile state (*1*).

Furthermore, the production of benzonitrile on Al_2O_3 by the reaction of adsorbed benzoate ion with ammonia is indicative of the reaction mechanism of the ammoxidation, in particular about the behavior of ammonia. The fact suggests that the conversion of benzoate ion into benzonitrile does not take place as a result of an oxidation reaction, because Al_2O_3 has only a low oxidizing activity in the oxidation of ammonia (*7*) as well as hydrocarbons (*8*). The reaction mechanism is then proposed as

$$\text{Ph–CH}_3 + (O^{2-}) \rightarrow (\text{Ph–COO}^-) + (OH^-), \quad (1)$$

$$NH_3 + (OH^-) \rightarrow (NH^+{}_4) + (O^{2-}), \quad (2)$$

$$(\text{Ph–COO}^-) + (NH^+{}_4) \rightarrow \text{Ph–CN} + H_2O. \quad (3)$$

As described above, toluene is oxidized in the side chain to form the adsorbed benzoate ion in the first place, which is accompanied with the increase of concentration of surface hydroxyls. Interaction of ammonia with hydroxyls may probably give ammonium ion on the surface. It is considered that the reaction of Ph–COO^- with $NH^+{}_4$ proceeds fast to form benzonitrile and water. As discussed above, the oxidative adsorption (1) may occur on V_2O_5, and following reactions (2) and (3) on Al_2O_3.

On the basis of this reaction mechanism, concentration of surface hydroxyls increases with the adsorption of toluene, and decreases with the reaction with ammonia. This consideration is well supported by the behavior of OH-band on V_2O_5/Al_2O_3, as shown in Fig. 1. The intensity of the OH-band on Al_2O_3, however, was increased by the contact of ammonia. It may therefore be said that hydroxyl ions produced in the benzonitrile formation on Al_2O_3 are not removed from the surface.

Ammoxidation of propylene is well known as a more typical process. Since Adams (*10*) and Sachtler and DeBoer (*9*) proposed the mechanism, it is believed that propylene initially gives a π-allyl intermediate on the surface. Although the following steps are needed to have a final product, the detailed scheme has not been necessarily clarified. One possible route may be via the carboxylate ion, i.e., adsorbed acrylate ion, from the viewpoint of above discussion. However, the adsorbed acrylate ion may be lacking in the stability necessary for observation by ir spectroscopy. Oxygen-containing intermediates should be taken into consideration to understand a whole reaction mechanism also in the ammoxidation of propylene.

REFERENCES

1. Murakami, Y., Niwa, M., Hattori, T., Osawa, S., Igushi, I., and Ando, H., *J. Catal.* **49**, 83 (1977).

2. Dent, A. L., and Kokes, R. J., *J. Amer. Chem. Soc.* **92**, 6709 (1970).

3. Kugler, B. L., and Kokes, R. J., *J. Catal.* **32**, 170 (1974).

4. Kubokawa, Y., Miyata, H., Ono, T., and Kawasaki, S., *J. Chem. Soc. Chem. Comm.* **1974**, 655.

5. Kuiper, A. E. T., Medema, J., and Van Bokhoven, J. J. G. M., *J. Catal.* **29**, 40 (1973).

6. Little, L. H., "Infrared Spectra of Adsorbed Species," Academic Press, London, 1966.

7. Germain, J. E., and Perez, R., *Bull. Soc. Chim. Fr.* 2042 (1972).

8. Moro-oka, Y., and Ozaki, A., *J. Catal.* **5**, 116 (1966).

9. Sachtler, W. M. H., and De Boer, N. H., *Proc. Int. Congr. Catal., 3rd, 1964* **1**, 252 (1965).

10. Adams, C. R., *Proc. Int. Congr. Catal., 3rd, 1964* **1**, 240 (1965).