

INTERMEDIATE IN
AMMOXIDATION OF TOLUENE INTO BENZONITRILE

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Ammoxidation of toluene into benzonitrile on V_2O_5/Al_2O_3
proceeds via an adsorbed benzoate ion as the reaction intermediate.

Detection of a reaction intermediate adsorbed on oxides during oxidation of propylene by infrared spectroscopy was done by Dent and Kokes,¹⁾ who showed the existence of π -allyl species over ZnO. Their clear result stimulates all of the scientists interested in this field, and the behaviors of this adsorbed species have been studied by Kugler²⁾ and Kubokawa et al.³⁾ However, there is little report about such an adsorbed species from aromatic hydrocarbon. The authors will report here the reaction intermediate adsorbed on V_2O_5/Al_2O_3 in ammoxidation of toluene.

The IR spectrum obtained by the adsorption of toluene (ca. 18 torr) on evacuated V_2O_5/Al_2O_3 catalyst (5 wt% of V_2O_5 is supported on Alon G) at 400°C, followed by evacuation at 400°C is shown in Fig. 1-b. This spectrum clearly shows the bands at 1550 and 1436 cm^{-1} which are ascribed to the asymmetric and symmetric stretching vibrations of carboxylate ion, and furthermore the absorptions of C=C and C-H stretching vibrations in the benzene ring are found at 1598, 1500, and 1453 cm^{-1} and 3086 cm^{-1} , respectively. The IR spectrum is essentially the same to that of the benzoate ion which are formed by the adsorption of benzaldehyde on alumina.⁴⁾ Therefore, this species can be identified as an adsorbed benzoate ion on V_2O_5/Al_2O_3 .

Ammonia was then allowed to contact with the catalyst for 10 min at 400°C and evacuated at 400°C. As shown in Fig. 1-c, the absorbance of the benzoate ion was decreased, and new absorption band was observed at 3338 and 1288 cm^{-1} which were due to adsorbed ammonia. Simultaneously, we found benzonitrile in the product of this reaction by gas chromatography. As a whole, above findings show that the adsorbed benzoate ion reacts with ammonia to give benzonitrile.

Murakami has already indicated that a stable adsorbed intermediate from toluene reacts with ammonia to give benzonitrile on V_2O_5/Al_2O_3 using pulse technique.⁵⁾ Kinetic measurements allow us to regard such an adsorbed species as a reaction intermediate in the ammoxidation of toluene also in the continuous-flow technique. We may therefore regard the benzoate ion detected by IR spectroscopy as a reaction intermediate in the ammoxidation of toluene over V_2O_5/Al_2O_3 .

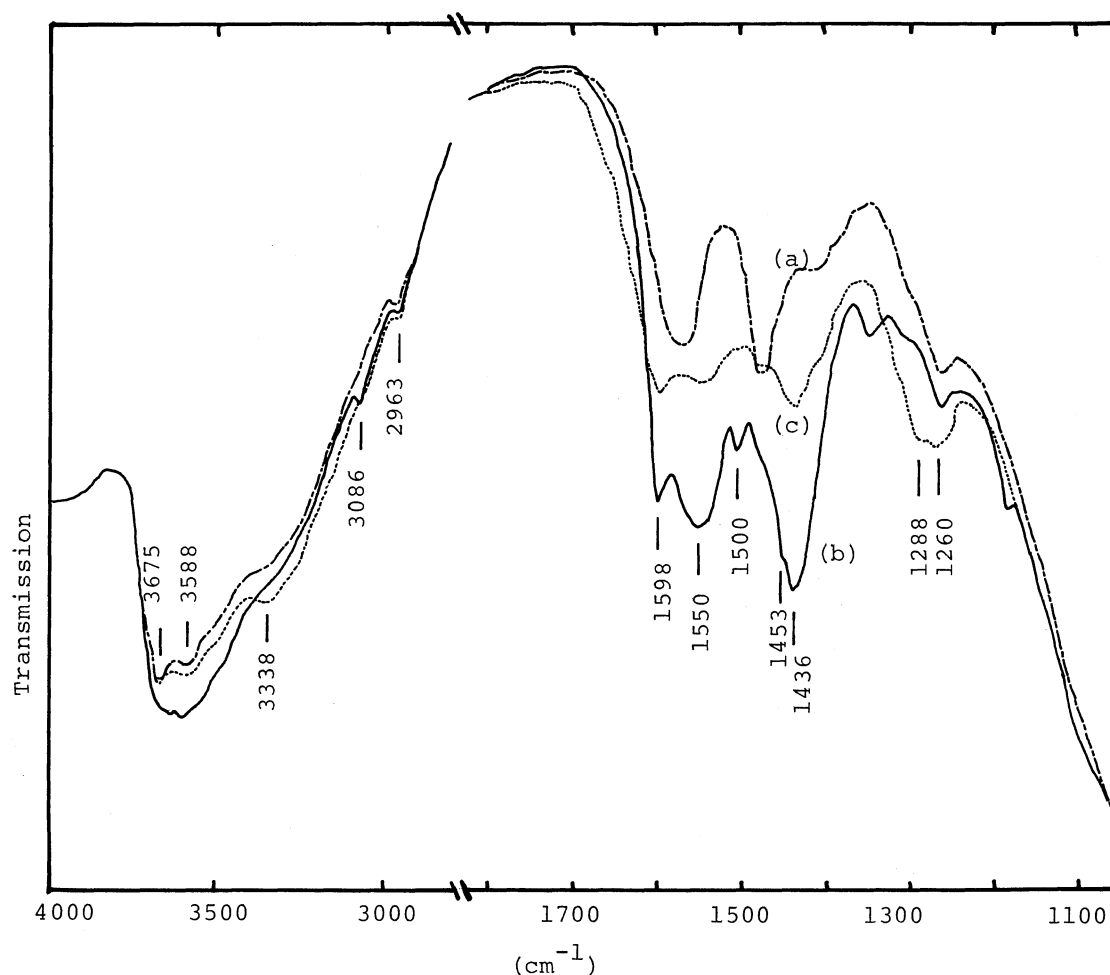


Fig. 1. IR spectra of toluene adsorbed on V₂O₅/Al₂O₃: (a) evacuated V₂O₅/Al₂O₃; (b) after adsorption of toluene, followed by evacuation; (c) after contact of ammonia, followed by evacuation.

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