APPLICATION OF EMISSIONLESS INFRARED DIFFUSE REFLECTANCE SPECTROMETRY FOR FOLLOWING REACTIONS OF ADSORBED ALCOHOLS ON AN ALUMINA CATALYST

T. Hattori, K. Shirai, M. Niwa and Y. Murakami

Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa, Nagoya 464, Japan

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IR spectra of adsorbed alcohols on alumina were measured under the reaction conditions at elevated temperatures. The transient response of IR absorption intensity indicates that alkoxides are reactive adsorbed species but carboxylates are not. The rate constants of surface reactions were calculated from the transient response.

IR spectroscopy would be a more powerful tool for the investigation of catalysis if IR spectra of reacting species could be measured while a reaction is in progress at elevated temperatures and if the reactivity of adsorbed species can be examined easily. For such purposes, we constructed an emissionless infrared diffuse reflectance spectrometer (EDR) /1/. It has been said that the infrared diffuse reflectance spectrometer would be useful for following the reactions of adsorbed species /2/, though no successful experiments have been reported. In the present study, the applicability of EDR for such purposes has been examined.
A mixture of fine powders of alumina catalyst, a reference catalyst of the Catalysis Society of Japan (JRC-ALO-2) /3/, and fine powders of Si were packed in an EDR sample holder and heat-treated at 638 K for 2 h in a flow of He. IR spectra were measured in a flow of a mixture of He and alcohols. The light path in an in situ EDR cell is so short that IR absorption by the gas phase alcohols can be neglected. The following bands ascribable to alkoxides were observed at 413 K: \( \nu \text{CH} \) at 2970, 2920 and 2860 cm\(^{-1}\), \( \delta \text{CH} \) at 1380 cm\(^{-1}\), and Al-O-C linkage at 1050 cm\(^{-1}\). Symmetric and asymmetric \( \delta \text{COO}^- \) bands at 1460 and 1570 cm\(^{-1}\) ascribable to carboxylates were observed at 558 K.

Figure 1 shows the transient responses of absorption intensities, that is, the changes of the absorption intensities at fixed wavenumbers with the sudden change of gas phase composition from a mixture of He and ethanol to He. The absorption intensities at 2970, 1380 and 1050 cm\(^{-1}\) decreased with time, while those at 1570 and 1460 cm\(^{-1}\) did not change. These results indicate that alkoxides are reaction intermediates, but carboxylates are not. The initial rapid decrease at 1050 cm\(^{-1}\) is due to a change of the background, and those at 2970 and 1380 cm\(^{-1}\), to the desorption of H-bonded or coordinatively adsorbed ethanol. The subsequent slow decreases at these wavenumbers are due to the reaction of alkoxide, because the rate depends on both temperature and alcohol. The rate constant of decomposition of alkoxide can be given as a function of the relative reflectance \( r \) and time \( t \) on the basis of the first order rate law and the Kubelka-Munk equation /4/

\[
k = \frac{1+r}{r(1-r)} \cdot x \frac{dr}{dt}
\]

The rate constants were calculated from the transient responses of the reflectance at 2970 cm\(^{-1}\) using Eq. (1) when the gas phase composition was changed from a mixture of He and alcohol to a mixture of He and \( \text{H}_2\text{O} \) (1.7 kPa). The change to He resulted in a change of temperature because of the difference in the thermal conductivity between He and alcohol. The empty symbols in Fig. 2 show the results