INFRARED STUDY OF COMPARATIVE ADSORPTION OF SOME ALCOHOLS AND THIOLS ON γ- ALUMINA

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Among the spectroscopic methods used for the characterization of the chemical nature of chemisorbed species, infrared transmission spectroscopy has certainly found the most frequent application. Adsorption of alcohols on alumina has been studied for many years. Despite this fact, even most fundamental questions concerning the system have not been yet answered. A most striking example is the process of adsorption (dissociation or coordination) and the nature of the adsorption sites on γ-Al₂O₃ surface. To solve this problem, we have undertaken a series of infrared experiments using non-deuterated and deuterated alcohols, the vibrational spectra of which had been previously reported in the gaseous and liquid state. Some experiments have been also carried out with methanethiol for comparison. A very detailed analysis of the spectra allows us to determine the nature of irreversible and reversible species. Poisoning experiments precise the mechanism of the adsorption process.

IRREVERSIBLE SPECIES

Alcohols

Infrared studies of alcohols on alumina at room temperature have shown that at least two types of chemisorbed species occurred: alkoxide species, resulting from a dissociative chemisorption and coordinated species, formed by chemisorption onto Lewis acid sites.
Carboxylate species are generally formed at higher temperatures. To distinguish between dissociative and coordinative chemisorption, the spectra have been carefully examined in two ranges:

a) in the 1500 - 1000 cm⁻¹ range, comparison between vibrational spectra of adsorbed ROH and ROD allows us to solve the problem:

- in \( R'CH_2OH \) or \( R'_nCHOH \) spectra, the \( \delta(OH) \) mode is coupled with the \( CH_2 \) or \( CH \) bending modes. If these alcohols are dissociatively adsorbed these couplings are suppressed and the spectra of the adsorbed species might be similar to those given by the corresponding ROD alcohols. This has been effectively observed for propargyl alcohol, and trichloro-2,2,2 or trifluoro-2,2,2 ethanols;

- in the case of tertiary alcohols, comparison between adsorbed ROH and ROD spectra in this range is also very helpful as shown for \((CF_3)_3COH\):

Fig. 1. : Comparative IR spectra of
a) \((CF_3)_3COH\)

b) \((CF_3)_3COD\)

irreversibly adsorbed on alumina (Degussa-C) dehydroxylated at 1150 K. Dotted line : background.