IR SPECTRA OF CATALYSTS AND ADSORBED MOLECULES.

33.* FORMATION OF NICKEL-COMPLEX CATALYSTS ON VARIOUS MINERAL SUPPORTS

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Synthesis in an adsorbed layer [2], where the initial substances are applied on a support from the gas phase and the complexing reaction is conducted on the surface, is one of the promising methods for production of complex catalysts on a support. The present study concerns the problem of determining the role of the support in adsorption of the components of a catalyst and complexing based on the example of obtaining a nickel-complex catalyst from nickel carbonyl and an allyl halide. Al₂O₃, SiO₂, and MgO, which significantly differ with respect to the nature of the hydrate-hydroxyl shell and the acid-base centers, were used as the supports.

EXPERIMENTAL

The Ni-complex catalysts were obtained by successive adsorption of Ni(CO)₄ and allyl chloride or bromide from the gas phase on a (Al₂O₃, SiO₂, MgO) support cooled to −10 to −5°C according to the method in [2]. Adsorption of the reagents was conducted in a vacuum adsorption installation connected to a quartz IR cell, which permitted conducting vacuum activation of the samples and taking spectra at temperatures from −70 to 600°C [3]. Preliminary activation of the supports (25 x 8 mm in size, weight of 10-20 mg/cm²) was conducted at 400-450°C in a vacuum of 10⁻⁴ torr. The support was then cooled to −10 to −5°C, and adsorption of first Ni(CO)₄ and then the allyl halide, or first the allyl halide and then the Ni(CO)₄ was conducted. *See [1] for Communication 32.
and the IR spectra were recorded at low and at room temperatures. Industrial γ-Al₂O₃, brand A-I, with a specific surface of 190 m²/g; SiO₂, Aerosil brand, with a specific surface of 300 m²/g; and MgO (obtained by decomposition of basic magnesium carbonate at 550°C), with a specific surface of 80 m²/g, were selected as the supports. The Ni(CO)₄ and allyl halides were distilled in a vacuum in glass tubes. The spectra were recorded on a modernized [3] UR-20 spectrophotometer in the 1000-3800 cm⁻¹ region. Samples of supports in which the OH groups had been replaced by OD groups by treating the samples with heavy water (D₂O) at 200-250°C with subsequent desorption at 450°C for 1-2 h were used in some cases.

DISCUSSION OF RESULTS

Adsorption of Nickel Carbonyl on the Surface of the Supports. The reaction of Ni(CO)₄ with γ-Al₂O₃ at a temperature close to 0°C resulted in a slight change in the shape of the absorption bands (AB) of the surface valence vibrations of the OH groups (Fig. 1). After adsorption of Ni(CO)₄ at 0°C for 1-3 min, the shape and intensity of the AB of the OH (OD) groups was not totally restored (see Fig. 1), and a single band for the carbonyl groups at 2065 cm⁻¹ was observed in the region of the valence vibrations of the CO groups. The absence of AB in the regions of 1800-1950 and 2000-2100 cm⁻¹ (with the exception of a band at 2065 cm⁻¹) indicated that the Ni(CO)₄ did not decompose during adsorption. The Ni(CO)₄ partially decomposed at higher temperatures in the case of Al₂O₃ (40-60°C), the transmission of the samples became worse (due to precipitation of metallic Ni), and AB appeared in the spectrum at 1860, 2020, and 2085 cm⁻¹, corresponding to adsorption of CO on Ni in the form of linear Ni–C=O and bridge Ni–CO–Ni structures [4, 5].

In adsorption of Ni(CO)₄ on the surface of SiO₂ (Fig. 2) and MgO, subsequent desorption at 20°C for 1-3 min resulted in total elimination of the Ni(CO)₄. In contrast to the SiO₂ and MgO supports on Al₂O₃, the AB at 2065 cm⁻¹ partially persisted in the spectrum even after the shape of the AB of the OH groups had been totally restored.

Nickel carbonyl is thus retained on the surface of SiO₂ and MgO either physically or by weak H bonds, and it is adsorbed without decomposing. Only part of the Ni(CO)₄ reacts with the OH groups on the surface of the Al₂O₃. The other part is probably adsorbed more stably on Lewis centers due to the reaction of the oxygen in the carbonyl group of Ni(CO)₄ with the surface of the Al₂O₃ or as a result of transfer of electron density from the nickel to the aluminum ion.

Adsorption of Allyl Halides on the Surface of the Supports. Adsorption of the allyl halides (C₃H₇Cl and C₃H₇Br) on the surface of previously deuterated Al₂O₃ resulted in perturbation of the OD groups. AB at 1250, 1300, 1380, 1420, 1460, 1580, 1640, 2860-3000, and 3100 cm⁻¹ were observed in the spectrum of the adsorbed allyl halide (in the presence of the gas phase) (see Fig. 1). Desorption at 20°C for 5 min resulted in a significant decrease in the intensity of the AB at 1250, 1300, 1420, 1640, and 2860-3100 cm⁻¹, while the intensity of the absorption bands at 1380, 1460, and 1580 cm⁻¹ did not change. The shape of the absorption bands of the surface OD groups became similar to the initial shape. There are thus at least two forms of adsorbed allyl halide on the surface γ-Al₂O₃: One of them is less stably bound and is characterized by absorption bands at 1250, 1300, 1420, 1640, 2860-3000, and 3100 cm⁻¹, while the second is more stably bound and has AB at 1380, 1460, and 1580 cm⁻¹, and weak bands in the 2860-3000 cm⁻¹ region (see Fig. 1). The bands of the weakly adsorbed form of the allyl halides were similar in position to the AB of the allyl halide (C₃H₇Cl, C₃H₇Br) in the gas phase. The antibiotic changes in the shape and AB of the OD groups and the absorption bands of the weakly adsorbed form during adsorption and desorption suggest that this form of adsorbed allyl halide is bound with the surface OD groups. A shoulder is also observed at 1420 cm⁻¹ in the region of the deformational vibrations of C–H in the spectrum of the allyl halides adsorbed on γ-Al₂O₃; it can be assigned to formation of a π-allyl complex on the surface, found in [6] in adsorption of propylene and C₃H₇Br on a gallium-molybdenum oxide catalyst. Formation of a structure of the type:

![Structure](image)

apparently requires cleavage of the halide atom. However, the presence of AB at 1250 cm⁻¹, characterizing the deformational vibration of C–H in the CH₃X fragment [7], indicates that