Characterization of the Pt–C bond of CO adsorbed by small Pt particles in a NaX zeolite by IR diffuse reflectance spectroscopy

V.B. Kazansky, V.Yu. Borovkov, N. Sokolova
Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow 117071, Russia

N.I. Jaeger and G. Schulz-Ekloff
Institut für Angewandte und Physikalische Chemie, FB 2 – Universität Bremen, D-28334 Bremen, Germany

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The unusual properties of small (1–2 nm) Pt particles within a zeolite support are documented by diffuse reflectance infrared spectroscopy of the metal–carbon bond of linearly adsorbed CO. The wave number of the metal–carbon stretching frequency is found to be about 60 cm⁻¹ higher compared to larger particles (2–3 nm) or to the bulk metal. The stronger bond is attributed to a negative charge on the small metal particles.

Keywords: CO chemisorption on Pt; carbon–Pt bond; IR diffuse reflectance spectroscopy

1. Introduction

Due to the narrow pore size distribution zeolites are unique supports for the preparation of metal dispersions with different though uniform sizes of the small metal particles under appropriate preparation procedures [1,2]. A common way to study their properties is the adsorption of CO as a molecular probe with IR control of the state of adsorbed species. The stretching frequency of the linear form of adsorbed CO was found to decrease with increasing dispersion of the platinum incorporated in the micropores of a faujasite matrix [3]. Similar effects in metal loaded zeolites were attributed to back donation of electrons resulting from the negative charging of small metal particles [4–7]. However, the C–O bond is not directly involved in adsorption. Therefore, its stretching frequency is rather insensitive to the nature and the state of the metal. More informative in this respect is certainly the Me–C stretching vibration that can be directly measured for CO adsorption on metal films and single crystals [8–11]. For supported metals the cor-
responding bands are hidden under intensive Me–O–Me bending modes of the oxide carriers. Therefore, for metal loaded zeolites the direct observation of the Me–C stretching vibrations was not yet reported.

Some new possibilities are provided in this context by the diffuse reflectance IR technique [12]. Due to the very high sensitivity it allows the observation of the combination of C–O and Me–C stretching bands that are about two orders of magnitude less intensive than the fundamental modes. The Me–C frequencies can then be easily obtained as the difference between the combination and the C–O stretching frequencies [11,12].

The aim of this paper is the application of this approach to the study of platinum loaded zeolites that have been investigated earlier in ref. [3].

2. Experimental

The Pt loaded NaX zeolite with a Si/Al ratio of 1.2 was prepared according to procedures described in refs. [2,13] by ion exchange with the tetraammine ion complex from aqueous solutions of the chloride. After ion exchange the samples were washed until complete removal of the chloride ions and dried at 353 K. The degree of ion exchange was equal to 10%.

The specimens were heated in flowing O2 up to 673 K (5 K min⁻¹) followed by treatment in flowing hydrogen at 573 K for 1 h [13]. The mean diameter of platinum particles after such treatment as evaluated from electron micrographs was equal to 1–3 nm (fig. 1).

IR diffuse reflectance spectra were recorded according to ref. [12] at room temperature for the original samples in the form of a powder and for small grains (0.25–0.5 nm in diameter) made from powder by pressing and subsequent crushing. The aim of the latter preparation was to reproduce thin pressed pellets that were used before for measurements of transmittance IR spectra in ref. [3].

Before diffuse reflectance IR measurements the samples were additionally evacuated and reduced in IR cells at 570 or 628 K for 2 h under static conditions ($P_{H_2} = 1.3 \times 10^4$ Pa). Then they were again evacuated for 1 h at the same temperature. Under these conditions an Ostwald ripening of the samples can be expected [13].

CO adsorption was carried out at room temperature at the equilibrium pressure of $1.3 \times 10^3$ Pa. IR spectra were also recorded at this temperature either in CO atmospheres or after evacuation at 298 K and different elevated temperatures.

3. Results and discussion

Evolution of IR spectra of CO adsorbed by the granulated sample at different surface coverages is presented in fig. 2. In the fundamental region of the C–O stretching vibrations a band with the maximum at 2080 cm⁻¹ with a low frequency