The adsorption of CO on an Rh foil and small Rh particles supported by Al₂O₃ polycrystalline surfaces was studied using the temperature programmed desorption (TPD). The supported Rh particles were prepared by evaporation, using the principles of electron bombardment. The activation energy of desorption was calculated. The results show the dependence on the CO exposure of the sample as well as the size effect. The desorption and the recombination peaks were measured. The dissociation of CO and the influence of C atoms on the surface are discussed.

1. Introduction

The adsorption and desorption of gases on the metal surfaces have been the subject of numerous surface analysis experiments. These studies, performed on well characterized surfaces (model catalysts), have made an important contribution to the heterogeneous catalysis understanding [1]. For the Rh-CO system a large body of data exists, mostly for the single crystals. In work [2] the dissociation of CO on Rh (210) single crystal was measured and the recombination peak (β) was found. The first extensive study of CO adsorption on supported Rh samples of various particle size was made by D. N. Belton and S. J. Schmieeg [3]. They prepared Rh particles of 2 and 7 nm average sizes, measured adsorption-desorption phenomena depending on CO coverage and calculated the activation energy of desorption $E_a$, using Redhead analysis for the first order desorption [4]. They compared the results for supported Rh particles with those obtained for single crystal Rh(111). Their values of $E_a$ obtained by the Redhead analysis for Rh(111), 7 and 2 nm particles were, respectively, 125.4 kJ/mol, 123.7 kJ/mol and 102.4 kJ/mol for saturation CO exposures and 131.7 kJ/mol; 131.7 kJ/mol and 127.5 kJ/mol for very low CO coverages.

This paper presents the results obtained on the Rh polycrystalline foil and Rh particles of various sizes evaporated on Al₂O₃ polycrystalline surface. Various CO exposures were used and the dependence of $E_a$ on them was studied. It was observed that $E_a$ changes with the size of particles and its value depends also on the temperature treatment of the sample. It is proposed to resolve the last phenomenon by C atoms which remain on the surface after the dissociation of CO molecules.
2. Experimental

The experiments were performed in a vacuum chamber with a base pressure of $2 \times 10^{-10}$ torr. TPD measurements were made with a quadrupole mass spectrometer which was placed in a differentially pumped chamber. This chamber is connected with the main one by a 3 mm hole, sample being held in front of it at a distance of about 3 mm. This set-up enables us to measure the gases desorbed from the sample only, the other desorbing gases being geometrically shielded. The CO exposure is made by the CO molecular beam, directed to the sample. This resulted in the possibility of high exposures of the sample, while the low pressure in the chamber is held.

The $\text{Al}_2\text{O}_3$ samples were prepared from Good-Fellows materials (GFM) 99.999% Al in the form of a plate $10 \times 10 \text{ mm}^2$, 1 mm thick. The samples were mechanically and chemically polished and oxidized at a higher temperature. A very thin chromel-alumel thermocouple was mounted inside a hole which was drilled into the sample before its oxidation. That is why the temperature could be comparatively accurately determined. Rh foil was also 99.999% GFM and the thermocouple was spot-welded to it. During TPD measurements all the samples were heated by conduction from a resistively heated Ta wire isolated from them by a 0.5 mm thick sapphire plate. The heating rates, used for these experiments, were about 5 K/s.

The Rh particles were evaporated in-situ from a cell, where a 99.999% Rh wire is heated by high voltage accelerated electrons emitted from a hot Re cathode. The evaporating rates, which were estimated by a quartz crystal film thickness monitor, were 0.2 nm/min and 0.08 nm/min. The temperature of the sample during the evaporation was held at 600 and 770 K. The average diameter of particles, determined by the electron microscope observation of the transfer carbon replica of the first sample, was 2.5 nm, the density of particles being $3.6 \times 10^{-11} \text{ cm}^{-2}$. These parameters were not determined in the case of the second sample (it was not possible to separate the replica from the substrate), but according to the preparation parameters we can assume that the particles are much larger. After the evaporation the samples were stabilized under the mixture of CO and O$_2$, the partial pressures of both being $3 \times 10^{-8}$ torr at a temperature of 770 K for one hour. Before the experiment the Rh foil sample was annealed for one hour in an O$_2$ atmosphere, the partial pressure being $3 \times 10^{-8}$ torr and the temperature 900 K.

The experiments with the Rh foil were performed on an annealed sample at first. Then the surface disorder was created by means of Ar ion bombardment ($E_i = 2 \text{ keV}, i_i = 1 \mu \text{A cm}^{-2}$) and the experiments were repeated.

3. Results and discussion

The CO desorption profiles as a function of temperature for different initial CO coverages were measured. Figure 1 shows the results obtained for a particle size of 2.5 nm (sample 1), the results obtained for larger particles (sample 2) and for