COMPARISON OF CHEMISORPTION AND HYDROGENOLYSIS OF ETHANE ON TRANSITION METALS

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Data on chemisorption of ethane on transition metal blacks have been correlated with hydrogenolysis activity measurements. On Pt and Pd the rupture of the C-C bond seems to be a hindered process. Desorption of methane requires larger activation on Co and Ni than on Ru, Rh or Ir blacks.

INTRODUCTION

Theoretical considerations /1/ have shown that the catalytic activity as a function of the strength of the catalyst-substrate interaction must pass through a maximum, i.e., from the viewpoint of catalytic activity both weak and strong interaction is disadvantageous. The hydrogenolysis activity of transition metals /2, 3/ passes through a maximum from left to right of the periodic table. In all reported cases, however, the catalytic activity and a "bulk" parameter of the catalyst were correlated. In our recent paper we intended to compare the chemisorption of ethane with catalytic activity measurements.
Catalytic activity measurements were described elsewhere /4/. The average H/C ratio in chemisorbed ethane was determined in a static system connected to an AEI MS 10 C 2 mass spectrometer introducing $2.4 \times 10^{19} - 7.2 \times 10^{19}$ molecules over the bare metal surface (3-6 m²). Desorption experiments /5/ were performed in a dynamic flow system: the flow rate of $H_2$ was 20 ml min⁻¹ and the heating rate 5 K min⁻¹. The preparation of metal blacks is given in earlier papers /4, 5/.

RESULTS AND DISCUSSION

The hydrogenolysis activity was characterized by the rate of ethane consumption at 523 K as well as by the threshold temperature ($T_{th}$), which is inversely proportional to the hydrogenolysis activity. The latter value was calculated for a reaction rate of 0.5% m⁻² h⁻¹. The activity pattern shown in the first two rows of Table 1 is in good correlation with Sinfelt's data /2/ measured on silica supported metals.

The average H/C composition of chemisorbed ethane was measured at 428 and 483 K on Co, Ni, Rh, Pd and Pt blacks. Results are shown in the 3rd and 4th rows, respectively. Ethane suffers "deep" dissociation on Co and Ni blacks, a much lower degree of C-H bond rupture on Pt, while Rh occupies a medium position.

The 5th row in Table 1 contains the temperatures at which the hydro-desorbed substrate contains 10 mol% methane, $T_{CH_4}^{10 \text{ mol%}}$. Chemisorption and hydro-desorption was performed under isothermal conditions. This temperature is the lowest for Ni, Co, Ir and Rh catalysts.

The position of the maximum rate of methane formation ($T_{CH_4}^{max}$) determined from TPD curves is summarized in the 6th row. The surface was saturated with ethane at 418-423 K for Co, Ni, Rh, Ru and Ir blacks, whereas at 473 K for Pt and Pd. Before switching on the TP the sample was cooled rapidly to room tem-