THIOPHENE HYDRODESULFURIZATION OVER TRANSITION METAL FOILS: COMPARISON WITH METAL SULFIDES

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The hydrodesulfurization (HDS) of thiophene has been investigated over polycrystalline metal foils of cobalt, molybdenum and rhenium. The measured activities for the Mo and Re foils are similar to those previously determined for low miller index single crystals of Mo and Re. In agreement with published results of HDS studies over unsupported and supported metal sulfides, the HDS activities of the three metal foils were found to increase in the order Co < Mo < Re. These results suggest that it is most probably correct to think of cobalt as a promoter of molybdenum in Co-Mo catalysts, and that metal surfaces are suitable substrates for model studies of HDS.

1. Introduction

The hydrodesulfurization (HDS) process by which sulfur is removed from crude oil feed stocks has been the subject of many surface science and/or catalytic studies using transition metal single crystals as model catalyst surfaces [1–3]. The majority of this research has been carried out under solely ultrahigh vacuum (UHV) conditions and has involved investigation of the bonding and stoichiometric reactions of simple, sulfur containing hydrocarbons with the metal surface. It is not readily obvious how this work relates to the catalytic reactions involved in HDS at high pressures. Work in our laboratory has concentrated on studying the catalytic hydrodesulfurization of thiophene over molybdenum and rhenium single crystals at relatively high pressures \( P_{\text{Th}} = 3.0 \text{ Torr}, \ P_{\text{H}_2} = 780 \text{ Torr} \) and relating results of this work to those of UHV studies of the bonding and reactions of thiophene and its HDS products on the same surfaces [1,4–10].

In this letter we report results from our laboratory on the HDS of thiophene over metal foils of cobalt, molybdenum and rhenium. The former two metals are

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of interest due to their great importance in the industrial HDS process and rhenium because it has been shown to be significantly more active than molybdenum when in sulfided form [11–13]. Metal foils were selected as model catalysts in this work because their polycrystalline nature suggests that they more closely model the heterogeneous structure of an industrial catalyst than do single crystals, which are relatively flat on the atomic scale. In addition, cobalt undergoes a phase transition from face centered cubic to hexagonal close packed structure at 693 K. If a cobalt single crystal is heated above 693 K and then cooled below the transition temperature, the sample is usually rendered polycrystalline. Hence it is impractical to use cobalt single crystals as they are difficult to clean below 693 K.

2. Experimental

The experiments described were carried out in a stainless steel, ultrahigh vacuum chamber (base pressure = 1 × 10⁻⁹ Torr) equipped with an isolation cell for carrying out catalytic reactions at atmospheric pressure and is described in detail elsewhere [14]. Cobalt, molybdenum and rhenium foils were cut from high purity sheets of the metals and were inserted into the UHV chamber without further treatment. The foils had thicknesses in the range 0.005–0.013 cm and areas of 1–2 cm². The molybdenum and rhenium foils were purchased from Alpha Products and the cobalt foil was obtained from the Materials Research Corporation. The metal foils were mounted onto the sample manipulator via 0.05 cm wires of the respective metals which were spot-welded along the length of the foils and attached to the heating feedthroughs by spot-welds. The temperature of the samples was monitored by means of a platinum-platinum 10% rhodium thermocouple spot-welded along the top edge of the foils.

The major impurities in the metal samples were found to be carbon and sulfur as determined by Auger electron spectroscopy (AES). The molybdenum and rhenium foils were cleaned by heating in oxygen (P_{O_2} = 10⁻⁸–10⁻⁵ Torr, T = 1100 K) followed by annealing to 1900 K in vacuum. The cobalt foil was cleaned by ion sputtering with argon (P_{Ar} = 5 × 10⁻⁵ Torr, E = 1.0 keV) followed by annealing to 800 K in vacuum. Following cleaning of the metal foils in UHV, they were enclosed in the atmospheric pressure cell and the reactor loop pressurized with thiophene and hydrogen (P_{Th} = 3.0 Torr, P_{H_2} = 780 Torr). The reactant gases were circulated in the reactor for 30 minutes prior to heating the metal sample to the reaction temperature of 613 K. Gas samples were injected into a gas chromatograph at 15 minute intervals and detected with a flame ionization detector. Catalyst activities were calculated using the product accumulation data from the first 90 minutes of reaction. Following completion of the data collection, the foils were cooled in the reaction mixture, the gases evacuated by means of