Catalysis Letters 3 (1989) 1-8

THIOPHENE HYDRODESULFURIZATION OVER TRANSITION METAL FOILS: COMPARISON WITH METAL SULFIDES

Mark E. BUSSELL * and Gabor A. SOMORJAI

Department of Chemistry, University of California, Berkeley
and Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720, U.S.A.

Received 22 March 1989; accepted 22 May 1989

Thiophene hydrodesulfurization, cobalt, molybdenum and rhenium foils as catalysts

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 ($P_{\mathrm{Th}} = 3.0$ Torr, $P_{\mathrm{H}_2} = 780$ 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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* Current Address: Laboratoire de Physico-Chimie des Surfaces, Ecole Nationale Supérieure de Chimie de Paris, 11, rue Pierre et Marie Curie, 75231 Paris Cedex 05, France.

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 heterogenous 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 cm^2. 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 ($P_{Ar} = 5 \times 10^{-5}$ 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

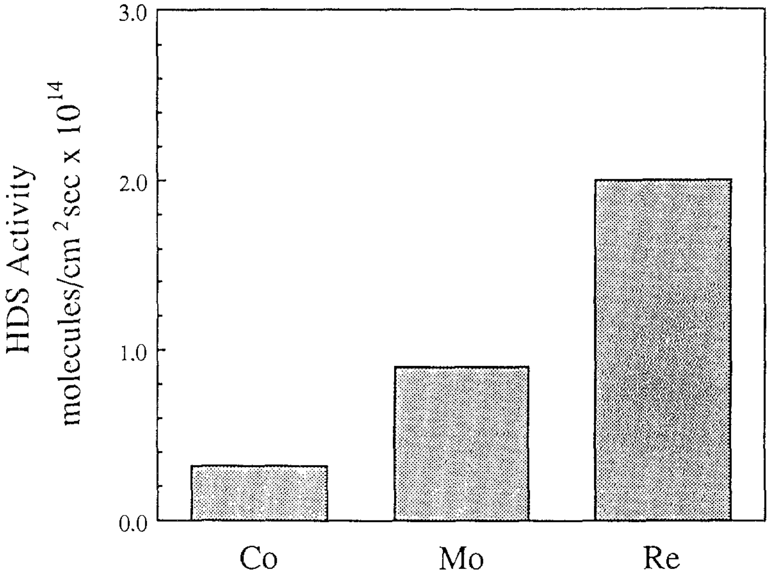

Fig. 1. Thiophene HDS activities for metal foils of cobalt, molybdenum and rhenium.

mechanical and oil diffusion pumps and the isolation cell opened to reexpose the foil to the UHV environment.

3. Results and discussion

The thiophene HDS activities for metal foils of cobalt, molybdenum and rhenium are compared in fig. 1 while typical product distributions obtained over the three metals are shown in table 1. To our knowledge, this is the first reported measurement of the thiophene HDS activity of a cobalt metal sample, whereas the activities of molybdenum and rhenium single crystals have been previously reported [1,7,8,15]. Thiophene HDS has been shown to be a structure insensitive reaction over molybdenum single crystals and the HDS activity of 0.9×10^{14} molecules/cm^{2}sec measured for a Mo foil in this current study agrees within

Table 1
Product distributions for thiophene HDS

Product	Metal foil		
	Cobalt	Molybdenum	Rhenium
butadiene	11.0%	2.5%	7.0%
1-butene	44.0	55.0	47.0
trans-2-butene	24.0	19.5	23.5
cis-2-butene	13.5	12.0	14.0
butane	7.5	11.0	8.5

uncertainty with the values of (1.1–1.2) × 10^{14} molecules/cm^{2}sec determined previously for the (111), (110) and (100) planes of molybdenum. On the contrary, thiophene HDS over rhenium single crystals is a structure sensitive reaction with measured activities of (1.2–7.3) × 10^{14} molecules/cm^{2}sec for the (0001), (1010), (1120) and (1121) faces of rhenium. The value of 2.0 × 10^{14} molecules/cm^{2}sec measured for the thiophene HDS activity of a Re foil falls within the range of activities. The fact that the rhenium foil has an activity between the two extremes measured for the single crystals indicates that the foil surface is composed of a distribution of crystallite faces, with the predominant one being the least active but thermodynamically most stable (0001) face. Based on the results discussed above, it can be concluded that surface defects are not a major factor in determining the activity of molybdenum and rhenium metal surfaces for thiophene HDS. If defect sites exhibited a far higher activity than sites found on a homogeneous surface, then the activity of a foil would be expected to be higher than that of a low miller index single crystal surface. Clearly, this was not observed in this study.

No significant differences were observed in the composition of the surfaces following a ninety minute thiophene HDS reaction. The surfaces of the metal foils were found to be covered with mixed overlayers of sulfur and carbon. Earlier studies using Mo and Re single crystals suggest that the post-reaction surface composition is an artifact which arises during evacuation of the reaction cell and that this composition is not representative of the catalyst surface composition during reaction [4,8]. In the case of molybdenum single crystals, the active catalytic surface was found to be composed of an overlayer consisting of primarily carbidic-type carbon while thiophene HDS over rhenium surfaces is believed to occur directly on the metal surface [4,8]. These differences in the composition of the active catalytic surfaces agree nicely with the observation that thiophene HDS is structure insensitive over molybdenum and structure sensitive over rhenium [1].

Comprehensive studies of hydrodesulfurization over transition metal sulfide catalysts have been carried out by three different laboratories [11–13]. In their pioneering work, Pecoraro and Chianelli measured the activities of unsupported sulfides of the first, second and third row transition metals for the HDS of dibenzothiophene. The research groups of Prins and Ledoux have carried out similar studies using transition metal sulfides supported on carbon and the HDS of thiophene as the test reaction. In each study, a volcano-type dependence of the HDS activity on periodic position was observed for the second and third row transition metal series. The authors are also in qualitative agreement for the trend in activities of the first row transition metal sulfides for which a two-humped curve is observed instead of a volcano curve. Despite these similarities in the shapes of the activity curves, there are considerable differences between the relative activities of specific transition metal sulfides. These discrepencies are most likely due to the difficulty of accurately measuring the active surface area of

Table 2
Comparison of HDS activities

Study	Cobalt	Molybdenum	Rhenium
[a] This work	1.0	2.8	6.3
[b] Ledoux	1.0	1.8	3.4
[c] Prins	1.0	0.55	1.8
[d] Chianelli	1.0	1.0	4.3
[e] Chianelli	1.0	5.7	28
[f] Chianelli	1.0	3.3	13.3

[a] Metal foils.
[b] Metal sulfides supported on carbon [13].
[c] Metal sulfides supported on carbon [12].
[d] Unsupported metal sulfides (rates normalized per m^2 of catalyst) [11].
[e] Unsupported metal sulfides (rates normalized per mmole of metal) [11].
[f] Unsupported metal sulfides (rates normalized per gram of catalyst) [11].

a sulfide catalyst. Pecoraro and Chianelli normalized their activities in three different ways: with respect to the catalyst BET surface areas, the number of millimoles of metal, and the number of grams of metal [11]. The relative activities of the different transition metal sulfides were found to change depending upon what normalization method was used. However, the pronounced volcano shape of the HDS activity versus periodic position curve was observed in each case. Prins and coworkers prepared their catalysts such that the final metal loading was 0.5 metal atom per nm^2 and normalized their HDS activities accordingly, while Ledoux et al. used low metal loadings and assumed complete dispersion of the metal on the catalyst support [12,13]. The advantage to using single crystals or metal foils as model catalysts is that the active surface area of the catalysts can be readily measured. This facilitates direct comparison of the HDS activities of the different metals.

The relative activities of the cobalt, molybdenum and rhenium catalysts measured in the present study using metal foils and also those from the studies employing metal sulfides are listed in table 2 where catalyst activities have been normalized with respect to cobalt. Three sets of activities are given from the work of Pecoraro and Chianelli corresponding to the three different methods of normalization used. It is clearly seen that whereas the trend is the same for the three sets of activities, the relationship between the activities of any two metal sulfides varies dramatically. Comparison of the results of the present study employing polycrystalline foils with the results of the other studies shows the trend in HDS activities to be similar. These results strongly suggest that transition metal surfaces (single crystals and polycrystalline foils) are suitable materials for model studies of hydrodesulfurization. It is not surprising that the results of the present study are not in close agreement with any of the others given the difficulty in normalizing the HDS activities of metal sulfides. However, recent electron microscopy results obtained by Ledoux and coworkers have allowed them to more accurately determine the active surface area of their catalysts, and the resulting ratio of HDS activities derived from this work is 1 : 3.2 : 4.7 for Co, Mo and Re respectively [16]. These results agree quite nicely with those of the present study employing metal foils. If the results of each of the studies listed in table 2 are compared with each other, what is surprising is the difference in the trend of activities measured by Prins and coworkers. Their results show cobalt sulfide to be about two times more active than molybdenum sulfide. In light of the fact that cobalt is generally considered to be a promoter of molybdenum sulfide in the industrial HDS catalyst, determination of the relative activities of cobalt and molybdenum alone is of considerable interest. In a more recent and detailed study of thiophene HDS over carbon supported Co and Mo catalysts, Prins and coworkers found cobalt sulfide to be nearly seven times more active than molybdenum sulfide which led them to propose that cobalt is in fact responsible for the high activity of Co-Mo catalysts and that the role of molybdenum is to keep the cobalt in a highly dispersed state [17]. The large variation of the HDS activities measured for cobalt sulfide is most likely associated with the difficulty of measuring the active surface area of the catalysts, as discussed earlier, but other explanations cannot be ruled out. One possible explanation is that thiophene HDS is a structure sensitive reaction over cobalt sulfide and that the distribution of crystal faces exposed on the catalysts of the various studies is different. Excluding this possibility, however, the results of the present study, those of Ledoux et al., and those of Pecoraro and Chianelli suggest that cobalt is indeed a promoter of Mo-Co HDS catalysts. Cobalt is less active than molybdenum in both metallic and sulfide forms and it seems unlikely, therefore, that cobalt alone is responsible for the high activities of Co-Mo catalysts.

Clearly, additional work needs to be done before the roles of cobalt and molybdenum in HDS catalysts are fully understood. To this end, we are currently investigating the promotional effects of cobalt in Co-Mo catalysts by depositing submonolayer amounts of cobalt on well-defined molybdenum substrates (single crystals and polycrystalline foils) and determining the catalytic properties of these surfaces for the HDS of thiophene.

Acknowledgements

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

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