Catalysis Letters 63 (1999) 21–26

Hydrodesulfurization of tetrahydrothiophene over evaporated Mo, Co and Mo–Co model catalysts

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Received 5 July 1999; accepted 11 September 1999

The hydrodesulfurization (HDS) of tetrahydrothiophene was studied over model catalysts prepared by deposition of Co and Mo thin films on a stainless-steel foil covered with graphite. There are three main findings: (1) the nominal turnover rate for the HDS reaction is approximately constant and independent of the Co to Mo ratio, (2) the main product was 1,3-butadiene for cobalt and 1,3-butadiene and 1-butene for molybdenum, and (3) the reaction is not poisoned by sulfur. The surfaces were characterized by Auger electron spectroscopy (AES) before and after reaction. The reactions were carried out under 2.6 kPa of tetrahydrothiophene and 100 kPa of H_2 at 613 K.

Keywords: hydrodesulfurization of tetrahydrothiophene, Mo model catalyst, Co model catalyst, Mo–Co model catalyst, hydrodesulfurization over Mo, hydrodesulfurization over Co, hydrodesulfurization over Mo–Co

1. Introduction

Sulfided Co–Mo/Al_2O_3 catalysts are extensively used in HDS processes. Over the past few decades, several different models have been proposed for explaining the promotional effect of cobalt. Some of these models include (1) Co–Mo–S model [1–4], (2) contact synergy or remote control model [5–7], (3) the electron-donation model [8,9], and (4) "Co only" model [10–13]. For a recent review of hydrotreating consult Topsøe et al. [14].

Because industrial catalysts have complex structures, it is difficult to characterize the state of the catalyst surface. The approach employed here, and used successfully in a number of systems [15], is one where a model catalyst is utilized for combined reactivity studies at high pressure and surface science studies. Molybdenum single crystals, molybdenum foil, and cobalt foil have been used as model catalysts for HDS studies [16–22]. However, because the industrial catalyst is composed of small particles on a support, another useful approach of modeling a catalyst is to deposit the active phase on a flat support [23]. In particular, a series of papers on Co–Mo–S catalysts using this approach have been published [24–30]. We undertook this work using a combined UHV/high-pressure system to try to gain a detailed understanding of the role of catalyst surface composition employing model Co–Mo catalysts supported on carbon. In this study, we will report the activity of films of Co and Mo for the HDS of tetrahydrothiophene. This molecule is comparatively easier to desulfurize than the thiophenes, benzothiophenes, and dibenzothiophenes present in the petroleum feed stock.

The catalysts were prepared by depositing Co–Mo thin films onto graphite in various compositions under UHV. The reactions were carried out under 2.6 kPa of tetrahydrothiophene and 100 kPa of H_2 at 613 K. Auger electron spectroscopy was used to get information about the composition of the catalyst surface.

In this study, we aimed to establish how the rate and product distribution varies as a function of the cobalt to molybdenum ratio in these thin films.

2. Experimental

2.1. Apparatus

All of the experiments were performed in a stainless-steel ultrahigh-vacuum (UHV) chamber (base pressure 1×10^{-9} Torr) equipped with a retarding grid Auger electron spectroscope (AES), an UTI 100C quadrupole mass spectrometer, metal deposition sources, and a retractable internal isolation cell for catalytic reactions. A stainless-steel reaction loop is connected to the isolation cell and is outfitted with a gas circulation pump and a sampling valve connected to a gas chromatograph. This UHV surface analysis/high-pressure catalytic reaction system has been described in detail elsewhere [31].

2.2. Preparation of catalysts

The sample was a $0.76\times0.76\times0.002$ cm graphite coated stainless-steel foil onto which cobalt and molybdenum were deposited. The stainless-steel foil was spot-welded to two 0.9 mm diameter stainless-steel 304 wires connected to a

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copper manipulator with rotary motion. A chromel–alumel thermocouple was spot-welded to the top edge of the foil for monitoring the sample temperature. The graphite coated stainless-steel foil was prepared by spraying it with Aerodag G (Acheson Colloids Company) followed by drying. Before cobalt and molybdenum deposition, the foil was annealed at 873 K for 5 min under UHV to remove any remaining alcohol and volatile impurities.

The absence of surface oxygen species from the graphite or Fe, Cr, and O from the stainless-steel substrate could be confirmed by AES as in the previous work by Jernigan et al. [32].

The Co–Mo thin films were prepared by deposition from two simultaneous evaporation sources. Cobalt deposition was performed by heating a 0.8 mm diameter tungsten wire wrapped with a 1 mm wide strip of 0.17 mm thickness cobalt foil (Materials Research Corporation). The source was resistively heated by a direct current power supply at 20 A and 1.2 V. Molybdenum deposition was performed with a rod-fed electron beam source (MDC e-vap 90). The deposition was made by heating a 1 mm diameter molybdenum rod (Thermo Shield) by means of electron bombardment (2 kV, 7.8–9.0 mA emission).

Before deposition, the cobalt and molybdenum evaporation sources were outgassed extensively with the sample shutters closed.

The cobalt and molybdenum covered graphite coated stainless-steel foil was then annealed at 700 K for 1 min allowing cobalt and molybdenum to diffuse on the graphite surface. The fraction of cobalt, molybdenum and carbon on the foil was followed by AES. According to the reference Auger spectra [33], the clean surface had less than 7% of a monolayer of sulfur and oxygen.

2.3. Characterization of the catalysts

Auger spectra were taken before and after each catalytic reaction. The cobalt to molybdenum ratio on graphite was calibrated by the ratio of the Co 755 eV AES peak height to the combined Co 755 eV + Mo 186 eV AES peak height since the sensitivity of the Co 755 eV AES peak is nearly equal to that of the Mo 186 eV AES peak [33].

The Auger spectrum after reaction was measured after evacuation of the reaction cell with a diffusion pump at room temperature and exposure of the sample to the main cell. After the vacuum reached about 1×10^{-7} Torr, the spectrum was measured.

2.4. Catalytic activity measurements

The catalytic activities of the catalysts for tetrahydrothiophene were measured in a batch reactor (reactor volume 400 cm^3). After the sample was prepared and characterized by AES in UHV, it was enclosed in the high-pressure cell. Tetrahydrothiophene (Kanto Chemical, 99+% purity) was degassed by freeze–thaw cycles before use and was introduced to the catalytic reactor system prior to hydrogen (Bay Air Gas, 99.99% purity). Hydrogen was passed through a liquid-nitrogen trap to remove volatile impurities. All of the activity measurements were carried out under reaction conditions of 2.6 kPa of tetrahydrothiophene and 100 kPa of H_2 at 613 K.

The product analysis was performed by an on-line gas chromatograph (Hewlett–Packard 5890-II) equipped with a frame ionization detector and a 7 feet long, $1/8$ inch wide stainless-steel packed column containing 0.19% picric acid on Graphpac-GC, 80/100 (Alltech Associates, Inc.). The reactant gases were circulated for 20 min before the foil was heated to reaction temperature to ensure good mixing. The first analysis was performed after 3 min of reaction and subsequent analyses were carried out at intervals of 18 min. Each reaction was carried out for about 75 min. The turnover rate was calculated from the slopes of product accumulation curves determined as a function of reaction time. In this paper, the rates were described as nominal turnover rates. The nominal turnover rates were calculated assuming that all surface metal atoms are active (cobalt and molybdenum) with a surface density of 1×10^{15} atoms/cm^2. Blank reaction studies, carried out over graphite coated stainless-steel foil without cobalt and molybdenum, revealed a background catalytic activity corresponding to 20% of the activity measured for the cobalt and molybdenum multilayer covered graphite coated stainless-steel foil. All results of the activity measurements were calculated by subtracting the blank activity.

It is important to report that we were not able to measure any activity on the Co and Mo thin films or foils for the HDS of thiophene. We have used the same conditions reported earlier by Gellman [16] and Bussell [17] for the HDS of thiophene on foils and single crystals.

3. Results and discussion

3.1. Co and Mo depositions onto graphite coated stainless steel

The measurement of AES was used for the characterization of the deposited films on graphite coated stainless-steel foil.

Figure 1 (a) and (b) shows the change of the Co 755 eV and C 272 eV Auger peak intensities as a function of deposition time. The curves can be interpreted by assuming a Frank–van der Merwe layer-by-layer growth mechanism [34,35]. By fitting straight lines we find breaks at 5 and 10 min metal evaporation time. The break at 5 min cobalt evaporation time is assigned to a coverage of one monolayer. Figure 2 (a) and (b) shows the change of the Mo 186 eV and C 272 eV Auger peak intensities as a function of deposition time. The curves can be interpreted by assuming a Frank–van der Merwe layer-by-layer growth mechanism similar to the one for cobalt deposition. By fitting straight lines we find breaks at 5 and 10 min metal

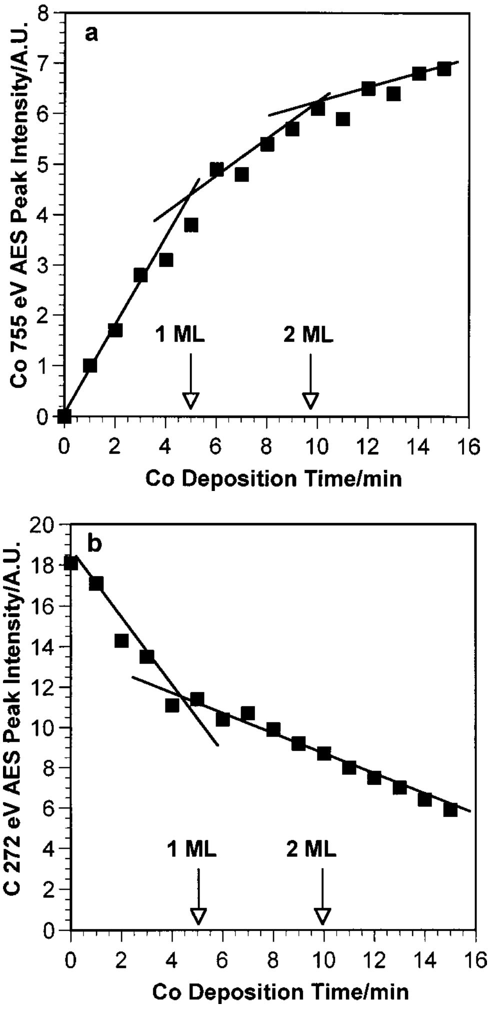

Figure 1. Variation of Auger signal intensity as a function of Co deposition time on a graphite coated stainless-steel foil: (a) cobalt 755 eV and (b) carbon 272 eV.

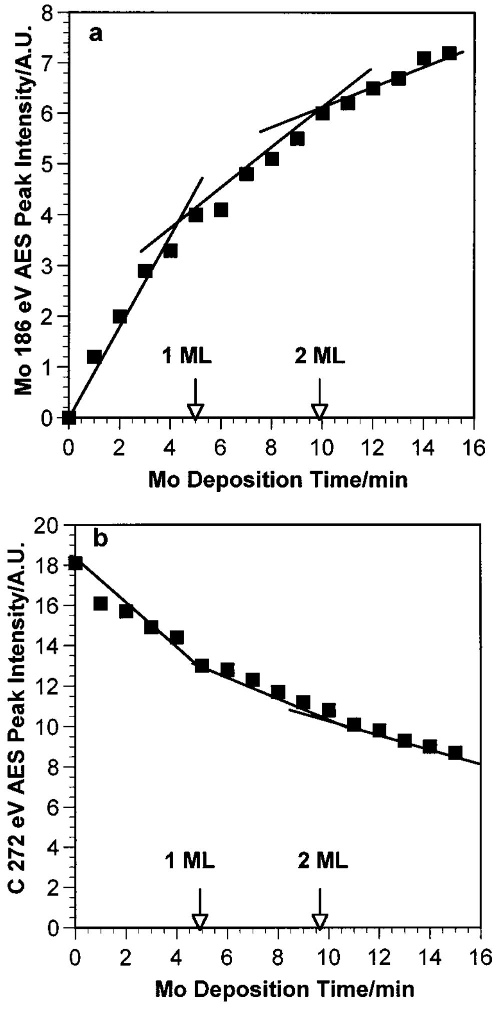

Figure 2. Variation of Auger signal intensity as a function of Mo deposition time on a graphite coated stainless-steel foil: (a) molybdenum 186 eV and (b) carbon 272 eV.

evaporation time. The break at 5 min molybdenum evaporation time is assigned to a coverage of one monolayer.

The effect of annealing on the Auger signals of both metal adlayers was also studied since the catalytic activity was determined after annealing of the sample. The Co/C and Mo/C Auger peak height ratios were investigated as a function of metal deposition time before and after the samples were annealed at 700 K for 1 min.

The results, which are given in figure 3 (a) and (b), show that the Co/C and Mo/C Auger peak ratios are unchanged before and after annealing. This indicates that island formation and migration of cobalt and molybdenum into the graphite do not occur.

Furthermore, the coverage of the cobalt and molybdenum on graphite coated stainless-steel foil was monitored by tetrahydrothiophene HDS reactions. Because the HDS reaction does not happen on graphite, if the surface of graphite is completely covered by each metal, the values of the nominal turnover rates should increase up to one monolayer and then it should remain constant. Figure 4 (a) and (b) shows the changes in the nominal turnover rates per total surface atom over the cobalt and molybdenum covered graphite coated stainless-steel foils as a function of deposition time. The nominal turnover rates of each foil increased with respect to the deposition time up to 5 min, at which point one monolayer is formed. The value of the nominal turnover rate was constant after this point.

The deposition time for the formation of one monolayer agrees with the value calculated from the AES measurements.

3.2. Tetrahydrothiophene hydrodesulfurization on Co and Mo system

The HDS reaction studies of tetrahydrothiophene were performed over the cobalt and molybdenum covered graphite coated stainless-steel foils. The deposition of cobalt and molybdenum was performed for 30 min. The product accumulation curves of the HDS of tetrahydrothiophene over each foil is shown in figure 5 (a) and (b). There are three important features: (1) the nominal turnover rates for HDS reaction on cobalt is nearly equal to those on molybdenum, (2) the product distributions differ signifi-

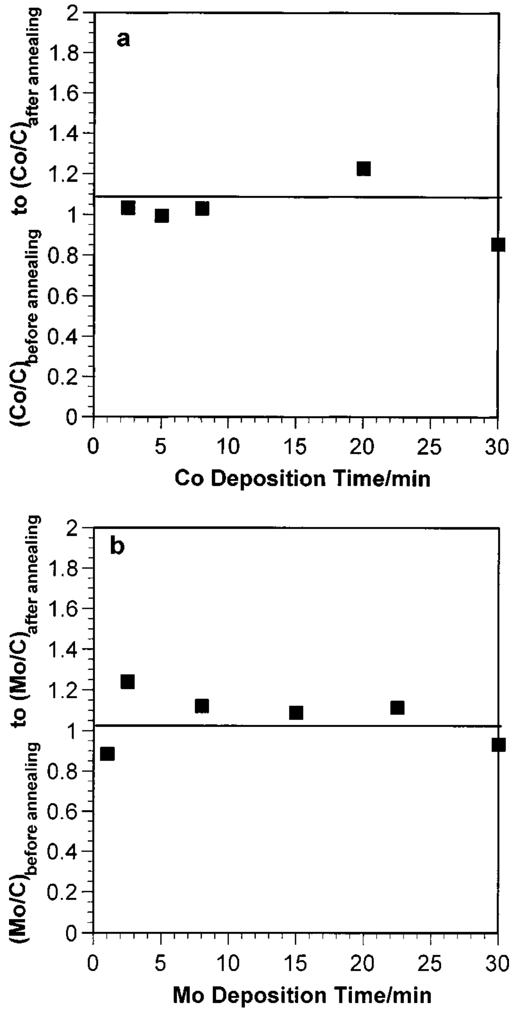

Figure 3. Ratio of Auger signal intensity before and after annealing at 700 K as a function of metal deposition time: (a) ratio of Co 755 eV to C 272 eV and (b) ratio of Mo 186 eV to C 272 eV.

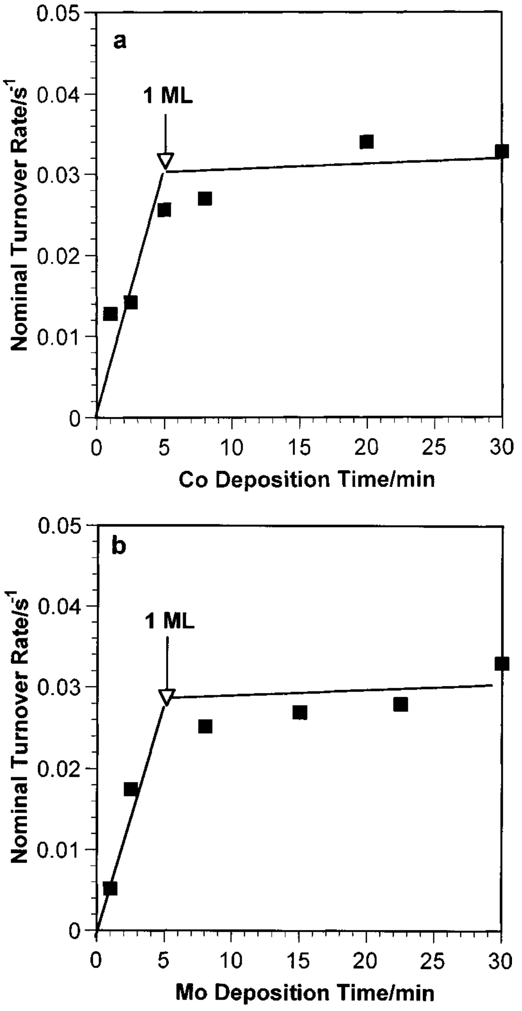

Figure 4. Nominal turnover rate for the hydrodesulfurization of tetrahydrothiophene over metal supported on graphite coated stainless-steel foil: (a) cobalt and (b) molybdenum. Reaction carried out at 2.6 kPa of tetrahydrothiophene, 100 kPa of H_2, at 613 K.

cantly for the two metals, and (3) poisoning does not occur over either metal.

The great difference between cobalt and molybdenum is the selectivity of 1,3-butadiene and 1-butene. In the case of cobalt, the reaction products were 1,3-butadiene, 1-butene, *trans*-2-butene, and *cis*-2-butene. The main product was 1,3-butadiene. No butane was found in the hydrocarbon products.

On the other hand, in the case of molybdenum, the reaction products were 1,3-butadiene, 1-butene, *trans*-2-butene, *cis*-2-butene, and a small amount of n-butane. The main products were 1,3-butadiene and 1-butene.

Moser et al. [36] studied the HDS reaction of tetrahydrothiophene over a commercial Co–Mo/Al_2O_3 using the temporal analysis of products (TAP) transient microreactor technique. Their results showed that 1,3-butadiene and butene were the only hydrocarbon HDS products and they assumed that the production of butene was not by way of production of 1,3-butadiene.

It is interesting to note again that this catalyst was not active for the hydrodesulfurization of thiophene. This property may be useful in the design of a selective HDS catalyst.

3.3. *Tetrahydrothiophene hydrodesulfurization on Co/Mo system*

The reaction studies of the conversion of tetrahydrothiophene were performed on various ratios for the cobalt and molybdenum covered graphite coated stainless-steel foil. The cobalt to molybdenum ratio was controlled by changing the emission current of the molybdenum deposition source. The deposition was performed for 30 min. The results are presented in figure 6 (a) and (b). As the ratios of the cobalt to molybdenum were changed, the turnover rates were not altered.

The amount of 1,3-butadiene increased steadily according to the increase of the amount of cobalt, while the amounts of 1-butene and *cis*-2-butene decreased. The amount of *trans*-2-butene was unchanged. No butane was found in the hydrocarbon products except for the molybdenum only film.

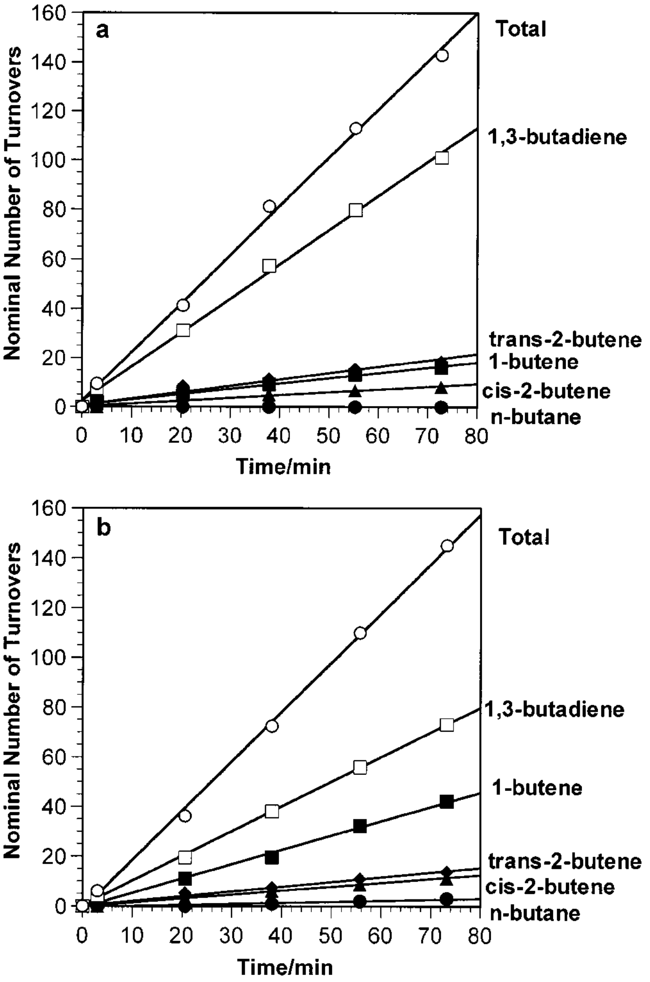

Figure 5. Product accumulation curves for the hydrodesulfurization of tetrahydrothiophene over metal supported on graphite coated stainless-steel foil: (a) cobalt and (b) molybdenum. Reaction carried out with 2.6 kPa of tetrahydrothiophene, 100 kPa of H_2, at 613 K. Number of turnovers is the number of molecules transformed per atom on the surface.

The reaction rate does not change as a function of the cobalt to molybdenum ratio, in contrast to an industrial catalyst where cobalt is a promoter. The difference in behavior is probably due to the different morphologies of the active phase. On the model catalyst mostly basal planes of MoS_2, with no edges available, are present; on the industrial catalyst, edge sites of MoS_2 decorated with Co sites are believed to be the active sites.

3.4. Sulfur surface concentrations on Co/Mo system after reaction

The amount of sulfur after reaction was investigated by AES. As shown in figure 7, the build-up of sulfur was detected on the catalyst surface. Also, the amount of sulfur does not change as a function of the cobalt to molybdenum ratio. Because the peak height ratio of the S 152 eV to the Mo 186 eV for a MoS_2 single crystal is about 13.8 [37], it seems that sulfur covers more than 50% of the catalyst surface. Nevertheless, because the turnover rates were not decreased, it is reasonable to conclude that sulfur does not

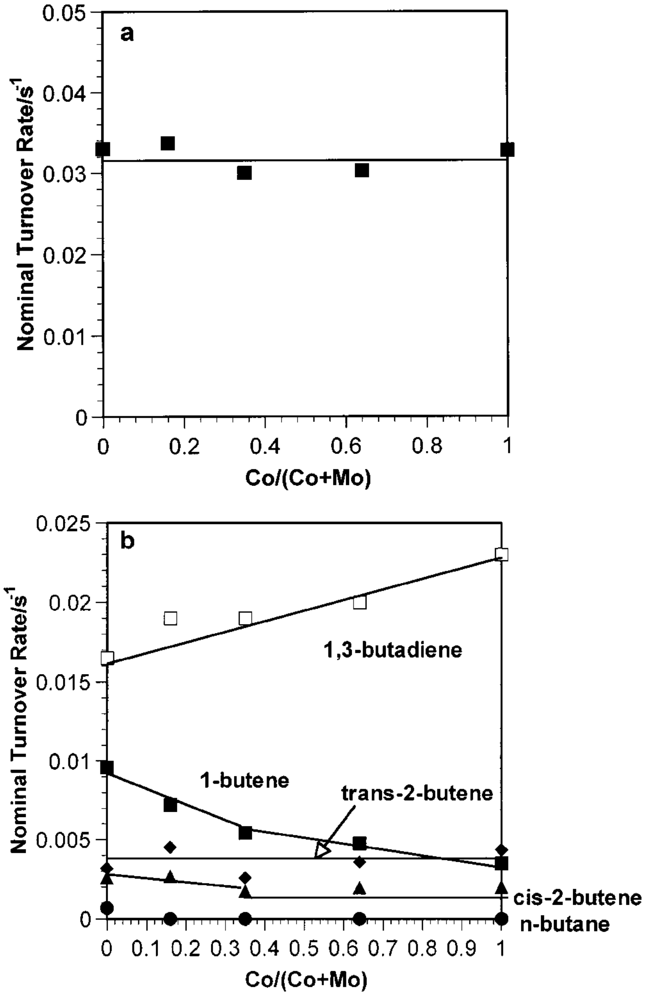

Figure 6. Nominal turnover rate: (a) total rate and (b) individual rates (1-butene, *n*-butane, *cis*-2-butene, *trans*-2-butene, and 1,3-butadiene) for the hydrodesulfurization of tetrahydrothiophene as a function of cobalt to molybdenum ratio. Reaction carried out with 2.6 kPa of tetrahydrothiophene, 100 kPa of H_2, at 613 K.

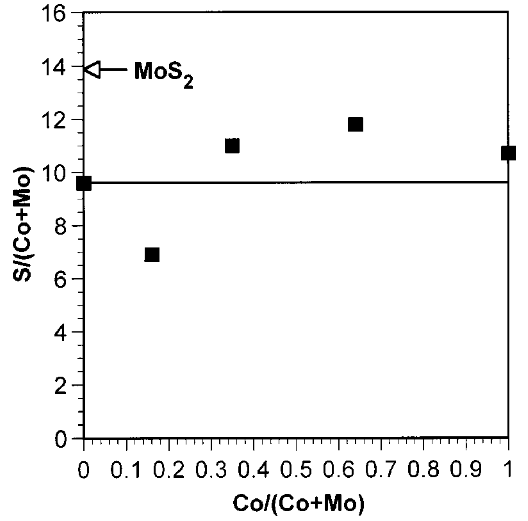

Figure 7. Ratio of S 152 eV to (Co 755 eV + Mo 186 eV) AES intensity after reaction as a function of cobalt to molybdenum ratio.

affect the catalytic activity. Bussell et al. [20] found that the reaction rate of thiophene HDS was decreased by the deposition of sulfur over the Mo(100) surface. It seems that the dependence of sulfur on the HDS reaction for thiophene is very different from the HDS reaction for tetrahydrothiophene.

4. Conclusions

The HDS turnover rate of tetrahydrothiophene on a Co thin film is the same as the one on a Mo thin film. Deposition of sulfur and carbon during reaction do not affect the catalytic rates. The turnover rate does not change as a function of the cobalt to molybdenum ratio on the HDS of tetrahydrothiophene over Co–Mo metal thin films. The reason for the absence of the promotional effect of Co on Mo may be due to the absence of edge MoS_2 sites on our samples.

Acknowledgement

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the US Department under Contract DE-AC03-76SF0098. TF acknowledges the financial support from Japan Cooperation Center for Petroleum Industry Development (JCCP) and Cosmo Oil Co., Ltd.

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