

# Thiophene HDS chemistry on monolayer Ni films on W(1 1 0) and Ru(0 0 0 1)

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## Abstract

The current paper presents a surface science study of the reaction pathways of thiophene on Ni/W(1 1 0) and Ni/Ru(0 0 0 1) surfaces. Using Auger electron spectroscopy (AES) and temperature-programmed desorption (TPD), we have shown that depositing Ni on a W(1 1 0) surface enhances the yield of the selective hydrodesulfurization (HDS) products, butene and butane. On Ni/W(1 1 0) surfaces with Ni coverages of 0.4 ML Ni, the butene product starts to desorb from the surface at ~178 K. In contrast, at Ni coverages above 2 ML, the butene product desorbs in two peaks at 209 and 259 K. When H<sub>2</sub> is pre-adsorbed on the Ni/W(1 1 0) surface, both butene and butane are detected at temperatures between 179 and 200 K on surfaces with Ni coverages between 0.3 and 0.5 ML Ni. For comparison, the Ni/Ru(0 0 0 1) surfaces also produce butene from the HDS of thiophene at temperatures below 300 K. However, pre-adsorbed hydrogen has only a relatively minor effect on the overall HDS activity of thiophene on the 1 ML Ni/Ru(0 0 0 1) surface.

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**Keywords:** Hydrodesulfurization (HDS); Bimetallic; Thiophene; Ni/W; Ni/Ru

## 1. Introduction

The implementation of more stringent emission regulations has increased the demand for more efficient catalysts to remove sulfur from petroleum feedstocks. Using the model reaction of thiophene hydrodesulfurization (HDS), one can gain a better fundamental understanding of the hydroprocessing of crude oil. Investigations of thiophene HDS on model surfaces can also help improve the understanding of HDS mechanisms on catalytic materials. For example, it is well known that bimetallic catalysts often exhibit enhanced activity and higher selectivity towards hydrogenation and HDS reactions compared to that of the pure metal systems [1]. Ideally, in HDS, the C–S bonds will be broken but the C–C will remain intact, forming hydrocarbon molecules. Nickel has been shown to be a promoter

in these catalytic reactions [2–4]. For this reason, we have performed a comparative study of the HDS activity and selectivity of Ni/W(1 1 0) and Ni/Ru(0 0 0 1) surfaces to determine the role of Ni in the HDS of thiophene through model surface science investigations.

Our previous study has shown that a Ni/Pt(1 1 1) surface, at 1 ML Ni coverage, exhibits HDS and hydrogenation activities at low temperatures [5,6]. Specifically, the HDS of thiophene is a thermodynamically favorable reaction and should be performed at low temperatures. However, the kinetics limits this reaction, forcing it to be run at high temperatures in industrial processes. As shown in our earlier study, on the 1 ML Ni/Pt(1 1 1) surface, atomic hydrogen is more weakly bonded to the surface than on either Pt(1 1 1) or thick Ni films. This weakly bonded hydrogen leads to the cleavage of C–S bonds of thiophene and the formation of C<sub>4</sub> hydrocarbons at temperatures as low as 230 K [5]. For comparison, the current paper will focus on the reactivity of Ni/W(1 1 0) and Ni/Ru(0 0 0 1) surfaces toward the low-temperature HDS of thiophene. Our interest in the HDS of thiophene on Ni/W(1 1 0) and Ni/Ru(0 0 0 1) is also related to the fact that Ni/W bimetallic sulfides are utilized in commercial HDS

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applications and that ruthenium sulfides are also known to be highly reactive towards the HDS reaction [7,8].

## 2. Experimental

The ultrahigh-vacuum (UHV) chamber used in the current investigation is a two-level stainless steel chamber (base pressure of  $1 \times 10^{-10}$  Torr) equipped with Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and temperature-programmed desorption (TPD). For the TPD experiments, the Ni/W(1 1 0) or Ni/Ru(0 0 0 1) surface was heated with a linear heating rate of 3 K/s. In addition, the opening of the random flux shield of the quadrupole mass spectrometer was placed at a distance of  $\sim 5$  mm from the sample surface. The experimental setup allowed us to monitor up to 12 masses simultaneously.

The W single crystal sample was a [1 1 0] oriented, 1.5 mm thick tungsten disk (99.999%), 8 mm in diameter. The Ru single crystal was a [0 0 0 1] oriented, 1.3 mm thick ruthenium single crystal (99.999%), 12 mm in diameter. The crystals were spot welded directly to two tantalum posts that served as electrical connections for resistive heating, as well as thermal contacts for cooling with liquid nitrogen. With this mounting scheme, the temperature of the crystals could be varied between 90 and 1200 K. The crystal surfaces were cleaned with O<sub>2</sub> treatment and by Ni sputtering, followed by annealing at 1200 K. Surface cleanliness was monitored using AES. For Ru(0 0 0 1), the Ru peak overlaps with the C peak, therefore O<sub>2</sub> was dosed and the reaction product CO (28 amu), was monitored using TPD to determine the cleanliness. The ratio of Ru (235 eV) and Ru (277 eV) AES peaks was calibrated on a clean Ru(0 0 0 1) surface; this ratio was used to verify the cleanliness of Ru(0 0 0 1) in subsequent experiments.

Thiophene (Aldrich, >99% purity) was purified by successive freeze–pump–thaw cycles prior to its use. The purity was verified in situ by mass spectrometry. Oxygen and hydrogen were research grade purity and were introduced into the UHV chamber without further purification. In all experiments, thiophene and hydrogen exposures were made at a crystal temperature of 110 K with the crystal surface located in front of a directional dosing tube of 8 mm in diameter. The directional dosing tube allowed a small dosage (0.5 L, 1 Langmuir (L) =  $1 \times 10^{-6}$  Torr s) to result in a multilayer coverage of thiophene. To avoid unnecessary confusion we will not use the Langmuir unit in the current paper. All surfaces described in the current paper were exposed to the identical exposure (0.5 L) that would result in multilayer coverage of thiophene.

The preparation and characterization of the Ni/W(1 1 0) surfaces has been described in detail previously [9]. On both W(1 1 0) and Ru(0 0 0 1) surfaces, the substrates were maintained at 600 K during Ni deposition to prevent CO adsorption. The Ni deposition was checked for uniformity on the W(1 1 0) and Ru(0 0 0 1) surfaces using AES. The coverage

of the Ni overlayer was estimated based on the reduction of the W (182 eV) [9] or Ru (277 eV) peak and the appearance of the Ni (60 eV) peak after the deposition of Ni.

## 3. Results and discussion

### 3.1. HDS activity of Ni/W(1 1 0) surfaces

The Ni/W(1 1 0) surface has been characterized extensively by various techniques in numerous research groups. We have utilized AES and XPS to characterize the Ni/W(1 1 0) surfaces with different Ni coverages [9]. Other groups have also studied the Ni/W(1 1 0) surface using various other techniques (STM, UPS, LEED) [10–17]. Briefly, these studies have shown that Ni grows on W(1 1 0) in a kinetically limited Stranski–Krastanov (SK) growth model. At temperatures below 300 K, the Ni grows in a layer-by-layer mode. However, annealing surfaces to 600 K and above with coverages above 1 ML results in island formation, with the first monolayer being stable upon annealing to 790 K [16]. XPS studies also indicate that there is negligible change in the core electron binding energy of Ni (2p) from 0.5 to 30 ML Ni/W(1 1 0) [9,11]. However, UPS studies show that the Ni band structure appears to be narrower at 1 ML Ni, but widens at Ni coverages above 2 ML [13,14]. Lastly, a significant amount of tensile strain is present due to the lattice mismatch on submonolayer Ni/W(1 1 0) surfaces. This strain arises with the presence of a (7 × 1) overlayer structure of Ni on W(1 1 0) at Ni coverages up to 0.4 ML [16].

In our previous study of cyclohexene chemistry on Ni/W(1 1 0), we first used hydrogen to probe the chemical properties of the surface [9]. Hydrogen desorbs at  $\sim 250$  K from Ni/W(1 1 0) surfaces with coverages up to 1 ML Ni [9,18]. On a 0.4 ML Ni/W(1 1 0) surface, cyclohexene hydrogenation occurs at  $\sim 234$  K. In contrast, cyclohexene hydrogenation does not occur on the clean W(1 1 0) surface or surfaces with Ni coverages above 1 ML [9,18]. In the current study, we have chosen the HDS reaction of thiophene as a probe reaction to determine the hydrogenation reactivity involving the cleavage of C–S bonds on Ni/W(1 1 0).

#### 3.1.1. TPD results of thiophene

Fig. 1 shows the desorption of thiophene (84 amu), hydrogen (2 amu), butene (41 amu) and butane (43 amu) from Ni/W(1 1 0) surfaces. Butadiene (39 and 54 amu), CO (28 amu) or H<sub>2</sub>S (34 amu) were not detected in the TPD measurements (spectra not shown). Fig. 1(a) shows that thiophene desorbs from all surfaces at 147 K (multilayer) and between 166 and 175 K (monolayer). The temperature for monolayer desorption is slightly higher for the clean W(1 1 0) surface (175 K) and slightly lower for Ni/W(1 1 0) surfaces (166–168 K). This additional molecular desorption peak at 166–175 K peak can be attributed to thiophene from either the first monolayer or strongly-bonded second layer. Fig. 1(b) shows the desorption of the H<sub>2</sub> product from the

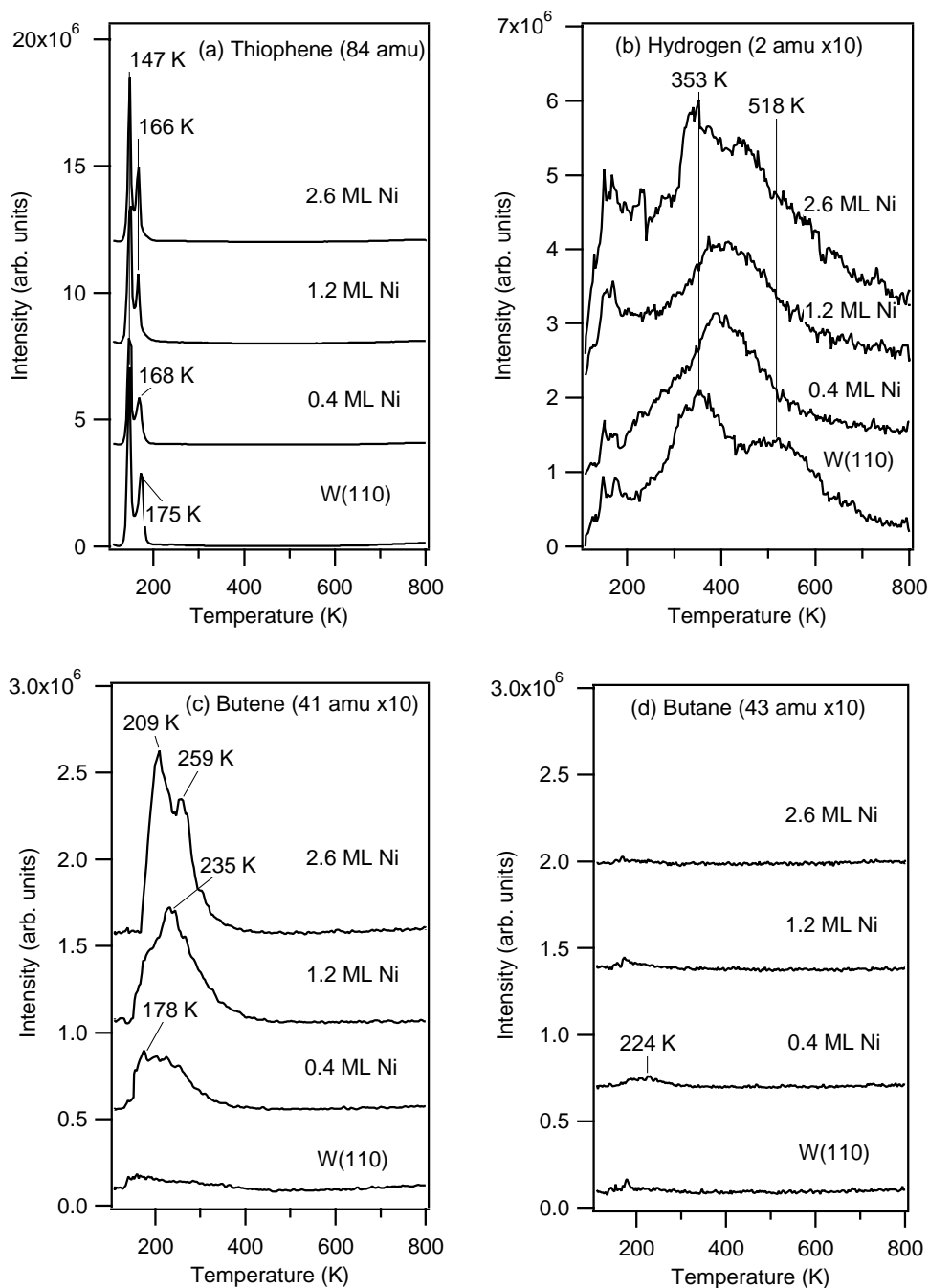


Fig. 1. Thiophene (84 amu) (a), hydrogen (2 amu) (b), butene (41 amu) (c) and butane (43 amu) (d) from multilayer thiophene exposure on Ni/W(110) surfaces as a function of Ni coverage.

surfaces. On W(110), hydrogen desorbs from the surface in two broad peaks, at 353 and 518 K. As shown in Fig. 1(c) and (d), C<sub>4</sub> products are not produced from the reaction of thiophene on clean W(110).

On the Ni/W(110) surfaces, a distinct difference is seen in the desorption products because thiophene undergoes HDS to form butene. Hydrogen desorbs in one broad peak, ranging from 300 to 500 K. On the 0.4 ML Ni/W(110) surface, the desorption of the butene product occurs as a broad peak

centered at ~210 K, although the onset temperature of desorption is as low as 178 K. The peak center increases to approximately 235 K on the 1.2 ML Ni/W(110) surface. When more Ni is deposited (2.6 ML Ni), two peaks appear at 209 and 259 K. The overall TPD peak shape of butene desorption at coverages above 2 ML Ni/W(110) is very similar to that observed on thick Ni(111) films deposited on Pt(111) [5]. Very small amount of butane is also observed on surfaces with 0.4 ML Ni.

### 3.1.2. Calculation of activity/selectivity of thiophene HDS on Ni/W(1 1 0)

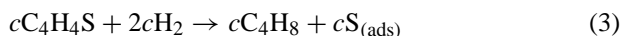
The reaction pathways of thiophene on a clean W(1 1 0) surface, a 0.4 ML Ni/W(1 1 0) surface, and a 1.2 ML Ni/W(1 1 0) surface are shown below, as seen in Fig. 1.



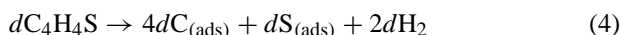
0.4 ML Ni/W(1 1 0) :



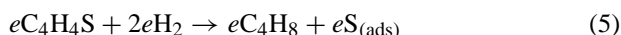
0.4 ML Ni/W(1 1 0) :



1.2 ML Ni/W(1 1 0) :



1.2 ML Ni/W(1 1 0) :



Since thiophene decomposition is the only reaction pathway present on the W(1 1 0) surface, the activity can be estimated from AES measurements. From the C/W AES atomic ratio (including the sensitivity factors of C and W) obtained after heating thiophene on a clean W(1 1 0) surface to 800 K, the activity toward thiophene decomposition (value  $a$ ) on W(1 1 0) was calculated to be 0.145 molecules/W atom (shown in Eq. (6)) where 0.6143 and 0.6527 are the Auger sensitivity factors for C (270 eV) and W (182 eV) obtained from the PHI AES handbook.

$$\frac{(\text{C AES}/0.6143)/(\text{W AES}/0.6527)}{4 \text{ carbon atoms}/\text{C}_4\text{H}_4\text{S molecule}} = \frac{0.57}{4} = 0.145 \quad (6)$$

On the 0.4 ML Ni/W(1 1 0) surface, the TPD peak area ratio of butane (43 amu)/butene (41 amu) was determined to be less than 0.10. Therefore, we assume that the amount of butane produced on the 0.4 ML Ni/W(1 1 0) surface is small and is not included to simplify the activity/selectivity calculations. In addition, it should be pointed out that from thiophene adsorbed on the Ni/W(1 1 0) surfaces, the highest theoretical selectivity towards HDS is 50%. This is because for every C<sub>4</sub>H<sub>8</sub> molecule that is produced, a C<sub>4</sub>H<sub>4</sub>S molecule has to decompose to produce the four H<sub>(a)</sub> atoms that are required for the production of butane.

In order to calibrate the production of butene on the Ni/W(1 1 0) surfaces, a O/W(1 1 0) surface was exposed to 1 L 1-butene at liquid nitrogen temperature, shown in Fig. 2. The O/W(1 1 0) surface was used because it is an inert surface, and all of the butene desorbed molecularly in the TPD measurement. After the TPD experiment, the surface was checked with AES, which confirmed that butene did not undergo decomposition, as indicated by the absence of carbon on the surface. The O/W(1 1 0) surface was exposed to 1 L 1-butene again and an AES measurement was taken at 90 K

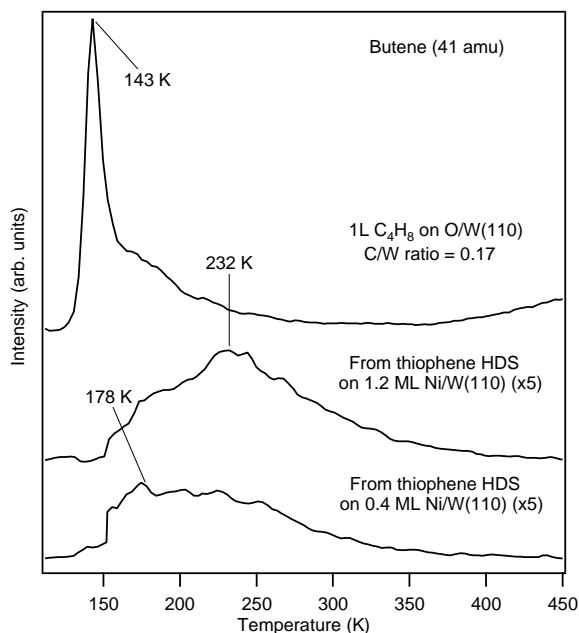


Fig. 2. Comparison of butene (41 amu) from 1 L exposure on O/W(1 1 0) with that of butene produced from a saturation exposure of thiophene on Ni/W(1 1 0) surfaces.

in order to estimate the amount of 1-butene on the surface. The peak area from that TPD corresponds to an atomic C/W ratio of 0.17, which corresponds to 0.043 1-butene molecules per W atom, based on the AES measurement.

Using this value (0.043) obtained from the C/W AES ratio and the ratio of peak areas of butene on Ni/W(1 1 0) and O/W(1 1 0) (shown in Eq. (7)), the activity towards hydrodesulfurization (value  $c$ ) was calculated to be 0.006 from the following equation:

$$\frac{\text{C}_4\text{H}_8 \text{ on } 0.35 \text{ ML Ni/W}(1\ 1\ 0)}{\text{C}_4\text{H}_8 \text{ on O/W}(1\ 1\ 0)} = 0.14 = \frac{c}{0.043} \quad (7)$$

Additionally, the activity for decomposition, value  $b$ , was calculated using the values for  $a$ ,  $c$  and the ratio between the H<sub>2</sub> peak areas from the clean W(1 1 0) and 0.4 ML Ni/W(1 1 0) surfaces, as shown in Eq. (8) as follows:

$$\frac{\text{H}_2 \text{ on W}(1\ 1\ 0)}{\text{H}_2 \text{ on } 0.35 \text{ ML Ni/W}(1\ 1\ 0)} = 1.8 = \frac{a}{b - c} \quad (8)$$

This leads to a value of  $b$  to be 0.087. In addition, the calculations for the activity and selectivity on the 1.2 ML Ni/W(1 1 0) surfaces were performed in the same manner as for the 0.4 ML Ni/W(1 1 0) surface (shown in Eqs. (9) and (10)), giving the values for  $d$  and  $e$  to be 0.120 and 0.009, respectively, from the following two equations:

$$\frac{\text{C}_4\text{H}_8 \text{ on } 1.2 \text{ ML Ni/W}(1\ 1\ 0)}{\text{C}_4\text{H}_8 \text{ on O/W}(1\ 1\ 0)} = 0.21 = \frac{e}{0.043} \quad (9)$$

$$\frac{\text{H}_2 \text{ on W}(1\ 1\ 0)}{\text{H}_2 \text{ on } 1.2 \text{ ML Ni/W}(1\ 1\ 0)} = 1.3 = \frac{a}{d - e} \quad (10)$$

These activity values, together with the corresponding selectivity values of selective HDS and complete decomposi-

Table 1  
Activity and selectivity of thiophene HDS on different Ni/W(1 1 0) surfaces

Surface	Activity (per W atom)			Selectivity (%)	
	Decomposition	C <sub>4</sub> H <sub>8</sub>	Total	Decomposition	C <sub>4</sub> H <sub>8</sub>
W(1 1 0)	0.145	–	0.145	100	0
0.4 ML Ni/W	0.087	0.006	0.093	93.5	6.5
1.2 ML Ni/W	0.120	0.009	0.129	93	7
H <sub>(a)</sub> /0.4 ML Ni/W	–	0.014	–	–	–

tion, are summarized in Table 1. As compared in this table, the Ni/W(1 1 0) surfaces are not very selective to C<sub>4</sub> production under UHV conditions. However, the important observation is the low-temperature HDS activity of the 0.4 ML Ni/W(1 1 0) surface, which shows an onset temperature for C<sub>4</sub> production as low as 160 K.

### 3.1.3. Effect of pre-adsorbed hydrogen on Ni/W(1 1 0)

Fig. 3 shows the effect of pre-adsorbed hydrogen on the W(1 1 0) and Ni/W(1 1 0) surfaces. In these experiments, the W(1 1 0) and Ni/W(1 1 0) surfaces were exposed to 0.5 L H<sub>2</sub>, corresponding to submonolayer coverage prior to the adsorption of thiophene. On the Ni/W(1 1 0) surfaces, the production of butene and butane occurs as sharp peaks at ~179 K. Based on the comparison of the TPD peak areas with and without hydrogen, the pre-adsorbed hydrogen increases the HDS activity for the production of butene on 0.4 ML Ni/W(1 1 0) by a factor of 2.4. At this Ni coverage, our previous study also showed a unique low-temperature cyclohexene hydrogenation pathway, which was tentatively attributed to the enhanced tensile strain of the Ni overlayer at 0.4 ML [9]. As more Ni is deposited, the intensity of the 179 K peak decreases, which is accompanied by a broadening of the butene desorption peaks. In addition to an increase in butene production, the formation of butane is also observed at ~179 K on all Ni/W(1 1 0) surfaces, indicating that the presence of pre-adsorbed H<sub>(a)</sub> enhances the production of the fully-hydrogenated HDS product.

### 3.2. HDS activity of Ni/Ru(0 0 0 1) surfaces

The Ni/Ru(0 0 0 1) surfaces have also been characterized by different surface science techniques by several research groups [19–23]. The electronic properties have been studied by XPS and angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) [19,21]. The XPS studies have shown a shift in the Ni 2p peak energy of 0.3 eV from a thick Ni film to 1 ML Ni/Ru(0 0 0 1), which is larger than that observed for Ni/W(1 1 0) [19]. Houston et al. have shown an increase in the density of d states near the Fermi level on the Ni/Ru(0 0 0 1) surfaces as compared to the bulk pure metals [21]. The physical properties of the surfaces were also studied using AES and STM [20,22,23]. At room temperature, Ni grows in a layer-by-layer growth. However, upon additional heating Ni agglomerates into large islands

at Ni coverages above 1 ML, although Ni/Ru(0 0 0 1) surfaces with submonolayer coverages were reported to be stable up to 1100 K [22].

On a clean Ru(0 0 0 1) surface, the only reaction pathway for thiophene is the complete decomposition to C<sub>(ads)</sub>, S<sub>(ads)</sub> and H<sub>2(g)</sub>. Tatarchuk and co-workers have conducted HREELS, XPS and TPD studies of thiophene decomposition on the Ru(0 0 0 1) surface. Using HREELS and XPS, they found that decomposition occurs at around 160 K for low coverages of thiophene and at about 260–280 K for higher coverages [24,25].

As shown in Fig. 4, the desorption of hydrogen, from the decomposition of multilayer thiophene on clean Ru(0 0 0 1), occurs as a broad peak at 258 K and as two weaker peaks ranging from 500 to 700 K. The desorption of H<sub>2</sub> from Ni/Ru(0 0 0 1) surfaces shifts up in temperature to ~338 K. The presence of Ni on Ru(0 0 0 1) results in the selective HDS of thiophene to produce butene (41 amu) at 200 and 290 K at low Ni coverages. As the coverage of Ni is increased, the desorption temperature and the peak ratios change slightly. By coverages of approximately 1 ML, the surface starts acting like that of Ni(1 1 1), with the main peak of butene desorption occurring at ~272 K [26]. The presence of Ni-like properties is also evident in hydrogen and CO desorption spectra at higher coverages of Ni on Ru(0 0 0 1) [27,28]. After TPD measurements, the overlapping AES (Ru + C) peak at ~270 eV showed an increase as compared to clean Ni/Ru(0 0 0 1), indicating that decomposition of thiophene occurred on the Ni/Ru(0 0 0 1) surface. However, we are unable to quantify the activity and selectivity for the decomposition of thiophene HDS due to the fact that the Ru AES peaks overlap with that of both sulfur and carbon.

For completeness, we have also investigated the effect of pre-adsorbed hydrogen on the 1 ML Ni/Ru(0 0 0 1) and clean Ru(0 0 0 1) surfaces, as shown in Fig. 5. On the Ru(0 0 0 1) surface, a trace amount of butene is detected from the surface at 202 K when H<sub>2</sub> is pre-adsorbed. However, this amount is negligible compared to the butene formation on the 1 ML Ni/Ru(0 0 0 1) surface. An exposure of 0.5 L H<sub>2</sub> (~50% of saturation coverage) enhances the production of butene at ~192 K on the 1 ML Ni/Ru(0 0 0 1) surface, although the higher temperature state (280 K) does not change significantly. The total amount of butene production increases by a factor of 1.5 as a result of pre-adsorbing H<sub>(a)</sub>. Compared to those surfaces without hydrogen, AES spectra revealed a

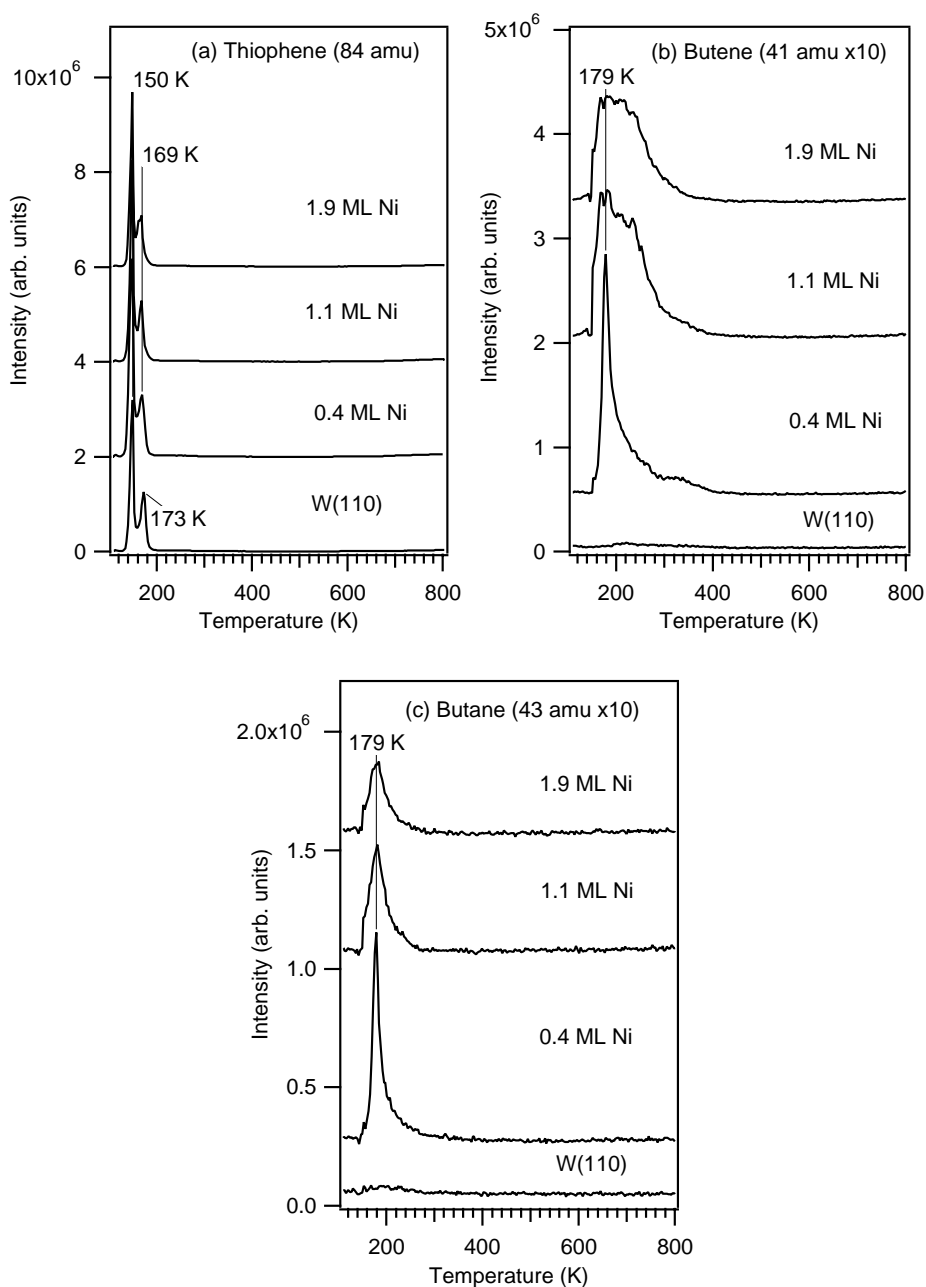


Fig. 3. Thiophene (84 amu) (a), butene (41 amu) (b) and butane (43 amu) (c) from submonolayer  $H_2$ /multilayer thiophene on Ni/W(110) surfaces as a function of Ni coverage.

smaller increase in the Ru + S peak at  $\sim 150$  eV, indicating that the overall degree of thiophene decomposition is less due to the presence of pre-adsorbed hydrogen.

### 3.3. Comparison with previous results

In our previous study of the thiophene HDS reaction on Ni/Pt(111) surfaces, thiophene undergoes low-temperature HDS with a Ni coverage of 1 ML. The desorption of the butene product from the 1 ML Ni on Pt(111), W(110) and Ru(0001) surfaces with and without hydrogen pre-adsorption is compared in Fig. 6. The relative intensity

for the Ni/Pt(111) and Ni/W(110) surfaces is normalized according to the calculated HDS activity. On Ni/W(110), Ni/Ru(0001) and Ni/Pt(111) surfaces, the HDS of thiophene, as indicated by the desorption of the butene product, occurs at temperatures below  $\sim 231$  K. Huntley et al. have shown that the butene product desorbs from a Ni(111) single crystal in one peak, centered between 250 and 300 K [26]. For comparison, the production of gas-phase butene on the Ni/W(110) surfaces occurs at significantly lower temperatures, indicating the more active nature of the Ni/W(110) surfaces toward the HDS of thiophene. Mullins and co-workers have also conducted a study of the

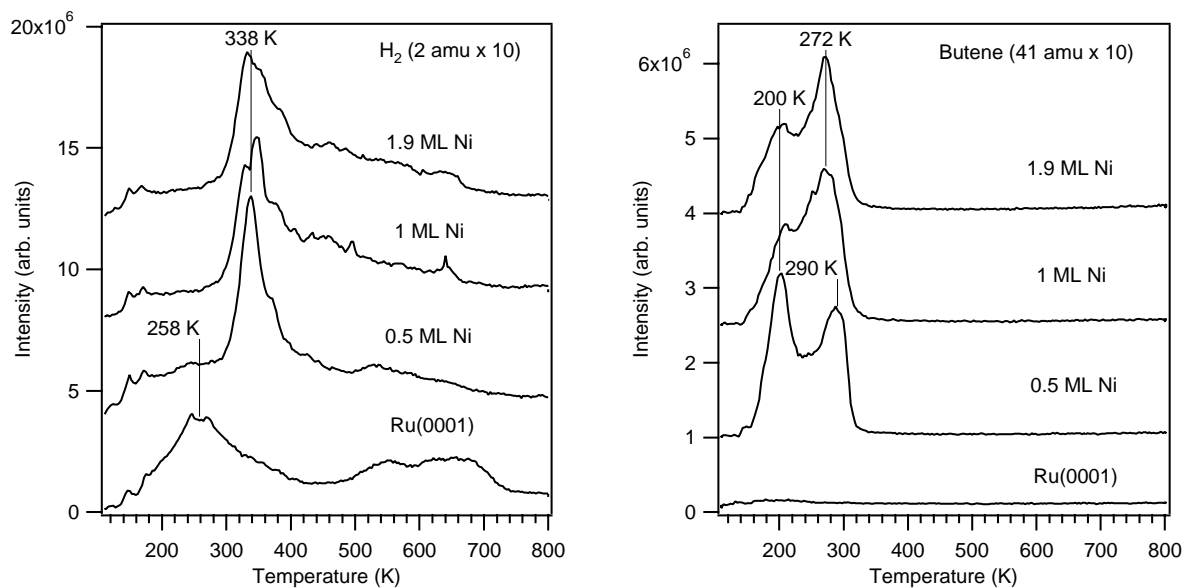


Fig. 4.  $H_2$  and butene desorption from multilayer thiophene TPDs on Ni/Ru(0001) surfaces as a function of Ni coverage.

influence of Ni on the chemical and electronic properties of a W(001) surface [29,30]. On the 1 ML Ni/W(001) surface, they observed an enhancement of methane formation from the reaction of methanethiol at low temperatures [30]. As shown in the current study, Ni also enhances the low-temperature formation of butene on W(110) and Ru(0001) at coverages ranging from 0.3 to 2.6 ML Ni. It is therefore evident that Ni plays an important role in the promotion of HDS reactions on these bimetallic surfaces.

The sharp desorption state of butene at  $\sim 179$  K, on the 0.4 ML Ni/W(110) surface with pre-adsorbed hydrogen (Fig. 3), is unlike that seen on either Ni/Pt(111) or

Ni/Ru(0001) surfaces. XPS studies of Ni 2p do not indicate an electronic modification of the core electrons at this coverage of Ni compared to that of a thick Ni layer [9,11,31]. However, Schmidthals et al. have previously found that a surface with Ni coverage of about 0.2–0.4 ML Ni shows significant tensile strain due to the lattice mismatch of Ni and W [16,17]. In our previous study of cyclohexene on Ni/W(110), we observe that the maximum hydrogenation activity occurs on the Ni/W(110) surface with coverage of 0.4 ML Ni [9]. Therefore, the sharp peak of butene desorption in the current study may also be related to the strain on the  $\sim 0.4$  ML Ni/W(110) surface.

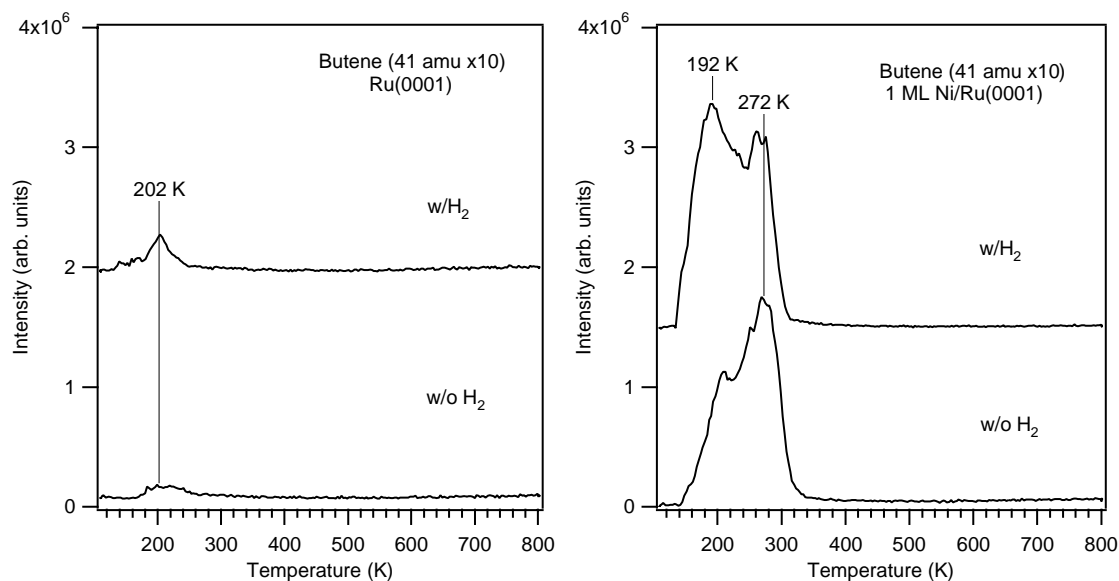


Fig. 5. Effect of pre-adsorbed hydrogen on the reaction of thiophene on Ru(0001) and Ni/Ru(0001) surfaces.

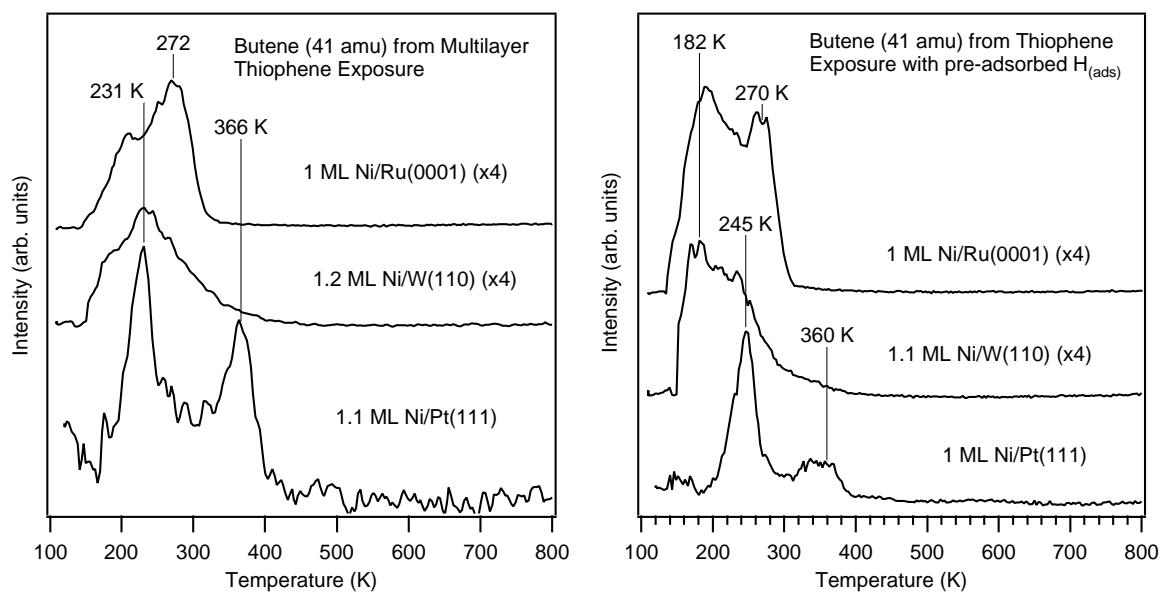


Fig. 6. Comparison of butene from thiophene reactions with and without pre-adsorbed hydrogen on the Ni/W(110), Ni/Ru(0001) and Ni/Pt(111) surfaces with approximately 1 ML Ni.

#### 4. Conclusion

In this paper, we have shown thiophene chemistry on surfaces covered with monolayer Ni films. Adding Ni to the closed-packed surfaces of W and Ru alters the HDS activity of these surfaces, and the resulting reactivity is unlike either pure metal. However, above 1 ML Ni, the Ni/W(110) surfaces begin to act like Ni surfaces. The presence of Ni increases the HDS selectivity of the W(110) surface from 0 to 7% C<sub>4</sub>H<sub>8</sub> on 1.2 ML Ni/W(110). On the Ru(0001) surfaces, Ni also promotes the HDS of thiophene, but at temperatures close to pure Ni surfaces. On the 0.4 ML Ni/W(110) surface, pre-adsorbed hydrogen results in thiophene undergoing HDS at a very low temperature, 179 K, and also increases the reactivity by more than two-fold. The promotion effect of Ni in HDS surface reactions, clearly seen on the Ni/W(110) and Ni/Ru(0001) surfaces, is consistent with the observation that Ni is a known promoter in commercial HDS applications.

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