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THE CHEMISORPTION AND SURFACE REACTIONS OF D_2 AND HYDROCARBONS ON THE Re(0001) SINGLE CRYSTAL SURFACE: WHEN CLEAN AND IN THE PRESENCE OF CO-ADSORBED SULFUR OR CARBON

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ABSTRACT

The chemisorption and surface reactions of thiophene, D_2 and the hydrodesulfurization products (1,3-butadiene and butenes) have been studied on Re(0001) at low ambient pressure (10^{-9} Torr) using thermal desorption spectroscopy (TDS), low energy electron diffraction (LEED), and Auger electron spectroscopy (AES). D_2 adsorption was found to be blocked by sulfur or carbon overlayers. Sulfur pre-adsorption induced small changes in the D_2 desorption energy and adsorption was completely blocked above 0.4 monolayers of sulfur (θ_s=0.4). Carbon pre-adsorption lowered the temperature of the desorption maxima (380K to 290K), and blocked D_2 adsorption nonlinearly. Sequential dehydrogenation of the adsorbed unsaturated hydrocarbons leading to complete decomposition at high temperatures (>700K) was observed on the clean Re(0001) surface. Addi-

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tion of sulfur or carbon blocked dehydrogenation. No changes in the dehydrogenation (yielding H_2) TDS peak temperatures were observed for both sulfur or carbon pre-adsorption. However, selective blocking of dehydrogenation states was observed for both sulfur or carbon pre-adsorption. In addition, carbon adsorption did allow hydrogenation of butadiene to occur. It is concluded that for all systems pre-adsorbed sulfur acts as a site-blocker for adsorption and dissociation with only small effects on bonding of adsorbed molecules on Re(0001). Although this also seems to be true for pre-adsorbed carbon as well, other subtle effects are observed which can change the surface chemistry of adsorbed molecules, as exemplified by the hydrogenation of butadiene.

1. Introduction

Rhenium is used as a catalyst for several important reactions in the chemical technology. With platinum it forms a bimetallic catalyst which is used for hydrocarbon reforming.[1] By itself, Re is also an active catalyst for hydrogenolysis.[1] In addition, its sulfided form catalyzes the hydrodesulfurization (HDS) reaction.[2] While the cobalt-molybdenum-sulfur system is used for HDS most frequently, sulfided rhenium appears to exhibit similar or superior activity.

The HDS of thiophene has been used as a test reaction to investigate the activity of model Mo(100) single crystal catalysts in our laboratory.[3,4,5] In order to gain a more complete understanding of this system we have also explored the surface chemistry of the reactants (thiophene and D_2), and the products of HDS (1,3-butadiene, butenes, and butane), by a combination of surface science techniques that include Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and thermal desorption spectroscopy (TDS).[6,7,8] It was found that the chemisorption and reactions of these molecules could be altered by co-adsorption with sulfur or carbon -- a condition usually encountered during HDS.

We have extended these studies (both at high pressure[9] and at low pressure) to the Re(0001) single crystal surface. In this paper we report studies on the chemisorption and surface reactions

of the reactants and products of thiophene HDS (D_2, butadiene, and butenes), when adsorbed on the clean surface or when co-adsorbed with sulfur or carbon. In addition, comparisons will be made with other metal surfaces where these hydrocarbons have been studied.

The surface chemistry of rhenium single crystals has not been extensively studied using surface science techniques. Most work has been confined to the study of CO and H_2 chemisorption on the basal plane (0001).[10,11] H_2 was found to desorb in one broad peak at 350K on the basal plane.[12,13] CO adsorbs molecularly at room temperature. Upon heating to 400K (during thermal desorption of the molecular species) a small amount dissociates, and then recombines to desorb at 780K. This behavior is consistent with the borderline position of Re in the periodic table in regards to CO dissociation.[14]

A few chemisorption[12,13] and high resolution electron energy loss spectroscopy (HREELS)[15] studies of hydrocarbons have been performed on Re(0001). Ethylene and acetylene were found to decompose to adsorbed carbon and hydrogen during thermal desorption similar to what has been found on most transition metal surfaces. In addition, HREELS of acetylene exhibited the most extensive rehybridization of the carbon-carbon triple bond on a close-packed surface seen to date, decreasing the ν(C-C) from 1974 cm^{-1} for gas phase aceytlene[16] to 1095 cm^{-1}, which is close to the single bond vibrational energy of ethane of 993 cm^{-1}.[17] This indicates strong interaction with the surface.

All unsaturated hydrocarbons that we studied were found to undergo sequential dehydrogenation during thermal desorption, which eventually lead to complete decomposition leaving surface carbon and adsorbed hydrogen (H_{ad}) which recombined and desorbed as H_2. Some similarities in dehydrogenation spectra (yielding H_2) of the unsaturated hydrocarbons were observed. At low hydrocarbon coverage the H_2 spectra are similar to those seen for H_2 chemisorption at low coverage.[12,13] As coverage increases individual H_2 desorption peaks are observed which are rate limited by C-H bond breaking (dehydrogenation-limited). These peaks fall in four regions for all the unsaturated hydrocarbons: 300K, 370-400K, 420K, and a long tail above 500K. Comparisons with other metals surfaces show some similarities, but because of the overlap in desorption peaks

no conclusions can be made concerning similar dehydrogenation mechanisms.

The adsorption of sulfur on the Re(0001) plane has not been studied previously. In another report, we present more details on this system,[18] but for now we summarize the results of direct interest here. We have found that sulfur forms several ordered overlayer structures on this surface. D_2 chemisorption was found to be blocked by pre-adsorbed sulfur. In addition, small shifts of the binding energy of D_2 were seen. As with other systems (S/Mo(100) in particular),[8] sub-monolayer coverage of pre-adsorbed sulfur block sites for hydrocarbon decomposition. This increases the amount of molecularly bound species which are physisorbed. In addition, small changes in molecular bonding and changes in the dehydrogenation spectra (yielding H_2), were found. Indicating that sulfur acts as a site-blocker for hydrocarbon chemisorption and surface reactions, with small binding energy shifts.

Pre-adsorbed carbon was also found to block hydrocarbon decomposition. In another study we report in more detail upon the nature of this carbon overlayer,[19] but here we will summarize the points of particular interest. Carbon was not found to form any ordered overlayers on this surface according to LEED, and the C(272eV) AES signal exhibited fine structure on the low energy side which is typical of "graphitic" carbon.[20] As expected from the nature of the overlayer, geometric site-blocking was observed. As with sulfur, the molecularly intact species was found to be physisorbed. However, this carbon overlayer was found to change the surface chemistry by lowering the binding energy of D_2. The same C - Re surface interaction which gives rise to the decrease in the deuterium bonding energy is also believed to be responsible for the increase in the hydrogenation of butadiene.

2. Experimental

The system used for these experiments has been described before.[8] Briefly, it consists of a stainless steel ultra-high vacuum chamber with a base pressure after bake-out of 3×10^{-10} Torr. It is equiped with LEED optics, a single-pass cylindrical mirror analyzer for AES, and a colimated mass spectrometer for TDS. The Re(0001) single crystal was $\sim$ 1 cm^2, and was heated resistively over the temperature range 130-1900K. The sample was cleaned by heating in 2×10^{-8} Torr of O_2

(to remove carbon), and then flashed to 1900K to remove the oxide (cleanliness was confirmed by AES).

The compounds studied (D_2, thiophene, 1,3-butadiene, 1-butene, trans-2-butene, cis-2-butene) were all adsorbed at approximately 140 - 170 K. The D_2 was obtained from Liquid Carbonic, the butadiene was obtained from Matheson, and the butenes were obtained from Linde. The purity of the compounds was determined by mass spectrometry. In addition, hydorcarbon purity was confirmed by gas chromatography.

The method of sulfur deposition and coverage calibration will be reported elsewhere.[18] Briefly, sulfur forms several ordered overlayers on Re(0001): a p(2×2) lattice at θ_s=0.25, a "$(3\sqrt{3}\times3\sqrt{3})R30°$" with missing spots at θ_s=0.35, a $\begin{pmatrix}3 & 1\\ 1 & 3\end{pmatrix}$ at θ_s=0.40, and $(2\sqrt{3}\times2\sqrt{3})R30°$ at θ_s=0.50, with saturation at approximately 0.6 - 0.7 monolayers.

Again, more detailed data will be presented elsewhere on the nature of the carbon overlayer.[19] Briefly, carbon overlayers were deposited by thermal decomposition to 900K of 1,3-butadiene. Other C_4 hydrocarbons were also used for carbon deposition, and there were no differences seen in the TDS of species adsorbed over the carbon, regardless of which C_4 hydrocarbon was the source of the carbon. LEED patterns have been seen by Ducros, et al[12] from the decomposition of ethylene and acetylene, but we did not see any from C_4 hydrocarbon decomposition for all coverages. In addition, AES peak shapes were analyzed over a range of carbon coverages and were found to compare well with those found for "graphitic" carbon.[20] Because of the lack of LEED structures no precise measure of carbon surface coverage was obtained. Based on comparisons of AES peak ratios of O, C, CO and comparison with previously determined CO coverages at saturation, an approximate measure has been made. First, we will assume the $\frac{C(272eV)}{Re(177eV)}$ ratio of 1.2 is 1 monolayer (further adsorption of butadiene does not result in any increase in carbon coverage). Second, we have found that $\frac{C(272)}{Re(177)}$= 0.3 corresponds to saturation CO coverage. From previous work[10,21,22] we will assume that the saturation CO coverage is 0.35 monolayers. Using the $\frac{C(272)}{Re(177)}$ ratio the carbon coverage is then linearly interpolated between these values.

This method is expected to give good accuracy at low carbon coverage (±10%), but at higher coverage the coverage determinations are expected to be more uncertain (±20%).

3. Results and Discussion

This section is organized as follows. First, a discussion of D_2 thermal desorption from the clean, sulfur covered, and carbon covered Re(0001) will be presented. Then a summary of the thermal desorption pathways of all the hydrocarbons on the different surfaces (clean, pre-adsorbed with sulfur, and pre-adsorbed with carbon) will be presented. This will be followed by a detailed account of the desorption behavior for each compound when it deviated significantly from the general behavior outlined above. A summary of desorption temperatures and products is presented in Table 1. These results will also be compared with results of similar studies on other metal surfaces.

3.1. D_2 Chemisorption on Re(0001)

H_2 chemisorption on the clean Re(0001) has been studied previously.[12,13] Our results using D_2 are in close agreement with these previous studies. The major distinction of our spectra is the 130-190K adsorption temperature of D_2. This results in a shoulder in the thermal desorption spectrum observed at low temperature (Fig. 1). The coverage dependence of these spectra is similar to those seen for Pt(111)[23] at low coverages; a decrease in the desorption maximum accompanied by a shoulder at low temperature. At very high exposures (>100L) it is possible that this low temperature state for H_2 on Re(0001) will be as intense as the low temperature state found for Pt(111).

Supression of both desorption states and a shift to lower temperature for the high temperature desorption is seen when D_2 is co-adsorbed with sulfur (Fig. 2a). At low sulfur coverage (θ_s=0.06) the peak temperature shifts to 350K. As sulfur coverage is increased through the p(2×2) phase no further shift was observed. A slight shift to higher temperature was observed near the appearance of the "$(3\sqrt{3}\times3\sqrt{3})R30°$" structure, but this may be caused by contributions to the TDS by desorption from the back face of the crystal, which does not have any sulfur pre-

adsorption.

A comparison of these results with data obtained from H_2 chemisorption on S/Ru(0001)[24] suggest that the effects seen above are caused by changes in relative D_2 coverage. The same peak temperature decrease as sulfur coverage increases was seen for the Ru system. Schwarz was able to show that the peak temperature decrease was similar to what would be expected if H_2 adsorption increased. Two possible ways to interpret this are: sulfur blocks metal sites, but does not cause any decrease in the amount of H_2 adsorbed at this low coverage. Therefore, as sulfur coverage increased the H_2 concentration increased relative to the available metal area. This hypothesis is corroborated by the constant amount of H_2 desorption up to θ_s=0.10. Another possibility is that similar to CO chemisorption on S/Re(0001)[18] the coverage effect of D_2 is caused by an electronic interaction with the adsorbed sulfur. The latter cause seems to be the most probable. The fact that an ordered overlayer of sulfur (p(2×2)) is present on the surface before D_2 adsorption suggests that D - D interactions should be decreased not increased (which is what a coverage effect would imply). Instead, there is an interaction of D_{ad} with S_{ad} which lowers the surface bonding energy of D_{ad}. Because of the experimental uncertainty in the peak areas we are unable to conclusivley determine that D_2 is blocked linearly by sulfur.

The surface area blocked by sulfur adsorption is different on Re and Ru (0001) faces. Whereas, Schwarz[24] showed that H_2 desorption on S/Ru(0001) stopped at completion of the p(2×2) structure, our data show that on Re(0001)-S-p(2×2) there is still $\frac{1}{3}$ to $\frac{1}{2}$ the amount of D_2 that there is at saturation on the clean surface (Fig. 3a). D_2 desorption is not completely inhibited until the $\begin{pmatrix} 3 & 1 \\ 1 & 3 \end{pmatrix}$ structure appears. This indicates that the blocking ability of sulfur for D_2 is less on Re(0001) than it is on Ru(0001).

Although pre-adsorbed carbon also blocks sites for D_2 adsorption on Re(0001) other effects are seen which cannot be explained by a geometric site blocking model. First, the thermal desorption spectra show a double peaked (290K, 470K) structure which was not seen on the clean or sulfur covered surface (Fig. 2b). Studies on other studies with "carbidic" carbon have shown no peak

shifts in the H_2 TDS.[25] In addition, H_2 chemisorption on carbon overlayers on Ru(0001) show no peak shift, just blockage of chemisorption. Other studies have shown that adsorption of hydrocarbons at room temperature on Re(0001) with subsequent decomposition to 800K produces "carbidic" carbon.[9] However, as mentioned previously (section 2.) the carbon overlayer on Re(0001) formed in this study was found to be "graphitic". Re is not known to produce any stable bulk carbides[26] except under extreme conditions.[27] The high temperature thermal desorption peak has been interpreted to be caused be desorption from the clean patches unaffected by carbon, since its desorption temperature is similar to that observed at low coverage on the clean surface. The low temperature thermal desorption peak is observed to decrease to a temperature lower than that seen on the clean or sulfur covered surface. We suggest that D_2 desorption from this peak is caused by regions strongly influenced by carbon adsorption (such as the periphery of carbon islands), where the desorption energy has been lowered with respect to the clean surface. Also, the amount of D_2 adsorbed was found to have a highly nonlinear dependence on carbon coverage on Re(0001) (Fig. 3b). Most (80%) of the adsorption sites are blocked by $\theta_c \simeq 0.4$.

3.2. Unsaturated C_4 Hydrocarbon Chemisorption on Re(0001)

3.2.1. The Clean Re(0001) Surface

On the clean Re(0001) surface all unsaturated C_4 hydrocarbons (thiophene, butadiene, and butenes) undergo thermal dehydrogenation until complete decomposition occurs resulting in desorbed H_2 and C_{ad}. Molecular desorption does not occur for the unsaturated hydrocarbons until multilayer coverage is attained, where desorption occurs from physisorbed states (150-180K). The hydrocarbons decompose to yield a carbon coverage of approximately $\frac{C(272)}{Re(177)} = 0.35$ which is $\theta_c = 0.4$. This coverage was independently confirmed by observing the $\frac{S(152)}{Re(177)}$ AES ratio after thiophene decomposition, which gives $\theta_s = 0.1$.[18]

The possibility of surface reactions other than dehydrogenation and desorption were also examined. Other masses: 16, 26, 39, 54, 56, and 58 were observed to determine if any cracking or hydrogenation was occuring which would lead to stable desorption products. Except for butadiene

hydrogenation, no extra peaks in the mass spectra appeared that were not present in the parent peak mass spectra.

Deuterium and hydrogen were co-adsorbed with all of the unsaturated C_4 hydrocarbons on the clean surface, and with some pre-adsorbed amounts of sulfur or carbon ($\theta_s \simeq 0.2$, $\theta_c \simeq 0.4$). This was performed to see if any hydrogenation would occur. In all cases, except butadiene on a surface pre-adsorbed with carbon, no extra hydrogenation products were observed.

The dehydrogenation spectra (yielding H_2) of unsaturated C_4 hydrocarbons on Re(0001) has some general features which are common to all (Fig. 4). At the C_4 hydrocarbon coverage where multilayer desorption occurs, these areas are: low temperature desorption at about 300K, an intermediate desorption (370-400K) area where the bulk of H_2 is desorbed, a shoulder at about 420K, and a long tail extending to 750K.

In order to understand the source of the features better, the dehydrogenation spectra (yielding H_2) of butadiene as a function of hydrocarbon coverage will be examined more closely (Fig. 5). The general features of the TDS as a function of butadiene coverage were also found for the other unsaturated hydrocarbons.

At low hydrocarbon coverage, H_2 desorbs at about 450-470K for all hydrocarbons. As discussed earlier, this also is true for low coverages upon H_2 or D_2 chemisorption (Fig. 1).[12,13] Therefore, these peaks are probably rate-limited by H_2 desorption and not dehydrogenation. Since these peaks are the only ones observed at low coverage, total dehydrogenation has occurred below the desorption temperature. This is similar to hydrocarbons on Mo(100)[8,28] and Ru(0001),[29] where H_2 desorption is rate-limited by desorption of H_2 and not dehydrogenation at low hydrocarbon coverage. This is similar to hydrocarbon adsorption on Pt(111)[30] and Rh(111),[31] but different from ethylene on Pt(111)[32] where no coverage dependence is seen.

As hydrocarbon coverage increases further, two H_2 desorption peaks are observed: first at 370K, then near multilayer hydrocarbon coverage and above at 300K. The lowest temperature desorption is slightly lower than the temperature at which desorption is seen for high coverages of chemisorbed D_2 (Fig. 1). The relative intensity of the two lowest temperature desorption maxima

are dependent upon the nature of the hydrocarbon, suggesting different dehydrogenation pathways for each hydrocarbon. The answer as to whether these peaks are rate-limited by desorption or dehydrogenation is difficult. The peak in the 370-400K region is probably rate-limited by C-H bond breaking for 1-butene, cis-2-butene, and thiophene because the desorption temperature is higher than the lowest desorption temperature upon D_2 chemisorption (Fig. 1), and this peak is very intense relative to the lowest temperature peak. However, it cannot be conclusively determined whether this is also true for butadiene and trans-2-butene. Partial dehydrogenation below the 300K desorption temperature affects the filling of the H_{ad} states on the surface. Partial dehydrogenation below this temperature would result in a low temperature H_2 desorption peak similar in intensity to that at 370K (butadiene and trans-2-butene), where the next step in partial dehydrogenation may occur. Suggesting that dehydrogenation for these compounds occur below the first desorption temperature (300K).

The high temperature tail appears in the hydrocarbon dehydrogenation spectra on many metal surfaces.[8,28,29,30,33,32,31,34] Desorption from this area is rate-limited by C-H bond breaking, because the desorption temperature is higher than that observed for H_2 or D_2 chemisorption.[12,13] The hydrocarbon fragments responsible for the desorption on other metal surfaces have been attributed to a metallocycle[28] or a C_xH species.[30,33,31] In at least one case,[8] the formation of the fragment is enhanced by a carbon overlayer. As will be shown below, this was also found to be true on Re(0001).

The dehydrogenation steps during thermal desorption for the butenes and butadiene on Pt(111) have been determined using HREELS by Avery and Sheppard.[30,33] In addition, extensive work on the dehydrogenation pathways of ethylene and propylene have been performed using HREELS by Bent et al on Rh(111).[31] HREELS of butenes and butadiene on Rh(111) have also been preformed, but analysis was focused on the species which form during thermal dehydrogenation above 500K.[34] On the left side of the periodic table, the thiophene dehydrogenation pathway on Mo(100) has been determined as well.[28] These studies have shown that the hydrocarbons chemisorbed on these surfaces go through sequential dehydrogenation as temperature increases so that

ultimately only "graphitic" (Pt(111), Rh(111)) or "carbidic" (Mo(100)) residues remain on the surface. The fact that sequential dehydrogenation is observed for all hydrocarbons on metal surfaces studied by HREELS to date supports the hypothesis that the separate peaks in the hydrocarbon dehydrogenation spectra on Re(0001) represent discrete steps in the process. In fact, the stoichiometry of the resulting fragments has been determined for hydrocarbons on Pt(111).[30,33] However, the overlapping desorption peaks has made it impossible here. This was also found to be true for ethylene on Ru(0001).[29]

The desorption spectra of the butenes and butadiene most closely resemble each other on the Rh(111),[31] and Re(0001) surfaces (Table 2).[35] Although the peaks in the desorption spectra of the hydrocarbons yielding H_2 on Mo(100) are at a lower temperature than those observed on the other surfaces, the general shapes of the spectra are similar to those observed on other surfaces. It is remarkable that these surfaces, which are very different from each other in terms of CO dissociation, exhibit dehydrogenation spectra with maxima at similar temperatures. Two explanations come to mind: one is that the dehydrogenation pathways are very similar, and the other is that the H_2 desorption and hydrocarbon dehydrogenation are so close in temperature that the partial dehydrogenation information is lost in the thermal desorption spectra. For ethylene, we have noticed that the dehydrogenation temperature to form the stable ethylidyne species decreases from Pt(111) (290K)[36] to Rh(111) (200K)[31] to Ru(0001) (150 - 280 K).[29] In addition, we have noticed that the thermal desorption peaks increasingly overlap from Pt(111) to Ru(0001). Based upon these observations we suggest that as one moves left across the periodic table the temperature for dehydrogenation decreases causing overlap in the H_2 desorption peaks. The similarity of the dehydrogenation spectra is also due to the complexity of the molecules. When a simpler compound such as ethylene is examined many differences in desorption maxima are seen between the surfaces mentioned (Table 2). However, as noted previously, the number of differences decreases for C_4 hydrocarbons. Therefore, any similarities or differences in the thermal dehydrogenation spectra (yielding H_2) of the C_4 hydrocarbons on various metals to the left of Rh in the periodic table must be viewed with caution when infering similarities or differences in dehydrogenation

pathways.

3.2.2. The Sulfur Covered Re(0001) Surface

Sulfur pre-adsorption acts to block unsaturated C_4 hydrocarbon dehydrogenation. Figure 6 shows the effect of sulfur coverage on the hydrogen yield from decomposition. Decomposition was found to be completely blocked by θ_s=0.4 (near the appearance of the $\begin{pmatrix} 3 & 1 \\ 1 & 3 \end{pmatrix}$ structure).[18] The effect of pre-adsorbed sulfur on the shape of the hydrocarbon dehydrogenation spectrum is illustrated with butadiene in Fig. 7a. Desorption in the low temperature region appears to be blocked first at low sulfur coverages, then the entire dehydrogenation spectrum is inhibited at higher coverages. This indicates that the first dehydrogenation step is blocked preferentially by sulfur. As can be seen in Table 1, the peak desorption for H_2 chemisorption is lower (350K) than that for butadiene chemisorption (370K). This suggests that this desorption is rate-limited by C-H bond breaking. The dehydrogenation of 1-butene shows a slightly different effect for increasing sulfur coverage, and will be discussed in section 3.3.3.

Additional evidence for the site-blocking nature of sulfur on hydrocarbons comes from reversible molecular adsorption. As stated earlier, molecular desorption occurs on the clean Re(0001) surface only above saturation coverage, and the low temperature of desorption 150-180K indicates that these reversibly bound species are physisorbed. For sulfur coverage up to 0.3 monolayers (Table 1), no changes in desorption temperature of the reversibly bound molecular species is observed while desorption from this state has increased (less dehydrogenation, therefore more molecular species). However, above this sulfur coverage the molecular desorption temperatures decrease by 20 to 30 K (Fig. 8). This unusual shift in the molecular physisorbed state is not easily explained, and has not been seen for hydrocarbon adsorption on sulfur covered surfaces to date.[8]

This inhibition in dehydrogenation observed here is in accord with what is seen on all other surfaces studied.[7,8,37,38] On some surfaces[7,8] sulfur acts only as a site-blocker, and no other chemical effects are seen. However, on Re(0001) sulfur induces some chemical effects in addition to being a site-blocker for adsorption and dissociation.

3.2.3. The Carbon Covered Re(0001) Surface

Pre-adsorbed carbon also blocks sites for dehydrogenation, but it does not show a blocking effect as drastic as that seen for sulfur. Nearly a monolayer is required to block decomposition completely. This difference is probably caused by the smaller size of the carbon atom.[39] It was also determined that the H_2 high temperature tail (from dehydrogenation) increases as carbon coverage increases.

Carbon is known to adsorb in two different forms depending on the metal and the crystal face: "graphitic" carbon, where strong C-C bonds are formed in addition to the C-M bonds,[40,41,42,43,44,45] and "carbidic" carbon, atomically bound to the metal with only long range C-C interaction.[45,46,47,48,49,50,51,52] The carbidic surface can moderate surface activity either by blocking dehydrogenation sites alone, with metal sites still available for bonding,[8,46,50,51,52] or by creating p-orbitals from the carbon (directed perpendicular to the surface) for bonding.[45] The graphitic overlayer is usually considered to be inert.[45] AES measurements on Re(0001) with pre-adsorbed carbon have shown that the carbon is "graphitic" in nature.[19] However, the carbon overlayer is observed to increase H_2 evolution (from hydrocarbon dehydrogenation) in the high temperature tail (Fig. 7b), which indicates that this overlayer does stabilize the formation of the hydrocarbon fragments which are stable to high temperature. This can be seen from the increased H_2 desorption from this portion of the spectrum. This type of fragment stabilization has been seen for hydrocarbon adsorption on Mo(100) where the type of carbon is "carbidic" in nature.[8] It is expected that the H_2 observed from decomposition in the high temperature tail or peaks observed on other surfaces[29,30,33,32,31,34] would also be stabilized by decomposed carbon.

The decrease in the number of dehydrogenation sites for the additive covered surfaces causes an increase in molecular desorption from these states. No changes in the temperature of the desorption is seen for all carbon coverages (except for thiophene as noted below). This is different from what has been studied previously. Chemisorption of these hydrocarbons on a "carbidic" carbon overlayer on Mo(100) produced reversibly adsorbed hydrocarbons with activation energies for desorption of 12 - 23 $\frac{\text{kcal}}{\text{mol}}$.[8] The carbon overlayer on Re(0001) did not have this effect on hydrocar-

bon chemisorption. Increasing carbon coverage merely increased the amount of physisorbed species which desorb (150-190K). This is similar to the effect of low coverages of sulfur, which is what is expected for inert "graphtitic" carbon.

3.3. Details of Unsaturated C_4 Hydrocarbon Chemisorption on Re(0001)

3.3.1. Thiophene Chemisorption on Re(0001)

Thiophene chemisorption has been studied on many metal surfaces.[53] Except for Cu (where it does not dehydrogenate during thermal desorption) it forms a complex dehydrogenation spectrum (yielding H_2), and molecular desorption occurs from a low temperature state. As has been discussed recently,[8,28] the orientation of the thiophene ring with respect to the surface is of importance in determining the decomposition pathway. Several studies suggest that the compound is adsorbed with the plane of the ring tilted with respect to the surface (Ni(100),[57,58] Mo(100),[28] and Pt(111)[55]). This facilitates electron donation from the metal surface d-band into the thiophene orbitals which are anti-bonding predominantly between the sulfur and carbon thus, leaving the carbon backbone intact. However, only on Pt and Pd[54] has desulfurization followed by hydrogenation to yield butadiene been observed in ultra-high vacuum. On some of these surface, desulfurization followed by metallocycle formation has been suggested to occur.[28,55,58] Usually the suggested metallocycle is one where the hydrogens α to the sulfur interact with the surface more strongly because they are closer. Therefore, dehydrogenation of the α-position is expected at a lower temperature than for the β-position if the desorption of H_2 is dehydrogenation-limited. Chemisorption and thermal dehydrogenation of thiophene-2,5-d_2 would be expected to exhibit differences in the H_2, HD, and D_2 desorption spectra. This has been observed on Ni(100),[54] and Mo(100),[8,28] but Pt(111)[54] did not show any α-β dehydrogenation specificity. In this case, H_2 desorption may be rate-limiting. Other surfaces where no structural studies have been performed also show α-β dehydrogenation specificity in the desorption spectra (Os(0001), Ru(0001), Ir(111), Pd(111), (100) and (110)[54]). In all of these studies the α-hydrogens dehydrogenate and desorb at lower temperatures than the β-hydrogens. As seen in Figure 9, this is also true for

Re(0001).

Focusing on the clean Re(0001) surface at low thiophene-2,5-d_2 coverage (0.1L) the desorptions of H_2, HD, and D_2 are very similar. The peak maximum of D_2 is a little lower (420K) than that seen for either HD or H_2 (450K). As thiophene coverage increases the effect of this preferential dehydrogenation increases as well. Up to 0.28L HD desorption (390K) is in between D_2 (350K) and H_2 (450K). These desorption temperature differences can have two possible sources: an isotope effect or α-dehydrogenation specificity. An isotope effect seems unlikely since H_2 would be expected to desorb at a lower temperture not D_2 as observed. However, at higher coverages the HD desorption spectra become a superposition of D_2 and H_2. This coincides with broadening of the H_2 desorption, and the appearance of the high temperature tail. As can be seen in figure 9, the D_2 spectrum has intensity only at low temperature, while the H_2 spectrum has intensity only at high temperture. This coverage behavior has been seen on Mo(100).[28] It has been interpreted in terms of two adsorption sites, one for complete decomposition, the other for partial step-wise dehydrogenation. However, we still observe an α-β dehydrogenation specificity even at low thiophene coverage, whereas Zaera et al[28] did not. Therefore, we suggest that thiophene dehydrogenates along the same thermal pathway at all coverages, but at low thiophene coverage H_2 desorption is rate-limiting.

Both pre-adsorbed sulfur or carbon act to inhibit the α-β dehydrogenation specificity. This similar to what has been seen on Mo(100).[8] As seen in Figure 10, the adsorption of thiophene-2,5-d_2 on either additive covered surface causes similar desorption peaks to appear in both the D_2 and H_2 spectra indicating a loss in α-β dehydrogenation specificity. This could be attributed to various causes: a change in dehydrogenation energy such that α and β hydrogens dehydrogenate below the H_2 desorption temperature, or a change in bonding which causes dehydrogenation to occur simultaneously. This is less pronounced on s sulfur covered surface where total dehydrogenation occurs at low temperatures, but only β-dehydrogenation occurs at higher temperatures.

Pre-adsorbed carbon was seen to create a low energy reversibly chemisorbed state for thiophene at $0.3 < \theta_c < 0.7$ (Table 1). Although this type of molecular chemisorption has been

seen for carbon on Mo(100),[8] we have not observed it for any other unsaturated C_4 hydrocarbons on Re(0001).

3.3.2. 1,3-Butadiene Chemisorption on Re(0001)

Unlike all other unsaturated C_4 hydrocarbons and surfaces studied herein, butadiene hydrogenates on a carbon pre-adsorbed Re(0001) surface (Fig. 7) to form butenes (70±20% 1-butene). On a surface witha small amount of pre-adsorbed carbon (θ_c=0.4) D_2 co-adsorption yielded a deuterated product which desorbed 70K lower than the hydrogenated product. Both the clean surface, and the one with pre-adsorbed sulfur showed no detectable hydrogenation. Two different hydrogenation mechanisms can be imagined; a two-step mechanism where butadiene first dehydrogenates then H_{ad} hydrogenates the intact butadiene, or a one-step mechanism where direct hydrogen transfer between molecules occurs. Previously, it was stated that the desorption temperature for butenes produced from butadiene hydrogenation is higher than observed from desorption of pre-adsorbed butene. Therefore, desorption of butenes from butadiene hydrogenation is reaction-limited. Co-adsortpion of D_2 with butadiene at sub-monolayer coverages of carbon produced deuterated butenes. This implies that hydrogenation of butadiene is a two-step process. In addition, the difference in desorption peak temperatures between the deuterated (180K) and nondeuterated (250K) butene shows that dehydrogenation of butadiene, and not hydrogenation is the rate-determining step. Assuming first order desorption kinetics, the activiation energy for dehydrogenation can be calculated to be 15 $\frac{\text{kcal}}{\text{mol}}$.[61] For hydrogenation, an activation energy of 10 $\frac{\text{kcal}}{\text{mol}}$ was calculated from the deuterated butene maximum assuming second-order desorption.[61] This is very different from what was found on Mo(100)[8] where hydrogenation was found to be the rate-dtermining step, and it was found to occur on surfaces with either pre-adsorbed sulfur or carbon. On this surface the metal sites were found to control the hydrogenation reaction. So, it is not suprising that hydrogenation on both sulfur and carbon covered surfaces was observed. However, consistent with our results we postulate that the carbon covered surface of Re(0001) lowers the activiation energy for hydrogenation. This could be accomplished by altering the binding state of butadiene. Although strong bonding on top of the carbon overlayer has been shown not to occur,

bonding along the periphery of the carbon islands should be significantly different from that on the clean metal patches. This area would be expected to increase the activiation energy for decomposition (due to weakening of the metal interaction). Note that the appearance of the high temperature H_2 peak from decomposition is enhanced by pre-adsorbed carbon. This effect is very different than that observed on Mo(100) where the additive covered patches acted only to block dehydrogenation, but they did not alter the activation energy for hydrogenation as the carbon covered Re(0001) surface did. It is interesting to note that the differences in hydrogenation ability at low pressure are similar to those observed catalytically.[62]

The hydrogenation mechanism also provides us with data on whether the first H_2 desorption (from hydrocarbon dehydrogenation) peak is rate-limited by C-H bond breaking or by H-M bond breaking for butadiene. Since hydrogen is available for hydrogenation by 250K, which is 50K lower than the observed H_2 desorption temperature, this H_2 peak is probably rate-limited by H-M bond breaking rather than C-M bond breaking.

3.3.3. Butene Chemisorption on Re(0001)

The dehydrogenation activity of these hydrocarbons depend upon the isomer. As seen in Figure 4, both 1-butene and cis-2-butene have the same H_2 desorption spectra, while trans-2-butene desorption spectra (yielding H_2) showed decreased intensity in the 380K peak relative to cis-2-butene and 1-butene. This indicates that molecular shape has an effect on the dehydrogenation pathway. The butene isomers have been observed to show different dehydrogenation spectra on Mo(100)[8] and Pt(111).[30,33,31] The differences in the dehydrogenation spectra on Pt(111) were caused by differences in the hydrocarbon fragment on this surface. It would be of interest to extend these studies to Mo(100) and Re(0001) and understand the molecular shape selectivity of the dehydrogenation pathways on these different metals.

The effect of sulfur pre-adsorption on 1-butene dehydrogenation is different than that seen for the other C_4 hydrocarbons. Instead of the low temperature dehydrogenation (300K) being blocked first, the intermediate dehydrogenation pathway is partially blocked at $\theta_s < 0.15$. Above this coverage the behavior of the dehydrogenation spectra (yielding H_2) is similar to the other C_4

hydrocarbons; the low temperature desorption is blocked preferentially. This implies that the pathway leading to formation of the intermediate dehydrogenation peak is separate from the pathway leading to formation of the low temperature dehydrogenation peak.

4. Summary and Conclusions

Re(0001) was found to dehydrogenate unsaturated C_4 hydrocarbons into C_{ad} and H_{ad}. Briefly, sulfur or carbon pre-adsorption on this surface blocked sites for adsorption and dehydrogenation.

This similar to what has been observed on other transition metal surfaces. The nature of chemisorbed carbon varies greatly with the position of the transition metal in the periodic table. The formation of "carbidic" or "graphitic" carbon on these surfaces greatly influences the chemistry of the carbon overlayer, and reinforces the concept of "active" versus "inactive" carbon. In general, we cannot make a definitive conclusion regarding the nature of the carbon overlayer formed in these studies on Re(0001). The site-blocking ability and the carbon AES both are typical for "inert" carbon. However, the lowering of the D_2 binding energy and the hydrogenation of butadiene suggest that the carbon overlayer is slightly "active". Below are summarized the main results and conclusions of adsorption on the clean, sulfur covered and carbon covered Re(0001) surface.

1) D_2 chemisorption on clean Re(0001) showed similarities to Pt(111). A low temperature state was observed for D_2 at high coverage.
    a) Pre-adsorbed sulfur was observed to block adsorption sites and lower the desorption temperature slightly (30K).
    b) Pre-adsorbed carbon also acts to block sites for adsorption, but it also lowers the lowest temperature for desorption to 290K form 315K.
2) Unsaturated hydrocarbons sequentially dehydrogenate during thermal desorption. The H_2 desorption spectra for these compounds exhibit peaks in the same temperature range : 300K, 350-380K, 420K, and a tail from 500-700K.
3) Pre-adsorbed sulfur acts to block sites for dehydrogenation, and enhances weak (9 - 10

$\frac{\text{kcal}}{\text{mol}}$)[61] reversible molecular adsorption.

5. Acknowledgements

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Table 1: Desorption temperatures (K) of various hydrocarbons and their desorption products from Re(0001) with various overlayers. Saturation coverage is used sith a heating rate of $10\frac{K}{s}$.

compound		surface		
adsorbed	desorbed	clean	sulfur θ_s=0.25	carbon θ_c=0.4
D_2	D_2	380 (1.5L) 200-250 (shldr) 315 (>10L)	350	290,450 200-250 (shldr)
thiophene	H_2 thiophene	400 (≃0.3L) 350, 450 (>0.4L) 180, 250	360, 510, 680 180	300, 480, 680 180, 230
thiophene-2,5-d_2	H_2 HD D_2	450 390 350	350, 480 360, 500 360	300, 450-700 300, 450, 600 300,700
1,3-butadiene	H_2 butadiene butene	300, 380, 420 150 -	370, 500 150 -	300, 420, 660 150 250
1-butene	H_2 butene	300, 380, 420 150	380, 420 150	300, 360 420, 680 150
trans-2-butene	H_2	300, 380, 420	380	300, 340, 420
cis-2-butene	H_2	300, 370, 420	360, 420	300, 350, 420

Table 2: Thermal desorption peak maxima (K) from the dehydrogenation of various hydrocarbons (yielding H_2) on various metal surfaces.

compound	metal surface			
	Rh(111)	Ru(0001)	Re(0001)	Mo(100)
ethylene	330, 385, 420[31]	355, 420[29]	300, 420[12,35]	270, 360[35]
1-butene	295, 345, 420[34]		300, 380, 420	260, 310, 350[8]
1,3-butadiene	290, 365, 415[34]		300, 390, 420	290, 360[8]
thiophene		380, 490[55]	350, 450	270, 360[8]

Figure Captions

Figure 1: Thermal desorption spectra of D_2 at various coverages on Re(0001). Species observed was D_2 (mass 4). Heating rate was $10\frac{K}{s}$.

Figure 2: Thermal desorption spectra of D_2 on Re(0001) as a function of sulfur (a) or carbon (b) coverage. Exposure was 1.5L. Species observed was D_2 (mass 4).

Figure 3: D_2 (mass 4) TDS peak areas on sulfur (a) and carbon (b) covered Re(0001) at an exposure of 1.5L.

Figure 4: Thermal desorption spectra of thiophene, 1,3-butadiene, 1-butene, cis-2-butene, and trans-2-butene at multilayer coverage on Re(0001). Species observed was H_2 (mass 2).

Figure 5: Thermal desorption spectra of 1,3-butadiene as a function of butadiene coverage on Re(0001). Species observed was H_2 (mass 2).

Figure 6: H_2 (mass 2) TDS peak areas of thiophene ⊡, 1,3-butadiene ⊙, and 1-butene △ at multilayer exposures nomalized to the clean Re(0001) surface as a function of sulfur coverage.

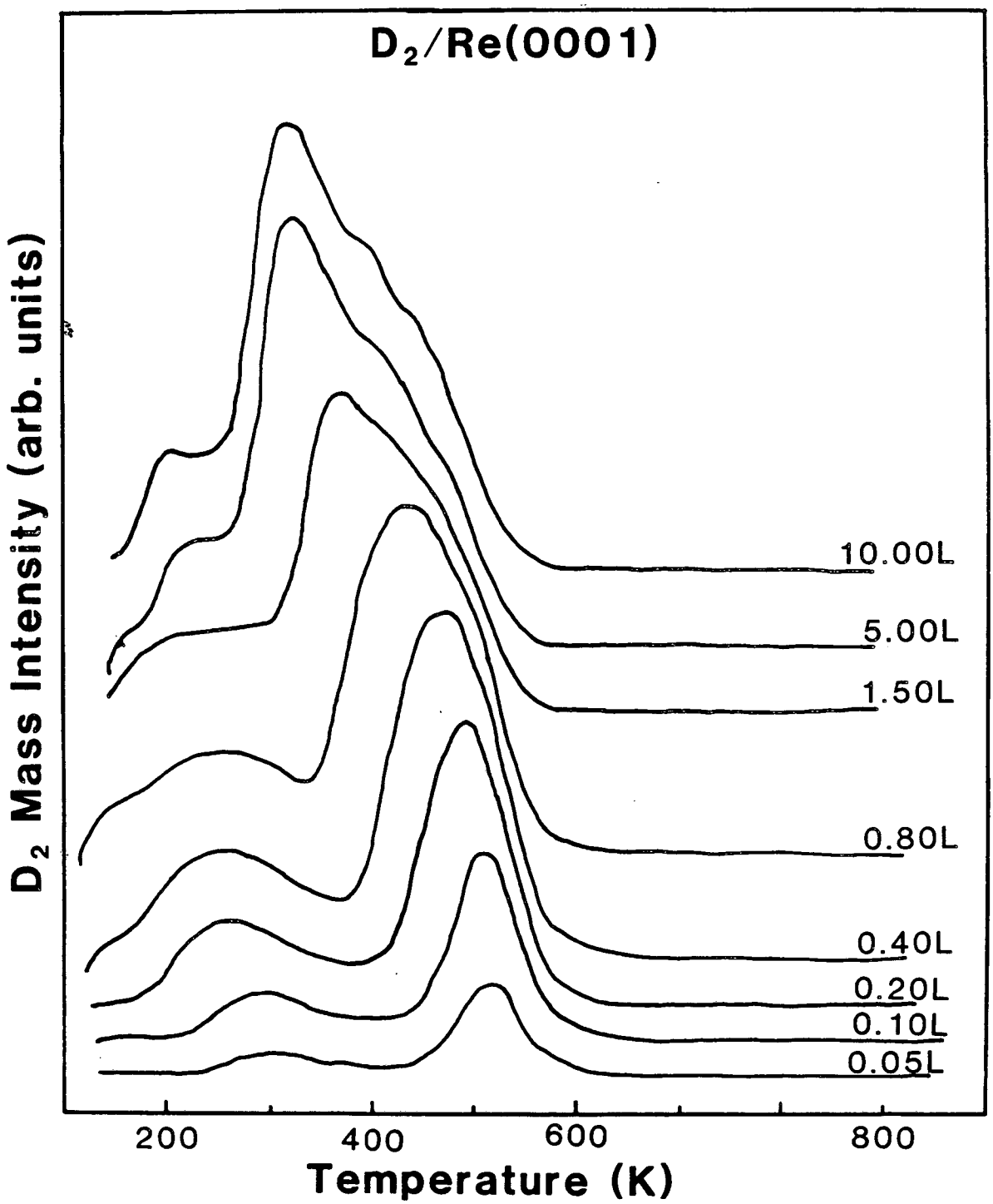
Figure 7: Thermal desorption spectra of 1,3-butadiene on Re(0001) as a function of sulfur (a) and carbon (b) coverage. Exposure is 0.25L. Species observed were H_2 (mass 2), butadiene (mass 54), and butene (mass 56).

Figure 8: Thermal desorption spectra of thiophene (a) and butene (b) at multilayer coverage on Re(0001) as a function of sulfur coverage. Species observed were thiophene (mass 84) (a) and butene (mass 56) (b).

Figure 9: Thermal desorption spectra of thiophene-2,5-d_2 on Re(0001) as a function of thiophene coverage. Species observed were H_2 (mass 2) and D_2 (mass 4).

Figure 10: Thermal desorption spectra of thiophene-2,5-d_2 on Re(0001) as a function of sulfur (a)

and carbon (b) coverage. Exposure is 0.35L. Species observed were H_2 (mass 2) and D_2 (mass 4).



XBL 873-1235

Fig. 1

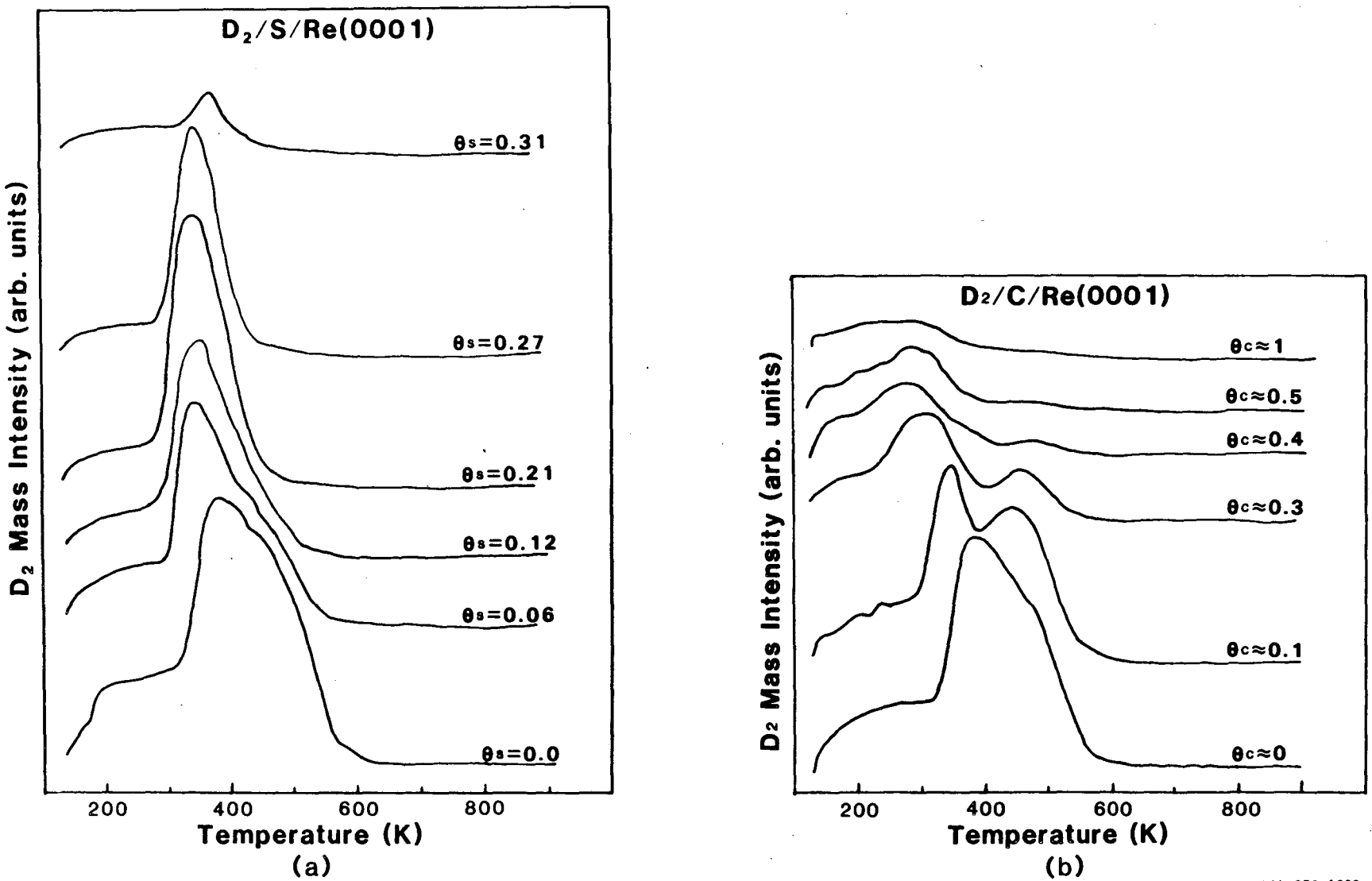


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Fig. 2

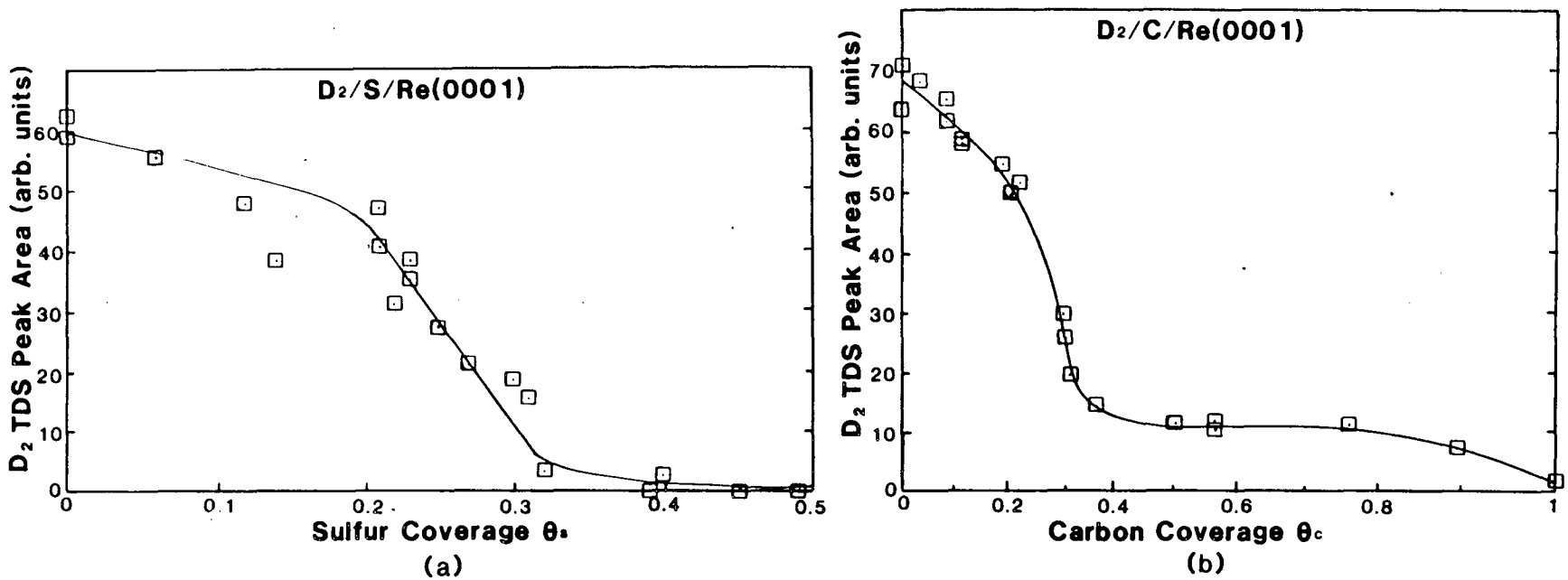

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Fig. 3

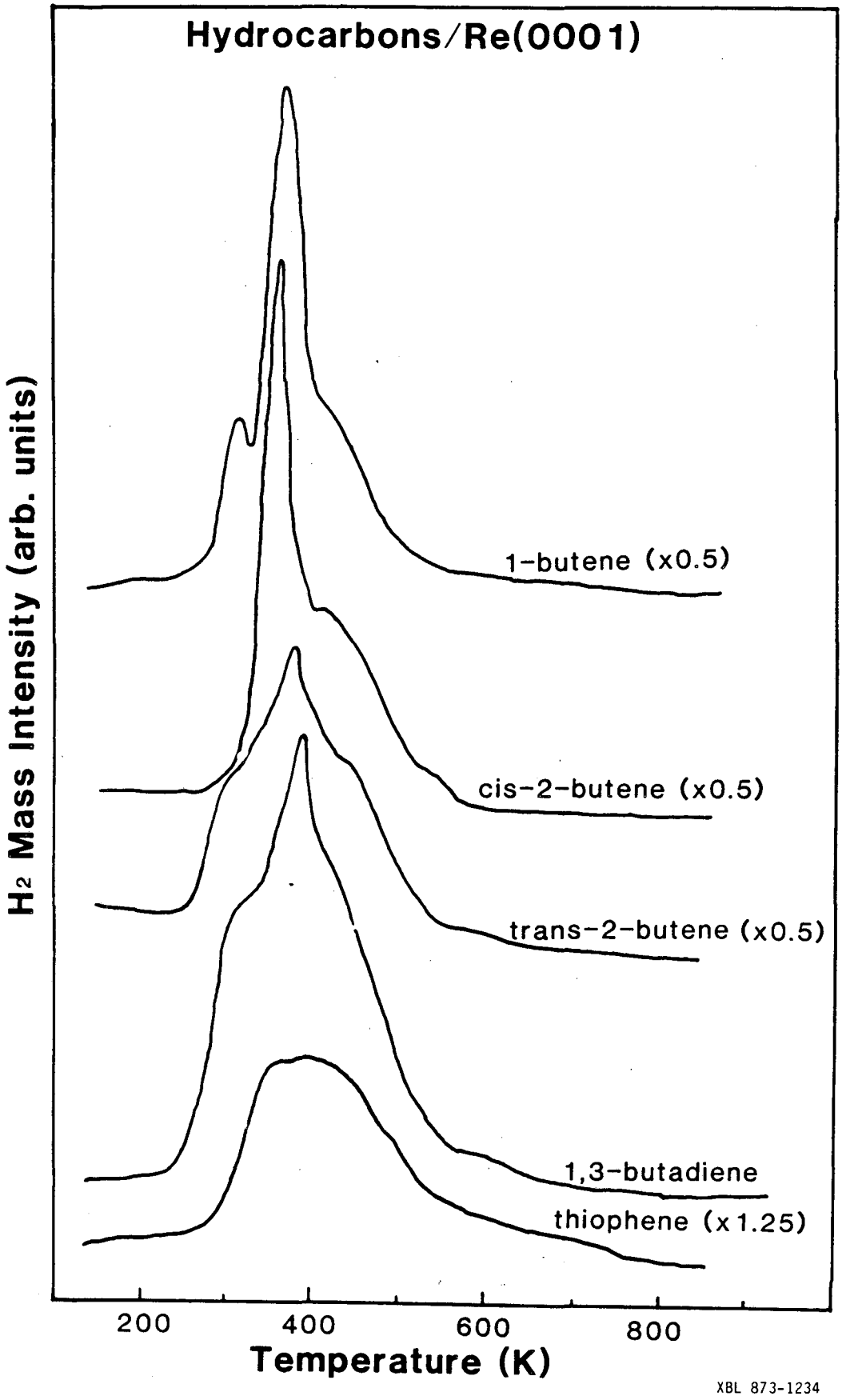

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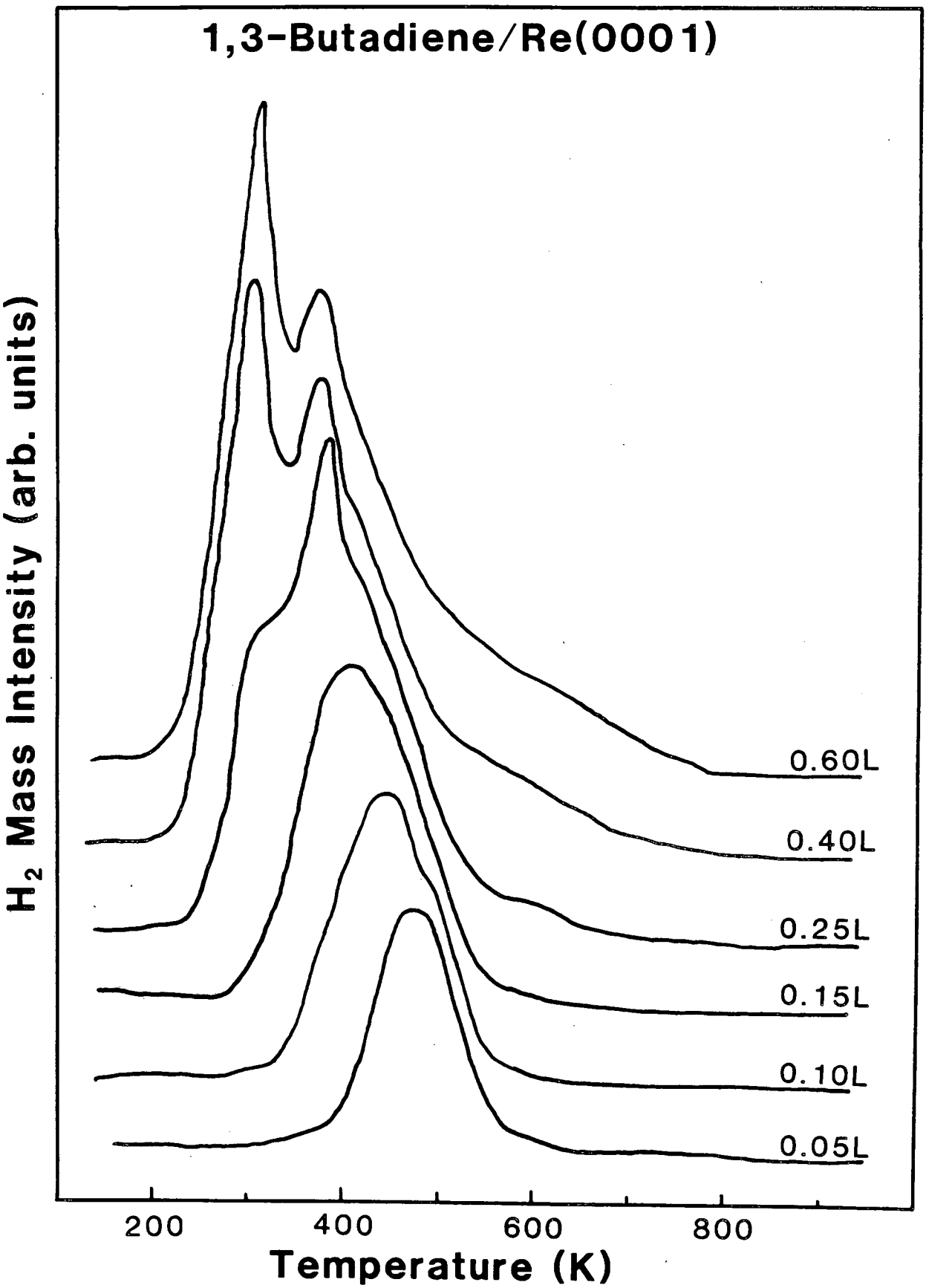
Fig. 4



XBL 873-1233

Fig. 5

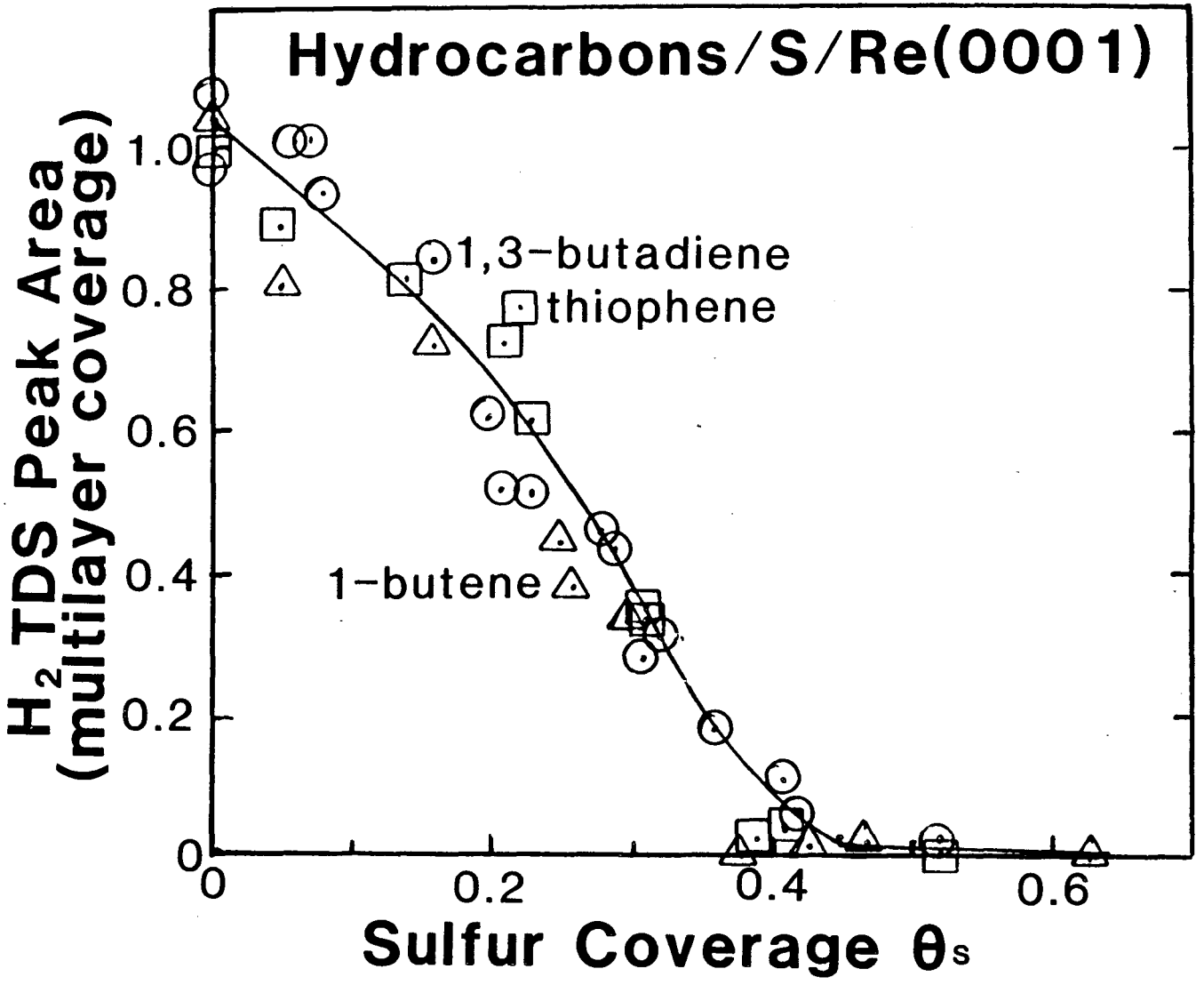


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Fig. 6

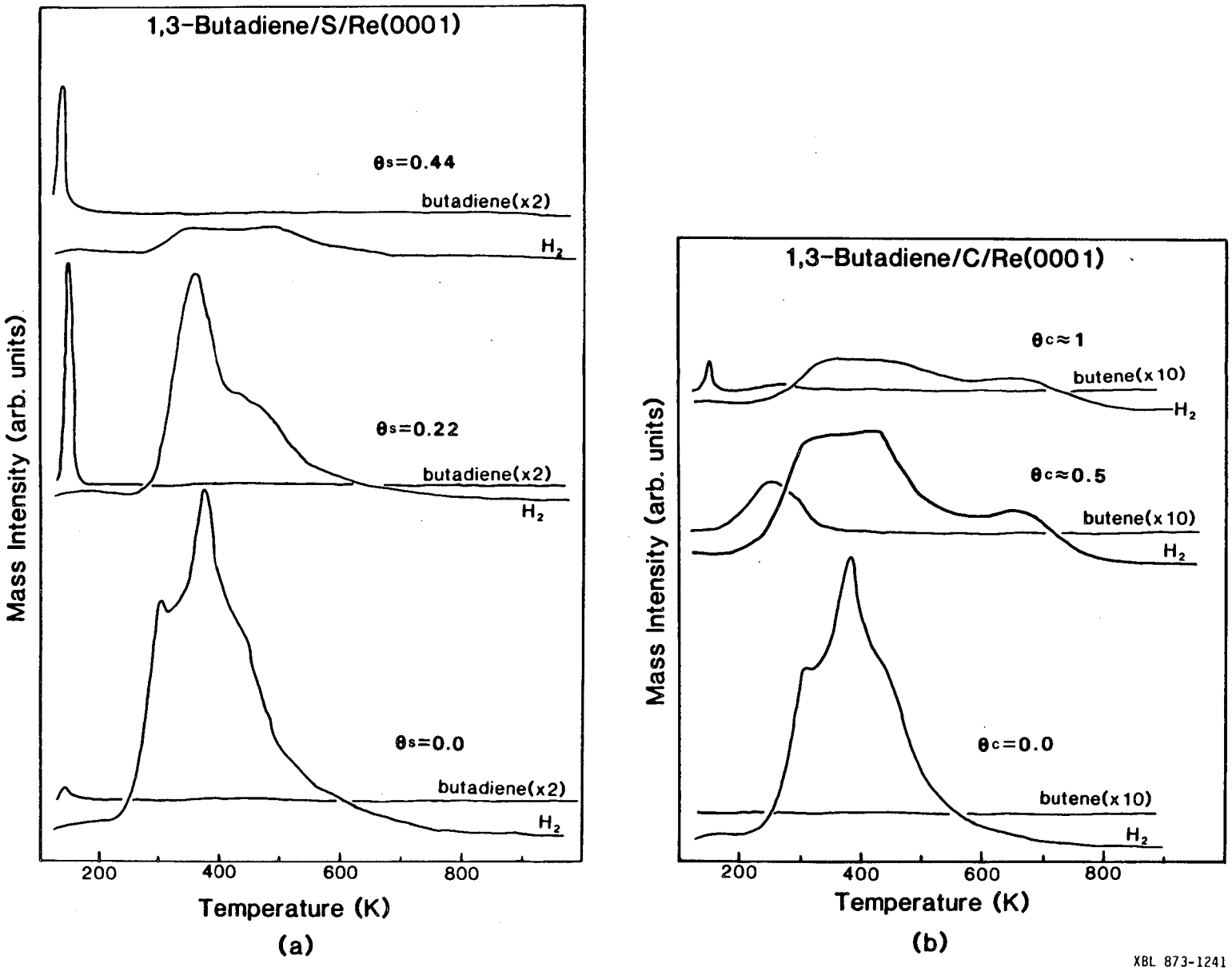

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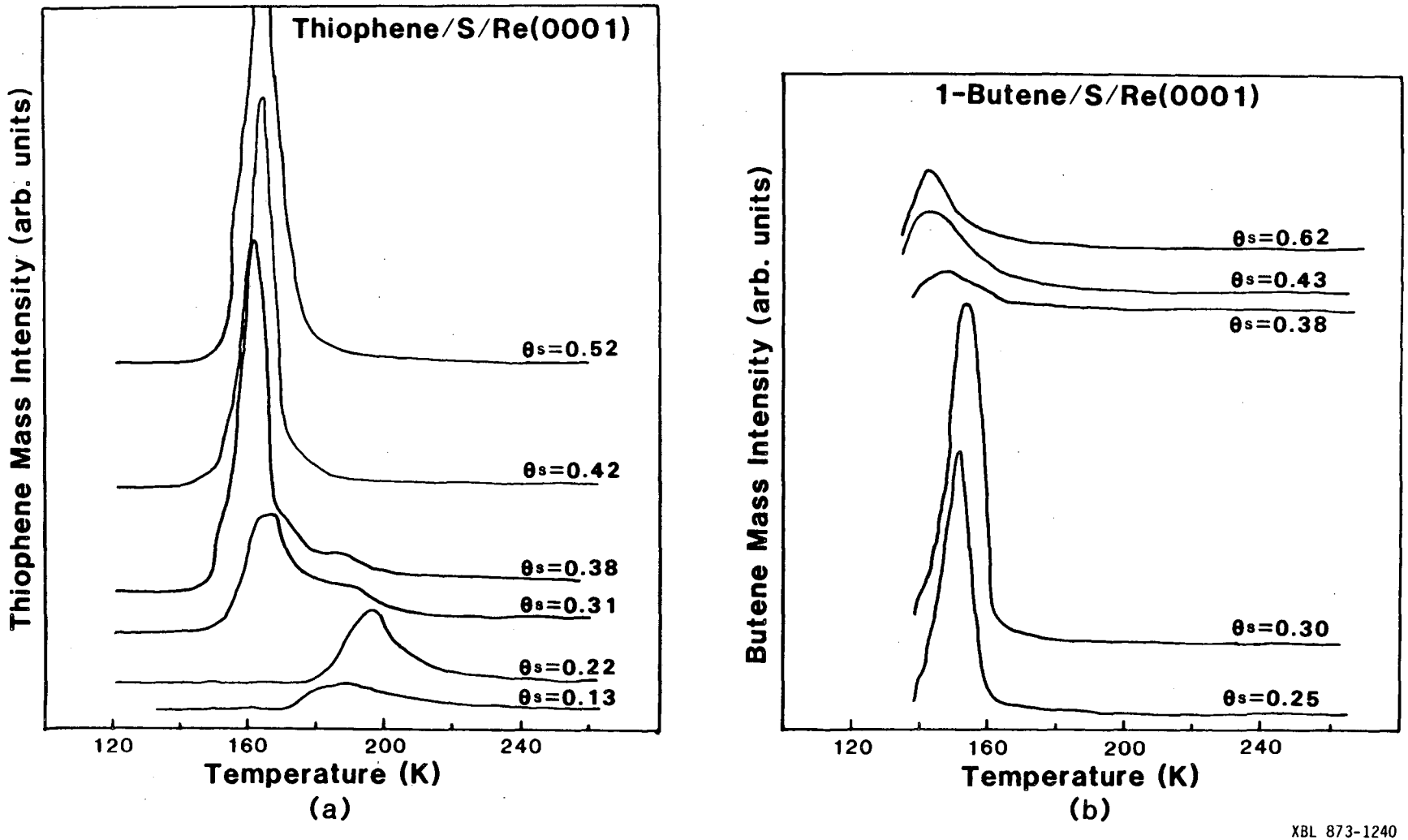
Fig. 7



XBL 873-1240

Fig. 8

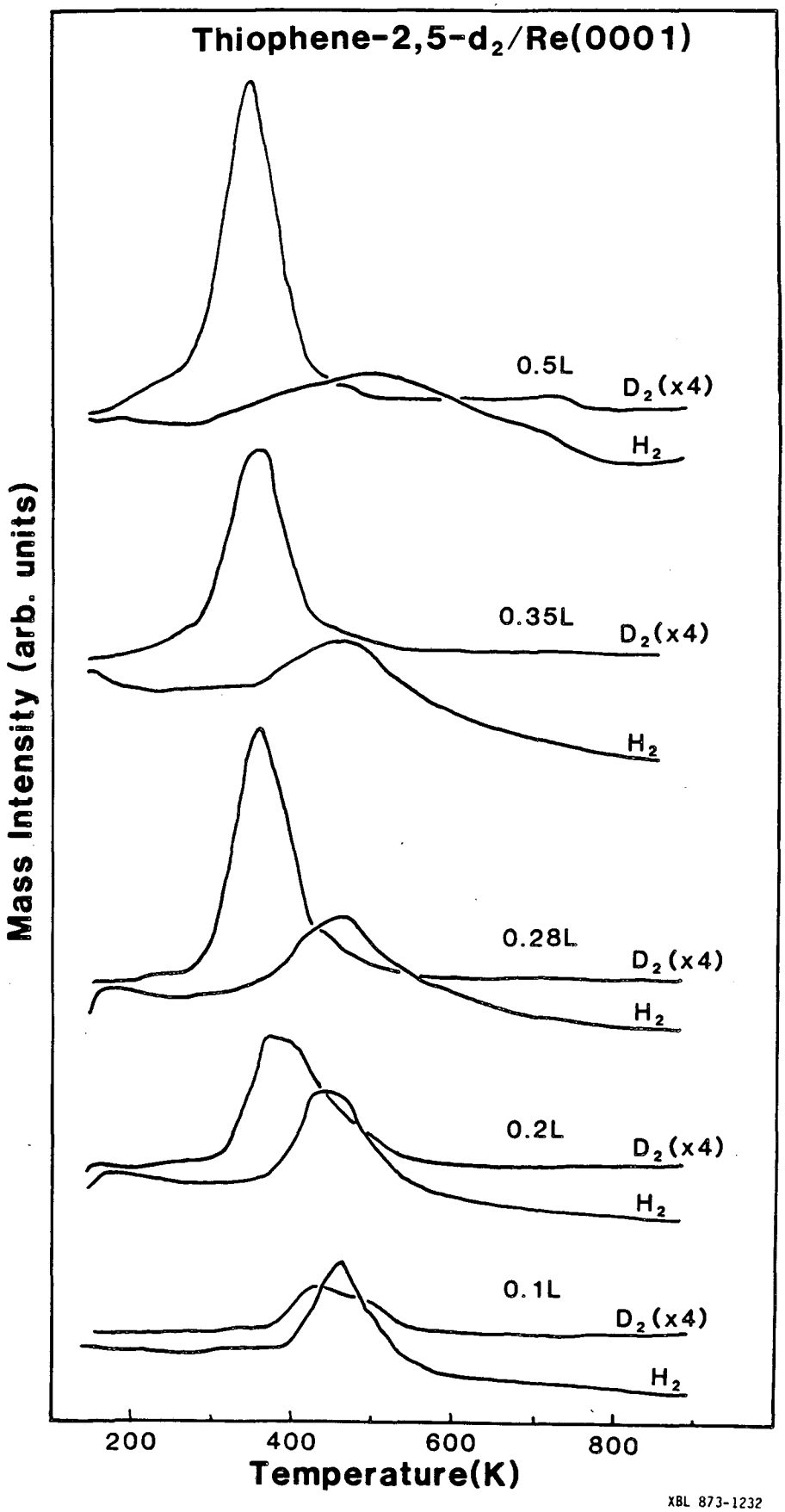
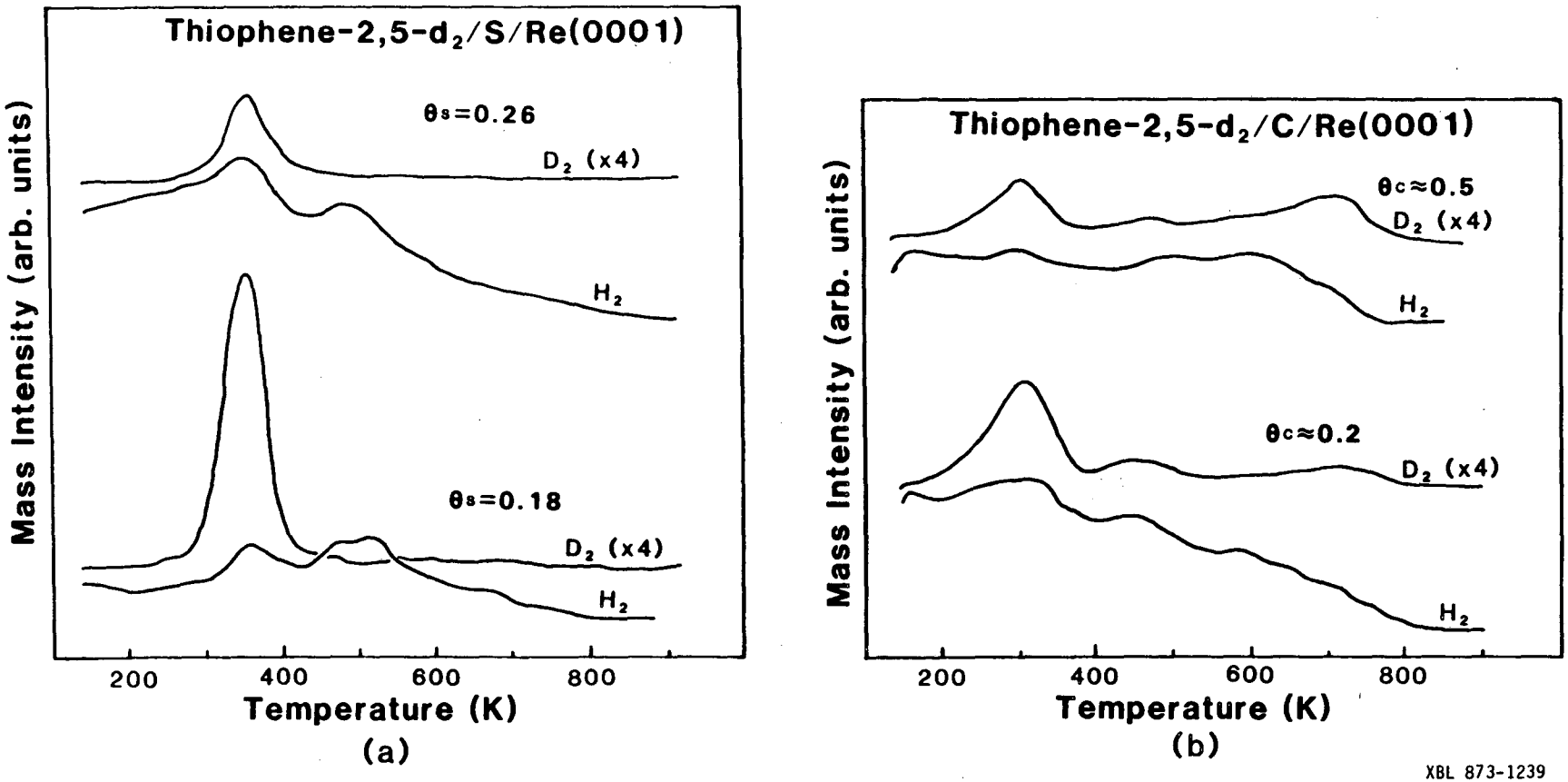

Thiophene-2,5-d2/Re(0001)
0.5L
D2(x4)
H2
0.35L
D2(x4)
H2
0.28L
D2(x4)
H2
0.2L
D2(x4)
H2
0.1L
D2(x4)
H2
Mass Intensity (arb. units)
200
400
600
800
Temperature(K)
XBL 873-1232

Fig. 9



XBL 873-1239

Fig. 10

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