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The hydrogenation and direct desulfurization reaction pathway in thiophene hydrodesulfurization over MoS_2 catalysts at realistic conditions: A density functional study

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Abstract

We present density functional theory (DFT) calculations of reaction pathways for both the hydrogenation (HYD) and direct desulfurization (DDS) routes in the hydrodesulfurization (HDS) of thiophene over the different MoS_2 edge structures, which will dominate under typical HDS reaction conditions. Contrary to the generally accepted view, we find that the HYD reaction path, which involves hydrogenation to 2-hydrothiophene followed by hydrogenation to 2,5-dihydrothiophene and subsequent S–C scission, can occur at the equilibrium Mo($10\bar{1}0$) edge without the creation of coordinatively unsaturated Mo edge sites. This is related to the presence of the metallic-like brim sites also observed in previous STM studies. It is found that the HYD reaction pathway also can occur at the S($\bar{1}010$) edge. At this edge, the equilibrium edge structure itself is not active, and sulfur vacancies must be created for the reaction to proceed. It is found that the effective energy barrier for vacancy creation depends on the H_2 partial pressure. The sulfur vacancies at the S($\bar{1}010$) edge are also found to be active sites for the DDS pathway. This pathway does involve an initial hydrogenation step to 2-hydrothiophene, followed by S–C scission. Analyzing the relative stabilities of reactants and intermediates suggests that a catalytic cycle may involve elementary steps that start at one type of edge and are completed at the other; for example, many intermediates are more stable at the S edge. The regeneration of the active sites is found to be a crucial step for all of the reaction pathways, and the importance of reactions at Mo brim sites is related to the observation that regeneration is least activated here. It is proposed that an important activity descriptor is the minimum energy required to either add or remove S from the different equilibrium edge structures.

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1. Introduction

As the global energy consumption rapidly increases and environmental legislation becomes stricter, the need to upgrade low-quality oil to clean transport fuels increases. To meet current environmental regulations, refiners must remove even the most refractory sulfur-containing species [1–6]. This is generating increased interest in obtaining a detailed description of the catalytic hydrotreating reactions occurring during desulfurization. Hydrodesulfurization (HDS) has been investigated for many decades, leading to increased insight into the structure of the active catalyst particles, their interactions with the support, the effect of promoters, and the kinetics of the reactions [7]. However, much less is known about the reaction mechanisms and the nature of the active sites, and many different views have been presented [6–12].

Thiophene is a suitable test molecule for studying the HDS reaction because it contains an S atom in a benzene-like ring and also is small. Therefore, thiophene HDS has been the most studied reaction; but there has been considerable debate regarding the mechanism [7,10,13–23]. For instance, it has been difficult to establish to what extent prehydrogenation to dihydrothiophene or tetrahydrothiophene may be necessary before S–C bond cleavage. It also appears that the observed reaction

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products depend on the reaction conditions [7,22,23]. Tetrahydrothiophene typically is not an intermediate at atmospheric pressure [23], but it may be a major intermediate at high pressure [17] and low temperature [10], because the formation of tetrahydrothiophene is equilibrium-limited at high temperature [10]. A detailed study of the HDS of 2-methylthiophene at high pressure [22] found that the splitting of the S–C bond in tetrahydro-2-methylthiophene (resulting in the formation of a thiol) is faster than the hydrogenation of the thiophene ring or of the pentene to yield pentane. Thus, the hydrogenation activity of the catalyst appears to be an important feature, which can influence the concentration of the reaction products. The proposed thiol intermediate was not observed, leading to the conclusion that the splitting of S–C bonds in thiols is very fast.

For the larger S-containing molecules like dibenzothiophene, it has been established that two parallel routes exist, a direct desulfurization route (DDS) through biphenyl and a hydrogenation route (HYD) in which one of the benzene rings is hydrogenated first [24]. In order to produce the clean transport fuels demanded today, even the very refractory sulfur compounds like 4,6-dimethyldibenzothiophene must be removed [1,2,4,5,7,19,25,26]. For such molecules, the HYD route may become more important than the DDS route, which dominates for unsubstituted dibenzothiophene [4,27]. Despite the established understanding of the pathways and the overall kinetics, little direct insight has been obtained regarding the reaction mechanisms and the surface sites involved in the DDS and HYD pathways. It has even been difficult to reach agreement on the mode of adsorption of the reactants. For instance, thiophene has been found to either exclusively adsorb in a so-called η_1 mode (e.g., standing up and binding only through S [28,29]) or adsorb primarily in a so-called η_5 mode (e.g., lying down, bonded through S and the four C atoms), with only a small fraction of the molecules being present in the η_1 mode [30].

Insight into the mechanism of HDS also has been obtained from numerous studies on activity correlations [7,31,32], which have been taken as evidence for MoS_2 edge vacancies being the active sites in HDS, because vacancy formation generally has been assumed to take place at the MoS_2 edges. In support of this, basal plane surfaces have been observed to be inactive [33]. For hydrogenation reactions, the activity also has been observed to correlate with the number of MoS_2 or WS_2 edges sites [34,35], and vacancies have been concluded to be the active sites for such reactions. However, in general it is difficult to draw firm conclusions from such activity correlations [7], because a variety of other species, like SH groups [36], also may be located at the edges. Further support for the importance of vacancies has been provided from experimental studies of the effect of prereduction temperature [37,38]. Moreover, the observed activity correlation with the metal–sulfur bond strength, leading to the formulation of the bond energy model (BEM), suggest that vacancy formation is a key aspect of HDS [39].

Because both HDS and hydrogenation activities have been observed to correlate with the number of MoS_2 (WS_2) edge sites, some authors have suggested [40,41] that the sites for the DDS route and the HYD route are similar. Indeed, kinetic models based on this proposal can provide a good fit of kinetic results. However, a number of effects strongly suggest that DDS and hydrogenation sites are not the same. For example, the presence of methyl groups in dibenzothiophene may severely reduce the activity for S removal via DDS without significantly affecting the hydrogenation activity [4]. In addition, H_2S is a strong inhibitor for S removal via DDS but has only a minor effect on hydrogenation [27]. Evidence for different sites for HYD and DDS also comes from studies of the effect of nitrogen compounds [7,26,42–52]. In contrast to the effect of H_2S, the presence of basic nitrogen compounds is observed to mainly inhibit the HYD route with only a moderate effect on DDS. The inhibiting effect was found to correlate with the proton affinity of the nitrogen compounds [44,45]; this result also suggests that different sites are involved in HYD and DDS. Based on the observation that quite large molecules may be desulfurized via the HYD route, Ma and Schobert [53] suggested that the hydrogenation sites are multiple vacancy sites on the Mo($10\bar{1}0$) edges capable of π-bonding the large molecules. The presence of such sites has been discussed in the literature [7], because the single-bonded sulfur atoms created by simply cleaving the bulk structures at the Mo($10\bar{1}0$) edges were proposed to be unstable.

Recently, it has become possible to use density functional theory (DFT) methods to address a number of issues relevant for HDS [54–72]. In the first DFT study of MoS_2 and Co-MoS structures, Byskov et al. [71] found that it is energetically very unfavorable to create the "naked" Mo edges, where Mo is exposed at the edge and only 4-fold coordinated, and they concluded that such structures probably are not present under realistic HDS conditions [71]. Subsequent DFT studies have supported this conclusion [56,67,70]. Even though multiple vacancy sites may be very reactive [59,62,64], they are expected to readily react with H_2S, and reactions involving such sites should be extremely strongly inhibited by H_2S. Because the hydrogenation reactions are not poisoned by H_2S, these results show that some other sites must be involved in HYD. The first study of mechanistic aspects of HDS using DFT was carried out by Neurock and Van Santen, who studied the HDS of thiophene over Ni_xS_y clusters [65]. Although the study does not directly relate to MoS_2 catalysts, coordinatively unsaturated Ni sites were found to be very reactive.

Recently, it has been possible to obtain important clues regarding the hydrogenation sites and the HYD pathway from scanning tunneling microscopy (STM) studies [61]. Such studies have provided atom resolved images of the MoS_2 nanostructures; when they are combined with DFT calculations, quite detailed information may be obtained from the images [56,57,61,73,74]. These combined studies clearly show that naked Mo($10\bar{1}0$) edges are not present at ultrahigh vacuum conditions. In contrast, the results show in agreement with the DFT calculations [54,56,63,69,71] that the Mo atoms will tend to maintain the full sulfur coordination of 6. This is achieved by extensive edge reconstruction. Quite surprisingly, it was found that these fully sulfur-saturated Mo($10\bar{1}0$) edges of MoS_2 have some sites with metallic character [56,73,75]. These so-called "brim" sites could bind thiophene and were observed to be involved in further hydrogenation reactions [61]. One S–C bond in thiophene appeared to be cleaved at the brim site, and the resulting ad-

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