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Atomic-scale insight into the origin of pyridine inhibition of MoS_2-based hydrotreating catalysts

Burcin Temel [a], Anders K. Tuxen [b], Jakob Kibsgaard [b], Nan-Yu Topsøe [a], Berit Hinnemann [a,*], Kim G. Knudsen [a], Henrik Topsøe [a], Jeppe V. Lauritsen [b,*], Flemming Besenbacher [b]

[a] Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Kgs. Lyngby, Denmark
[b] Interdisciplinary Nanoscience Center (iNANO), and Department of Physics and Astronomy, Aarhus University, DK-8000 Aarhus C, Denmark

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ABSTRACT

Basic nitrogen-containing compounds such as pyridine are well known to be inhibitors of the hydrodesulfurization (HDS) reaction for the MoS_2-based catalysts. From an interplay of scanning tunneling microscopy (STM) experiments and density functional theory (DFT) calculations, atomic-scale insight into pyridine adsorption on MoS_2 is obtained. In agreement with previous IR-spectroscopy and DFT studies, the STM results show that the pyridine molecule itself interacts weakly or not at all with the MoS_2 nanoclusters. However, in the presence of hydrogen at the MoS_2 edges, adsorbed species are revealed by STM also at the edges. The calculated DFT energies and simulated STM images allowed us to conclude that these species are pyridinium ions located at the catalytically active brim sites. Furthermore, the DFT results for the vibrational modes of the adsorbed pyridinium species agree well with those observed in earlier IR experiments on high surface alumina-supported MoS_2 catalyst. The adsorption sites appear to be very similar to the brim sites involved in hydrogenation reactions in HDS. Thus, the combined STM and DFT results provide new atomic-scale insight into the inhibition effect of basic N-compounds in HDS and the first direct observation of the adsorption mode of basic N-compounds on the catalytically active MoS_2 edges. Our results lend further support to previously reported correlations between inhibiting strength and proton affinity for the N-containing compounds.

1. Introduction

The increasingly more stringent legislative demands for removing sulfur and producing cleaner fuels have introduced new hydrotreating challenges for the refining industries [1]. Specifically, in order to meet present and future specifications [2] for ultra-low sulfur fuels [1,3–11] with low levels of sulfur and nitrogen compounds, improved activity and selectivity of the HDS catalysts are required. Consequently, increased research efforts are devoted to obtain an improved atomic-scale understanding of the structure, reactivity and inhibition mechanism of MoS_2-based hydrotreating catalysts.

Much of the earlier research has suggested that hydrodesulfurization (HDS) reactions of sulfur-containing compounds occur at characteristic brim sites at the edges of MoS_2 nanoclusters and that HDS can take place following two different pathways: the hydrogenation (HYD) pathway, in which several hydrogenation steps precede sulfur extrusion, and the direct desulfurization (DDS) pathway [1,12,13]. For simple S-compounds, the DDS pathway has been shown to be the most important route [1,4,12]. However, this pathway is often suppressed for sterically hindered alkyl-substituted compounds such as 4,6-dimethyldibenzothiophene (DMDBT), and the HYD pathway may become the dominating route since it is less sensitive to steric effects [4]. Thus, as crude oils become heavier and contain an increasing amount of refractory compounds, the HYD activity is becoming increasingly more important [4,5,7,14]. However, an efficient use of the HYD pathway is complicated by the fact that heterocyclic nitrogen-containing compounds such as pyridine or quinoline, which are typically present in heavy crude oils, severely inhibit the HYD route [1,7,10,15–25]. Ideally, one could alleviate this problem by removing these N-compounds by hydrodenitrogenation (HDN) processes before sulfur is removed by HDS [1,3–5,7,10,12,14–16,20–22,24,26–33], but, HDN is often slower than HDS, and it is therefore imperative to understand the origin of the N inhibition in order to minimize its effect.

For non-sterically hindered heterocyclic compounds with nitrogen in a six-membered ring, it has been shown that the equilibrium adsorption constants, which are used as a measure of

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* Corresponding authors. Fax: +45 45279999 (B. Hinnemann), +45 86120740 (J.V. Lauritsen).

E-mail addresses: behi@topsoe.dk (B. Hinnemann), jvang@inano.au.dk, jvang@phys.au.dk (J.V. Lauritsen).

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inhibition strength, correlate well with proton affinities of the inhibitor molecules [16,26]. It was proposed that this correlation is due to the interaction of nitrogenous molecules with Brønsted acid sites on the edges of the MoS_2 nanoclusters and that those species that tend to get protonated easier adsorb on the catalyst surface more strongly. Subsequent IR studies [34] of pyridine adsorption on alumina-supported MoS_2 catalyst did indeed show the presence of Brønsted acid sites as indicated by the presence of pyridinium ion, which gives rise to a characteristic IR band at $1546\ \mathrm{cm}^{-1}$. The fact that the pyridinium ion was not observed at room temperature but first at higher temperatures indicated that the protonation was activated such that high temperature was required to activate the proton transfer from the SH group to pyridine [18,34].

The nature of the active sites for the HYD and DDS pathways has been much debated in the literature. Early studies [1,31,35] have considered multiple vacancy sites or "naked" MoS_2 edge sites, i.e., the Mo-edge in its stoichiometric termination without the presence of the strongly bonded sulfur atoms [36]. Recently, combined STM [37–40] and DFT studies [41–48] have allowed one to revisit many of the earlier proposals for HYD and DDS sites since these methods have provided unique insight into the structures of MoS_2 nanoclusters. Extensive edge reconstructions may take place, and the structures are typically very different from those proposed in the past (as in the "naked" Mo-edges) where it was assumed that the edges have structures with atoms occupying bulk-like lattice positions [44,45,47]. It was furthermore revealed that the shape of MoS_2 nanoclusters depends significantly on the composition of the surrounding gas that is whether they are exposed to sulfiding or reducing gas conditions. Specifically, MoS_2 clusters may have a triangular shape with only the $(10\bar{1}0)$ Mo-edge exposed under sulfur-rich conditions, whereas they depict a hexagonal morphology and expose both the Mo-edge and the $(\bar{1}010)$ S-edge under HDS conditions. Surprisingly, high resolution images also revealed a characteristic bright brim structures at the edges of MoS_2 nanoclusters (referred as the brim sites) [37,38,40–44,49], which were identified by DFT to be metallic edge states. Subsequent STM and DFT studies showed that these sites may play an important role for both hydrogenation and C–S bond scission.

Based on the improved atomic-scale understanding of the MoS_2 edges, it has recently been possible to provide insight into the details of active sites and reaction pathways for both the HYD and the DDS pathway of thiophene [31,50]. Pyridine inhibition was treated in a DFT study by Logadottir et al. [51]. They found that the pyridine molecule only interacts weakly with the MoS_2 nanoclusters. However, on the Mo-edge, pyridine can be protonated to pyridinium with a very low barrier, and the resulting pyridinium binds much stronger than pyridine. In contrast, on the S-edge, formation and binding of pyridinium was not found to be favorable. These results provided additional evidence for pyridinium formation as the main origin of the inhibition and furthermore pointed out that inhibition is different at the two edges.

Although the previous studies have provided evidence for pyridinium formation on MoS_2, the exact bonding configuration has never been addressed directly. In the present combined STM and DFT study, we provide the first direct evidence for the presence and location of pyridinium on MoS_2. In addition, we have carried out a detailed DFT analysis of the vibrational frequencies of different adsorbed species to further elucidate the previous IR results on pyridine adsorption [34]. Finally, the DFT results also allow us to gain more fundamental atomic-scale insight into the interaction of pyridine with MoS_2 nanoclusters and the origin of the inhibiting role of N-containing cyclic compounds. We find that only protonated pyridine species (pyridinium, $C_5H_5N–H^+$), and not pyridine itself, adsorb strongly and especially block the active hydrogenation sites on the Mo-edge of MoS_2 under all relevant catalytic conditions.

2. Methods

2.1. Scanning tunneling microscopy experiments

The STM experiments were performed on a HDS model system consisting of MoS_2 nanoclusters synthesized on a chemically inert Au substrate in an ultra-high vacuum (UHV) chamber with a base pressure below 1×10^{-10} mbar. The experimental setup was equipped with standard utilities for surface preparation and characterization, and the home built variable temperature Aarhus STM [52] that has been proven capable of routinely achieving atomic resolution on MoS_2 nanoclusters in a number of recent studies (see e.g. [6,38,39]). In the study, the STM image was recorded at temperatures ranging from 160 K to room temperature.

The sample was a planar model catalyst system consisting of highly dispersed perfectly crystalline single-layer MoS_2 nanoclusters that are found to adopt characteristic triangular equilibrium shapes under the present sulfiding conditions. The crystalline MoS_2 nanoclusters were synthesized by evaporating metallic Mo onto an Au(1 1 1) substrate followed by post-annealing the sample at 673 K in a sulfiding H_2S atmosphere. In several past studies, this procedure has proven to lead to very uniform and well-characterized ensembles of MoS_2 nanoclusters with a known atomic structure at the edges of the clusters edges. These MoS_2 nanoclusters are ideally model systems suited for addressing the atomic-scale details of the active sites on MoS_2 in HDS. The full details concerning the preparation and characterization of the HDS model system and the atomic details of the MoS_2 nanoclusters have been published previously [40,52]. Pyridine (C_5H_5N) (Sigma Aldrich, 99% purity) was purified by several freeze-pump-thaw cycles and dosed into the UHV chamber through a leak-valve and a stainless steel tube directed toward the sample. The substrate temperature during pyridine exposure was throughout the experiments controlled by cooling a separate sample stage with liquid nitrogen, and molecules could be dosed at here sample-temperatures ranging from 200 K up to room temperature. We used the maximum temperature of the sample recorded during pyridine dosage as the experimental adsorption temperature and not the actual temperature of STM imaging that was 20–30 K lower.

The role of sulfur vacancies and S–H groups as Brønsted acid sites for protonation of the adsorption of pyridine on the edges was systematically investigated by exposing the MoS_2 nanocluster to atomic (pre-dissociated) hydrogen, with hydrogen being pre-dissociated on a hot (~2000 K) tungsten filament. Molecular hydrogen generally does not lead to the formation of S–H groups and vacancies at UHV-compatible pressures less than 1×10^{-6} mbar, since the hydrogen adsorption at the fully sulfided Mo-edge was shown to be endothermic in a previous study [39]. The atomic H flux was obtained by a standard procedure involving backfilling of the UHV chamber with hydrogen to a pressure of 1×10^{-6} mbar while a very hot tungsten filament used for dissociating the H_2 gas was kept at a 100 mm distance of the sample.

2.2. Density functional theory

The density functional theory (DFT) calculations were carried out using an infinite stripe model of MoS_2, analogous to the results in Refs. [42,44,53]. The equilibrium $(\bar{1}010)$ S-edge and $(10\bar{1}0)$ Mo-edge of the stripe are shown in Fig. 1. To enable the correct sulfur dimer pairing at the edges, the slab should contain even number of Mo atoms in the x-direction. The supercell in this study contained four Mo atoms both in the x and in the y-directions, in order to avoid replica interactions and to ensure sufficient decoupling between the Mo- and S-edges. Some of the calculations were also repeated with a 4×6 supercell; however, the differences in