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Sulfide Catalysis without Coordinatively Unsaturated Sites: Hydrogenation, Cis−Trans Isomerization, and H_2/D_2 Scrambling over MoS_2 and WS_2

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Supporting Information

ABSTRACT: Simple test reactions as ethene hydrogenation, 2-butene cis−trans isomerization and H_2/D_2 scrambling were shown to be catalyzed by MoS_2 and WS_2 in surface states which did not chemisorb oxygen and were, according to XPS analysis, saturated by sulfide species. This is a clear experimental disproof of classical concepts that require coordinative unsaturation for catalytic reactions to occur on such surfaces. It supports new concepts developed on model catalysts and by theoretical calculations so far, which have been in need of confirmation from real catalysis.

The catalytic properties of MoS_2 and WS_2 ("MS_2") have attracted tremendous attention due to their importance for hydrorefining catalysis.[1] There has been general agreement that these catalysts operate via coordinatively unsaturated sites (cus)[2] at the edges of their layered structures,[3] and detailed assignments as to which reaction requires which extent of coordinative unsaturation were proposed.[4−6] In the past decade, different views on the active sites on MS_2 have emerged from work with model catalysts and from theoretical studies. On single, fully saturated MoS_2 slabs, a metallic state extending on the basal plane adjacent to the slab edge was observed by Scanning Tunneling Microscopy (STM),[7,8] and theoretical calculations suggested potential catalytic activity of these "brim" sites.[8] Although this was supported by STM images showing adsorbed thiophene to be cleaved on them in presence of atomic hydrogen,[9,10] the gap between model situation and real catalysis remains formidable, calling for experimental support for the relevance of these structures under real conditions. At the same time, theoretical studies have demonstrated the ability of various sulfur species at saturated MoS_2 edges to adsorb and dissociate H_2 without any coordinative unsaturation,[10−12] although the adsorption of hydrocarbons has not been discussed so far. Another recent concept at variance with the classical cus models is based on the observation that the surface layers absorbs carbon during interaction with real feeds, and the activity is assigned to Mo carbide like active species.[13,14]

We are reporting here that both MoS_2 and WS_2 can catalyze simple test reactions like ethene hydrogenation (EH), cis−trans isomerization of 2-butene (CT), and H_2/D_2 scrambling (H_2D_2) in surface states that do not exhibit any oxygen chemisorption capacity (OCS) which might indicate coordinative unsaturation. XPS intensity data and reactivity experiments confirm that the catalytic effect originates from a saturated surface containing hydrogen. Although it is not yet possible to identify the sites operating in our catalysts with any of the theoretical models, our results strongly support the new concepts according to which saturated sites make major contributions to sulfide catalysis.

MS_{2+x} were prepared by thermal decomposition of $(NH_4)_2MS_4$ in inert gas. Inspired by Afanasiev's work,[15] series of samples with varying S/M ratios were made by varying the decomposition temperatures.[16,17] Here, data will be presented from samples with S/Mo = 2.56 and S/W = 2.24 ("$MoS_{2.55}$", "$WS_{2.25}$"), while more details and data on the remaining materials will appear elsewhere.[16,17] Basic characterization included elemental analysis, XRD, N_2 physisorption and TEM. XRD revealed the 2H-MS_2 structure of the sulfides (Figure S1), their small particle sizes in stacking direction (on average 3.4 and 3.8 nm for $MoS_{2.55}$ and $WS_{2.25}$), and eventually lattice plane bending (slight shift of (002) reflections to lower angles). These observations are confirmed by TEM images (Figure S2).

OCS and catalysis were studied in a setup allowing easy switch between flow and recycle modes.[6] Samples were reduced in dilute H_2 (10% in He) or thermoevacuated at various temperatures (xyz K: $\mathbf{R}_{xyz}$, $\mathbf{V}_{xyz}$) before the OCS capacity was measured (pulse mode, 273 K). The adsorbed oxygen was removed by a mild hydrogenation at 473 K ($\mathbf{IR}_{473}$), which did not change the OCS capacity. Thus, the $\mathbf{V}_{xyz}$ pretreatment involved a final contact with H_2 at 473 K. Catalytic studies were made in recycle mode (see Supporting Information). The absence of any oxygen traces that could interfere with the OCS measurements was scrupulously examined (cf. refs 16, 17). Thus, a $MoS_{2.15}$ sample that yielded zero OCS capacity after thermoevacuation ($\mathbf{V}_{723}$ without subsequent $\mathbf{IR}_{473}$) was recovered from the reactor via a glovebox, and studied by XPS after sample transfer without air contact: No indication for oxidation neither of Mo nor of S were found, and the minor O 1s sample present already in the as-prepared material was not increased. This measurement showed the near-surface region stronger enriched in sulfur than even in the initial sample ($(S/Mo)_{XPS}$ = 2.52 vs 2.42, bulk ratios −1.91 and 2.17,

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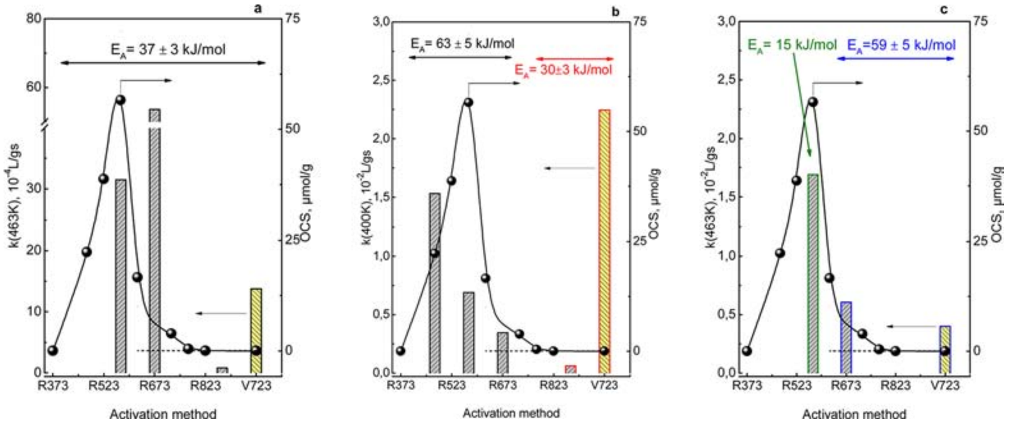

Figure 1. Catalytic activity and OCS capacity of $MoS_{2.55}$ after different pretreatments. (a) Ethene hydrogenation, T_{cat} = 463 K; (b) cis−trans isomerization of 2-butene, T_{cat} = 400 K; (c) H_2/D_2 scrambling, T_{cat} = 463 K. Activation energies resulting from different pretreatments shown in the panels.

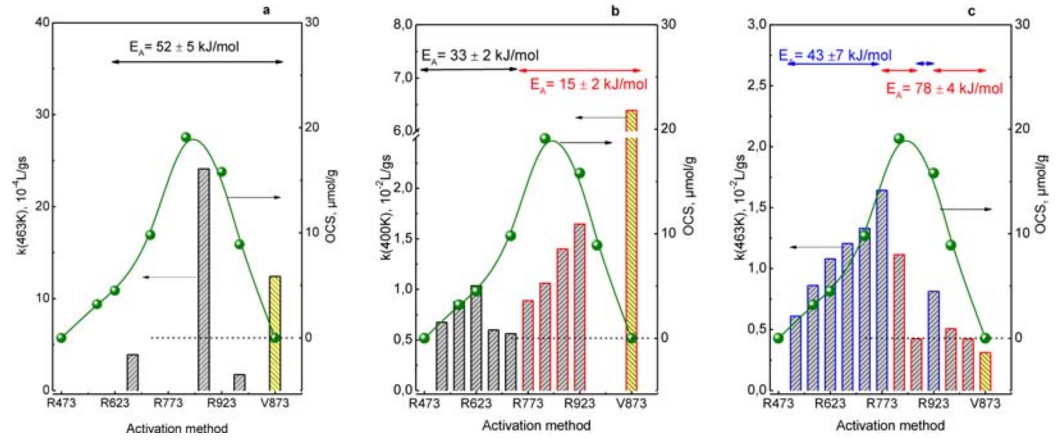

Figure 2. Catalytic activity and OCS capacities of $WS_{2.25}$ after different pretreatments. (a) Ethene hydrogenation, T_{cat} = 463 K; (b) cis−trans isomerization of 2-butene, T_{cat} = 400 K; (c) H_2/D_2 scrambling, T_{cat} = 463 K. Activation energies resulting from different pretreatments shown in the panels.

respectively): Apparently, thermoevacuation leads to a saturated surface, the vacancies being distributed into the bulk.

During the activation treatments, textural properties (BET surface area, stacking height) and composition of the materials varied in a complex manner, which has no obvious relation to the catalytic properties. Upon reduction, the BET surface area of $MoS_{2.55}$ exhibited a monotonous increase from 5 m^2/g ($\mathbf{R}_{473}$) to >60 m^2/g ($\mathbf{R}_{773}$), while a shallow maximum at 72 m^2/g was found for $WS_{2.25}$ after $\mathbf{R}_{573}$ (see Figure S3). Stacking heights started to grow moderately at reduction temperatures T_{red} > 573 K ($MoS_{2.55}$) and >823 K ($WS_{2.25}$). Reduction caused sulfur loss, but with different patterns.[16,17] Falling to 1.91 already after $\mathbf{R}_{573}$, the S/Mo ratio of $MoS_{2.55}$ went through a minimum of 1.65 after $\mathbf{R}_{773}$ returning to 1.87 after $\mathbf{R}_{923}$, whereas the S/W ratio of $WS_{2.25}$ never fell below 2. Analogously, a monotonous decay above S/M = 2 was observed with MoS_{2+x} of small S excess, and a pronounced S/W minimum with WS_{2+x} of large S excess.[16,17] We assign this to sulfide mobility at higher temperatures (>723 K) where more stable structures may delay loss of sulfur.[16,17] This mobility may also explain the pronounced peaks in the temperature dependence of the OCS capacities (Figures 1 and 2). Thermoevacuation resulted in nearly stoichiometric samples (S/Mo − 1.98, S/W − 1.96).

In Figure 1, activity data (first-order rate constants at a reference temperature T_{cat}) of $MoS_{2.55}$ are summarized and compared with the OCS capacities. The range of activation energies E_A observed is also reported. After a pronounced maximum at T_{red} = 523 K (56.6 μmol/g), the OCS capacity fell to zero at 823 K. After $\mathbf{V}_{723}$, the OCS capacity was zero as well, directly after evacuation, after the $\mathbf{IR}_{473}$ step (see above) and after catalysis.

The hydrogenation activity (Figure 1a) initially increased with T_{red}, in contrast to the drastically decreasing OCS capacity as reported in Polyakov et al.[6] Upon more severe reduction, the hydrogenation activity dropped as well, but remained measurable even at T_{red} = 873 K where the OCS capacity had vanished. With the same zero OCS capacity, $MoS_{2.55}$ exhibited an almost 20-fold activity when activated by $\mathbf{V}_{723}$. All these treatments resulted in activation energies scattering around 37 kJ/mol (±3 kJ/mol) although the OCS capacity span a range from ≈57 to 0 μmol/g. The CT activity (Figure 1b) declined with increasing reduction severity as described in Polyakov et al.[6] A dramatic change of the activation energy from ≈60 to ≈30 kJ/Mol was noted after $\mathbf{R}_{873}$. After $\mathbf{V}_{723}$, the activity was much larger, but the activation energy remained close to that after $\mathbf{R}_{873}$. In H_2D_2 (Figure 1c), activity started high and at a very low activation energy (15 kJ/mol) after $\mathbf{R}_{573}$ as found in our earlier work.[6] Already at T_{red} = 673 K, the activity had decreased and the activation energy had increased four times. After $\mathbf{V}_{723}$, the activity was even smaller, but E_A remained the same as after $\mathbf{R}_{673}$.

With other initial S/Mo values, similar tendencies were observed, with characteristic deviations though in details (Figure S4, see also refs 16, 17). CT activity was always higher after $\mathbf{V}_{723}$ than after any reductive activation, and H_2D_2 activity was lower. Hydrogenation activity after $\mathbf{V}_{723}$ exceeded that after activation in H_2 at low initial S/Mo ratio and dropped below the latter at high initial S/Mo ratio.

Analogous data for $WS_{2.25}$ are depicted in Figure 2. The OCS on tungsten sulfides exhibited similar trends as on MoS_{2+x}, but peak capacities were lower and required higher reduction temperatures.[16,17] $WS_{2.25}$ had a peak OCS capacity of 19 μmol/g at T_{red} = 823 K, a temperature where $MoS_{2.55}$ did not adsorb oxygen any more (Figures 1 and 2). The OCS capacity of $WS_{2.25}$ did not vanish at $T_{red} \leq 1023$ K although its decrease was obvious. After $\mathbf{V}_{873}$, the OCS capacity was zero as in case of the MoS_{2+x} catalysts.

Unlike with $MoS_{2.55}$, the hydrogenation activity of $WS_{2.25}$ nearly paralleled the OCS capacity with variation of T_{red} (Figure 2a). Again, however, a sizable activity was measured with the thermoevacuated sample, which did not adsorb oxygen. In the limits of experimental error, all treatments resulted in the same activation energy irrespective of the OCS capacity achieved. Changes in E_A occurred for the CT and H_2D_2 reactions (Figure 2b,c) as observed with $MoS_{2.55}$ (Figure 1b,c). In CT, the activation energy dropped to ca. 50% at higher reduction temperatures and remained low after $\mathbf{V}_{873}$ (Figure 2b). As with $MoS_{2.55}$, the activity after thermoevacuation was the highest observed for CT. The behavior of the H_2D_2 reaction was very complex (Figure 2c). A shift from lower to higher activation energy (≈45 to ≈75 kJ/mol) occurred with increasing reduction severity, but E_A reproducibly shifted back to the lower level in a narrow range of T_{red} around 923 K. As with $MoS_{2.55}$, the H_2D_2 activity after thermoevacuation was smaller than achieved after reductive activations.

These data show that EH, CT, and H_2D_2 can proceed on MoS_2 and WS_2 surfaces which do not adsorb oxygen. Oxygen chemisorption is generally accepted to indicate coordinative unsaturation of Mo(W) sites, and our XPS analysis clearly supports that surfaces with zero oxgen chemisorption capacity are saturated. Therefore, our reactions obviously can proceed on saturated surfaces, that is, on exposed sulfide species. This is what the recent studies under model conditions and theoretical investigations predict, although it is not yet possible to identify which kind of saturated sites is operative in our real catalysts. It includes actually also Mo carbide sites although their formation from the adsorbed hydrocarbon species should be less likely under our mild reaction temperatures, which are well below those in hydrorefining processes.

The invariability of the EH activation energy over a wide range of activation conditions is a further remarkable result. This "universal" activation energy changes with the initial S/Mo ratio, from 73 kJ/mol for $MoS_{2.15}$ to ca. 40 kJ/mol for $MoS_{2.55}$ and $MoS_{2.75}$ (refs 16, 17, Figure S4). The range of OCS capacities achieved by these activations is sometimes enormous as seen in Figure 1a where the activation energy does not respond to a change of the OCS capacity between 0 and almost 60 μmol/g. Similar observations were made with the WS_{2+x} samples.[16] Such result can be reconciled with a competition between two different reaction paths (over 3-fold unsaturated and over saturated sites) only if both routes present the same activation energy. We rather suggest that hydrogenation activity may not be related to oxygen chemisorption at all. We propose therefore that EH always proceeds on saturated sites: those observed in surface states without OCS capacity—brim sites or hydrogen activating sulfide species. As to CT, the different activation energies in catalyst states with high or zero OCS capacity (Figure 1b) suggest that the reaction rate is contributed from different sites, one of which might be a ^{1}M site as proposed earlier.[6] The case of H_2D_2 reaction is very complex, and further work is in progress. There is competition between different reaction mechanisms as well, the contributions of which may be very sensitive to details of the activation procedure, which results in unexpected switches of E_A. H_2D_2 can also proceed in absence of OCS capacity, but at a relatively low reaction rate (Figures 1c and 2c).

While the contribution of saturated sites to catalysis over MS_2 appears to be well supported by our data (including those from three more MoS_2 and two more WS_2 catalysts (refs 16, 17, Figure S4)), it is not yet possible to discriminate contributions from them and from other types of sites because there is not yet a tool to count those saturated sites that are involved in the catalytic reactions. As mentioned with regard to EH, we are skeptical on the relevance of OCS as an indicator for active sites. Theoretical work has cast doubt on the traditional mechanisms of H_2D_2[4,18] by showing the minor stability of Mo−H species[19,20] and of multiple vacancies on Mo,[20] and the variety of sulfur species capable of splitting dihydrogen[10−12] may well give rise to the observed changes in the activation energy without any need for cus. The above-mentioned reference to ^{1}M sites which would host the half-hydrogenated intermediate of CT is an unproved suggestion.

Still, one may wonder why EH should not proceed on cus on surfaces offering huge OCS capacities (Figure 1a). We found evidence that OCS may count not only cus, but cover also a secondary reaction with adsorbed H. Actually, using our textural data and a stoichiometry of 1 O per missing S^{2-}, one may estimate that with our peak OCS capacity of 57 μmol/g (thought to arise from edge planes) the edge Mo atoms are all exposed.[16,17] This is certainly unrealistic. When we performed the $\mathbf{IR}_{473}$ treatment in D_2 and repeated the OCS run, we could indeed detect D_2O in the effluent, see Drescher et al.[17] This evidence (though as yet qualitative) for a rapid reaction of chemisorbed oxygen with surface hydrogen at room temperature suggests that OCS overestimates the cus to an extent depending on the availability of surface hydrogen. The details are subject to ongoing research. Because of the minor role ascribed by us to OCS as a tool for the detection of active sites, this finding does not invalidate our major conclusions.

Another important observation concerns the role of surface hydrogen in hydrogenation. The appreciable (in case of $MoS_{2.15}$ actually very high[17]) hydrogenation activity after thermoevacuation contradicts observations in Polyakov et al.[6] where low hydrogenation activities after $\mathbf{V}_{723}$ were obtained in catalytic runs immediately following the activation, that is, without intermediate contact with hydrogen by $\mathbf{IR}_{473}$ (see above). Reproducing this, we found an extremely low activity of $MoS_{2.15}$ directly after thermoevacuation, which increased by almost 2 orders of magnitude when the catalyst was treated in H_2 at 473 K (for details see ref 17). In this treatment, the catalyst adsorbed hydrogen without acquiring any OCS capacity. This observation suggests the existence of a surface hydrogen species acting as a co-catalyst in hydrogenation, quite reminiscent to the report of the Besenbacher group about the importance of surface hydrogen for the adsorption of thiophene on the single-slab model catalysts.[9,10] In our case, however, the coexistence of ethene with hydrogen in the gas phase appeared to prevent the formation of the co-catalyst.[17] The experiment also shows that OCS does count coordinative unsaturation: The surface hydrogen did not react with the oxygen offered in the OCS run. Obviously, there is no reaction between surface hydrogen and oxygen if the latter is not activated by adsorption onto cus.

In conclusion, ethene hydrogenation, 2-butene cis−trans isomerization, and H_2/D_2 scrambling were observed over MoS_2 and WS_2 catalysts in surface states in which oxygen chemisorption, a proven indicator for coordinative unsaturation, did not occur. Obviously, the reactions can proceed on saturated sites, which is of considerable importance for the understanding of catalysis on sulfides although the surface states of our catalysts certainly deviate from those under real hydrorefining conditions due to differences in temperature and conditions of the gas phase. Ethene hydrogenation exhibits the same activation energy over catalyst states with widely varying OCS capacities, whereas changes in E_A were found for cis−trans isomerization and H_2/D_2 scrambling, indicating the relevance of more than one type of active sites. These observations suggest that ethene hydrogenation may occur on saturated sites only, whereas other types of sites are also available for the remaining reactions. Ethene hydrogenation is strongly accelerated by the presence of a specific surface hydrogen species, the identity of which is being further investigated.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Sample preparation, characterization techniques, description of catalytic experiments. Characterization data of $MoS_{2.55}$, $WS_{2.25}$: XRD in initial state, TEM after $\mathbf{R}_{573}$ ($MoS_{2.55}$), $\mathbf{R}_{873}$ ($WS_{2.25}$), development of BET surface area with reduction temperature. Summary of catalytic data of ethene hydrogenation for all MoS_x catalysts. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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