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Reactive and Non-reactive Interactions of Thiophene with WS_2 Fullerene-like Nanoparticles: An Ultra-high Vacuum Surface Chemistry Study

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Abstract The adsorption kinetics of thiophene on WS_2 nanoparticles with fullerene-like (onion-like) structure has been studied at ultra-high vacuum conditions by sample temperature ramping techniques. At low temperatures, thiophene adsorbs molecularly. The formation of H_2S and alkanes is evident at greater temperatures on fully sulfided as well as reduced and oxidized WS_2 nanoparticles.

Keywords Hydrodesulfurization · Thiophene · Hydrogen · CO · Oxygen · WS_2 nanoparticles · Kinetics · Thermal desorption spectroscopy · TDS

1 Introduction

Due to the importance of the hydrodesulfurization (HDS) of sulfur-containing compounds for refining fuels and chemical feedstock (plastics, paint, etc.), HDS has been studied for decades, as reviewed in refs. [1–3]. In model studies, thiophene is the probe molecule of choice since it is the smallest sulfur-containing compound present in naturally occurring oil. In surface chemistry studies, research focused initially on single crystal systems including MoS_2 (see e.g., refs. [4, 5]) and Mo (see e.g., refs. [6, 7]) surfaces. A variety of mechanisms have been proposed [1–3], mostly assuming a bond activation in thiophene (C_4H_4S) on S-vacancy sites of MoS_2 systems (i.e., on metallic Mo sites). Recently studies on single crystals have been extended by studying Mo nanoclusters obtained by ultra-high vacuum (UHV) vapor deposition [8–10]. Accordingly, fully sulfided Mo clusters are catalytically active due to the formation of brim sites (one-dimensional electronic edge states with a distinct metallic character) along the rim of the Mo clusters. Naturally, the discovery of carbon and inorganic nanotubes [11] triggered catalysis related research [12] on nanostructured catalysts. For example, the HDS activity of hollow MoS_2 nanoparticles was linked to an interplay of defect and confinement effects [13]. The enhancement of methanation activity in MoS_2 nanotube-powder-catalysts has been reported too, and was assigned to confinement effects [14].

Comparatively, few studies about the adsorption of thiophene on tungsten-based catalysts have been published [1–3]. Thiophene already partially decomposes at 90 K on W(110) surface and more strongly when the surface temperature is increased to 200 K; carbon and sulfur have been detected on the surface as well as sulfur and hydrogen desorption [15]. Kinetic studies at high pressures of thiophene and hydrogen on supported and unsupported tungsten sulfide powders suggested the formation of H_2S and butane as well as tetrahydrothiophene as parallel reaction pathways [16]. The reactivity decreases as $WS_2 > WS_2/Al_2O_3 > WS_2/C > WS_2/SiO_2$.

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In this study we present UHV kinetics experiments on WS_2 nanoparticles (hereafter IF-WS_2 or IF for inorganic fullerene-like particles) supported on silica. These nanoparticles, which exhibit hollow and closed-cage structure are generally synthesized in large amounts from tungsten oxide nanoparticles [11, 17]. The non-reactive and reactive adsorption of thiophene on the IF nanoparticles has been characterized by sample temperature ramping experiments. Even at UHV conditions some catalytic activity for HDS was evident.

2 Experimental Procedures

2.1 Experimental Techniques

IF-WS_2 nanoparticles (diameter of 60–120 nm) were synthesized in “NanoMaterials, Ltd.” (www.apnano.com) following a procedure given in ref. [17]. The kinetics experiments have been conducted (at NDSU) by means of a standard UHV apparatus, including a shielded mass spectrometer for temperature ramping experiments such as thermal desorption spectroscopy (TDS) and reactive TDS [18]. The reading of the thermocouple has been calibrated (±5 K) in situ by TDS measurements of condensed hydrocarbons. A background has been removed from the TDS curves, conserving, however, the curve shapes; the heating rate amounts to 2 K/s. The exposures are given in Langmuir ($1\ \mathrm{L} = 1$ s gas exposure at 1×10^{-6} mbar). Scanning electron microscopy (SEM) images of the WS_2 powders and supported samples were obtained at PNNL before the start of the UHV experiments utilizing a Zeiss LEO 982 FE-SEM (2–20 keV). Furthermore, a SEM post-characterization was conducted at the Weizmann Institute (SEM, LEO model Supra, 7426). Energy dispersive X-ray spectroscopy (EDS, Oxford model INCA) has been utilized to characterize the chemical composition of the samples after the UHV experiments, as compared with results from fresh samples.

2.2 Materials

The IF-WS_2 nanoparticles have been supported on a silica wafer by the drop-and-dry technique (see, e.g., ref. [19]) using 2-propanol as a solvent for the suspension. Solvent test indicated that longer chain alcohols lead to the best dispersion (for example, propanol works better than ethanol) of the IF-WS_2; alkanes were less efficient, and water led to the formation of a gel. The suspension has been mildly sonicated with a bench top sonicator. The wafers (10 by 10 mm, from MEMS and nanotechnology Exchange, VA, USA) were specified as a 300 nm thick SiO_2 layer on n-type Si(111) (bluish color, 1–10 Ωcm). Thiophene (C_4H_4S from sigma-aldrich, 99+%) has been purified by pump freeze-thaw cycles. Several IF-WS_2/silica samples were studied; some of them baked in a tube furnace (in a gas stream of Ar at 570 K for 30 min) before mounting in the UHV chamber. Data for two samples (baked/unbaked) are explicitly shown, as indicated in the figure captions. The samples were degassed in UHV by flashing the samples to increasingly higher temperatures (up to 700 K). During the first degassing cycles, desorption signals at $m/e = 18$ and 16 were present, i.e., mostly water and oxygen (in the form of O_2^{-2}) desorbed. For all experiments with hydrogen shown, hydrogen has been partially dissociated by a hot W-filament. Please note that the filament of the mass spectrometer and ion gauge can lead already to the formation of some atomic hydrogen [20]. No adsorption of molecular hydrogen has been detected (when dosing H_2 with all filaments switched off), as expected. Some samples were annealed in UHV in an ambient of CO, oxygen, and hydrogen in order to activate the catalyst (gases from Praxair, 99.99% or better).

3 Presentation and Discussion of the Results

3.1 Sample Characterization by SEM and EDS

Figure 1 depicts SEM images (scale bars indicated) of the IF supported on silica before (a–c) and after (d/e) the UHV experiments; data of baked and unbaked samples are shown (see figure captions). However, no differences in the appearance and the composition of the IF nanoparticles are evident. Furthermore, SEM/EDS analysis shows that the dispersion of the IF nanoparticles appears to be unaffected by the annealing process in the tube furnace or in the UHV chamber. The support is well covered (see Fig. 1a) by the IF-WS_2, i.e., a few layers of the IF nanoparticles were present (see Fig. 1e). The baked and unbaked samples have been analyzed after the UHV experiments by EDS analysis averaged over an area of 200 × 200 nm. The W-to-S ratio did not change significantly when annealing the samples in the tube furnace ($W/S_{EDX} = 0.43$ (baked) vs. 0.40 (unbaked)) and agreed with the ratio obtained for a fresh sample ($W/S_{EDX} = 0.42$) which had not been studied in UHV. Thus, the baking and the UHV experiments did not significantly alter the chemical composition of the samples as judged by EDS. Water desorption from the IF nanoparticles is nevertheless observed [21]. Besides a silica peak, no further structures were present in the EDS scans, indicating a high purity of the samples.

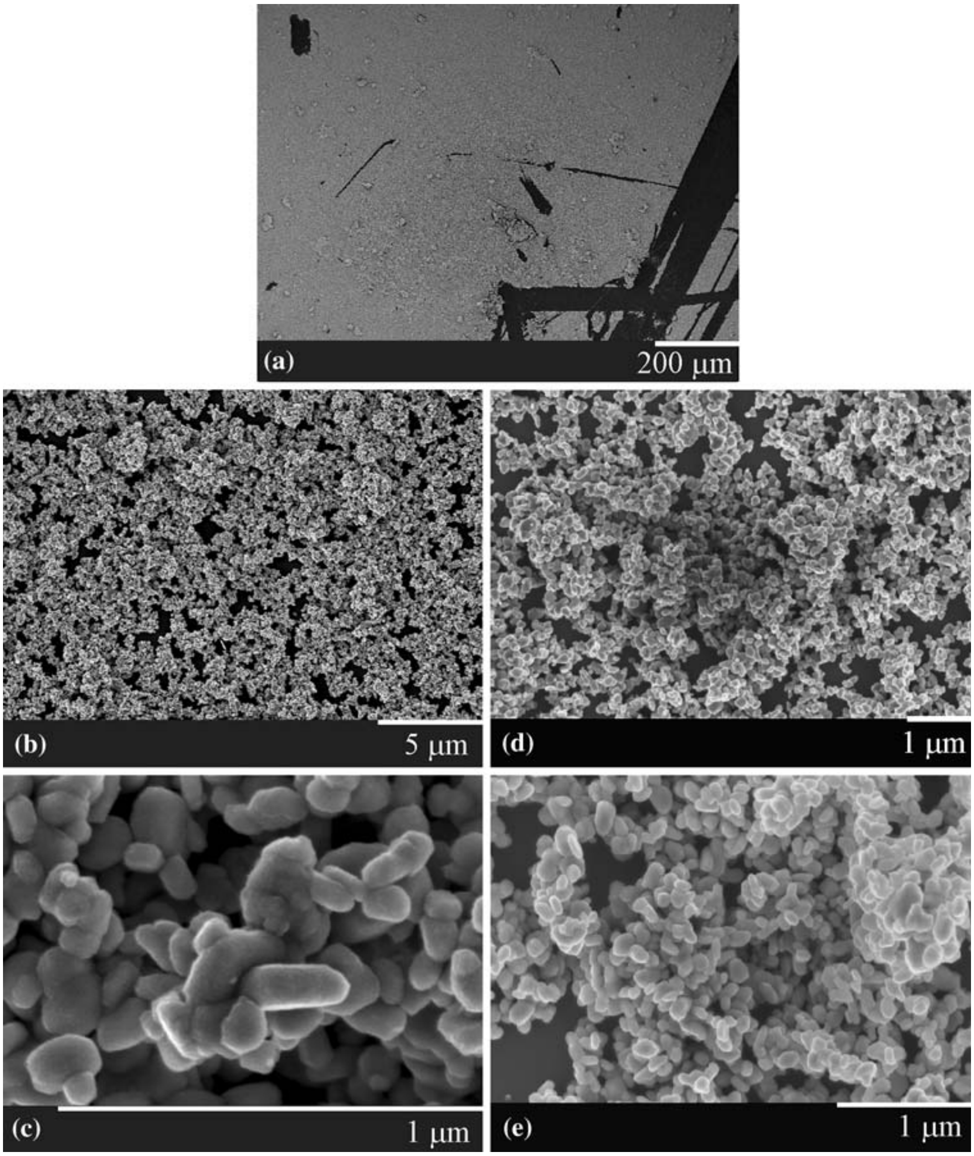
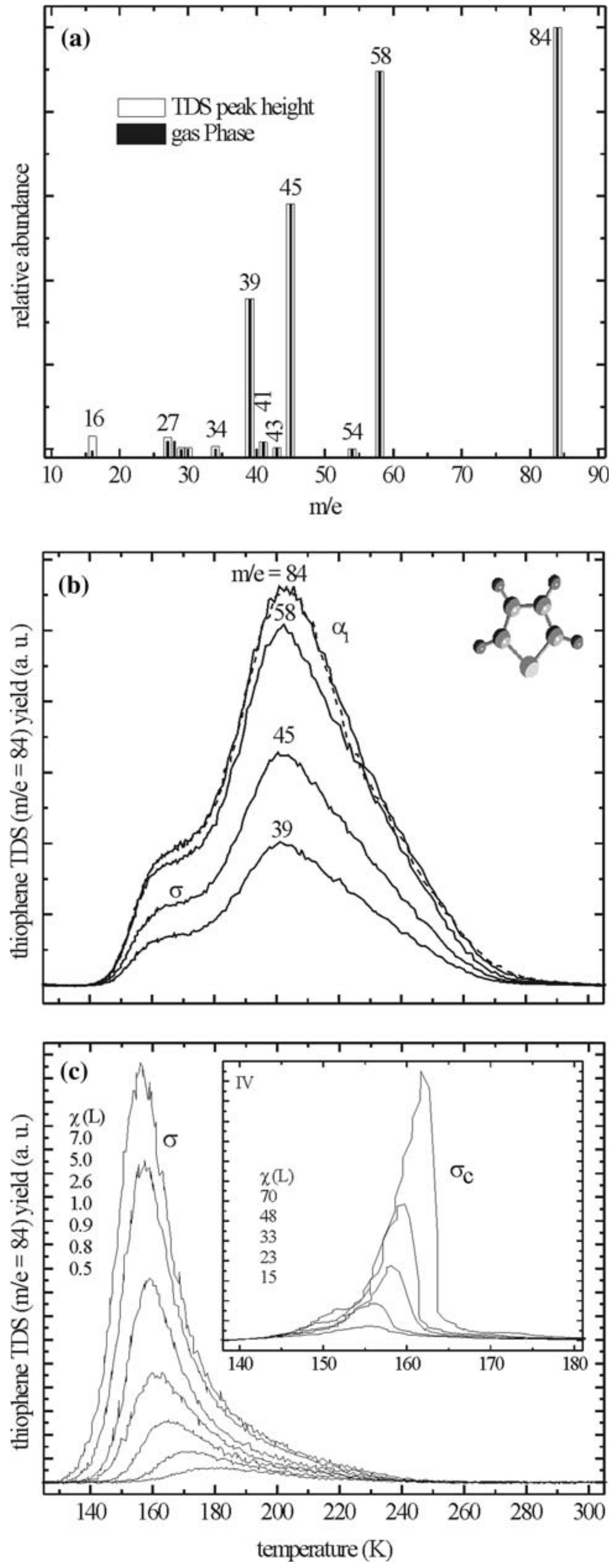


Fig. 1 Scanning electron microscopy (SEM) images of WS_2 nanoparticles supported on a silica wafer. (**a–c**) Unbaked before UHV experiments and (**d/e**) unbaked/baked after UHV experiments. Magnification is indicated

3.2 Molecular Adsorption of Thiophene at Low Temperatures

In order to determine whether or not thiophene adsorbs molecularly on the supported IF-WS_2 samples, multi-mass TDS scans for constant thiophene exposures have been collected. In Fig. 2a, the peak intensities of the most intense thiophene fragments (open bars), as determined in TDS runs, are compared with the fragmentation pattern of gaseous thiophene (solid lines). The multi-mass TDS pattern matches that of gaseous thiophene and is similar to tabulated mass scans (see NIST library [22]). In addition, the TDS peaks detected for the most abundant thiophene fragments are centered at the same desorption temperature (see Fig. 2b), with curve shapes similar to TDS traces of the thiophene parent mass ($m/e = 84$). Thus, molecular adsorption/desorption of thiophene is concluded. In contrast, bond activation and/or HDS would lead to TDS features at, for example, $m/e = 34$ (for H_2S), $m/e = 43$ (for alkanes), and $m/e = 86$, 60 (for H_8C_4S), which have not been observed. A minor (<5% of the thiophene parent mass) and nonspecific feature at $m/e = 16$ (corresponding to ${O_2}^{2-}$ fragment), which has already been seen while degassing the sample, was present throughout the project and is assumed to be the result of oxygen desorption, signifying oxygen desorption from the hollow core of the nanoparticles or from defects [21].

Inspecting the TDS curves in Fig. 2b more closely reveals two structures in thiophene desorption, a peak at 200 K (α_1 peak) and a shoulder at 160 K (σ peak). Blind experiments where thiophene has been dosed on a clean silica support are shown in Fig. 2c as a function of exposure [23]. A comparison of the two data sets suggests assigning the σ-peak to molecular thiophene desorption



◀ **Fig. 2** (**a**) Comparison of TDS peak intensities (open bars) with the mass spectrometer signal (solid bars) for gaseous thiophene. (**b**) TDS curves (thin line) for some of the thiophene fragments and 5 L C_4H_4S. Dotted line (m/e = 84) indicates how well the data can be reproduced (same sample, different TDS runs). (Unbaked sample.) (**c**) TDS curves for silica [23] as a function of χ. (**d**) Data for large thiophene exposures on silica

from uncovered areas of the silica support. (See ref. [23, 24] for a detailed characterization of the adsorption kinetics of some small organic molecules on silica wafers.) The α_1 peak (Fig. 2b) is assigned to molecular desorption of thiophene from the IF-WS$_2$ nanoparticles; the σ_c peak (Fig. 2d), detected at larger exposures, corresponds to thiophene condensed on silica.

3.3 Kinetic Parameters of Thiophene Adsorption

Figure 3 shows thiophene TDS of the IF-WS$_2$/silica as a function of exposure, χ. Within the range of small exposures, the TDS peaks shift to lower desorption temperatures (from 232 K to 174 K) with increasing H_4C_4S exposure (from 1.8 to 15 L, see Fig. 3b), which is consistent with either the effect of repulsive lateral interactions or a superposition of desorption events from kinetically distinct adsorption sites on the IF-WS$_2$. The inset (Fig. 3b) depicts data obtained for a second IF-WS$_2$ sample. The TDS peak shapes obtained for these two samples (cf., Fig. 3a/b) are very similar except for a variation in the σ-to-α_1 TDS peak intensity ratio. This result is plausible and simply indicates differences in the dispersion of the IF-WS$_2$ nanoparticles on the support for the two different samples. (The σ TDS peak is related to the silica support, as described above.) The TDS peak positions obtained for the two samples agree within ±10 K for exposures larger than ~4 L, reflecting the uncertainty in the temperature measurements. At very small exposures, the TDS peak positions obtained for the different samples differ more distinctly (up to 30 K). However, this result may also be expected, since TDS curves at small exposures are dominated by the effect of high binding energy (defect) sites, which will differ significantly for systems as inhomogeneous as the IF-WS$_2$ samples studied here. No systematic variations in TDS data obtained for baked (in the tube furnace) or unbaked samples have been recognized.

At larger thiophene exposures, a low temperature TDS peak (α_2 peak) is present, which shifts to higher temperatures with increasing exposure. The low-temperature leading edges line up. This indicates a condensation of thiophene, consistent with 0th order kinetics.

A Redhead analysis of the TDS peak positions has been used to determine the coverage, Θ, dependent heat of adsorption, E_d, of thiophene (assumed pre-exponential 1×10^{13}/s). The coverage has been obtained by integrating the TDS curves and assigning an apparent coverage of 1 ML (Mono Layer) to the TDS curve detected just before the onset of the condensation peak (labeled by "*" in

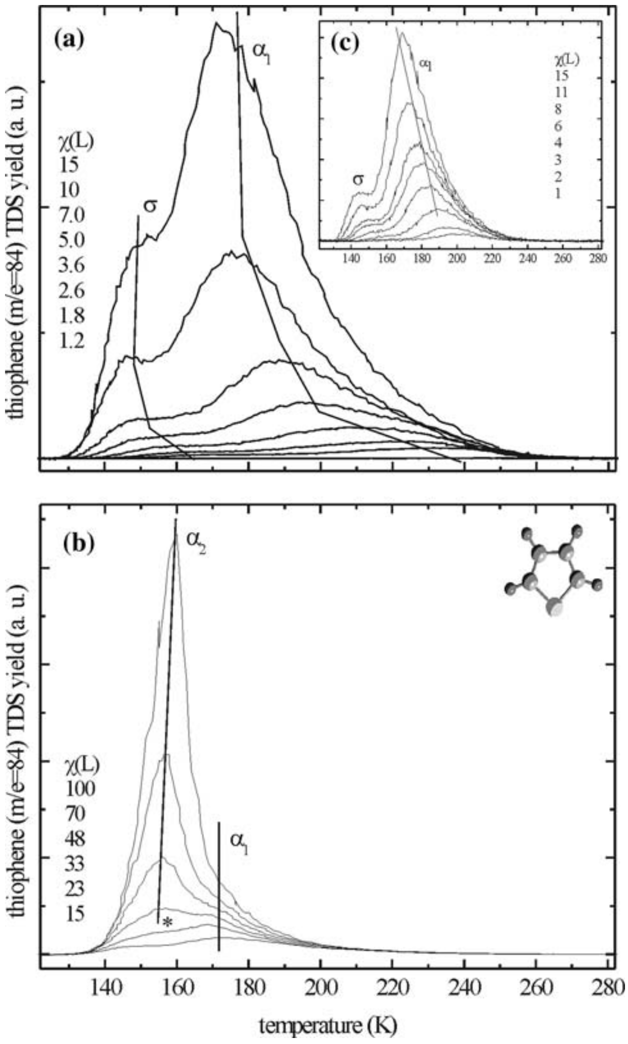


Fig. 3 TDS curves as a function of thiophene exposure, χ, for (**a**) small, (**b**) large exposures (unbaked sample). The inset (**c**) shows the corresponding data for a second sample (baked)

Fig. 3c). One ML simply corresponds to a saturated layer of thiophene on the IF-WS_2/silica sample. The results for two different IF-WS_2 samples are depicted in Fig. 4, together with the data for a clean silica support [23]. Accordingly, E_d for thiophene/IF-WS_2 initially decreases with Θ, and levels out at 41 kJ/mol for large exposures. This $E_d(\Theta)$ curve shape is often observed for molecular adsorption/desorption of small organic molecules (see, e.g., refs. [25, 26]). A decrease in E_d with Θ is consistent with repulsive lateral interactions. The initially steep decrease ($\Theta < 0.3$ ML) is typically related to the effect of high energy (defect) binding sites. As already described above, significant variations in $E_d(\Theta \rightarrow 0)$ for different IF-WS_2 samples are expected. (A "defect" concentration of ~0.3 ML appears plausible.) However, the shapes of TDS curves (Fig. 3a/b) and large coverage binding energies (41 ± 1.3 kJ/mol) were easily reproducible for different samples, i.e., the IF-WS_2 synthesis leads to a consistent and reproducible quality of nanoparticles. The error bars in Fig. 4 correspond to an uncertainty in the temperature reading of ±5 K (or ±1.3 kJ/mol).

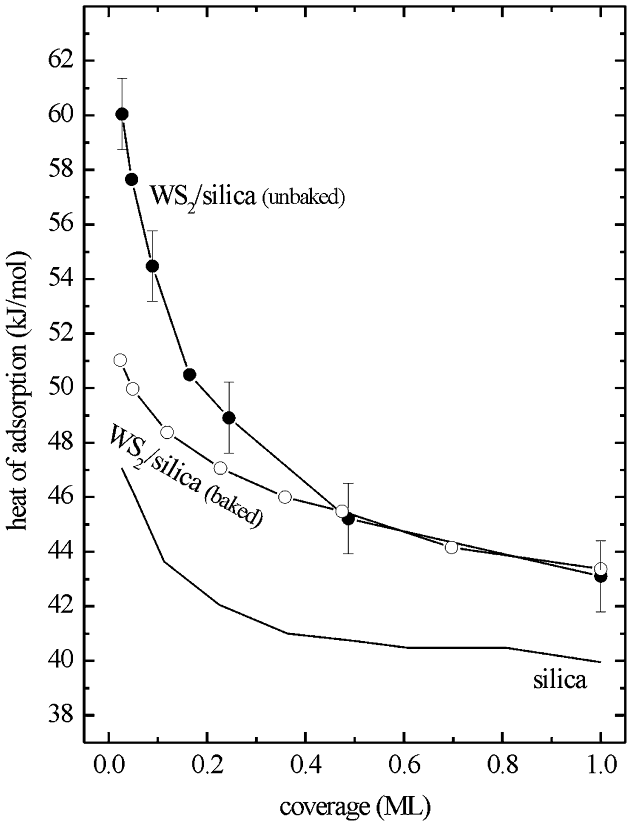


Fig. 4 Heat of adsorption of thiophene as a function of coverage. (*solid circles*) WS_2-IF/silica (unbaked); (*open circles*) WS_2-IF/silica (baked); (*solid line*) silica

3.4 Reaction Kinetics—Reactivity Screening

A number of different types (as well as combinations) of kinetic experiments have been conducted to eventually discover a catalytic activity of IF-WS_2 nanoparticles/silica towards thiophene HDS. Briefly they are: (1) reactive TDS experiments, i.e., hydrogen (dissociated on a hot W-filament) and thiophene have been adsorbed at low temperatures followed by ramping up the sample temperature and simultaneously recording typical HDS reaction products [27], (2) quenching experiments, i.e., dosing (dissociated) hydrogen and thiophene at high temperatures (at reaction conditions) followed by cooling the sample down fast and collecting subsequently multi-mass TDS data; a similar methodology has been used in prior STM studies of sulfided Mo nanoparticles [8, 9], (3) titration experiments, i.e., pre-exposing (dissociated) hydrogen and then post-dosing thiophene (or vice versa) and monitoring simultaneously the reaction products as a function of time and at constant temperature [27], (4) quasi steady-state experiments, i.e., annealing the sample in a H_2/thiophene mixture and looking for reaction products (in addition switching on/off a filament to dissociate H_2), (5) pressure jump experiments, i.e., recording reaction products at constant temperature while increasing the (dissociated) hydrogen/thiophene gas pressure step-wise. In addition, samples have been annealed in oxygen, hydrogen (H_2 and H), and CO to eventually activate the catalyst.

Unfortunately, the catalytic activity of the IF-WS_2 samples studied here (at UHV conditions) was close to the detection limit of the mass spectrometer.

3.4.1 Pristine (Fully Sulfided) IF-WS_2

As an example, Fig. 5a shows typical results of temperature ramping experiments where the sample was kept in a reactive (dissociated) H_2 (7×10^{-8} mbar)-thiophene (1×10^{-7} mbar) gas mixture while increasing the surface temperature at a rate of 2 K/s. (A hot W-filament has been used in order to dissociate H_2.) The desorption of hydrocarbons ($m/e = 43$), H_2S ($m/e = 34$), and H_8C_4S ($m/e = 60$) was detected for temperatures above 600 K. Switching off the gas exposure (see dashed line in Fig. 5a) leads to a drop in the signals, which is uniquely correlating the catalytic activity of the sample with the effect of the reactive gas mixture. Similarly, the results of isothermal pressure jump experiments are shown in Fig. 5b. (A hot W-filament has been switch on and off in order to dissociate H_2, as indicated in Fig. 5b) The formation of alkanes and H_2S has been seen and is clearly related to the exposure of thiophene and atomic hydrogen. (Note that the ion gauge filaments and the mass spectrometer filament already generate atomic hydrogen [20].) Thus, fully sulfided IF-WS_2 shows some activity for HDS even at UHV conditions, which is in agreement with recent STM studies on sulfided-Mo clusters [8, 9]; however, the reaction rates are very small.

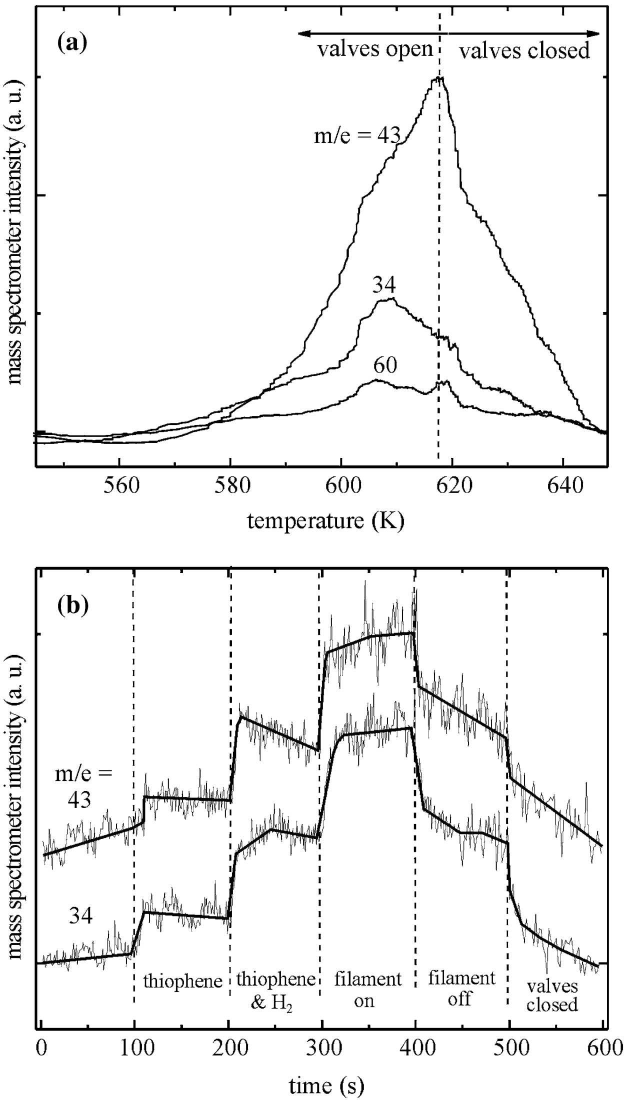


Fig. 5 Reactivity screening. (**a**) Temperature programmed reaction; sample heated at a rate of 2 K/s in a mixture of 7×10^{-8} mbar H_2 (W-filament on) and 1×10^{-7} mbar thiophene. The gas exposure has been stopped, as indicated. (**b**) Pressure jump experiments at 690 K. Gas valves have been opened and closed as indicated. (2×10^{-6} mbar H_2 [W-filament on] and 1×10^{-6} mbar thiophene.)

3.4.2 Annealed IF-WS_2 Samples

Atomic hydrogen dosed on IF-WS_2 samples leads to a broad H_2 TDS peak (150–500 K). No adsorption of molecular hydrogen was detected, as expected.

Annealing the sample in (dissociated) hydrogen (1×10^{-6} mbar, 400 K, 0–95 min), CO (1×10^{-6} mbar, 5 min at 300 K), or oxygen (1×10^{-6} mbar, 10 min, 300 K) resulted in a shift of the α_1 TDS peak (monolayer thiophene adsorption) to larger temperatures in subsequent thiophene TDS experiments (peak shifts: 100 K for CO, 30 K for H/H_2, 50 K for O_2 annealing). The position of the σ-shoulder TDS peak (from the silica support) remained mostly unaffected. Thus, it appears that fully sulfided IF-WS_2 nanoparticles are catalytically less active (smaller binding energy) towards thiophene adsorption than partially reduced/oxidized IF-WS_2 particles, as perhaps expected.

Desorption of H_2S ($m/e = 34$) and alkanes ($m/e = 43$) has been detected for the reduced (CO, H annealed) samples; however, not with significantly larger intensities than for the pristine (sulfided) samples. After a number of thiophene adsorption/desorption cycles with reduced samples, their initial state could be restored, as judged by TDS.

Interestingly, oxygen annealed samples showed some thiophene desulfurization activity too; a mass spectrometer signal at $m/e = 43$ (alkanes) has been detected in thiophene TDS experiments with oxygen annealed IF-WS_2. However, the initial state of the IF-WS_2 could not be perfectly restored again. Thiophene TDS on oxidized samples consisted of three broad overlapping structures, two similar to the σ and α_1 TDS peak (silica and sulfided-IF-WS_2 peaks), and a new feature between those peaks which is perhaps related to thiophene desorption from partially oxidized IF-WS_2 nanoparticles.

4 Summary

The following information was obtained:

- The morphology and chemical composition of IF-WS_2 has been characterized by EDS and SEM before and after UHV kinetics experiments. No significant changes in the morphology or chemical composition were present.
- Thiophene adsorbed molecularly on pristine ("fully sulfided") IF-WS_2 samples at low temperatures, as verified by multi-mass TDS.
- Thiophene binding energies are in the range of (43–60) kJ/mol, depending on coverage and studying two samples in detail.
- A reactivity screening of pristine IF-WS_2 as well as reduced and oxidized IF-WS_2 has been conducted.
- The HDS activity of pristine IF-WS_2 at UHV conditions was close to the detection limit of the mass spectrometer used. However, H_2S and alkane fragments were detected.
- Partially reduced and oxidized samples are catalytically active too (towards HDS), but with small reaction rates, similar to those detected for fully sulfided IF-WS_2.
- It may be expected that a distinct HDS activity would be present at high pressure conditions.[1] The IF-WS_2 appears to be very stable at reducing conditions.

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[1] Alkane formation rates were detectable only above 600 K. At these large surface temperatures the coverage of the reactants on the surface is very small which limits the product formation rates. This problem can be overcome by increasing the gas pressure of the reactants in a high-pressure chemical reactor.