Catal Lett (2009) 129:66–70
DOI 10.1007/s10562-009-9880-7

Adsorption of Thiophene on Inorganic MoS_2 Fullerene-Like Nanoparticles

M. Komarneni · A. Sand · U. Burghaus

Received: 29 December 2008 / Accepted: 26 January 2009 / Published online: 5 February 2009

Abstract The catalytic activity of a rather new nanomaterial, IF-MoS_2 (inorganic fullerene-like nanoparticles), towards hydrodesulfurization (HDS) activity has been characterized at ultra-high vacuum conditions. Thiophene TDS as well as quasi steady-state kinetics experiments have been conducted. The IF-MoS_2 nanoparticles were supported on sapphire and silica.

Keywords Inorganic fullerenes · MoS_2 nanoparticles · Thiophene · Hydrodesulfurization · Kinetics · Thermal desorption spectroscopy

1 Introduction

Inorganic MoS_2 fullerene-like nanoparticles (IF-MoS_2) have so far mostly been utilized as solid lubricants and high-strength nanocomposites [1, 2]. However, recently the application of nanomaterials for hydrodesulfurization (HDS) has been studied by a number of groups: clean [3] and metal supported carbon nanotubes [4–6] as well as IF-WS_2 [7] and MoS_2/WS_2 nanotubes [8, 9] were considered. In this study we explore the application of IF-MoS_2 in catalysis for processes such as the HDS of sulfur containing compounds. In doing so, thiophene (C_4H_4S) is commonly used as the probe molecule since it is the smallest sulfur containing compound present in naturally occurring oil. A variety of mechanisms have been proposed for HDS [10–12], most of them assume the formation of metallic sites on MoS_2 catalyst in a hydrogen ambient. Subsequent bond activation in thiophene on these S-vacancies fills the defect sites again with sulfur. Alkanes, as desulfided thiophene fragments, leave the catalyst. Thus, a catalytic cycle consisting of the formation and healing of S-vacancy sites is formed. Therefore, we attempted in this project to distinguish metallic and sulfur like adsorption sites with thiophene as the probe in TDS (thermal desorption spectroscopy) experiments by studying pristine ("fully" sulfided) IF-MoS_2 and hydrogen/oxygen annealed samples in order to characterize the active sites for HDS with IF-MoS_2. Other models proposed HDS activity of fully sulfided MoS_2 catalysts [13], a mechanism which may be related to an interplay of the catalyst particles and the support. Therefore, we used different supports, namely silica and sapphire; sapphire is common in the industrial HDS process and silica is conveniently used as a support in nanoscience. In addition to the TDS experiments, the formation of alkanes by thiophene HDS has been studied at quasi-steady state conditions.

The inorganic MoS_2 fullerene-like nanoparticles, IF-MoS_2, used in this study were synthesized at ApNano Materials by evaporating first MoO_3 powder and subsequently sulfiding the MoO_{3-x} nanoparticles in an H_2/H_2S ambient at high temperatures ($\sim$1,100 K) using a quartz reactor as described in ref [14, 15]. The structure of IF-MoS_2 has recently been studied by aberration-corrected high-resolution transmission electron microscopy combined with simulations of the images [16]. Accordingly, the nanoparticles with a typical size of 50–70 nm consist of closed MoS_2 layers. Each shell is made of a central Mo layer sandwiched between an outer and inner sulfur layer. Each Mo atom in a shell is coordinated by six S atoms. The optical absorption of the IF-MoS_2 nanoparticles suggests that, in analogy to the bulk materials, they are indirect

M. Komarneni · A. Sand · U. Burghaus (✉)
Department of Chemistry and Molecular Biology,
North Dakota State University, Fargo, ND 58108, USA
e-mail: uwe.burghaus@ndsu.edu
URL: www.chem.ndsu.nodak.edu

semiconductors with a bandgap smaller than the bulk 2H-MoS_2 [17]. The structure of the smallest IF, a rectangular bipyramid (nanooctahedron) of 3–6 nm size, synthesized by LASER ablation, consists of 3–5 MoS_2 shells held together by van der Waals interactions. It appears that the building blocks of the nanooctahedral IF are triangular monolayers of MoS_2. Some types of inorganic IF are in the meanwhile commercially available ("NanoLub") in bulk quantities, which makes it attractive to explore also applications in heterogeneous catalysis.

2 Experimental Procedures

Approximately 2 mg of the IF-MoS_2 powder was dissolved in 20 mL isopropanol and mildly sonicated at room temperature with a bench top sonicator [18]. Two 50 μL aliquots were dropped-and-dried on silica (SiO_2/p-Si(111) from MEMS nanotechnology Exchange, VA, USA) [19, 20] and sapphire (Al_2O_3(0001) from Crystal lab. Inc., FL, USA) supports. Four different samples have been studied; no significant differences were observed. The kinetics experiments were conducted in two UHV (ultra-high vacuum) systems, one of them equipped with a retarding field auger electron spectrometer (AES). The TDS (thermal desorption spectroscopy) set up is discussed in ref [21]. A heating rate of 2 K/s has been used; the exposures χ, are given in Langmuir (1 L = 1 s gas exposure at 1×10^{-6} mbar). Thiophene has been cleaned by pump-freeze-thaw cycles; hydrogen has been dosed on the surface by means of a capillary doser to which a hot W filament for partially dissociating the hydrogen was attached. SEM (scanning electron microscopy) and EDX (energy-dispersive X-ray spectroscopy) characterization has been provided by R. Tenne's group at Weizmann Inst. (Israel).

3 Results and Discussion

Figure 1 shows typical SEM images of IF-MoS_2 supported on silica. As evident the support is entirely covered by the nanoparticles. Figure 2a and b depict thiophene TDS data for IF-MoS_2 supported on sapphire (panel I) and silica (panel II); the insets display data for small exposures. Panel III shows the results of blind experiments (thiophene TDS) with a clean silica support. The supported IF-MoS_2 samples have been annealed for 5 min at 800 K in UHV and are referred hereafter as pristine (or as-received) samples. As evident, three TDS peaks, labeled as T, S, and Mo are present for both IF-MoS_2 samples (independent of the support), and the peak positions agree within ±10 K. Thus, the support has little effect on the adsorption kinetics of thiophene. In addition, the blind experiments show only

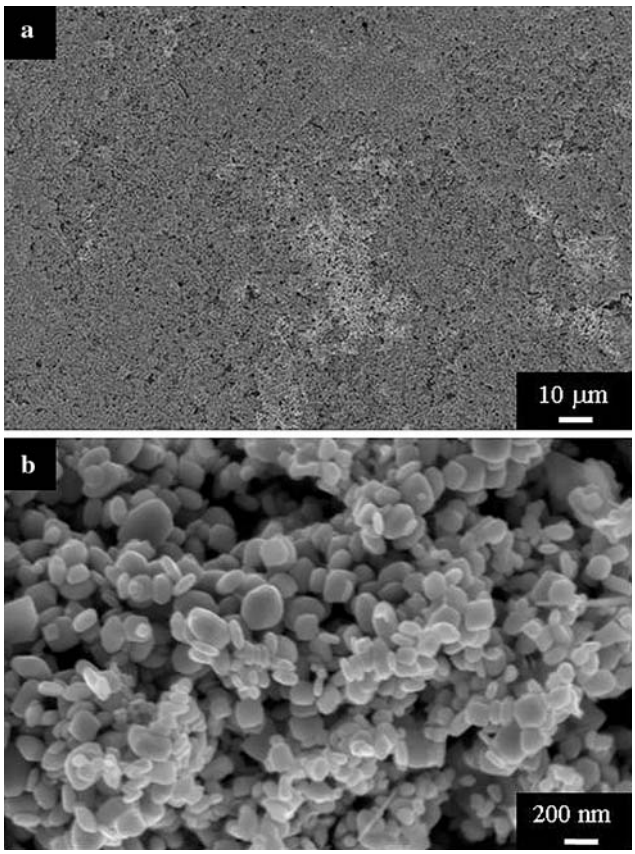

Fig. 1 SEM images with different magnification of IF-MoS_2 supported on silica

one structure, i.e., the kinetics data are not obscured by adsorption on eventually non-covered areas of the support. Note that SEM images indicate a closed layer of IF-MoS_2 as well as the total surface area of the IF exceeds the area of the support by at least an order of magnitude.

The low temperature edges of the T peaks line up, identifying this structure (observed only at low temperatures and large exposures) as the signature of thiophene condensation, obeying 0th order kinetics.

The position of the S and Mo TDS peaks are approximately independent of exposure, consistent with 1st order kinetics and small effects of lateral interactions. In addition, the gas-phase fragmentation pattern of thiophene agrees with the one obtained in multi-mass TDS scans not explicitly shown). Therefore, we conclude that 1st order adsorption/desorption kinetics is obeyed for the S and Mo TDS peaks. Assuming a standard preexponential of 1×10^{13}/s results in binding energies of 46 and 52 kJ/mol for the S and Mo TDS features (at ~180 and ~200 K), respectively. Slightly larger binding energies of 60 kJ/mol have recently been determined for thiophene/IF-WS_2 [7].

In order to identify the TDS peaks, the samples have been annealed in UHV, H_2, O_2, and H_2S. Typical results are presented in Fig. 3. Extensive annealing of the samples

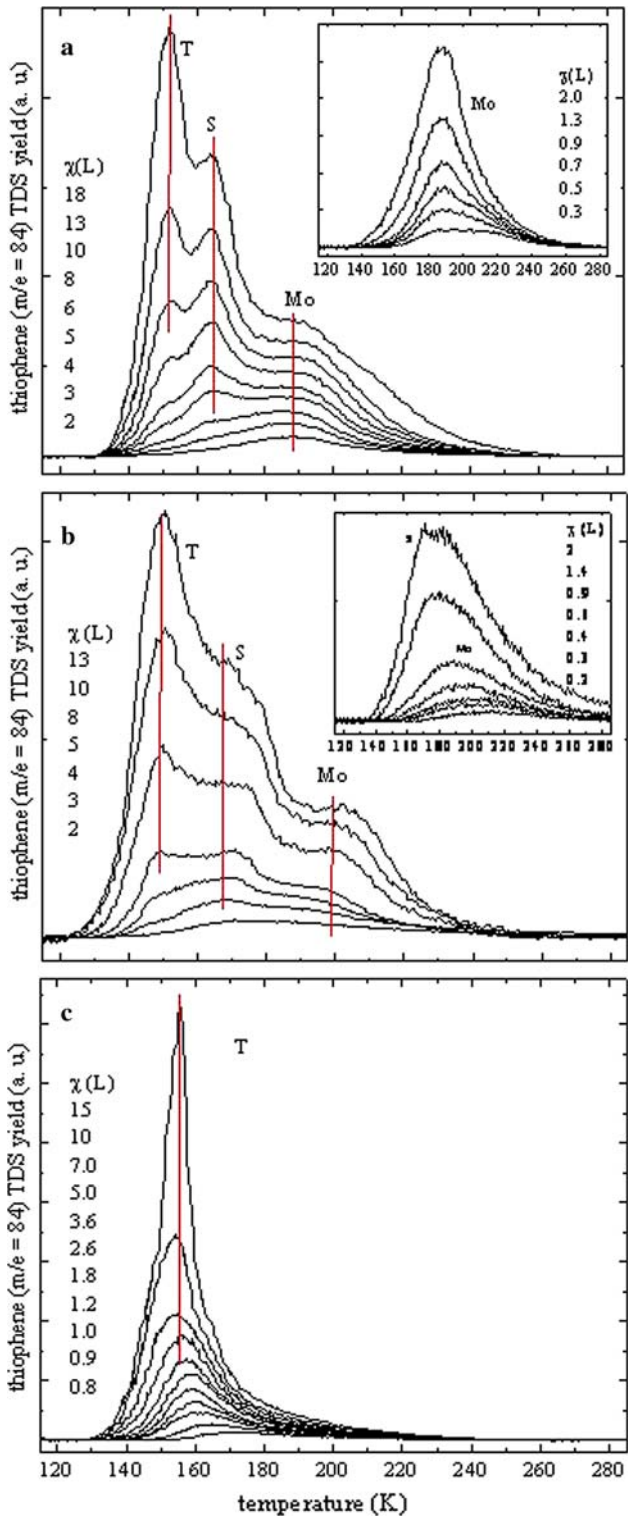

Fig. 2 Thiophene TDS data for **a** silica and **b** sapphire supported IF-MoS_2, as a function of exposure. **c** Thiophene TDS on a clean silica support (blind experiment) from Ref. [19]

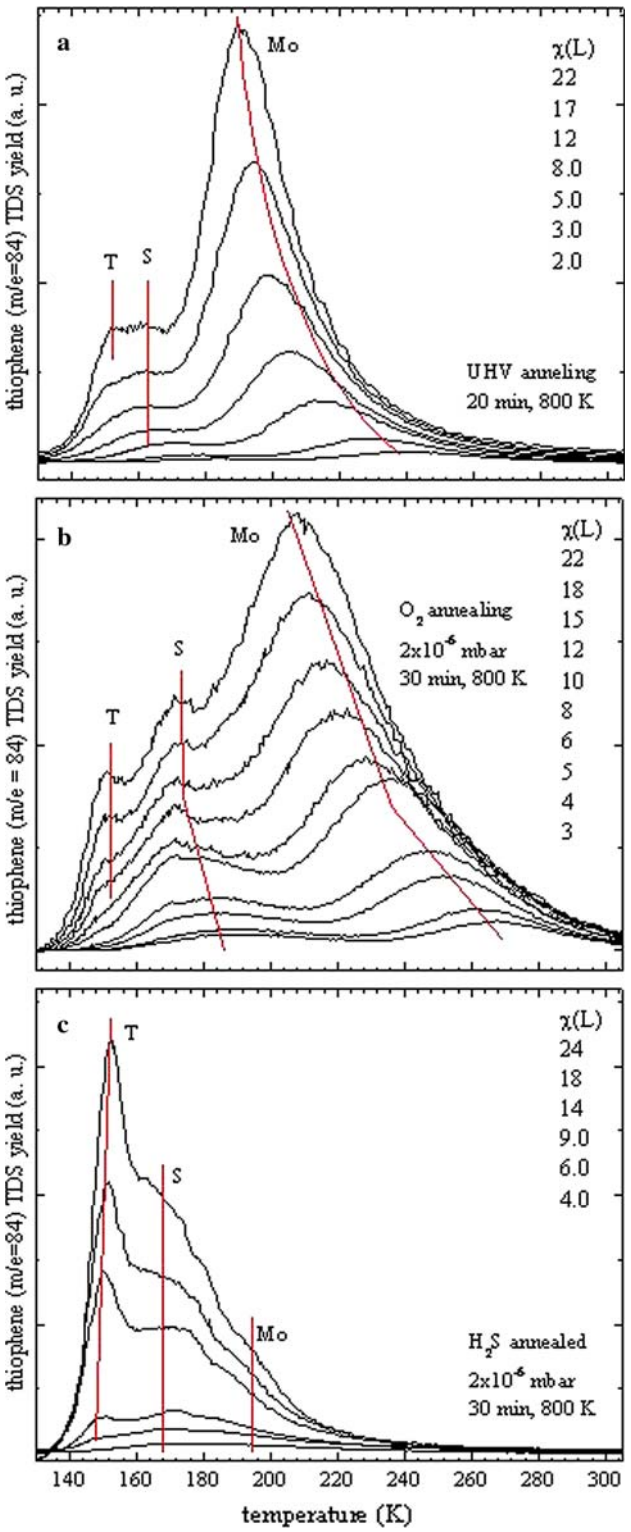

Fig. 3 Thiophene TDS of **a** UHV annealed, **b** oxygen annealed, and **c** H_2S annealed IF-MoS_2 supported on silica

in UHV (Fig. 3a), or in a hydrogen (H_2/H) ambient, results in TDS curves dominated by a structure similar to the Mo TDS peak. (After hydrogen annealing of the samples, H_2S has been identified in the residual gas.) Interestingly, this high temperature feature shifts now to lower desorption temperatures with increasing exposure. This shift would be

consistent with repulsive lateral interactions of thiophene. However, a TDS peak shift was absent for the pristine sample. Therefore, is appears more likely that kinetically distinct adsorption sites formed while reducing the sample in hydrogen. Similarly, oxidizing the sample in oxygen ambient, leads to an enhancement in the Mo TDS peak intensity with respect to the S TDS peak (Fig. 3b). In contrast, annealing a reduced sample in H_2S (Fig. 3c) appears to convert the reduced surface back to the pristine state. At least TDS curves detected for H_2S annealed samples are quite similar to those obtained for an as-received sample, cf. Fig. 1a and b with Fig. 3c. Thus, reduction of the samples enhances the Mo TDS peak whereas sulfiding the samples reduced the Mo TDS peak intensity with respect to the S TDS peak. Another hint for assigning the Mo and S TDS features came from AES data collected for reduced/oxidized (O_2/H_2 annealed) and sulfided (H_2S annealed) samples. Hydrogen annealing (30 min, 800 K, 2×10^{-6} mbar) reduced the S AES peak by 20% while subsequent H_2S annealing leads to an increase in the S-AES peak intensity (compared to the pristine case). Therefore, it is plausible to assign the S TDS peak to sulfur-like adsorption sites and the Mo TDS peak to Mo/MoO_x-like sites on the IF-MoS_2 samples.

Finally, pressure jump transients have been recorded to characterize the HDS activity of the supported IF-MoS_2 samples. Typical examples for sapphire supported samples are summarized in Fig. 4. (Comparing absolute intensities obtained for different samples is problematic but very similar results have been obtained for silica supported IF-MoS_2 samples.) In section A and B of the transient the sample was kept in UHV. At 200 s, H_2/H was dosed at a pressure of 2×10^{-6} mbar (section B) via a leak valve; at 400 s thiophene was additionally dosed at 1×10^{-6} (section C); at 600 s the hydrogen stream was stopped by closing the leak valve (section D); and at 800 s also the thiophene flux was stopped. Five different transients are shown: two for the pristine surface, two for the reduced surface (two H annealing cycles), and one for the sulfided surface, as indicated. While dosing these gases, the formation of alkanes has been detected by monitoring the m/e = 43 signal vs. time. (H_2S vs. time transient similar to these shown in Fig. 4 have also been detected). As evident, even at rather high pressure in a UHV chamber, HDS activity has been observed since the formation of alkanes is clearly detectable when hydrogen and thiophene are dosed together (section C). After stopping the H flux, a few minutes are required to drop the hydrogen background pressure in the vacuum chamber entirely. Therefore, in section D, HDS activity is seen. Similarly, an unavoidable thiophene background pressure results in some HDS activity already in section B. Please note, that reversing the exposure order, i.e., dosing first only thiophene and afterwards hydrogen and thiophene together also leads to some initial formation of alkanes which is certainly expected. Hydrogen is the largest component of the residual gas in every vacuum chamber. Furthermore, the sample heating filament, pressure gauge filament, and mass spectrometer filament always generate some atomic hydrogen. In addition, pristine samples (supposing nearly fully sulfided) show distinct HDS activity. However, for hydrogen annealed samples, the alkane intensity roughly doubles. Sulfiding the samples, reduces the HDS activity again back to the reactivity of the pristine samples. Thus, it appears that Mo/MoO_x sites enhance the HDS activity (consistent with traditional HDS models) but also nearly fully sulfided samples are catalytically active. No indication for a catalyst poisoning was evident in our experiments. Except some intensity variations (compare the two traces for the pristine catalyst in Fig. 4), pressure jump experiments could be well reproduced.

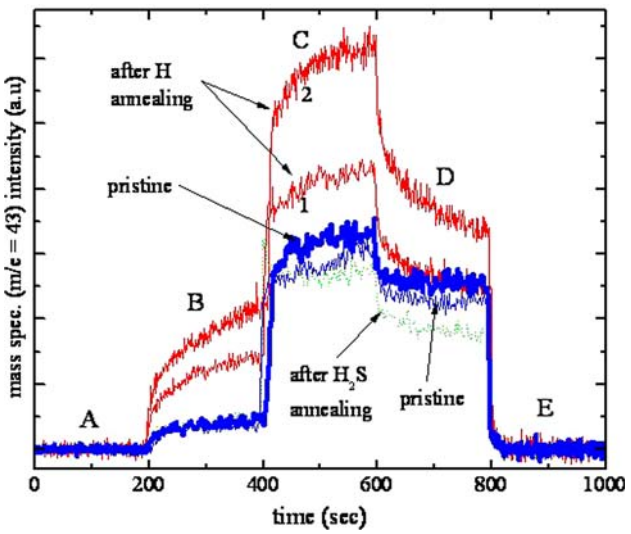

Fig. 4 Pressure jump experiments (at 350 K) for reduced and sulfided IF-MoS_2 samples. The formation of alkanes is monitored by recording mass m/e = 43. *A* Valves closed, *B* 2×10^{-6} mbar H_2/H, *C* 2×10^{-6} mbar H_2/H and 1×10^{-6} mbar thiophene, *D* 1×10^{-6} mbar thiophene, *E* valves closed

4 Summary

The following information has been gathered.

- The catalytic activity of a rather new nanomaterial IF-MoS_2 (inorganic fullerene like nanoparticles) towards (HDS) activity has been characterized at UHV conditions.
- Thiophene adsorbed molecularly on IF-MoS_2 at low adsorption temperatures. Besides a condensation peak (at 150 K), two thermal desorption spectroscopy (TDS)

features were observed corresponding to binding energies of 46 and 52 kJ/mol (1×10^{13}/s preexponential).
- Kinetics experiments with reduced and sulfided samples as well as spectroscopic data (Auger electron spectroscopy) suggest assigning the TDS peaks to sulfur and Mo/MoO_x like adsorption sites.
- HDS activity was present for both reduced and sulfided samples, but the largest HDS activity was seen for reduced samples.

Acknowledgments We acknowledge generous support by R. Tenne (Department of Materials and Interfaces, Weizmann Institute of Science, Israel) including sample fabrication and SEM characterization by R. Rosentsveig (Weizmann Institute of Science). Financial support from the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, Office of Science, US Department of Energy is acknowledged by NDSU (DE-FG02-08ER15987).

References

1. Rapoport L, Bilik Y, Feldman Y, Homyonfer M, Cohen SR, Tenne R (1997) Nature 387:791
2. Chhowalla M, Amaratunga GAJ (2000) Nature 407:164
3. Goering J, Burghaus U (2007) Chem Phys Lett 447:121
4. Dong K, Ma X, Zhang H, Lin G (2006) J Nat Gas Chem 15:28
5. Li X, Ma D, Chen L, Bao X (2007) Catal Lett 116:63
6. Song XC, Zheng YF, Zhao Y, Yin HY (2006) Mater Lett 60:2346
7. Goering J, Burghaus U, Arey BW, Eidelman O, Zak A, Tenne R (2008) Catal Lett 125:236
8. Dhas NA, Suslick KS (2005) J Am Chem Soc 127:2368
9. Chen J, Li SL, Xu Q, Tanaka K (2002) Chem Commun 16:1722
10. Friend CM, Chen DA (1997) Polyhedron 16:3165
11. Topsoe H, Clausen BS, Massoth FE (1996) Hydrotreating catalysts, science and technology, vol 11. Springer, Berlin
12. Prins R, Beer VHJd, Somorjai GA (1989) Catal Rev Sci Eng 31:1
13. Lauritsen JV, Bollinger MV, Laegsgaard E, Jacobsen KW, Norskov JK, Clausen BS, Topsoe H, Besenbacher F (2004) J Catal 221:510
14. Zak A, Feldman Y, Alperovich V, Rosentsveig R, Tenne R (2000) J Am Chem Soc 122:11108
15. Rosentsveig R, Margolin A, Gorodnev A, Popovitz-Biro R, Feldman Y, Rapoport L, Naveh G, Tenne R [(2009) submitted]
16. Sadan MB, Houben L, Enyashin AN, Seifert G, Tenne R (2008) PNAS 105:15643
17. Frey GL, Elani S, Homyonfer M, Feldman Y, Tenne R (1998) Phys Rev B 57:6666
18. Funk S, Hokkanen B, Nurkig T, Burghaus U, White B, O'Brien S, Turro N (2007) J Phys Chem C 111:8043
19. Funk S, Goering J, Burghaus U (2008) Appl Surf Sci 254:5271
20. Funk S, Nurkic T, Burghaus U (2007) Appl Surf Sci 253:4860
21. Wang J, Hokkanen B, Burghaus U (2005) Surf Sci 577:158