Journal of Catalysis 329 (2015) 49–56

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

# *In situ* scanning tunneling microscopy of the poisoning of a Co(0001) Fischer–Tropsch model catalyst by sulfur

M. Ehrensperger [a], J. Wintterlin [a,b,*]

[a] Department Chemie, Ludwig-Maximilians-Universität München, Butenandtstr. 5-13, 81377 Munich, Germany
[b] Center for NanoScience, Schellingstr. 4, 80799 Munich, Germany

ARTICLE INFO

*Article history:*
Received 6 March 2015
Revised 22 April 2015
Accepted 23 April 2015
Available online 16 May 2015

*Keywords:*
Cobalt
Fischer–Tropsch
High-pressure STM
*In situ* STM
Sulfur poisoning
Co(0001)
Scanning tunneling microscopy
XPS

ABSTRACT

The poisoning of a Co(0001) model catalyst for the Fischer–Tropsch reaction by sulfur was investigated by *in situ* scanning tunneling microscopy (STM). Experiments were performed under syngas at pressures around 10 mbar and at sample temperatures around 500 K under methanation conditions. After the reaction experiments, the surface was analyzed by X-ray photoelectron spectroscopy. Mass spectrometry showed that the sample was poisoned when hydrogen with <0.5 ppm of sulfur was used in the syngas. STM images recorded under these conditions showed a strong restructuring of the surface into small terraces. The terraces were fully covered by a stable surface phase, displaying small ordered areas with $(2 \times 2)$ and $(\sqrt{19} \times \sqrt{19})R23.4°$ structures. The observations contrast with the flat terraces covered by a mobile adsorption layer when sulfur-free hydrogen was used. The poisoned surface state is interpreted as a mixed sulfur/carbon layer that additionally involves a reconstruction of the Co(0001) surface.

© 2015 Elsevier Inc. All rights reserved.

## 1. Introduction

The cobalt- or iron-catalyzed Fischer–Tropsch synthesis of liquid fuels from syngas,

$$n\mathrm{CO} + (2n+1)\mathrm{H}_2 \rightarrow \mathrm{C}_n\mathrm{H}_{2n+2} + n\mathrm{H}_2\mathrm{O},$$

is strongly and irreversibly poisoned by sulfur, a particularly harmful effect for the expensive cobalt-based catalysts [1–3]. Sulfur compounds have therefore to be removed from the CO/$H_2$ mixtures fed into Fischer–Tropsch reactors to extremely low contents. Maximum tolerable concentrations of 20 ppb [1] or similarly low values have been reported [4,5]. In the technical process, this is achieved in several cleaning steps, until, at the last step, most of the remaining sulfur is adsorbed on ZnO [6].

How such low concentrations of sulfur can deactivate a cobalt Fischer–Tropsch catalyst has been mainly studied with supported catalysts, by adding small amounts of sulfur compounds to the feed gas, or to the catalyst material during preparation, and measuring the decrease in activity. In an experiment, in which methanation conditions on a supported Co catalyst were applied, it was found that adding only 13–87 ppb of $H_2S$ to the syngas led to a drop of the methanation rate by more than four orders of magnitude [7]. The sulfur coverage responsible for this deactivation was estimated from the amount of $H_2S$ consumed and from Auger electron spectra (AES) of the catalyst taken out of the reactor. It was found that the surface was saturated with sulfur, corresponding to a coverage of S atoms of $\Theta = 1/2–2/3$ of a monolayer (ML) with respect to the Co surface atoms. Similarly strong deactivation effects of low amounts of sulfur have also been observed in several studies performed under Fischer–Tropsch conditions [3,8–12]. That the sulfur coverages are so high already at extremely low partial pressures of sulfur compounds can be explained by the high binding energy of adsorbed S atoms. A value is available for the $(2 \times 2)$S structure on Co(0001) for which DFT calculations obtained 5.3 eV per S atom [13,14].

That poisoning is caused in a nonselective way by a closed layer of sulfur atoms is consistent with a local deactivation mechanism, either by a simple geometric site blocking, or by local electronic changes at the Co atoms directly bonded to the S atoms [13]. An electronic effect can be understood within the “d band model”, according to which adsorbed sulfur causes a downshift of the energy of the d band of a transition metal with more than half-filled d band [15]. As a consequence, the dissociation barrier for molecules—in the present case the dissociation of CO is a critical step—can become higher at the directly bonded metal atoms. A local poisoning mechanism was also supported by adsorption

---

* Corresponding author at: Department Chemie, Ludwig-Maximilians-Universität München, Butenandtstr. 5-13, 81377 Munich, Germany.

*E-mail address:* wintterlin@cup.uni-muenchen.de (J. Wintterlin).

http://dx.doi.org/10.1016/j.jcat.2015.04.028
0021-9517/© 2015 Elsevier Inc. All rights reserved.

experiments on a Co(0001) surface in which adsorption sites for $D_2$ and CO were found to be blocked by preadsorbed S atoms [16,17].

However, the picture of nonselective poisoning by a closed layer of S atoms may not be fully adequate for the Fischer–Tropsch synthesis on cobalt. It does, e.g., not include effects on the morphology of the Co catalysts. The dissociation of CO molecules on cobalt, most likely an essential step in the reaction sequence, is strongly structure sensitive [18], so that sulfur-induced changes of the surface morphology could be important. Moreover, adsorbed sulfur is known to enhance the surface self-diffusion of metal surfaces [19–21], which may accelerate sintering of supported Co catalysts. In other systems, there are also indications of heterogeneous distributions of sulfur. Using steady state isotopic transient kinetic analysis and Fourier transform infrared spectroscopy on the methanation on a supported Ni catalyst, it was found that sulfur did, in fact, block CO adsorption sites, but that surprisingly the active sites for the reaction partially seemed to remain uncovered [22]. One may also question the chemical nature of the poisoned surface. The reported sulfur coverages of $\Theta = 1/2–2/3$ of a ML in the deactivated state [7] are significantly higher than $\Theta = 25\%$ of a ML of adsorbed sulfur atoms in the $(2 \times 2)$S structure on Co(0001), the only experimentally known ordered phase of adsorbed sulfur on cobalt [13,16,17]. Because of the almost complete lack of direct surface information under reaction conditions, the actual state of the poisoned catalyst surface is still obscure.

Here we present results of high-pressure high-temperature scanning tunneling microscopy (STM) experiments, performed in a syngas atmosphere, on the poisoning of a Co(0001) surface by sulfur. Atomic resolution was achieved under reaction conditions in the methanation limit of the Fischer–Tropsch synthesis. The data provide, to our knowledge, the first atomic scale, *in situ* insight into sulfur poisoning of a Fischer–Tropsch catalyst. The images show that minute amounts of sulfur in the syngas drastically change the surface morphology. These changes are in strong contrast to a recent *in situ* STM study in which we have shown that, under methanation conditions in the absence of sulfur, the Co(0001) surface morphology was unchanged with respect to the state under ultra-high vacuum (UHV) [23]. With sulfur, we observed, in addition, so far unknown surface structures that can be explained by a mixed sulfur/carbon layer on a reconstructed surface.

## 2. Experimental

The experiments were performed using an apparatus consisting of a UHV chamber and a high-pressure cell housing the STM that has been described in detail previously [24]. In short, the UHV chamber is equipped with X-ray photoelectron spectroscopy (XPS) and a monochromatized X-ray source, low-energy electron diffraction (LEED), quadrupole mass spectrometry (QMS), and an ion gun. The STM in the high-pressure cell can be operated at pressures between $10^{-10}$ mbar and 1 bar, during heating of the sample with an infrared laser. The gas composition in the cell was measured by QMS using a bypass to a leak valve at the UHV chamber. For details of the preparation of the Co(0001) single crystal by Ar ion sputtering and annealing we refer to an earlier paper [23].

Gases used were 99.9999% $H_2$ (Alphagaz 2, Air Liquide), the same gas as in our previous study [23,25], 99.999% $H_2$ (lecture bottle, Linde), and 99.97% CO (lecture bottle, Linde). After experiments in the mbar regime with the hydrogen from the lecture bottle, both in syngas mixtures and in $H_2$ only, XP spectra showed a distinct sulfur signal. By contrast, after experiments with the Alphagaz 2 hydrogen, the surface was free of sulfur. As the same gas inlet was used in both cases, we rule out a sulfur source in our experimental setup. The sulfur must be contained in the hydrogen gas in the lecture bottle. Since no sulfur compounds are given in the list of residual contaminants provided by the supplier, the maximum sulfur content must be below 0.5 ppm of hydrocarbons, the lowest concentration of other foreign components listed. Mass spectra of the hydrogen gas from the lecture bottle showed no sulfur compounds, in particular no $H_2S$ signal above the background level at $m/z = 34$. The sulfur content must therefore be below $\sim$1 ppm, a similar limit as from the above estimate. That the Alphagaz 2 hydrogen does not contain sulfur contaminations is explained by an extra low temperature purification step applied by the producer that freezes out sulfurous compounds.

The CO gas, stored in an aluminum lecture bottle, was introduced into the stainless steel gas inlet only directly before an experiment to avoid accumulation of Ni carbonyls. In no case a nickel signal was detected by XPS on the sample surface. Experiments with CO alone did not lead to a sulfur signal in XPS.

Experiments were typically performed by cleaning the sample in UHV, transferring it to the STM cell, adjusting the $H_2$ and CO pressures between $p(H_2):p(CO) = 4:1$ to 40:1 and at $p_{total} = 10–14$ mbar, and heating the sample to $T = 493–523$ K. Then, the STM or QMS data were taken. The cell was not pumped during the STM and activity experiments, which thus correspond to batch conditions. After the experiments, the STM cell was evacuated, the heating was stopped, the sample was transferred to the UHV chamber and quickly reheated, a sequence during which the temperature intermediately dropped by roughly 100 K. Finally, XP spectra were taken. The C 1s, O 1s, S 2p, and Co 2p peaks in XPS were analyzed as described previously [23]. Survey scans did not show any other foreign elements.

To further characterize the surface structures observed by STM, a supporting $H_2S$ adsorption experiment was performed in another UHV chamber. This chamber was equipped with STM, AES, LEED, and QMS. $H_2S$ was formed by reaction of $Na_2S$ with phosphoric acid and filled into a glass tube that was mounted to a leak valve at the chamber. The so-produced $H_2S$ contained a small amount of air. $H_2S$ was dosed at a sample temperature of 300 K until AES indicated saturation. Then, the sample was flash-annealed to 650 K to decompose the adsorbed $H_2S$ and desorb $H_2$.

## 3. Results and discussion

### 3.1. Reference experiments with sulfur-free hydrogen

For reference purposes, Fig. 1 shows two STM images of the Co(0001) surface, recorded in a syngas atmosphere with the Alphagaz 2 hydrogen [$p_{total} = 10$ mbar, $p(H_2):p(CO) = 40:1$, $T = 493$ K]. Images like these were typical for the active state of the surface and have been analyzed in detail earlier [23]. The surface in this state was characterized by several 100 Å wide terraces, most of which were separated by monatomic steps of irregular directions. The low hillocks are caused by Ar atoms implanted into the bulk of the crystal during ion sputtering and not completely removed in the annealing step. (Because of the hcp-to-fcc phase transition of cobalt, the temperature had to be kept well below 695 K [26].) Also the many screw dislocations are explained by the low preparation temperatures. This morphology was indistinguishable from the morphology of the freshly prepared surface under UHV at room temperature.

The XP spectra recorded thereafter (Fig. 2, spectra 1) only showed a small C 1s signal at 283.3 eV in the range of “carbidic” carbon (8% of a ML), and a broad peak at 285.1 eV, in the range of “graphitic” carbon ($\leqslant$7% of a ML). The significant O 1s signal (main peak at 529.6 eV and a second peak at 530.7 eV, 17% of a ML) is most likely due to atomic oxygen formed from water adsorption after the experiment during pump down of the STM

Download English Version:

https://daneshyari.com/en/article/60794

Download Persian Version:

https://daneshyari.com/article/60794

Daneshyari.com