Influence of the support on sulfur poisoning and regeneration of Ru catalysts probed by sulfur K-edge X-ray absorption spectroscopy

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ABSTRACT

Catalyst supports are known not to be inert, but react with some gases, such as sulfur species. Understanding the interaction of sulfur species with the supports is necessary to design improved catalysts or optimize regeneration protocols. We investigated the oxidation state of sulfur on supported Ru catalysts and blank supports during methanation, sulfur poisoning, oxidative regeneration, and subsequent reacitvation by sulfur K-edge X-ray absorption spectroscopy (XAS). We found that oxide (Al_2O_3 and ZrO_2) supported Ru forms sulfides on the Ru and sulfates on the support during poisoning. Upon regeneration, sulfur is transported from the Ru to the support, and is transported back upon subsequent reducing conditions, impeding complete regeneration. On C-supported Ru, not all sulfur is removed by oxidation, making regeneration by oxidation under the tested conditions impossible.

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1. Introduction

While heterogeneous catalysis is usually described in terms of the interaction between the reactants (gaseous or liquid) and the solid catalyst (often a metal, metal oxide, or metal sulfide), it is known that the catalyst support can have an influence on the reaction. Catalyst supports include porous oxide structures, zeolites, or active carbon. The interaction of the support can influence the reaction, for example, by influencing the catalyst size or shape [1], by providing O_2 for the reaction [2], or by formation of an alloy of the metal with the support [3]. Modification of the support can improve the catalyst performance, for instance, by improving tolerance towards sulfur poisoning of the metal catalyst [4].

It is known that materials which are frequently used as catalyst supports are not inert towards sulfur. Al_2O_3 for example, one of the most frequently used catalyst supports, is also used as a catalyst for the oxidation of H_2S to elemental S (Claus reaction) [5]. The surface chemistry of Al_2O_3 in the presence of sulfur has been the subject of many infrared spectroscopy studies [5–11]. Activated carbon, another widely used catalyst support, is used for the

catalytic oxidation of H_2S [12] or the removal of SO_2 from stack gases via adsorption [13].

Sulfur is also a catalyst poison, which is known to poison metal catalysts, for instance, Ni- or Ru-based methanation catalysts [14,15] or Fischer–Tropsch catalysts [16]. Since sulfur is always contained in natural feedstocks like coal or biomass, minimizing sulfur poisoning or regeneration of poisoned catalysts used for the conversion of coal or biomass is an important research topic [17].

The interaction of the catalyst and its support with sulfur species is especially important for applications where sulfur is either the main component in the gas feed, or a relevant minority species. The effect of sulfur on benzene hydrogenation over Pt or Ir was studied on different supports, and it was found that the acidity of the support influences the toxicity of sulfur [18]. On alumina-supported palladium catalysts that were poisoned by H_2S, sulfite and sulfate species were found after poisoning, which were attributed to reaction of the Al_2O_3 support with sulfur [19]. A positive effect of an alumina support was reported for sulfur poisoning of Pd catalysts, where the deactivation was slower compared to SiO_2-supported Pd due to "trapping" of sulfur on the Al_2O_3 support [20].

One direct way to experimentally probe the sulfur speciation on catalysts is X-ray absorption spectroscopy (XAS) at the sulfur K-edge (2474 eV) [21]. In contrast to infrared spectroscopy, XAS has in principle no temperature limit, and allows the presence of large amounts of steam in the reactor. While ex situ experiments

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are straightforward to conduct, they do not offer time resolution and preserving the in situ state is difficult, due to rapid oxidation of the sample in air. A recent ex situ XAS study at the sulfur K-edge suggested that sulfur poisoning of Al_2O_3 supported Ni reforming catalysts at 900 °C produced mostly sulfides and sulfates, while sulfates were formed after regeneration in H_2O or $H_2O + O_2$ [22]. Even though in situ XAS studies are an excellent tool to study sulfur speciation under operating conditions, few in situ sulfur XAS studies have been reported. This is probably due to the limited number of beamlines, which allow access to the sulfur K-edge. In addition, such studies present high requirements from the experimental side; not only needs the reactor to be tight against high vacuum, but also the windows need to be transparent to the low-energy X-rays, temperature resistant, chemically inert, and must not contain elements which absorb in the desired energy range. Recently, in situ S-XAS studies were performed using different reactor designs, allowing insights into sulfur transport over catalysts or sulfur absorber materials [23,24].

In a previous study, we investigated the Ru K-edge during sulfur poisoning of the methanation activity of a Ru/Al_2O_3 catalyst and subsequent regeneration [25]. It was found that regeneration with O_2 initially restores activity by removing sulfur from the Ru surface, but the catalyst deactivates even in the absence of sulfur in the feed. We ascribed this to the buffering of sulfur on the Al_2O_3 support, which prevents complete sulfur removal from the system in O_2, and releases sulfur under reducing conditions. A similar sulfur "trapping" function of the Al_2O_3 support was proposed for sulfur poisoning of Pd catalysts [20]. While the detection of the formation and disappearance of a Ru-sulfide species upon poisoning and regeneration, respectively, was possible with Ru K-edge XAS, no direct information on the storage effect of the support was obtained.

In this work, we used sulfur K-edge XAS to study sulfur speciation of supported Ru catalysts in situ, during methanation, sulfur poisoning, oxidative regeneration, and subsequent re-activation. This allows proposing a mechanism for sulfur poisoning and regeneration, taking into account the role of the support. We found that sulfur is stored on the support, from which it is not removed upon oxidative regeneration. Under subsequent reducing conditions, sulfur is transported back from the support to the catalyst, poisoning its activity.

2. Experimental

2.1. Materials

Ru catalysts supported on different supports, and the blank supports, were investigated in this study. One of the most common catalyst supports is γ-Al_2O_3, while activated carbon exhibits remarkable stability under certain conditions, such as gasification in supercritical water [26,27]. Ru/Al_2O_3 (2 wt.% loading) and Ru/ZrO_2 (2 wt.% loading) were prepared by wet impregnation of Ru-nitrosyl-nitrate (Sigma–Aldrich) on blank Al_2O_3 and ZrO_2 supports, respectively, and both catalysts were calcined. A Ru/C catalyst (2 wt.% loading) was provided by BASF, which has been investigated extensively before, exhibiting a particle size of approximately 1 nm [27].

2.2. XAS measurements

In situ XAS at the sulfur K-edge (2472 eV) was carried out at the PHOENIX beamline X07MB of the Swiss light source. Fluorescence XAS was acquired with a single element, silicon drift detector (Roentec) that was placed at 90° angle with respect to the X-ray beam. The detector and the in situ reactor (see next Section 2.3)

were kept in a vacuum chamber. The optical design of the PHOENIX beamline is similar to the layout of the LUCIA beamline, that is now located at SOLEIL, France [28]. All XAS spectra were background corrected and normalized to the count rate above the absorption edge, at 2495 eV to avoid introduction of artifacts due to fitting of a background function. The Si double crystal monochromator was calibrated with a Ru metal foil at the Ru L_{III} edge (2838 eV).

2.3. In situ reactor

10–15 mg of the catalyst sample were filled between plugs of quartz wool in a plug flow reactor described elsewhere [29]. In short, the reactor consists of three plates made of stainless steel. In the central plate there is a rectangular aperture, which mimics a plug flow reactor. On both ends of the aperture, 1/16 in steel lines are connected for inlet and outlet of the gases. The two other steel plates, having openings at the place of the central's plate aperture, are then mounted on both sides of the central plate. Between the central plate and the two outer plates are polyimide (Kapton) foils, which seal the reactor against the ambient atmosphere, and act as X-ray windows. The reactor was mounted on a XYZ sample stage in a vacuum chamber (pressure 10^{-5}–10^{-4} mbar) at a 45° angle with respect to the X-ray beam. The Kapton foils (Goodfellow) had a thickness of 13 μm on the X-ray exposed window and 25 μm on the opposite window of the reactor.

2.4. Gas mixing and analysis

Product gases were dosed with mass flow controllers (Bronkhorst) and analyzed with a quadrupole mass spectrometer (Max 300-LG, Extrel). All stainless steel tubes outside the actual reactor were coated with quartz to minimize sulfur adsorption (Restek). The following gases were used for the in situ experiments: 5000 ppm H_2S/He, 5% O_2/He, 10% H_2/Ar, 10% CO/He. To dilute the gases to the desired concentration, they were mixed with He.

2.5. H_2S and SO_2 uptake of blank supports

The uptake of H_2S and SO_2 by the blank supports was tested at 300 °C. The amount of the adsorbed gases was calculated in comparison to a measurement of the empty tube. The supports were exposed to 1000 ppm H_2S and 8% O_2 + 80 ppm SO_2, respectively at a total flow of 25 ml min^{-1}.

2.6. In situ experimental procedure

After the reactor was cleaned by sonication in deionized water and filled with a fresh sample, it was mounted in the vacuum chamber and tested for tightness. Subsequently the vacuum chamber was evacuated to 10^{-5}–10^{-4} mbar, and the reactor was heated up to 300 °C under He atmosphere and at a pressure of 0.5–1 bar (against ambient pressure). If not indicated otherwise, spectra were measured subsequently under the following conditions, with a total flow rate between 20 and 26 ml min^{-1}, and balance inert gas:

- fresh catalyst under He
- reduction in 2% H_2
- methanation conditions: 2% H_2 + 0.2% CO (10:1)
- sulfur poisoning conditions: with 96 ppm H_2S added to the H_2/CO feed
- regeneration conditions: 0.4% O_2 (at 200–400 °C)
- methanation conditions: 2% H_2 (+0.2% CO).

Our previous study (see [25]) showed that approximately 70% of the surface Ru atoms are bound to a sulfur atom (based on