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Distinct spatial changes of the catalyst structure inside a fixed-bed microreactor during the partial oxidation of methane over Rh/Al_2O_3

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Abstract

During the catalytic partial oxidation (CPO) of methane to hydrogen and carbon monoxide distinct spatial changes of the catalyst structure in a microreactor containing a fixed-bed of 2.5 wt% Rh/Al_2O_3 were observed depending on temperature and space velocity. The variation of the catalyst structure along the catalyst bed was determined by X-ray absorption spectroscopy. In a first step the catalyst bed was scanned with a small X-ray beam. Then, more detailed information on the oxidation state of Rh along the catalyst bed was extracted by recording absorption images using a position sensitive X-ray camera. The studies were combined with on-line mass spectrometry providing information on the catalytic performance of the catalyst simultaneously.

Mainly oxidized Rh-particles were found below the ignition temperature (310 °C) of the partial oxidation of methane to hydrogen and carbon monoxide. Hardly any structural changes were observed when oxidation to water and carbon dioxide occurred, but strong variations over the catalyst bed were detected when the CPO-reaction started. In the entrance zone of the catalyst bed the rhodium species were mainly in oxidized state, whereas they were in metallic state towards the end of the catalyst bed. Usually, a steep gradient within less than 100 μm was observed. Furthermore, at higher temperature, a characteristic cone towards the inlet of the spectroscopic cell was observed. Upon temperature increase the gradient zone moved towards the inlet. The variation of the space velocity also resulted in a shift as well as a change in the shape of the profile.

Keywords: *In situ* X-ray absorption spectroscopy; Catalytic partial oxidation of methane; Rhodium catalysts; 2D-imaging; Spatially resolved XAS; Micro EXAFS; XANES

1. Introduction

In situ or *operando* spectroscopic studies are used to gain mechanistic insight into the structure and working mechanisms of heterogeneous catalysts [1–7]. Spectroscopic studies under reaction conditions are vital since the structure is often more dynamic than anticipated [8–10]. However, only little attention has been paid to changes in the solid catalyst on a microscale up to now [11–18]. Usually, the *in situ* studies are performed in an integral way neglecting variations of the gas composition, the use of pre-shaped particles (extrudates, shell-impregnation), or the change of the temperature over the catalyst bed. Only recently, it was shown that molecular information on a microscale is of importance also under *in situ* conditions, *e.g.*, during catalyst preparation [15,19–21] and in the catalytic reactor during operation [16,18,22].

Spatially resolved X-ray absorption spectroscopy is among other techniques such as micro XRD, micro infrared, micro UV–vis, and micro Raman spectroscopy a well suited tool for this purpose since it is element-specific and both amorphous and crystalline samples can be investigated [4,23–26]. Two different approaches have been reported: either the use of highly focused beams and scanning over the sample or the use of a two-dimensional position sensitive X-ray camera that allows recording X-ray images behind the sample. Nowadays, hard X-ray beams can be focused to less than 1 μm and information both in transmission and fluorescence can be obtained in this way on a micrometer scale [13,27–31]. Position

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sensitive X-ray cameras can also give spatially resolved information [18,32]. In this case, the spatial resolution is on the 1–10 μm scale. For studying the structural changes over a catalyst bed, the use of a charged coupled device (CCD) camera compared to scanning with a microbeam has distinct advantages [18,32]: the absorption can be determined using the X-ray transmission images with and without sample and thus recording the absorption of the sample as function of the location (x, y) and energy E. This leads to a significantly faster measurement due to the parallel acquisition of the data points.

Recently, we observed a strong spatial change of the oxidation state of rhodium in Rh-based catalysts during the partial oxidation of methane [16,18]. Both a catalytic combustion and reforming (CCR) and a direct partial oxidation (DPO) mechanism have been proposed [33,34].

Catalytic combustion and reforming (CCR)

1. Combustion of methane:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O, \qquad \Delta_r H = -801.7\,\mathrm{kJ/mol}.$$

2. Reforming of methane:

$$CH_4 + H_2O \rightarrow CO + 3H_2, \qquad \Delta_r H = 206.1\,\mathrm{kJ/mol}$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2, \qquad \Delta_r H = 247.5\,\mathrm{kJ/mol}.$$

Direct partial oxidation of methane (DPO)

Partial oxidation of methane:

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2, \qquad \Delta_r H = -35.5\,\mathrm{kJ/mol}.$$

From experimental and modelling studies [33–37], it is concluded that both the temperature and the flow (space velocity) influence the relative distribution of the gas composition during the catalytic partial oxidation of methane significantly. Hence, we investigated in this study the influence of both parameters on the structural composition of the catalyst in a fixed-bed. Moreover, if this technique is to be combined with tomography to obtain the three-dimensional distribution of the oxidation states inside a microreactor, the recording time required for a complete profile must be short. Therefore, ways to achieve this, such as reduced energy sampling or smaller energy intervals are also discussed in this contribution.

2. Experimental

The reaction was conducted using a 2.5 wt% Rh/Al_2O_3 catalyst in a quartz glass capillary microreactor (Markröhrchen, Hilgenberg GmbH, ca. 1 mm diameter, 20 μm wall thickness) as described in Ref. [38]. The *in situ* spectroscopic cell is similar to the one that has been originally proposed for *operando* XRD measurements [39,40] and was later used by a number of groups for *operando* EXAFS [38,41,42] even in fluorescence mode [43–45], SAXS [46] and even combined EXAFS/XRD [8] measurements. The 2.5 wt% Rh/Al_2O_3 catalyst was prepared by flame spray pyrolysis using a solution of Rh(III)acetylacetonate and aluminium-*sec*-butoxide in xylene sprayed in the flame (cf. Refs. [47,48]), which resulted in a high surface area and microcrystalline material (130 m^2/g determined by BET, Rh-particle size of 2–3 nm as evidenced by electron microscopy). Pre-mixed 6% CH_4/3% O_2/He was used as reaction gas and flows were controlled by mass flow controllers (Brooks, 0–50 ml/min). The outlet of the quartz glass microreactor was connected to a mass spectrometer (Balzers Thermostar). The microreactor was heated using an air blower with a controlled air flow regulated by a mass flow controller (Brooks, 0–2000 ml/min). The temperature of the heater was measured by a thermocouple (K-type) at the heating element (ring cartridge, SUVAG, Zurich, 300 W/230 V) in order to control a linear temperature ramp. The actual sample temperature was monitored just below the sample. The microreactor was additionally enclosed in a Kapton cap just above the heater where the hot air stream passed out of the oven. The whole assembly (*in situ* cell, heater) was mounted on a small stage (Huber, provided by HASYLAB) that allowed one to align the microreactor horizontally and vertically in the X-ray beam.

Spectroscopic information on the Rh-oxidation state was obtained in two ways. During dynamic changes of the reaction conditions (change in temperature, variation of the space velocity of the reaction mixture) the microreactor was scanned by an X-ray beam of 1 mm × 1 mm. By recording the intensities before and after the sample as a function of energy information on the oxidation state could be extracted from the XANES spectra at a spatial resolution of about 1 mm. After equilibration of the catalyst under the new experimental conditions more detailed spatially resolved X-ray absorption information from the reactor could be obtained by placing a two-dimensional position sensitive X-ray camera behind the reactor. A remote-controlled positioning system allowed us to move the camera in and out of the beam. In this way, either the camera or the ionization chamber I_1 behind the camera could be used for transmission measurements (Fig. 1). The setup has been described in more detail in Ref. [18]. In brief, the X-rays are converted in the detector into visible light in a thin single crystal scintillator that is imaged onto a CCD camera by a visible light microscope optic [49]. The effective pixel size is 3.5 μm. The energy was scanned in the XANES region around the Rh K-edge in steps of 1 or 2 eV (from 23190 to 23350 eV). At each energy E, an X-ray image was recorded with and without the capillary, effectively measuring the transmitted intensity $I_1(E, x, y)$ and incident intensity $I_0(E, x, y)$ in each pixel, where x and y denote the coordinates of the pixel. The exposure time for each image was 30 s. The reaction conditions of six selected investigations including the experimental parameters are summarized in Table 1. Obviously, we changed both the number of images and flat-fields and also the incoming intensity was varied by a different detuning of the monochromator crystal. The images were dark-field corrected, *i.e.*, the influence of the CCD dark current and read-out noise were removed by subtracting an averaged dark image (without X-rays) from each of the images. From the dark-field corrected transmission and flat-field images, the absorption along the