



## Methanol oxidation over model cobalt catalysts: Influence of the cobalt oxidation state on the reactivity

S. Zafeiratos<sup>a,\*</sup>, T. Dintzer<sup>a</sup>, D. Teschner<sup>b</sup>, R. Blume<sup>b</sup>, M. Hävecker<sup>b</sup>, A. Knop-Gericke<sup>b</sup>, R. Schlögl<sup>b</sup>

<sup>a</sup> LMSPC, UMR 7515 du CNRS, 25 Rue Becquerel, 67087 Strasbourg, France

<sup>b</sup> Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

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### ABSTRACT

X-ray photoelectron and absorption spectroscopies (XPS and XAS) combined with *on-line* mass spectrometry were applied under working catalytic conditions to investigate methanol oxidation on cobalt. Two cobalt oxidation states ( $\text{Co}_3\text{O}_4$  and  $\text{CoO}$ ) were prepared and investigated as regards their influence on the catalytic activity and selectivity. In addition adsorbed species were monitored in the transition of the catalyst from a non-active state, to an active one. It is shown that the surface oxidation state of cobalt is readily adapted to the oxygen chemical potential in the  $\text{CH}_3\text{OH}/\text{O}_2$  reaction mixture. In particular, even in oxygen-rich mixtures the  $\text{Co}_3\text{O}_4$  surface is partially reduced, with the extent of surface reduction following the methanol concentration. The reaction selectivity depends on the cobalt oxidation state, with the more reduced samples favouring the partial oxidation of methanol to formaldehyde. In the absence of oxygen, methanol effectively reduces cobalt to the metallic state, also promoting  $\text{H}_2$  and  $\text{CO}$  production. Direct evidence of methoxy and formate species adsorbed on the surface upon reaction was found by analysing the O 1s and C 1s photoelectron spectra. However, the surface coverage of those species was not proportional to the catalytic activity, indicating that they might also act as reaction inhibitors.

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### 1. Introduction

Our current understanding of heterogeneous catalysis is to a large extent built on post-reaction (*ex situ*) analysis of the catalysts and deductions based on kinetic experiments. A key problem was the lack of surface-sensitive techniques that could provide spectroscopic information at pressures relevant to the catalysis process. The situation in catalyst characterization is gradually changing, and today a variety of techniques are available that may provide detailed atomic-scale structural and chemical insight into complex heterogeneous catalysts exposed to controlled environments that closely match the working conditions [1–3]. These studies showed that the structure of a heterogeneous catalyst is dynamic and is intimately dependent on the reaction conditions. Such dynamic changes have, for example, been observed on a Cu and Ru catalyst during methanol oxidation, indicating that the active state of the catalyst exists only during the process of catalysis [4–7].

Cobalt and its oxides ( $\text{CoO}$  and  $\text{Co}_3\text{O}_4$ ) exhibit interesting electronic and magnetic properties and are used as catalysts in a range of reactions. Perhaps the major application of cobalt-based catalysts is in the Fischer–Tropsch synthesis, since cobalt has been shown to efficiently convert syn gas ( $\text{CO} + \text{H}_2$ ) to methane or liquid

fuels [8–11]. Other applications of cobalt catalysts include partial oxidation reactions [12] and decomposition of methane to form hydrogen and carbon nanotubes or filamentous carbon [13,14]. Recently cobalt has been proposed as a very promising catalyst to replace noble metals for  $\text{H}_2$  production by steam reforming of ethanol [15,16]. Pure cobalt oxide surface phases have seldom been investigated with respect to their catalytic properties [17–19] and always by *ex situ* methods. While this has provided valuable information, the question of whether or not the active surface state “survives” after reaction remains unanswered.

In the present work, ambient pressure photoelectron and soft X-ray absorption spectroscopies were applied under working catalytic conditions, to investigate methanol oxidation on cobalt. Previous studies of methanol adsorption on  $\text{Co}(0001)$  surface indicated dissociative adsorption and decomposition of methanol to  $\text{CO}$  and  $\text{H}_2$  upon annealing [20]. On the other hand, on cobalt oxide surfaces methanol is molecularly chemisorbed at room temperature, while dissociation and formation of formate and formaldehyde species was observed upon annealing [19]. In the presence of oxygen both, partial (carbon monoxide, formaldehyde ext) and complete, oxidation products (carbon dioxide) can be produced depending on the conditions. A detail description of the most prominent reaction paths has been given elsewhere [5–7]. Our previous *in situ* photoelectron spectroscopy studies of methanol oxidation on Ru and Cu suggested that the active catalyst state is

\* Corresponding author.

E-mail address: [spirosz@ecpm.u-strasbg.fr](mailto:spirosz@ecpm.u-strasbg.fr) (S. Zafeiratos).

neither the metal nor the stoichiometric oxides, but rather a “transient oxidized state” controlled by the chemical potential of gas phase oxygen [2 and reference therein].

Acquiring fundamental understanding of the reaction networks of methanol on cobalt is important for further development of processes such as production of formaldehyde and for operation of direct methanol fuel cells. On the other hand, methanol may also serve as a simple model compound for the study of the oxidation of the other, more complex alcohols, like ethanol and glycerol [21]. The aim of this work is to discover if cobalt undergoes dynamic variations under reaction conditions and to understand the role of different cobalt oxidation states in the reaction pathways.

## 2. Materials and methods

In situ X-ray photoelectron and absorption spectroscopies (XPS and XAS, respectively) were performed at ISSS beamline at BESSY in Berlin, in a setup described elsewhere [2,4]. The soft X-ray absorption spectra of the Co  $L_{3,2}$  edges were recorded in the Total Electron Yield (TEY) mode, enhanced by additional electrons created by ionization of the gas phase above the sample. The 0.5 mm thick and 5 mm diameter Co(0001) single crystal was placed on a sample holder, which could be heated from the rear by an IR laser (cw, 808 nm). The temperature was measured by a K-type thermocouple fixed onto the sample surface. The Co crystal was pre-treated in the XPS reaction cell by oxidation (0.2 mbar  $O_2$  at 520 K) and reduction (0.2 mbar  $H_2$  at 520 K) cycles, until all residual surface carbon disappeared. The same procedure was repeated after each reaction cycle to “refresh” the surface. The reaction mixture was introduced after cooling down the sample at 300 K with an overall pressure of 0.1–0.3 mbar. Consequently the sample was heated to 520 K (by 5 K/min) where photoemission and absorption spectra were recorded. Preparation of  $Co_3O_4$  and metallic Co surfaces was attained after 30 min annealing in 0.2 mbar  $O_2$  and  $H_2$  respectively, at 520 K. The CoO surface was formed by heating metallic Co at 450 K in 0.2 mbar  $H_2$  and consequently introducing traces of  $O_2$  (~5–10% of the hydrogen pressure). Few minutes under these conditions were adequate to form a thick CoO layer on the Co crystal, as judged by XPS.

$CH_3OH$ ,  $O_2$  and  $H_2$  gas flow into the reaction cell was controlled using calibrated mass flow controllers. A differentially pumped quadrupole mass spectrometer (QMS) was connected through a leak valve to the experimental cell and the gas phase composition was simultaneously monitored by *on-line* mass spectrometry to the spectroscopic characterization of the surface. The decrease of  $CH_3OH$  ( $m/e = 31$ ) QMS intensity was used to calculate  $CH_3OH$  conversion under reaction conditions. Relative product selectivities were calculated by the increase of the  $H_2$  ( $m/e = 2$ ), CO ( $m/e = 28$ ),  $CH_2O$  ( $m/e = 30$ ) and  $CO_2$  ( $m/e = 44$ ) QMS intensities induced by the catalytic reaction. A correction of the ion current signals of  $m/e = 28$  and 30 due to  $CH_3OH$  fragment (20% and 25% of  $m/e = 31$ , respectively) was also taken into account. It should be noted that, since QMS signals are not calibrated to the sensitivity factor of each gas, only the comparison of selectivities between various conditions (*relative selectivity*), and not absolute values are considered here. For the sake of simplicity we refer only to selectivity in the following.

Photoemission spectra were recorded both during temperature rising and stationary conditions. The typical duration of an experiment was about 90 min, while the acquisition time of each spectrum was between 1 and 2 min. Therefore, the same energy region (e.g. Co  $2p_{3/2}$ ) was recorded in different stages of the stationary experiments. As a consequence, whenever combined catalytic and spectroscopic data are presented they refer to the same

experimental stage. Two methanol-to-oxygen mixing ratios (MR) 1:5 and 2:1 were studied and are referred to here as MR = 0.2 and 2, respectively. The Co 2p, O 1s and C 1s spectra were recorded using appropriately selected photon energies, resulting in photoelectrons with two characteristic kinetic energies for each spectrum, namely 180 and 580 eV ( $\lambda_{180\text{eV}}/\lambda_{580\text{eV}} = 0.56$ , where  $\lambda$  is the photoelectron attenuation length) [22]. In that way, information of two different depths was collected providing a non destructive depth analysis. For the calculations all spectra were normalized by the storage ring current and the energy-dependent incident photon flux, which was measured prior to the measurements using a gold foil with known quantum efficiency. The photon flux obtained has been corrected for higher diffraction orders that contribute only to the background but not to the peak intensity in XPS. The spectra presented here are rescaled to facilitate the observation of peak characteristics. The binding energy (BE) scale was calibrated with respect to the Fermi level of the electron analyzer. The oxidized surface showed no electrostatic charging. Curve fitting of the O 1s and C 1s peaks was performed based on a mixed Gaussian/Lorentzian function. XPS and XAS peaks of Co were fitted using line shapes recorded on reference samples. Background subtraction was carried out by using the Shirley method. Quantitative calculations were performed using normalized Co 2p, O 1s, C 1s intensities, taking into account the photon-energy dependence of the atomic subshell photoionization cross sections [23].

## 3. Results

### 3.1. The dynamic transformation of cobalt upon changes in the reaction mixture

There are two stable bulk phases of cobalt oxide, i.e., the fcc-type rocksalt structure of CoO and the cubic spinel structure of  $Co_3O_4$ . The thermodynamically stable form of cobalt oxide under ambient temperature and pressure conditions is the  $Co_3O_4$  spinel phase [9,24]. Therefore, initially we investigated how pre-oxidized cobalt surfaces respond to different reactant-mixing ratios (MRs). Two MRs (0.2 and 2), as well as pure methanol, were studied at separate reaction cycles. Fig. 1 displays photoemission and absorption spectra of Co 2p core level ( $L_{3,2}$  edge in absorption spectroscopy nomenclature) obtained from a cobalt crystal at 520 K, under various gas phase environments.

The photoemission data of cobalt oxides published previously (see Table 1) provide the necessary basis for identification of the cobalt oxidation state [24–30]. In pure  $O_2$ , the Co  $2p_{3/2}$  photoemission peak at 779.6 eV is accompanied by a weak, broad satellite (marked as S in Fig. 1a) characteristic of the  $Co_3O_4$  spinel phase [24–26]. In agreement, the  $L_{3,2}$  edge fine structure (Fig. 1b) is very similar to that previously obtained on  $Co_3O_4$  reference compounds [27,28]. Finally, the Co/O atomic ratio calculated from the Co 2p and O 1s peaks was found  $0.69 \pm 0.08$ , within experimental error of the nominal value for  $Co_3O_4$  (0.75). All spectroscopic results are consistent with the complete transformation of cobalt surface to  $Co_3O_4$  when heated in  $O_2$  at 520 K. The thickness of the oxide layer exceeds 4 nm which is the estimated probing depth of the absorption spectra [31]. However, the cobalt crystal is still metallic in the bulk, since photoemission spectra showed no electrostatic charging, as would occur for the electrically insulating bulk  $Co_3O_4$  oxide [26 and reference therein].

The spectroscopic characteristics undergo significant modification in oxygen-methanol mixtures. The Co  $2p_{3/2}$  photoemission peak (Fig. 1a) is shifted to higher energies (780.6 eV) and the satellite structure becomes broader and more intense, especially for MR = 2. The difference curve (third spectra from the top), obtained

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