Direct comparison of the reactivity of the non-oxidic phase of Ru(0001) and the RuO$_2$ phase in the CO oxidation reaction

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ABSTRACT

Applying in situ surface X-ray diffraction (SXRD) together with on-line mass spectrometry during the CO oxidation over Ru(0001) allows a direct comparison of the reactivity of the non-oxidic state with that of the RuO$_2$(110) covered surface. This comparison reveals that the RuO$_2$(110) surface is a catalytically active phase at least as active as the non-oxidic phase. At high CO and O$_2$ pressures of 200 mbar and temperatures above 550 K, the CO oxidation reaction does not proceed isothermally on the RuO$_2$(110) surface. The released reaction heat leads rather to an increase of the sample temperature of up to 130 K accompanied by a self-acceleration of the CO oxidation reaction.

The identification of the active phase of a catalyst under practical reaction conditions forms the basis for the development of an even more efficient catalyst in the future [1]. Frequently, the catalytically active phase is only stable under reaction conditions and may even change when the reactant mixture and/or the reaction temperature is varied. All these complications call for in situ surface structure characterization of the catalytic system [2,3]. In order to attain full access to the atomic scale structure of the catalyst one has to study model catalysts with low structural complexity such as single crystalline films and single crystal surfaces.

The CO oxidation reaction is the prototype (model) reaction in surface chemistry. While the CO oxidation reaction itself is simple, the full system consisting of CO, O$_2$ and CO$_2$ in the gas phase together with a solid state catalyst may exhibit a quite complex behavior. A particular interesting situation is encountered with the CO oxidation over Ru(0001). While the activity of Ru(0001) is exceedingly low at low pressures (close to UHV conditions), Ru turns into a very efficient oxidation catalyst at high-pressures [4]. Recently, it has been shown that RuO$_2$, which may form at the Ru(0001) surface under reaction conditions [5], is very active in the oxidation of CO [6]. However, even more recently this conclusion was challenged [7] on the basis of earlier ex situ AES data [4], claiming that "the steady-state activity of RuO$_2$ at elevated temperatures/pressures and near stoichiometric reaction conditions is decidedly below that of the oxygen-covered surface..." [7]. This unsatisfying situation called not only for a public discussion in the Journal of Surface Science [8] but calls also for in situ characterization of the active phase of Ru(0001) under realistic reaction conditions to clarify the nature of the active phase under reaction conditions.

In this paper, the complex structure–activity correlation in the CO oxidation on Ru has been elucidated for temperatures above 500 K with in situ surface X-ray diffraction (SXRD) and on-line mass spectrometry. Temperatures above 500 K were chosen in order to allow the model catalyst Ru(0001) either to be in the reduced or in the oxidized state depending on the composition of the reaction mixture and the surface temperature [9,10]. We will unambiguously demonstrate that the oxidized state is active in the oxidation of CO and above 550 K the oxidized phase is significantly more active than the non-oxidic state. At high CO and O$_2$ pressures of 200 mbar and temperatures above 550 K the CO oxidation reaction ignites so that the sample temperature increases by up to 130 K due to the released reaction heat at the surface. The ignition of the CO oxidation reaction occurs only on the oxidized state of the catalyst's surface.

With the unique high-pressure chamber of ID03 at ESRF [11] we were able to follow simultaneously the surface structure of the Ru(0001)-based model catalyst by SXRD and the reaction rate of the product formation (CO$_2$) via on-line mass spectrometry (MS) during the CO oxidation reaction over RuO$_2$(110)/Ru(0001) under practical reaction conditions. Therefore this experimental set-up allows us to identify structure–activity correlations. The sample was mounted on a BN-encapsulated heater, the temperature was

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measured by a Re/W W5 thermocouple 2 mm away from the sample position on the heater plate. In the reaction experiments the high-pressure cell with a volume of about 0.8 dm^3 served as a batch reactor. The chamber could be separated from the pumping system by a gate valve. By leaking the gas mixture from the batch reactor into the differentially pumped MS chamber, the gas composition was monitored on-line, with a delay time of <5 s. For more details see Ackermann, Ph.D. thesis [12]. Without the sample practically no activity in the CO oxidation was observed in the batch reactor up to 100 mbar and temperatures as high as 750 K. For the SXRD experiments, a photon energy of 17 keV was selected with a Si(111) monolithic channel cut monochromator corresponding to a wave length of 0.73 Å.

In reciprocal space, **H** and **K** are the in-plane lattice vectors corresponding to the in-plane lattice vectors **A$_1$** and **A$_2$** of the Ru(0001) surface (with a length of 2.71 Å), and **L** is the reciprocal out-of-plane vector corresponding to **A$_3$** (with a length of 4.28 Å). The reciprocal lattice vectors of the tetragonal RuO_2(110) on Ru(0001) are given in fractions of **H**, **K** and **L**, and are referred to as **h**, **k**, **l**, where **h** is parallel to **H** and **k** is equivalent to the **H** + **K** (by mirror plane symmetry) direction (cf. Fig. 1) while **l** is aligned along the **L** direction. For more details the reader is referred to Ref. [9]. A typical h-scan of the non-oxidic and the oxide phase are shown in Fig. 1. The RuO_2(110) oxide reveals a characteristic diffraction peak at h = 0.73, while the peak at h = 1.0 is related to diffraction from the Ru(0001) substrate. In the l-scan of RuO_2(110) taken at h = 0.73 appears a pronounced maximum at l = 1.3 which is characteristic of the oxide. In the following, we will use repetitively recorded l-scans to monitor the oxidation state of the surface during the reaction with a time resolution of 100 s.

The Ru(0001) sample was prepared by Ar-ion etching (U = 2 kV, I = 1 µA/cm^2, P(Ar) = 10^{-5} mbar, for 20 min at 760 K) and oxygen treatment cycles at elevated temperatures. The structure–activity experiments were performed by exposing the sample in the batch reactor to various O_2 and CO partial pressures (ranging from some 30 mbar to 300 mbar) at sample temperature ranging from 500 to 750 K. It turned out that above a threshold temperature of about 500 K, the reaction rate, as seen from the partial pressure time evolution of the reactants and the product, is increased exactly when the oxide is detected by SXRD.

Fig. 2 shows a direct comparison of the activity of a thick RuO_2(110) film with that of the non-oxidic phase starting with a reaction mixture of P(CO) = 20 mbar and P(O_2) = 10 mbar for two specific temperatures, i.e. T = 530 K and T = 603 K. The activity for other temperatures are summarized in a comparative Arrhenius plot in Fig. 3. A thick oxide was prepared at 700 K. A thick oxide instead of a thin oxide was chosen as this surface does not expose areas with (1 × 1)O phase. We may note that for thinner oxide film of only 1.6 nm and typical preparation temperatures of 600–650 K the area of (1 × 1)O is already very low as indicated by a previous high resolution core level shift study [13]. In Fig. 2 the partial pressures of CO, O_2 and CO_2 together with the calculated turnover frequencies (TOF) are shown as a function of reaction time t. From the partial pressure P(CO_2) the TOF, i.e. the number of produced CO_2 molecules per active site and second, is calculated from the following formula:

$$TOF = \frac{V \cdot L}{R \cdot T} \cdot \frac{1}{\#Cat} \cdot \frac{dP(CO_2)}{dt} \qquad (1)$$

with V = volume of the batch reactor (0.8 dm^3), L = Avogadro's number = 6.022 × 10^{23} 1/mol, R = general gas constant = 8.4135 J/(Kmol), T = gas temperature = 300 K, #Cat = number of active catalyst sites = 10^{15} (the sample area is 1 cm^2).

This comparison shows clearly that the thick oxide film is at 530 K similarly active as the non-oxidic phase but the activity of the oxide phase is significantly higher than the non-oxidic phase for temperatures above 550 K. Already these experiments invalidate the recent statement in Ref. [7] "… the steady-state activity of RuO_2 at elevated temperatures/pressures and near stoichiometric reaction conditions is decidedly below that of the oxygen-covered surface …". From the Arrhenius plot in Fig. 3 an activation energy of 75 kJ/mol can be estimated for the thick oxide layer in the temperature range 500–574 K. For temperature higher than 570 K we observe a roll over of the reaction rate, still substantially higher than for the non-oxidic phase. The chemical nature of the non-oxidic phase is not clear at the moment. All what we know
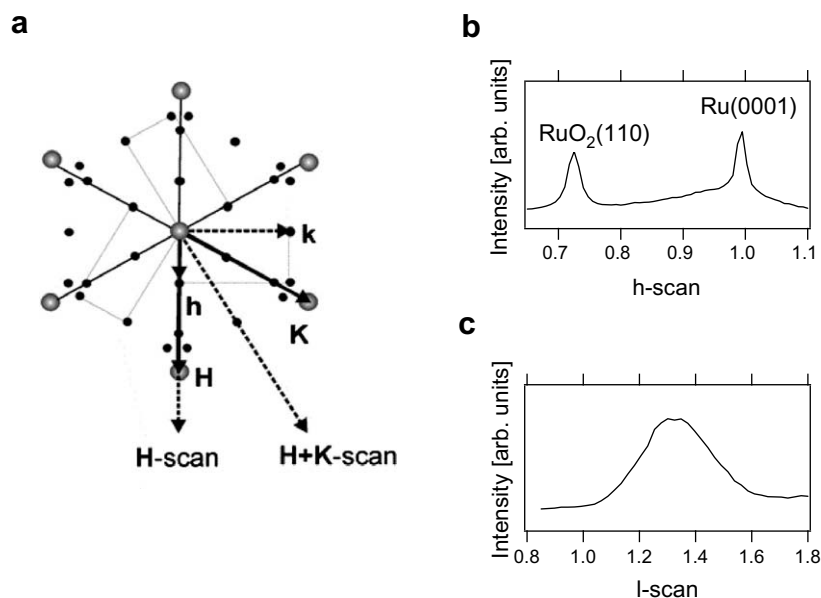

Fig. 1. (a) Schematic LEED pattern of Ru(0001) (open discs) and the incommensurately grown RuO_2(110) layer on Ru(0001) (small solid discs). In reciprocal space the in-plane high-symmetry direction are denoted by **H**, **H** + **K** for Ru(0001) and **h**, **k** for RuO_2(110). (b) h-scan at l = 1.3 of a RuO_2(110) coated Ru(0001) surface together with an l-scan for h = 0.73. (c) The l-scan of RuO_2 indicates a pronounced maximum at l = 1.3 which is indicative of RuO_2(110). From the full width at half maximum (FWHM) of this peak an averaged thickness of the RuO_2(110) layer of 1.6 nm can be deduced.