Heterogeneous Catalysis

Understanding the Structural Deactivation of Ruthenium Catalysts on an Atomic Scale under both Oxidizing and Reducing Conditions**

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The science and technology of catalysis are of central practical importance. About 80% of all industrial chemicals are manufactured by utilizing (heterogeneous) catalysis. Besides activity and selectivity, catalyst deactivation during use is a key issue in practical catalysis. “The importance of understanding and being able to predict loss of activity during catalyst usage must not be under-estimated”[1] since replacement of a catalyst means high operational costs. Industrially used catalysts are, however, far too complex to allow for a microscopic understanding of why a catalyst deactivates. This knowledge calls rather for the use of model catalysts (such as single-crystalline surfaces) and their investigations under well-controlled ultrahigh vacuum conditions. The trade off for this so-called surface-science approach[2] is the introduction of a pressure and a materials gap by which catalytic properties determined under well defined conditions may not be extrapolated to those at realistic reaction conditions.[3]

For a ruthenium-based catalyst, activity loss was reported for the CO oxidation reaction. In particular, under oxidizing reaction conditions the activity of supported ruthenium catalysts declines substantially.[4,5] This finding has been quite puzzling as recent investigations clearly indicate that RuO_2 is much more active than ruthenium in the oxidation of CO.[6] Since the pressure and materials gap for the CO oxidation over ruthenium are considered to be bridged[7] we can utilize the surface-science approach to clarify the microscopic processes determining the structural deactivation of ruthenium-based catalysts and how this atomic-scale knowledge is used to optimize the performance of practical ruthenium catalysts.

We concentrate herein mainly on polycrystalline RuO_2 powder which is calcined at 573 K, resulting in a specific surface area of $0.9\,m^2\,g^{-1}$. Complementary data of supported ruthenium catalysts are provided in the Supporting Information. The mean diameter of the particles in the RuO_2 powder is about 1 μm. Therefore RuO_2 powder represents a natural link between single–crystal ruthenium model catalysts and ruthenium catalysts supported on SiO_2 or MgO with an active surface area of $10\,m^2\,g^{-1}$.[8] Applied partial pressures of CO and O_2 are in the range of 5–35 mbar.

Figure 1 a displays the conversion of CO over oxidized RuO_2 polycrystalline powder as a function of time on stream, using a stepwise temperature variation and a CO/O_2 feed ratio of 1:2. During the first temperature cycle each temperature jump is accompanied by a rapid increase of the CO conversion followed by a transient decrease of the CO conversion whose steady state is not reached within 1 h. This deactivation process occurs faster at higher temperatures, whereas the extent of deactivation increases with higher concentrations of O_2 (see Supporting Information). For all investigated CO/O_2 feed stocks it is found that the conversion

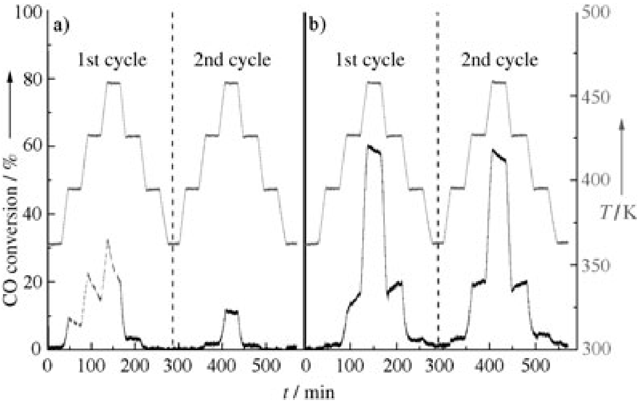

Figure 1. Conversion of CO over a) oxidized polycrystalline RuO_2 powder and b) pre-reduced polycrystalline RuO_2 powder as a function of time on stream and temperature. The applied cyclic temperature program (363 K–456 K) is shown in the gray trace (right-hand axis). The total flow rate was $50\,mL\,min^{-1}$ with a CO/O_2 feed ratio of 1:2 (1.8% CO/3.6% O_2). The transient decrease of the CO conversion is indicated as a broken curve in the first cycle of Figure 1 a.

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of CO is significantly lower when reaching 363 K for the second time, and that almost no further deactivation takes place during the second temperature cycle. The highest CO conversion is accomplished with a stoichiometric CO/O_2 gas feed.

The oxidation state of the RuO_2 powder catalyst is determined by temperature programmed reduction (TPR) in H_2 (see Figure 2 trace a). The consumption of H_2 by water formation is a direct measure of the oxygen capacity in the ruthenium particle and therefore of the O/Ru ratio. For instance, after running the RuO_2 powder catalyst with net oxidizing gas feeds at 453 K, the O/Ru ratio turns out to be 2:1, consistent with fully oxidized RuO_2.

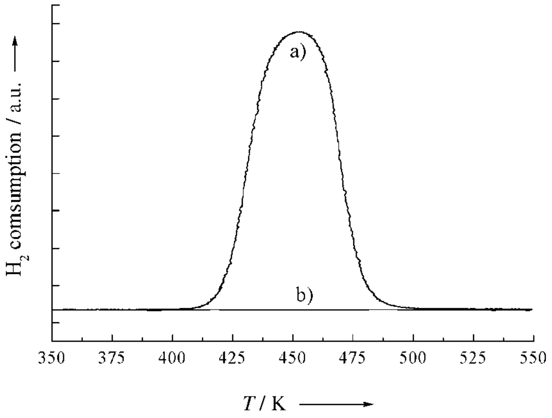

Figure 2. TPR (in H_2) profiles of polycrystalline RuO_2 after oxidizing CO at 453 K under net oxidizing conditions (CO/O_2 reactant feed ratio of 1:2) for 2 h: a) using a pre-oxidized RuO_2 catalyst; b) using a pre-reduced RuO_2 catalyst. The pre-reduced RuO_2 catalyst was prepared by purging the RuO_2 powder at 750 K in H_2 (30 mbar) for 2 h prior to the CO oxidation reaction.

To identify the microscopic processes that lead to the deactivation of a RuO_2-powder catalyst and also to find efficient measures to impede its deactivation we invoke the surface science approach. The initial oxidation of a macroscopic Ru(0001) single crystal proceeds by various characteristic stages.[6] First, oxygen from the gas phase adsorbs dissociatively on the Ru(0001) surface, forming distinct ordered O overlayers. All these Ru(0001)–O overlayers are inactive in the oxidation of CO molecules because of the strong O–Ru bonding. Below 500 K oxide formation does not set in, even under oxygen pressures of 10^{-2} mbar. At 650 K oxide formation proceeds in an autocatalytic process,[9] resulting in an ultra thin RuO_2(110) layer on Ru(0001) (typical thickness of 1 nm). This thin RuO_2(110) layer is extraordinarily active in the oxidation of CO. At higher temperatures (above 800 K) the RuO_2 film grows thicker under oxidizing conditions and is observed to roughen. CO adsorption and reaction experiments indicate that a very rough RuO_2 film on Ru(0001) is practically inactive in the oxidation of CO, that is, the RuO_2 film deactivates.

Excessive exposure of an Ru(10$\bar{1}$0) surface to oxygen at 650 K leads also to the growth of an ultra thin RuO_2 film that is oriented along the (100) direction and which is as active as RuO_2(110) in the oxidation of CO.[10] However, under oxidizing conditions and temperatures above 800 K the RuO_2(100) film grows thicker and transforms irreversibly from the catalytically active RuO_2(100) phase into a reconstructed c(2 × 2) phase which is unable to convert CO into CO_2.[11]

What is the reason for the deactivation of a rough RuO_2 film on Ru(0001), where as a flat RuO_2(110) surface is extraordinarily active in the oxidation of CO? The scanning tunneling microscope (STM) images in Figure 3 visualize the initial roughening of the RuO_2(110) surface. The flat regions in Figure 3a are the catalytically active RuO_2(110) areas. However, the rough part of the surface with a height of 8 nm above the flat region (Figure 3d) exposes RuO_2(100) facets. Zooming into this facet we can identify (Figure 3b, c) the catalytically inactive c(2 × 2) regions which are separated by narrow RuO_2(100) stripes. Similar STM images were reported for the growth of RuO_2(100) on Ru(10$\bar{1}$0).[11] Since the c(2 × 2) patches are inactive in the CO oxidation, a rough RuO_2 film on Ru(0001) becomes gradually inactive. Finally a thick RuO_2 film is completely covered by these c(2 × 2) domains and therefore catalytically inactive.

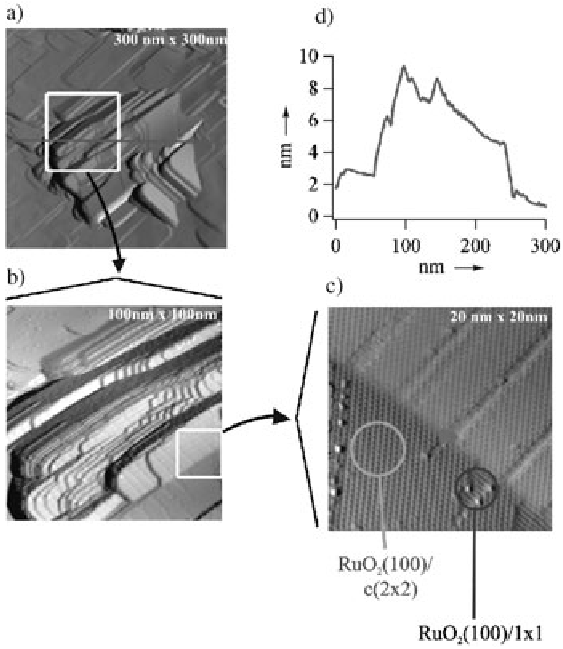

Figure 3. The initial roughening of a RuO_2(110) film on Ru(0001). a) STM image (300 nm × 300 nm). b) and c) close-up images of the rough region (STM image: 100 nm × 100 nm (b), 20 nm × 20 nm (c)) indicating that the facets are oriented along the (100) direction and reconstructed into a c(2 × 2) phase. d) a line profile across the facetted region along the line shown in (a).

Under reducing reaction conditions the RuO_2(110) surface will first be depleted of bridging O atoms. CO molecules adsorb strongly (binding energy = 180 kJ mol^{-1} [12]) into such bridging O vacancies, thereby stabilizing the mildly reduced RuO_2(110) surface. Nevertheless, this mildly reduced RuO_2(110) surface is still active in the oxidation of CO.[7] Only at temperatures above 450 K and under reducing reaction conditions does the mildly reduced surface decompose into a metallic and an oxide surface phase[11] until the $RuO_2(110)$ film is buried under a catalytically inactive Ru(0001)–O layer.

Therefore, the deactivation of the RuO_2-powder catalyst under reducing reaction conditions is straight forwardly explained by the presence of catalytically inactive Ru(0001)-O domains on the surface of the catalyst (see Figure 4). To comprehend the deactivation of the RuO_2 powder catalyst (and also supported ruthenium catalysts) under net oxidizing conditions we transfer knowledge gained from the surface-science approach across the materials and pressure gap as summarized in Figure 4. The RuO_2 particles expose preferentially (110) and (100) facets. Upon CO oxidation at net oxidizing conditions, the active $RuO_2(100)$ facets of the RuO_2 particle transform into the inactive $RuO_2(100)$-c(2 × 2) phase. But also the $RuO_2(110)$ facets will deactivate partly under oxidizing conditions. The $RuO_2(110)$ facets roughen considerably, thereby forming additional $RuO_2(100)$ facets (Figure 3) which reconstruct into the inactive c(2 × 2) phase. Both deactivation processes are the more efficient the higher the temperature is, consistent with the deactivation behavior of RuO_2 powder and supported ruthenium catalysts. Eventually the RuO_2 particle exposes predominantly catalytically inactive $RuO_2(100)$-c(2 × 2) facets and only small areas of active $RuO_2(110)$ facets.

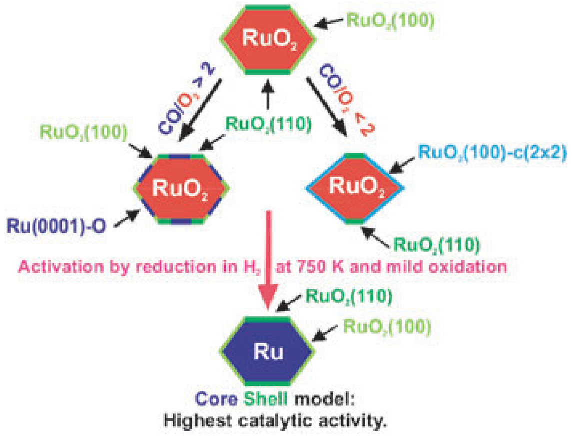

Figure 4. Core–shell model for RuO_2 powder catalysts: The degree of surface oxidation is determined by the CO/O_2 reactant feed ratio and the temperature. The inactive $RuO_2(100)$–c(2 × 2) (light blue) surface facets are formed under oxidizing conditions ($CO/O_2 < 2$), whereas low-activity metallic ruthenium surfaces (Ru(0001)–O) (dark blue) are exposed under net reducing conditions ($CO/O_2 > 2$). The most active state is an ultrathin RuO_2 (light and dark green: thickness 1–2 nm) layer supported on a metallic ruthenium core. This state is achieved by complete reduction of the RuO_2 particle followed by a mild re-oxidation below 500 K.

Is there any remedy to impede the deactivation of the RuO_2 powder catalyst? Again we will find the answer by transcribing the knowledge from the surface-science approach to the practical RuO_2 catalyst. We know that ultrathin RuO_2 films (thickness 1–2 nm) both on Ru(0001) and on Ru(10$\bar{1}$0) are extremely active in the oxidation of CO.[10] We know also that for reaction temperatures below 650 K these active RuO_2 films are stable under oxidizing reaction conditions. This suggests the following recipe to prepare an active and stable RuO_2 powder catalyst. First we fully reduce the RuO_2 particles to metallic ruthenium by purging the catalyst in H_2 at 750 K. Then we re-oxidize the ruthenium particles under gentle reaction conditions, say temperatures below 500 K. This procedure indeed results in a very active and also stable RuO_2 powder catalyst as indicated in Figure 1 b: Note that the conversion of CO is enhanced by a factor of three. The oxidation state of this catalyst is determined by TPR (Figure 2 trace b). Only a little oxygen is present in/on the ruthenium particle consistent with a ruthenium particle that is covered by only an ultrathin RuO_2 layer.

We can safely assume that the metallic ruthenium particles in the fully reduced RuO_2 powder catalyst, expose preferentially (0001) and (10$\bar{1}$0) facets, since those are the surfaces with lowest surface energies (see Supporting Information). Under mild reaction conditions the ruthenium particle will oxidize by growing a $RuO_2(110)$ layer on the Ru(0001) facets and a $RuO_2(100)$ layer on the Ru(10$\bar{1}$0) facets. This RuO_2/Ru core–shell particle (see Figure 4) reveals the highest activity in the CO oxidation (see Figure 1 b).

The stability of this RuO_2/Ru core–shell particle is controlled by kinetics. For ruthenium particles with a mean diameter of 1 μm (reduced RuO_2 powder) or for the macroscopic Ru(0001) and Ru(10$\bar{1}$0) single crystals the oxidation of ruthenium stops at a thickness of 1–2 nm as long as the temperature does not exceed 650 K. Therefore the active state of the reduced RuO_2 powder catalyst is maintained under oxidizing reaction conditions. In contrast, for supported ruthenium catalysts, the ruthenium nanoparticles with active $RuO_2(110)$ and $RuO_2(100)$ layers surrounding the metallic ruthenium core are instable under both reducing and oxidizing reaction conditions (see Supporting Information). Either the nanoparticle reduces, exposing inactive ruthenium domains, or it oxidizes completely, exposing predominantly inactive c(2 × 2) domains.[13]

The atomic-scale information of the deactivation of ruthenium-based catalysts upon CO oxidation can be utilized for practical applications. If the size of the ruthenium nanoparticles is about 3 nm (typical size of supported ruthenium catalysts[8]), the catalyst should be run under alternating reducing and oxidizing conditions about the CO/O_2 gas feed ratio of 2:1 to maintain the active RuO_2/Ru core–shell particle with its high conversion rate. The supported ruthenium catalyst is more stable if the ruthenium particles are larger. The high catalytic activity is, however, balanced by the inferior surface-to-bulk ratio of larger particles, so that an optimum particle size is expected to be in the order of 10 nm.

The deactivation of RuO_2 is not restricted to the CO oxidation reaction. The RuO_2 coated electrodes used in the electrochemical evolution of chlorine[14] may also deactivate under oxidizing conditions. In industrial chemistry ruthenium-based catalysts are currently discussed as promising candidates for a green chemistry route of the aerobic alcohol oxidation.[15,16] The deactivation of the ruthenium-based catalyst through full oxidation of the ruthenium particles is an important issue to be settled for future application.

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