On the Nature of the Active State of Supported Ruthenium Catalysts Used for the Oxidation of Carbon Monoxide: Steady-State and Transient Kinetics Combined with in Situ Infrared Spectroscopy[†]

Jens Assmann,[‡] Vijay Narkhede,[‡] Lamma Khodeir,[‡] Elke Löffler,[‡] Olaf Hinrichsen,[‡] Alexander Birkner,[§] Herbert Over,[⊥] and Martin Muhler^{*,‡}

Lehrstuhl für Technische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany, Lehrstuhl für Physikalische Chemie I, Ruhr-Universität Bochum, D-44780 Bochum, Germany, and Physikalisch-Chemisches Institut, Justus-Liebig-Universität, D-35392 Giessen, Germany

Received: February 26, 2004; In Final Form: May 11, 2004

The oxidation of CO over Ru/MgO and Ru/SiO₂ catalysts was used as a simple model reaction to derive turnover frequencies at atmospheric pressure, which were observed to agree with kinetic data obtained under high-vacuum conditions with supported ruthenium catalysts and the RuO₂(110) single-crystal surface. Thus, it was possible to bridge both the pressure and the materials gap. However, a partial deactivation was observed initially, which was identified as an activated process, both under net reducing and net oxidizing conditions. Temperature-programmed reduction (TPR) experiments were performed subsequently in the same reactor, to monitor the degree of oxidation, as a function of the reaction temperature and the CO/O₂ reactant feed ratio. Using in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements, the structural changes of the ruthenium catalysts during the oxidation of CO were confirmed, under relevant reaction conditions. Under net reducing conditions, only domains of RuO₂ seem to exist on the metallic ruthenium particles, whereas, under net oxidizing conditions, the ruthenium particles were fully oxidized to bulk RuO₂ particles, which may expose less-active facets, such as the RuO₂(100) $-c(2 \times 2)$ surface.

1. Introduction

Supported ruthenium catalysts,^{1–6} and especially ruthenium single crystals,^{7–13} have received much attention recently, because of their high activity in oxidation reactions. Originally, ruthenium single-crystal surfaces had been classified to be very poor catalysts for the oxidation of CO under ultrahigh vacuum (UHV) conditions,^{14,15} until it was shown that the RuO₂(110) single-crystal film formed autocatalytically on Ru(0001) under strongly oxidizing conditions is highly active.¹³ By means of kinetic investigations under well-defined high-vacuum conditions in the temporal-analysis-of-products (TAP) reactor, the active phase of supported ruthenium catalysts was identified as RuO₂.¹

The deactivation of the supported ruthenium catalysts during the oxidation of CO is not well understood so far, which was observed at atmospheric pressure^{16,17} as well as under highvacuum conditions.¹ Cant et al.¹⁶ concluded that portions of the metallic ruthenium surface are covered by an inactive oxide layer, whereas Kiss and Gonzalez suggested that the partial deactivation of Ru/SiO₂ is a result of the formation of lattice oxygen.¹⁷ However, the duration of the deactivation period, the influence of the support and of the experimental conditions such as temperature and the CO/O₂ reactant feed ratio has not yet been studied in detail. Furthermore, no attempt has yet been made to quantify the degree of oxidation of the supported ruthenium catalysts. Thus, an extensive investigation of the deactivation phenomena is of major importance to establish a suitable model of the active state of the catalyst, taking results from recently published RuO₂ single-crystal studies into account.

The present work is focused on the deactivation phenomena of two differently supported ruthenium catalysts during the oxidation of CO. The Ru/MgO and Ru/SiO2 catalysts were prepared by the molecular organic chemical vapor deposition (MOCVD) method, resulting in a mean ruthenium particle size of 2 nm.¹ The oxidation of CO was monitored during continuous temperature cycles. Thus, it was possible to determine the duration of the deactivation and to correlate it with the experimental conditions. To the best of our knowledge, turnover frequencies for the oxidation of CO at atmospheric pressure were derived for the first time using Ru/MgO. In addition, the transient behavior of preoxidized catalysts was investigated. In a series of temperature-programmed reduction (TPR) measurements, the degree of oxidation was determined as a function of the reaction temperature and the pretreatment conditions, using the same experimental setup. Thus, it was possible to derive the degree of oxidation immediately after the catalytic oxidation of CO without any artifacts, because of a lengthy sample transfer. A shrinking metallic core model is proposed, which attributes the lower catalytic activity of fully oxidized RuO₂ particles to the presence of inactive faces such as the RuO₂(100) $c(2 \times 2)$ surface. Finally, this model was confirmed by an in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) study of the oxidation of CO under relevant reaction conditions.

[†] Part of the special issue "Gerhard Ertl Festschrift".

^{*} Author to whom correspondence should be addressed. Telephone: +49 234 32 28754. Fax: +49 234 32 14115. E-mail address: muhler@techem. rub.de. URL: http://www.techem.rub.de.

[‡] Lehrstuhl für Technische Chemie.

[§] Lehrstuhl für Physikalische Chemie I.

^a Lenistuni für Physikansche Che

[⊥] Justus-Liebig-Universität.

2. Experimental Section

2.1. Catalyst Preparation and Characterization. The catalysts Ru/MgO and Ru/SiO2 were prepared by the MOCVD method.^{1,18} The Ru₃(CO)₁₂ precursor (supplied by Strem) was deposited on MgO (ALFA, purity of 99.9955%) and on SiO₂ (Aerosil 200, from Degussa). The adsorbed precursor was thermally decomposed in a quartz ampule on a vacuum line under high-vacuum conditions by executing a multistage temperature program up to 723 K. Ruthenium loadings of 3.0 and 3.2 wt% were determined for Ru/SiO2 and Ru/MgO, respectively. A sieve fraction of $250-355 \,\mu\text{m}$ was used for the TPR and catalytic activity measurements. Using transmission electron microscopy (TEM), X-ray diffraction (XRD), and H₂ chemisorption, the size of the reduced metallic ruthenium particles was determined to be approximately equal to or smaller than 2 nm.1 For the determination of the ruthenium particle size after reaction, a Hitachi model H-8100 TEM system, operated at 200 kV, was used. Prior to the TEM investigations, the oxidation of CO was performed in the fixed-bed microreactor described below. The subsequent transfer of the ruthenium samples to the TEM equipment was performed in inert gas without contact with air, using a glovebox and a special TEM vacuum transfer holder.

2.2. Catalytic Activity Measurements. The oxidation of CO was conducted at atmospheric pressure and at temperatures in the range of 298–423 K, using a fixed-bed microreactor under plug-flow conditions. Different amounts of catalysts (12.5-50 mg) of the 250–355 μ m sieve fraction were placed in the quartz reactor, and these samples were diluted with quartz particles of the same sieve fraction. The temperature was measured directly below the fixed bed, using a thermocouple that was placed in the hollow shaft of the reactor. The following gases and gas mixtures (supplied by Messer Griesheim) were used: argon (>99.999% purity), 5.2% H₂ in argon (hydrogen purity, >99.9%), 10.0% CO in neon (CO purity, >99.997%; neon purity, >99.99%), and 10% O2 in neon (oxygen purity, >99.995%). The total flow rates maintained by three mass flow controllers were in the range of 50-150 NmL/min. (Note: NmL represents milliliters normalized to 273.15 K and 1 atm.) The CO and CO₂ gas concentrations were measured using an Uras 14 infrared analyzer module, and the O2 concentration was measured using a Magnos 16 analyzer (both supplied by Hartmann & Braun).

Prior to the steady-state oxidation of CO, the supported ruthenium catalysts were heated to 773 K in a 5.2% H₂/Ar gas mixture, using a heating ramp of 5 K/min, and kept at this temperature for 1 h. The reactor with the reduced samples was then purged in argon and cooled to the desired starting temperature. These conditions are known to result in a fully reduced and adsorbate-free state of the ruthenium catalysts.¹⁸ The CO/O₂ reactant feed ratios were changed in the range between 4 and 0.5, using partial pressures of CO and O₂ in the range of 5–35 mbar.

The conversion of CO was calculated as follows:

conversion of CO (%) =
$$\frac{C_{\rm CO}^{\rm in} - C_{\rm CO}^{\rm out}}{C_{\rm CO}^{\rm in}} \times 100 \qquad (1)$$

where C_{CO}^{in} is the inlet concentration of CO and C_{CO}^{out} is the outlet concentration of CO. The calculation of the yield of CO₂ was based on the inlet concentration of CO (C_{CO}^{in}):

yield of CO₂ (%) =
$$\frac{C_{CO_2}^{out} - C_{CO_2}^{ut}}{C_{CO}^{in}} \times 100$$
 (2)

where $C_{CO_2}^{in}$ is the inlet concentration of CO₂ and $C_{CO_2}^{out}$ is the outlet concentration of CO₂. Turnover frequencies were derived for low conversions of CO after steady state had been reached.

2.3. Temperature-Programmed Reduction. The temperature-programmed reduction (TPR) experiments were conducted in the same experimental setup as that already described previously. According to the suggested criteria for highly resolved TPR experiments, ^{19,20} the concentration of H₂, the flow rate, and the heating ramp were correlated with the amount of catalyst (55-215 mg). The measurements were performed using the 5.2% H₂/Ar mixture at a flow rate of 20 NmL/min. The temperature was first held for 30 min at 300 K, and then was linearly increased up to 773 K with heating ramps of 5-10K/min. The consumption of H₂, the reaction products such as water and methane, and desorbing molecules such as CO and CO2 were monitored using a calibrated quadrupole mass spectrometer (Thermostar, from Pfeiffer Vacuum). The consumption of hydrogen was additionally analyzed by a thermal conductivity detector (Binos, from Fisher-Rosemount). The TPR measurements were conducted after the supported ruthenium catalysts had been oxidized in pure O₂ at different temperatures, as well as after the oxidation of CO had been monitored for over 12 h under different reaction conditions. Based on the consumption of H_2 and the formation of CH_4 , the degree of oxidation of the ruthenium particles was calculated. H₂, which was consumed for the methanation of adsorbed CO_{ads} (eq 3) or CO_2 (eq 4) formed by the decomposition of carbonates, was subtracted from the total consumption of hydrogen:

$$CO_{ads} + 3H_2 \rightleftharpoons CH_4 + H_2O$$
 (3)

$$\mathrm{CO}_2 + 4\mathrm{H}_2 \rightleftharpoons \mathrm{CH}_4 + 2\mathrm{H}_2\mathrm{O} \tag{4}$$

The corrected amount of the hydrogen consumption was then correlated with the reduction of RuO_x (eq 5):

$$RuO_{x} + xH_{2} \rightleftharpoons Ru + xH_{2}O$$
 (5)

2.4. In Situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). DRIFT spectra were recorded using a Nicolet Protegé 460 spectrometer that was equipped with a diffuse reflectance accessory, a Harrick low-temperature reaction chamber, and an MCT detector. The sample cup was covered by a water-cooled stainless-steel dome with KBr windows. The coolant temperature was maintained at 303 K. The sample temperature was controlled by a thermocouple that was in direct contact with the catalyst. The heating element and a second thermocouple were connected to a temperature controller. The inlet and outlet of the DRIFTS cell were connected to the same setup that was used for the investigation of the CO oxidation kinetics. For the in situ DRIFTS measurements, all catalysts were used as powders. Prior to the oxidation of CO, both ruthenium catalysts were pretreated as follows:

(1) Heating in a 5.2% H_2/Ar mixture at a rate of 10 K/min up to 773 K and holding at this temperature for 30 min.

(2) Purging with argon at 773 K for 30 min.

(3) Cooling in argon down to 323 K.

This procedure ensured a complete reduction of the ruthenium catalysts. Subsequently, the oxidation of CO was started with different CO/O₂ feed ratios, using a total flow rate of 150 mL/ min at 323 K. After holding this temperature for 30 min, it was



Figure 1. Conversion of CO over 50 mg of the Ru/MgO catalyst diluted with 150 mg of quartz, as a function of the temperature using heating and cooling ramps as indicated. The total flow rate was 50 NmL/min with a CO/O₂ reactant feed ratio of 2.1 (1.8% CO/0.85% O₂).

successively increased, using a heating ramp of 2 K/min up to 343, 363, and 423 K. At 423 K, feed-switching experiments that used an excess of oxygen and an excess of CO were performed without additional purging in argon. The DRIFT spectra were recorded as single-beam spectra in the series mode of the spectrometer, using a resolution of 4 cm⁻¹ and an average of 150 scans. To obtain the spectrum of the catalyst, the single beam spectrum of the sample was divided by the background spectrum (KBr). The spectra are presented in apparent absorption units (-log *R*).

3. Results

3.1. Catalytic Activity and Deactivation. The conversion measurements were performed with both prereduced supported ruthenium catalysts, changing between decreasing and increasing temperatures in a cyclic way. To achieve a steady-state conversion of CO, each temperature was held constant for 2 h. This period of time was not sufficient when reducing the temperature, because of the typical ignition/extinction behavior²¹ that is observed for highly exothermic heterogeneous oxidation reactions. Figure 1 illustrates the ignition/extinction phenomenon using 50 mg Ru/MgO and a CO/O₂ reactant feed ratio of 2.1. When heating from 320 K up to 425 K (heating ramp of 0.5 K/min), the ignition of the reaction was observed at \sim 370 K. The maximum theoretical conversion of CO was reached at 375 K. Cooling to the initial temperature, using a cooling ramp of 0.5 K/min, no decrease of the conversion was observed at temperatures of >355 K. This temperature difference in the hysteresis is caused by the heat-transfer limitations at full conversion. The presence of a hot spot was indicated by an increase of the reactor temperature, relative to the furnace temperature. Calculating the heat-transfer coefficient and considering the diagnostic criteria for heat-transport limitations in fixed-bed reactors (Reynolds number of Re = 0.13, Prandtl number of Pr = 0.47, and Nusselt number of Nu = 0.43,^{22,23} the heat-transfer resistance in the boundary layers adjacent to the particle must be taken into account at high conversion. However, at low conversion (<10%), an influence of heattransfer limitations can be excluded.

In the following, the results of catalytic activity measurements that were performed with the diluted Ru/MgO catalyst, are shown. In Figure 2a, the conversion of CO is shown for Ru/MgO as a function of time and temperature, using a CO/O_2 reactant feed ratio of 2/1. The starting temperature was 373 K, which was increased stepwise to 423 K and subsequently



Figure 2. Conversion of CO for the oxidation of CO over 12.5 mg of Ru/MgO diluted with 75 mg of quartz, as a function of time and temperature. The temperature program is displayed by the gray trace. The total flow rate was 50 NmL/min, with a CO/O_2 reactant feed ratio of (a) 2.0 (1.8% CO/0.9% O₂), (b) 1.0 (1.8% CO/1.8% O₂), (c) 0.5 (1.8% CO/3.6% O₂), and (d) 4.0 (1.8% CO/0.45% O₂).

reduced to the initial temperature. This procedure was repeated in a second cycle. During the first increase in temperature, the

conversion decreased slowly after every increase in temperature, and steady state was not reached within 2 h. The ignition of the reaction was observed at >393 K, which led to full conversion of CO. During the cooling period, a delayed decrease of the conversion was monitored, which can be explained by the extinction phenomena already mentioned previously. At the initial temperature of 373 K, the conversion of CO was lower in the second cycle, compared to the beginning of the reaction, and no further deactivation was observed during the second heating ramp, i.e., after every increase in temperature, steady state was reached immediately. The ignition temperature was slightly shifted to higher temperatures, in comparison to the first cycle, and after cooling again to room temperature, it was observed that the conversion of CO was similar to that observed at the beginning of the second cycle. Thus, the deactivation observed under the chosen reaction conditions is restricted to the initial period of the time-on-stream (first cycle).

The same temperature program was chosen for measurements that were conducted in an excess of oxygen with CO/O2 reactant feed ratios of 2/2 and 2/4. The corresponding conversion of CO is shown in Figure 2b and 2c. During the first heating ramp, a decrease in the activity can be observed again after every increase in temperature. This deactivation process seems to be accelerated by the higher concentration of O2. Moreover, the conversion of CO decreases as the concentration of oxygen increases. After the ignition of the reaction, full conversion was not reached at 423 K. Maximum CO conversions of ~85% and 55% were obtained for CO/O2 reactant feed ratios of 2/2 and 2/4, respectively. In contrast to the measurements with the stoichiometric CO/O2 reactant feed ratio of 2/1, where full conversion was reached below 423 K, it was possible to observe the ongoing deactivation process also after reaching the highest temperature step. The extent of the deactivation at this temperature was much higher, in comparison to the lower temperatures with lower degrees of conversion. In the second cycle, no further deactivation was observed during the heating ramp for the first two temperature steps (see Figure 2b and 2c). After reaching a temperature of 423 K, the decrease of the conversion of CO is lower, in comparison to the first cycle, and the degrees of conversion of the following cooling steps are similar to those measured during the heating ramp in the second cycle. These observations imply that, under net oxidizing conditions, the deactivation is restricted to the first cycle.

The oxidation of CO was also performed using the same temperature program in an excess of CO (CO/O₂ reactant feed ratio of 4). As a consequence of the net reducing conditions, the maximum theoretical conversion of CO was restricted to 50%. Figure 2d shows the conversion of CO as a function of time and temperature. An enhanced deactivation during the first increase in temperature is observed. However, this process is again restricted to the initial period of the time-on-stream (first cycle), because it did not appear during the second cycle, during which steady state was reached immediately after every increase in temperature. To restore the high initial activity, the reduction in H₂/argon at 773 K had to be repeated, independent of the CO/O₂ reactant feed ratio, which had been applied during the reaction. The subsequently observed deactivation was again controlled by the reactant gas mixture and the temperature.

To study the role of the degree of oxidation in more detail, the reduced Ru/MgO sample was oxidized at room temperature and subsequently purged in argon. The oxidation of CO then was monitored using the same temperature program and the stoichiometric CO/O_2 reactant feed ratio of 2, which were each applied for the measurements with the initially reduced catalyst



Figure 3. Conversion of CO over 12.5 mg of Ru/MgO preoxidized at room temperature and diluted with 75 mg of quartz, as a function of time and temperature. The temperature program is displayed by the gray trace. The total flow rate was 50 NmL/min, with a CO/O₂ reactant feed ratio of 2.0 (1.8% CO/0.9% O₂).



Figure 4. Conversion of CO over 12.5 mg of Ru/MgO diluted with 75 mg of quartz at 423 K, using a total flow rate of 50 NmL/min as a function of time. The CO/O₂ reactant feed ratio was changed systematically: (a) CO/O₂ ratio = 2 after oxidation of the catalyst at room temperature, (b) CO/O₂ ratio = 1 after that described in trace a, (c) CO/O₂ ratio = 0.5 after that described in trace b, and (d) CO/O₂ ratio = 2 after that described in trace c.

(see Figure 2a). The result of this measurement, which is shown in Figure 3, is hardly distinguishable from the results obtained during the second cycle, using the reduced Ru/MgO catalyst (see Figure 2a); i.e., no deactivation was observed during the first heating period after reaching the next temperature step, and the degrees of conversion agreed with those of the deactivated catalyst within 2%. Obviously, the oxidative pretreatment did result in the same less-active state of the Ru/MgO catalyst. The degrees of conversion obtained during the initial period were strongly dependent on the pretreatment conditions: starting the oxidation of CO with a reduced catalyst leads to a higher initial activity but includes a deactivation process. On the other hand, the initial activity of the preoxidized catalyst is stable, but rather low. Control experiments were also performed, using temperature programs starting at 423 K, which showed again that the degree of deactivation is determined by the highest reaction temperature and not by the sequence of increasing and decreasing temperatures.

Because the catalytic activity was observed to be strongly influenced by the CO/O_2 reactant feed ratio under net oxidizing conditions (see Figure 2b and 2c), flow-switching experiments were performed with both supported ruthenium catalysts at 423 K to study the dynamics of this inhibition. Figure 4 shows the results obtained with the Ru/MgO catalyst. Using a stoichiometric CO/O₂ reactant feed ratio of 2/1, full conversion of CO was observed, even after an oxidizing pretreatment at room



Figure 5. Arrhenius plot of the rates of CO_2 formation (TOF denotes the turnover frequency, defined as the number of CO_2 molecules formed per metal surface site per second) over the supported ruthenium catalysts (Ru/MgO and Ru/SiO₂) for different CO/O₂ reactant feed ratios and in dependence on total pressure. Data obtained on Ru(0001) at high pressure,¹⁵ on a silica-supported ruthenium catalysts prepared by impregnation,¹⁶ and TOFs over supported rhodium catalysts^{16,17} also are included.

temperature (see trace a in Figure 4). Switching to a CO/O_2 reactant feed ratio of 2/2 led to a decrease of the conversion of CO to ~70% (see trace b in Figure 4). After increasing the O_2 concentration further (a CO/O_2 reactant feed ratio of 2/4 was used), the conversion of CO decreased to ~30% (see trace c in Figure 4). Switching back to the stoichiometric CO/O_2 reactant feed ratio restored the initial activity after a period of ~4 h (see trace d in Figure 4), indicating a reversible change of the state of the catalyst under net oxidizing conditions.

Turnover frequencies (TOFs), which represent the number of CO₂ molecules formed per metal surface site per second, were calculated for low and steady-state conversion for the deactivated state of the Ru/MgO catalyst. The TOFs obtained from measurements with a CO/O2 reactant feed ratio of 2 are plotted for Ru/MgO and Ru/SiO2 in an Arrhenius diagram (shown in Figure 5). Also, TOFs obtained in a high-pressure single-crystal study¹⁵ and TOFs found in a recent high-vacuum TAP reactor study that used the same supported ruthenium catalysts (Ru/MgO and Ru/SiO_2)^1 are included in this figure. The results show that an influence of the support on the activity at atmospheric pressure can be neglected. In addition, the activation energy of ~82 kJ/mol for Ru/MgO is in very good agreement with both the single-crystal data and the TAP results, indicating the absence of a pressure gap. A comparison with supported rhodium catalysts (also included in Figure 5) reveals a much higher activity of the ruthenium catalysts.

3.2. Temperature-Programmed Reduction (TPR) and Transmission Electron Microscopy (TEM) Measurements after Reaction. The degrees of oxidation of the supported ruthenium catalysts were determined using the TPR method. The TPR profiles obtained after oxidation of the Ru/SiO₂ sample at room temperature and at 473 K in flowing O2 are presented in Figure 6. After oxidation at room temperature (Figure 6a), the TPR profile consists of only one peak at \sim 360 K, whereas after oxidation at 473 K, a sharper peak was observed at 413 K, in addition to the peak at lower temperatures. The total consumption of H₂ yielded O/Ru ratios of 1.3 and 1.5, respectively. For Ru/MgO, the same O/Ru ratios were determined. However, no consumption of hydrogen was observed at >300 K for the Ru/MgO sample that was oxidized at room temperature; i.e., it was fully reduced already at room temperature when switching to H₂/Ar. The TPR profile of the Ru/ MgO sample oxidized at 473 K (not shown) was observed to



Figure 6. TPR profiles obtained with Ru/SiO_2 oxidized at (a) room temperature and (b) 473 K. The K-factor¹⁹ and P-factor²⁰ were 83 s and 13.8 K, respectively.



Figure 7. TPR profiles obtained after CO oxidation at 423 K under net oxidizing conditions (CO/O₂ reactant feed ratio of \leq 2): (a) Ru/ SiO₂ (213 mg), (b) Ru/SiO₂ (99 mg), (c) Ru/MgO (201 mg), and (d) Ru/MgO (103 mg). The gray trace displays the formation of methane, multiplied by a factor of 4.

consist of the same two peaks as those of the Ru/SiO₂ catalyst (Figure 6b) but with lower intensity. In addition to the consumption of H_2 at 360 and 413 K, H_2 was already consumed at the initial temperature of 300 K during the TPR experiment, resulting in the same O/Ru ratio of 1.5 calculated for both catalysts that were oxidized at 473 K.

The results of the TPR measurements, after reaction at 423 K under net oxidizing conditions (CO/O2 reactant feed ratio of <2), are shown in Figure 7 for both supported catalysts. Under the conditions applied for the oxidation of CO, full conversion was observed, inducing strong heat production. The shape of the TPR profiles of the Ru/SiO₂ sample (see Figure 7a and 7b) is similar to those obtained after oxidation in pure O₂; however, the height of both peaks at 383 and 415 K is significantly increased. The TPR profiles of the Ru/MgO sample after reaction display an additional feature (see Figure 7c and 7d). In addition to the consumption of H_2 at 300 K and at ~360 and 415 K, a broad shoulder appeared at \sim 490 K. The desorption of methane produced during the reduction process was detected by mass spectroscopy at the same temperature of 490 K (see gray trace in Figure 7d). Assuming the methanation of CO_2 , a H₂/CH₄ ratio of 4 must be considered. Multiplying the amount of methane by a factor of 4 indicates that the methanation of CO2 fully accounts for the additional consumption of H2 at 490 K. After subtracting the amount of H₂ consumed for the latter reaction, O/Ru ratios were calculated. Independent of the support, O/Ru ratios equal to 2 were observed, indicating the presence of fully oxidized RuO₂ particles under net oxidizing reaction conditions.



Figure 8. TPR profiles obtained after CO oxidation at 423 K under net reducing conditions (CO/O₂ reactant feed ratio of >2): (a) Ru/ MgO (103 mg) and (b) Ru/SiO₂ (100 mg). The gray traces display the formation of methane, multiplied by a factor of 3.

The TPR profiles of the Ru/MgO and Ru/SiO₂ catalysts after reaction under net reducing conditions (CO/O₂ reactant feed ratio of 2.2) are shown in Figure 8. In contrast to the TPR profiles presented in Figure 7, only one TPR peak was observed, at 500 and 453 K for Ru/MgO and Ru/SiO₂, respectively. At the same temperatures, the desorption of methane was monitored. Assuming the methanation of adsorbed CO (eq 3), a H₂/CH₄ ratio of 3 must be considered. Multiplying the amount of methane by a factor of 3 led to almost-coincident traces, as shown in Figure 8 (gray traces in Figure 8a and 8b). Thus, no significant oxidation of the ruthenium particles was observed under net reducing conditions at high conversion. Therefore, it is reasonable to assume that only a few RuO₂ domains are present on the surface of the metallic ruthenium particles under these conditions.

The TEM images of the ruthenium catalysts were recorded after the oxidation of CO at 423 K in an excess of O₂. Under these reaction conditions, fully oxidized RuO₂ particles are present, as shown by the TPR results. Figure 9a and 9b respectively show the TEM micrograph and the corresponding particle size distribution of the RuO₂/SiO₂ sample. The latter displays two maxima, at ~2.5 and 4.5 nm. The comparison with the particle size distribution of the reduced Ru/SiO₂ sample obtained prior to reaction¹ reveals minor sintering of the ruthenium particles in the oxidized state, as a consequence of the net oxidizing conditions and the high temperatures applied during the oxidation of CO.

3.3. In Situ DRIFTS Measurements. The oxidation of CO was also investigated using the in situ DRIFTS cell as a reactor. The deactivation phenomena were observed to be similar, in comparison to the results obtained under plug-flow conditions in the fixed-bed reactor, whereas the degrees of conversion were consistently lower. The IR spectra in the carbonyl region obtained with the Ru/MgO and Ru/SiO2 catalysts recorded at 423 K, using a CO/O_2 reactant feed ratio of 1/2, are shown as dotted traces in Figure 10. The spectra are characterized by two bands, at \sim 2130 and \sim 2070 cm⁻¹, and a weak shoulder at \sim 2000 cm⁻¹. As demonstrated in a recent DRIFTS study,¹ these bands can be assigned to C-O vibrations of CO adsorbed on a RuO_2 surface layer, which is comparable to the $RuO_2(110)$ single-crystal surface. Both high-frequency bands are assigned to a multicarbonyl species formed by the binding of two or three CO ligands to a Ru site, which may be similar to the 1-fold coordinatively unsaturated Ru site present on the RuO₂(110) single-crystal surface.^{12,24} The weak shoulder at \sim 2000 cm⁻¹ is assigned to C-O vibrations of CO adsorbed in an asymmetric bridge position on oxygen vacancies in the RuO₂ film.^{1,24} The



Figure 9. (a) TEM micrograph and (b) corresponding particle size distribution of the Ru/SiO_2 catalyst obtained after CO oxidation at 423 K using a CO/O_2 reactant feed ratio of 0.5.



Figure 10. DRIFT spectra obtained during CO oxidation at 423 K using a total flow rate of 150 NmL/min with CO/O₂ ratios of 0.5 (1.7% CO/3.4% O₂, dotted traces) and 4.0 (1.7 CO/0.43% O₂, solid traces) over (a) Ru/MgO and (b) Ru/SiO₂.

low intensity of this band is obviously due to the low CO/O_2 reactant feed ratio. The assignment of the bands is summarized in Table 1.

In contrast to these results, the DRIFT spectra recorded at 423 K in an excess of CO revealed different bands in the carbonyl region, as shown in Figure 10 (solid traces). These spectra were normalized using the second high-frequency band observed in an excess of oxygen. Independent of the support, an additional band at ~2050 cm⁻¹ is observed. This band is assigned to CO adsorbed linearly on reduced metallic Ru sites, in agreement with the C–O vibration frequency of CO adsorbed on the Ru(0001) single-crystal surface.²⁵ In addition to the observed presence of metallic Ru sites, evidence is also provided

TABLE 1: Assignment of the Bands of Adsorbed CO Observed during CO Oxidation over the Ru/MgO and Ru/SiO₂ Catalysts at 423 K, Using a Total Flow Rate of 150 NmL/min with CO/O₂ Ratios of 0.5 (1.7% CO/3.4% O₂) and 4.0 (1.7% CO/0.43% O₂)

	RuO ₂ Assignment (cm ⁻¹)		metallic Ru,
CO/O ₂ ratio	multicarbonyl	asymmetric bridge	on-top (cm ⁻¹)
	Ru/M	IgO Catalyst	
0.5	2125/2067	1990	
4.0	2125/2067	1990	2043
	Ru/S	iO2 Catalyst	
0.5	2127/2078	2010	
4.0	2134/2078	2010	2051

for the presence of oxidized Ru^{n+} sites by the two highfrequency bands at ~2130 and ~2070 cm⁻¹. Thus, RuO_2 domains are present, leading again to an assignment of the band at 1990 cm⁻¹ in the spectra of Ru/MgO to CO adsorbed on oxygen vacancies of the RuO₂ surface.¹

According to the DRIFTS results, the active state of the ruthenium catalysts in an excess of O_2 is characterized by the presence of RuO₂ surfaces that are similar to the RuO₂(110) single-crystal surface, whereas, under net reducing conditions, mildly reduced RuO₂ domains and metallic ruthenium surfaces coexist. In the case of Ru/SiO₂, the metallic ruthenium surfaces seem to be dominant, as shown by the higher intensity of the band at 2051 cm⁻¹ in Figure 10b (solid trace).

4. Discussion

The results of the catalytic activity measurements presented for the Ru/MgO sample indicate the influence of the CO/O_2 reactant feed ratio, the temperature, and the pretreatment of the sample on the rates of CO oxidation. The results obtained with the Ru/SiO₂ sample were determined to be in good agreement with those of the Ru/MgO catalyst, as shown by the good agreement between the turnover frequencies plotted in Figure 5. Thus, a significant influence of the support on the deactivation behavior and the CO conversion can be ruled out. The turnover frequencies are also independent of the total pressure, which is illustrated by the good agreement with the TOFs obtained in a recent high-vacuum TAP reactor study.¹

The TOFs were determined after the deactivation process had been finished. The repetition of heating and cooling cycles (up to four cycles) provided clear evidence that the deactivation of the pre-reduced supported ruthenium catalysts is restricted to the initial period of the time-on-stream. This is valid for all CO/O2 reactant feed ratios, which determined the extent and rate of deactivation. The preoxidized sample had a lower initial activity and did not deactivate during the first increase in temperature; instead, a rather slow activation process was observed. No difference in the conversion of CO was observed during the second cycle of the catalytic activity measurements that were performed with a stoichiometric CO/O₂ reactant feed ratio. Obviously, the active state of the catalyst after the termination of the initial period is independent of the pretreatment. Therefore, we can assume a partial reduction of the oxidized ruthenium surface and a partial oxidation of the reduced ruthenium catalyst during the first cycle when a CO/O₂ reactant feed ratio of ≥ 2 is used. The state of the catalyst with the highest activity seems to be metallic bulk ruthenium that was covered by a partially reduced RuO2 surface layer. Correspondingly, a re-reduction of the used catalysts in H2 at 773 K was determined to be necessary to restore the initial high activity, in good agreement with the observations by Kiss and Gonzalez.¹⁷

This hypothesis is supported by the results of TPR measurements. An O/Ru ratio of 1.3 was derived from the quantitative

analysis of the TPR measurements for both ruthenium catalysts that were preoxidized at room temperature, which is in agreement with O_2 chemisorption measurements.¹ This ratio is equivalent to a RuO₂ surface layer when the dispersion of ruthenium (\sim 65%) is taken into account. After the oxidation of CO under net reducing conditions and at high conversion, no indication for oxidized ruthenium particles was observed by the TPR experiments within the experimental accuracy, because the total consumption of H₂ was due to the methanation of adsorbed CO. Note that the amount and the peak temperature of the methane desorption were dependent on the support. For the Ru/MgO sample, a larger amount of methane was observed, compared with the Ru/SiO₂ sample. Moreover, the methanation occurs at higher temperatures for Ru/MgO. This observation suggests that CO is slightly stronger bound onto the surface of Ru/MgO and, therefore, less reactive for the methanation reaction, which is in agreement with recent infrared studies.¹

In contrast, even in a small excess of O2, the ruthenium particles were completely oxidized to RuO₂. As shown by the TEM measurements, the fully oxidized RuO₂ particles were still rather small (<5 nm), even after reaction at 423 K and under strong oxidizing conditions. Sintering of the RuO₂ particles during the oxidation of CO had indeed occurred to a minor extent, as judged by the bimodal particle size distribution with maxima at 2.5 and 4.5 nm in the case of Ru/SiO₂. Thus, the two TPR signals observed at \sim 370 and 415 K can be assigned to the different rates of reduction of smaller and larger RuO₂ particles, respectively. The observation of only one TPR peak at ${\sim}360~K$ after oxidation of the Ru/SiO_2 sample at room temperature is in agreement with this interpretation, because sintering of the particles is only favored at higher temperatures. By means of a series of O₂ and H₂ chemisorption measurements, it was shown that oxidation at room temperature causes no agglomeration of the ruthenium particles.¹ For significantly larger oxidized ruthenium particles, TPR maxima at >473 K were observed.2

The consumption of H₂ at room temperature observed for the Ru/MgO sample either in the preoxidized state or after CO oxidation under net oxidizing conditions can be rationalized by recent single-crystal studies on the interaction between H₂ and the RuO₂(110) single-crystal surface.⁹ Dissociatively adsorbed hydrogen was observed to desorb completely only at temperatures of >350 K. Up to this temperature, dihydride species formed from H₂ and a coordinatively unsaturated O surface atom transform to monohydride before water molecules desorb at ~400 K. Based on this single-crystal study, the consumption of H₂ at <300 K in the case of Ru/MgO is assigned to the dissociative adsorption of H₂ on the supported RuO₂ particles, probably leading to the formation of dihydride or monohydride species.

The results of the in situ DRIFTS experiments correspond well with the conclusions drawn from the kinetic investigations. The observed CO bands clearly indicate that the active surface is RuO₂ under net oxidizing conditions. Furthermore, the coexistence of metallic ruthenium islands and RuO₂ domains was observed for CO/O₂ reactant feed ratios of ≥ 2 at high temperatures and high conversion. The influence of the CO/O₂ reactant feed ratio on the nature of the Ru surface sites and the total degree of oxidation found in the DRIFTS and TPR measurements is in agreement with theoretical calculations,¹⁰ which demonstrated the influence of the CO/O₂ ratio on both the surface structures and the stability of bulk RuO₂. Both the theoretical predictions and our results reveal the importance of phase coexistence conditions that lead to enhanced dynamics



Figure 11. Schematic of the shrinking metallic core model. The degree of oxidation is determined by the CO/O_2 reactant feed ratio and the temperature. The most active state is represented by a partially reduced RuO_2 surface layer supported on a metallic ruthenium core. The formation of inactive RuO_2 surface facets is favored under net oxidizing conditions, leading to bulk RuO_2 particles, whereas hardly active metallic ruthenium surfaces are exposed under net reducing conditions.

at the catalyst surface. These changes are presumably more pronounced at higher temperatures and are very sensitive to the $\rm CO/O_2$ reactant feed ratio. Drastic surface morphology changes have been observed for the mildly reduced RuO₂(110) single-crystal surface after annealing to 600 K.²⁶ As a consequence of this annealing process, a restored oxide with holes and small ruthenium clusters was formed.

An illustration of the processes that occur and the parameters that control the changes of the supported ruthenium catalysts is presented in Figure 11. The pre-reduced ruthenium particles are initially very active for the oxidation of CO. Even under net reducing conditions, the ruthenium particles are covered by a RuO₂ surface layer. The rate of its formation and its thickness are controlled by the CO/O₂ reactant feed ratio. Increasing the temperature under net reducing conditions leads to a partial reduction of the RuO₂ layer. Thus, hardly active metallic Ru sites are exposed to the gas phase, as confirmed by the in situ DRIFTS measurements. Increasing the temperature under net oxidizing conditions leads to an ongoing oxidation of the ruthenium particles, which are finally fully oxidized to bulk RuO₂.

Based on this shrinking-core model, the restriction of the deactivation to the initial period during the time-on-stream (first cycle) is comprehensible. Under net oxidizing conditions, the highest temperature applied for the oxidation of CO determines the maximum degree of oxidation. Cooling and then heating again has no more influence on the degree of oxidation of the ruthenium particles. In consequence, steady-state conversion is immediately observed. Under net reducing conditions, the degree of oxidation is also changed in a continuous way, which is controlled by the temperature. At low conversion, the active catalyst is covered by a highly active RuO₂ surface layer, which is partially reduced. Only at high conversion and under net reducing conditions, the reduction of the RuO₂ surface layer is faster than its reoxidation, a process that was also observed for the oxidation of methane over Ru/Al₂O₃.²

Finally, the question must be addressed as to why the fully oxidized RuO₂ particles are less active catalytically. RuO₂ single-crystal studies showed that two different phases coexist on the RuO₂(100) surface.^{26,27} This surface is characterized by an (1×1) phase that is as active as the RuO₂(110) surface, and a $c(2 \times 2)$ phase that is inactive for the adsorption of CO. Furthermore, the formation of the inactive $c(2 \times 2)$ phase is favored under oxidizing conditions and higher temperatures. Thus, also inactive surface planes are assumed to be present on the supported RuO₂ particles to an increasing extent with decreasing CO/O₂ reactant feed ratio. Based on the structure

sensitivity found on RuO_2 single-crystal surfaces, the shrinking metallic core model is extended by taking the different possible surface structures of the RuO_2 layer into account. The higher the degree of oxidation, the more inactive RuO_2 planes are exposed, leading to an overall lower catalytic activity.

Further studies that apply in situ extended X-ray absorption fine structure (EXAFS) and DRIFTS combined with O_2 TPD and O_{ads} + CO temperature-programmed surface reaction (TPSR) measurements are underway, to provide additional evidence for the model of the active state and its different methods of deactivation (shown in Figure 11).

5. Conclusions

(1) By optimizing the experimental conditions in a fixedbed reactor operated at atmospheric pressure, it was possible to derive turnover frequencies (TOFs) for the oxidation of CO over Ru/MgO at low conversion. The good agreement with kinetic data obtained with the RuO₂(110) single-crystal surface and with Ru/SiO₂ under high vacuum conditions demonstrates that both the materials and the pressure gap were successfully bridged. The support is necessary to maintain a high dispersion of the ruthenium particles but has no direct influence on the catalytic activity.

(2) The systematic investigation of the deactivation process revealed that it is affected by the CO/O_2 ratio and the reaction temperature, and, in particular, that it is limited to the initial period of the time-on-stream.

(3) Based on temperature-programmed reduction (TPR) measurements that were performed in the same reactor after the oxidation of CO, the degree of oxidation of the ruthenium particles was derived. When starting in the metallic state under net reducing conditions, the formation of a partially reduced highly active RuO₂ surface layer was detected. Under net oxidizing conditions, the ruthenium particles were determined to be completely oxidized to bulk RuO₂.

(4) The dynamic changes of the surface structure of the ruthenium catalysts, as a function of the CO/O_2 reactant feed ratio, were demonstrated by in situ diffuse reflectance infrared Fourier spectroscopy (DRIFTS) experiments conducted under reaction conditions. Obviously, the highest catalytic activity is correlated with the presence of a partially reduced RuO₂ surface layer supported on metallic bulk ruthenium. Further reduction of this RuO₂ surface layer was observed under net reducing conditions at higher temperatures, leading to a deactivated state of the catalysts due to exposed metallic ruthenium surfaces. Based on the structure sensitivity of the CO oxidation over RuO₂

surfaces, the decrease of the activity under net oxidizing conditions is rationalized by assuming that bulk RuO_2 particles expose less-active facets such as the $\text{RuO}_2(100)-c(2 \times 2)$ surface.

Acknowledgment. The authors gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft (DFG, SPP 1091).

References and Notes

(1) Assmann, J.; Löffler, E.; Birkner, A.; Muhler, M. Catal. Today 2003, 85, 235.

- (2) Balint, I.; Miyazaki, A.; Aika, K. J. Catal. 2003, 220, 74.
- (3) Balint, I.; Miyazaki, A.; Aika, K. React. Kinet. Catal. Lett. 2003, 80, 81.
- (4) Snytnikov, P. V.; Sobyanin, A. V.; Belyaev, D. V.; Tsyrulnikov, G. P.; Shitova, B. N.; Shlyapin, A. D. *Appl. Catal.*, A **2003**, *239*, 149.
- (5) Han, Y.-F.; Kahlich, M. J.; Kinne, M.; Behm, R. J. Phys. Chem. Chem. Phys. **2002**, *4*, 389.
- (6) Zang, L.; Kisch, H. Angew. Chem. 2000, 112, 4075; Angew. Chem., Int. Ed. 2000, 39, 3921.
 - (7) Over, H.; Muhler, M. Prog. Surf. Sci. 2003, 72, 3.
 - (8) Wendt, S.; Seitsonen, A. P.; Over, H. Catal. Today 2003, 85, 167.
 - (9) Wang, J.; Fan, C. Y.; Sun, Q.; Reuter, K.; Jacobi, K.; Scheffler,

M.; Ertl, G. Angew. Chem. 2003, 115, 2201.

- (11) Reuter, K.; Scheffler, M. Phys. Rev. Lett. 2003, 90, 046103.
- (12) Fan, C. Y.; Wang, J.; Jacobi, K.; Ertl, G. J. Chem. Phys. 2001, 114, 10058.
- (13) Over, H.; Kim, D. Y.; Seitsonen, P. A.; Wendt, S.; Lundgren, E.; Schmid, M.; Varga, P.; Morgante, A.; Ertl, G. Science **2000**, 287, 1474.
- (14) Lee, H. I.; White, J. M. J. Catal. 1980, 63, 261.
 (15) Peden, C. H. F.; Goodman, D. W. J. Phys. Chem. 1986, 90, 1360.
- (16) Cant, N. W.; Hicks, P. C.; Lennon, B. S. J. Catal. 1978, 54, 372.
- (17) Kiss, J. T.; Gonzalez, R. D. J. Phys. Chem. **1984**, 88, 892.
- (18) Bielawa, H.; Hinrichsen, O.; Birkner, A.; Muhler, M. Angew. Chem. 2001, 113, 1093; Angew. Chem., Int. Ed. 2001, 40, 1061.
 - (19) Monti, D. A. M.; Baiker, A. J. Catal. **1983**, 83, 323.
- (20) Malet, P.; Caballero, A. J. Chem. Soc., Faraday Trans. 1988, 84, 2369.
- (21) Assovskii, I. G. Combust., Explos. Shock Waves 2003, 34, 163.
- (22) Mears, D. E. Ind. Eng. Chem. Process Des. Dev. 1971, 10, 541.
- (23) Mears, D. E. J. Catal. 1971, 20, 127.
- (24) Seitsonen, A. P.; Kim, Y. D.; Knapp, M.; Wendt, S.; Over, H. Phys. Rev. B 2002, 65, 035413.
- (25) Peden, C. H. F.; Goodman, D. W.; Weisel, M. D.; Hoffmann, M. Surf. Sci. 1991, 253, 44.
- (26) Over, H.; Knapp, M.; Lundgren, E.; Seitsonen, A. P.; Schmid, M.; Varga, P. Chem. Phys. Chem. 2004, 5, 10.
- (27) Kim, Y. D.; Schwegmann, S.; Seitsonen, A. P.; Over, H. J. Phys. Chem. B 2001, 105, 2205.