

CO oxidation on a model Cu/Rh(100) catalyst

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The reaction between carbon monoxide and molecular oxygen on a model Cu/Rh(100) bimetallic catalyst was studied at 455 K using a $\text{CO}/\text{O}_2 = 2$ reactant gas mixture at a total pressure of 10.0 Torr. A maximum in the initial activity was observed at a Cu coverage of 1.3 monolayers. However, the Cu overlayers were found to be unstable at the reaction conditions employed in that the Cu films interact strongly with surface oxygen to form three-dimensional CuO_x clusters. The morphological modifications were found to influence markedly the catalytic properties of the surface. However, the initial catalytic activity and surface morphology of the Cu films could be restored by flashing the sample to > 750 K.

Keywords: CO oxidation; bimetallic catalysis; Cu/Rh(100)

1. Introduction

The catalytic oxidation of CO has received considerable attention because of the emphasis on the reduction of the CO levels emitted by automobiles and heavy industry [1–3]. A further incentive to study this reaction is the relative simplicity of CO oxidation which makes it ideal to investigate the basic phenomena of heterogeneous catalysis. In practice, supported noble metal catalysts of Pt, Pd and Rh are used for CO oxidation, and consequently extensive studies on both supported [4,5] and model single crystal [6–14] catalysts of these metals have been carried out. The reaction has been found to be structure insensitive and observed to follow a Langmuir–Hinshelwood mechanism [8,10,11]. Furthermore, the reaction rate at conditions near stoichiometry is CO desorption limited as a result of the strong adsorption of CO onto Pt, Pd, and Rh. Dissociative adsorption of O_2 is rapid on the CO-free surface sites, while the subsequent reaction between adsorbed carbon monoxide, CO(a) , and adsorbed oxygen, O(a) , is quite facile. The observed positive order in O_2 partial pressure and negative order in CO partial pressure are a consequence of the relatively weak adsorption of O_2 compared to the relatively strong adsorption of CO.

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The high cost of Pt, Pd, and Rh is a strong driving force for the development of improved catalysts with high CO oxidation activities and resistance to catalyst poisons. In this regards bimetallic catalysts often exhibit higher activities and/or selectivities or resistance to catalyst poisons thus making them superior in many cases to the single component systems [15,16]. Optimum catalytic properties can be achieved for certain reactions by combining two or more metals enabling one to tailor catalysts for specific reactions [17,18]. The microscopic details, however, of the improved functionality of mixed-metal catalysts is at present poorly understood.

Recent work in our laboratories, using an array of surface science techniques, has shown that the electronic and chemisorptive properties of a monolayer of one metal supported on a dissimilar metal substrate are markedly different from the corresponding properties found for the pure overlayer metal [16]. For example, the interaction between monolayer Cu and Rh(100) leads to an increase of ≈ 75 K in the peak desorption temperature of CO from Cu/Rh(100) compared to CO desorption from pure Cu [19]. Because of the modified electronic and chemical properties observed for ultra-thin films of Cu on Rh and the essential role that CO adsorption plays in the kinetics of CO oxidation, studies of this reaction were initiated on various Cu/Rh(100) model bimetallic catalysts.

In this letter we report the effect that the addition of Cu to Rh(100) has on its relative activity for the CO + O₂ reaction. The relative stabilities of the Cu overlayers under reaction conditions have also been investigated and are discussed.

2. Experimental

The experiments were carried out in a combined elevated pressure reactor-ultrahigh vacuum (UHV) surface analytical chamber which has been described in detail elsewhere [20]. The UHV surface analytical chamber, with a base pressure of $< 3 \times 10^{-10}$ Torr, is equipped with Auger electron spectroscopy (AES), temperature programmed desorption (TPD), ion sputtering as well as metal- and gas-doser capabilities. The Rh(100) sample was heated resistively by tantalum leads attached to the back of the crystal, and the crystal temperature was monitored by a W-5%Re/W-26%Re thermocouple spotwelded to the edge of the sample.

The Rh(100) crystal was cleaned by repeated cycles of oxidation at 800 K in 10^{-7} Torr O₂ followed by annealing at 1200 K in the ambient vacuum for 2 min. Cu was deposited onto the Rh(100) surface at a substrate temperature of 300 K from a Cu(OFHC)-wrapped tungsten filament. The cleanliness of the crystal and the Cu coverage were monitored by AES. The absolute coverage of the deposited Cu was determined using the coverage calibration of ref. [19]. Following

the cleaning of the Rh(100) and the deposition of Cu, the sample was transferred into an elevated pressure reaction chamber. This reaction chamber is connected to a gas handling system and a gas chromatograph (GC) equipped with a flame ionization detector (FID).

Upon completion of a reaction, the reactant-product gas mixture was evacuated through a liquid-nitrogen-cooled sample loop, a procedure which ensured the efficient trapping of the product CO₂. The CO₂ was injected into the GC by rapidly heating the trap to temperatures > 350 K and then passed through a methanizer. The CO₂, in turn, was converted quantitatively to CH₄ and detected as such by the FID.

Research purity (> 99.999%, Matheson) CO and O₂ were used in these studies. CO was further cleaned by passing it through a 142 K *n*-pentane/liquid-nitrogen slurry trap in order to remove transition metal (Ni, Fe) carbonyl impurities. O₂ was used as received without further purification. CO/O₂ reactant gas mixtures with different ratios were prepared and stored after thorough mixing in glass bulbs. Following each reaction the sample was returned to the UHV chamber for surface analysis by AES.

3. Results and discussion

The catalytic activities for CO oxidation of a series of Cu/Rh(100) catalysts are shown in fig. 1 as a function of Cu coverage. The data were acquired at 455 K using CO/O₂ = 2 reactant gas mixtures at a total pressure of 10.0 Torr (1 Torr = 133.32 Pa). The catalytic activity for CO oxidation shows a maximum at an initial Cu coverage of approximately 1.3 monolayers (ML). The deposition of Cu onto the Rh(100) surface results in a sharp increase in the CO oxidation activity up to an optimum coverage of 1.3 ML, where the activity is higher by a factor of 13 compared to the clean Rh(100) surface. A further increase in the deposited Cu results in a sharp decrease in catalytic activity; however, it should be noted that the Cu/Rh(100) catalysts exhibit higher activities than clean Rh(100) even at Cu coverages > 3 ML.

It is noteworthy that steady-state activities are not observed initially as is apparent in fig. 2. Beginning with an initial Cu coverage of 1.2 ML, the catalytic activity is attenuated with each successive reaction until approximately the eighth sequence. Concomitantly, the Cu/Rh Auger ratio decreased from an initial value of 0.55 to 0.16 after 12 consecutive reaction sequences. This sharp decrease in the Cu/Rh Auger ratio is not due simply to the removal of Cu from the Rh(100) surface in that flashing the sample to > 750 K restored both the initial Cu/Rh Auger ratio and the initial catalytic activity. The dashed line in fig. 2 corresponds to the point in this series of experiments where the sample was heated to 750 K in the ambient vacuum.

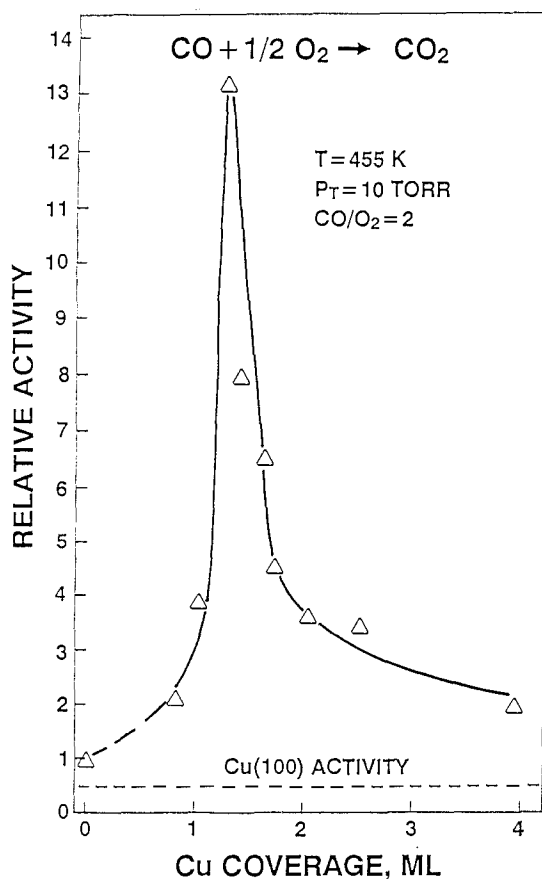


Fig. 1. Relative CO₂ formation rate versus initial Cu coverage for CO oxidation on Rh(100). The catalyst was preconditioned in the reactant gas mixture at the reaction temperature for 15 min prior to the activity measurements. $T = 455$ K; $\text{CO}/\text{O}_2 = 2$; and $P_T = 10.0$ Torr. The rates have been normalized to the TOF of 0.325 s^{-1} of Rh(100). The reactant time was 5 min in each sequence.

The Cu overlayers on Rh(100) interact with surface oxygen resulting in the agglomeration of the Cu into 3D clusters. AES following reaction shows residual oxygen consistent with the Cu being oxidized during the course of the reaction. Under the reaction conditions implemented in these experiments, the clean Rh(100) has been shown to be oxygen-free following reaction [11], thus this surface oxygen is assumed to be associated with the overlayer Cu in the form of Cu oxide (CuO_x) clusters.

The time-dependent catalytic activity and surface composition were monitored for two catalysts with different initial Cu coverages. The relative catalytic activities and the Cu/Rh and O/Cu Auger ratios are shown in figs. 3 and 4 as a function of reaction time for Cu_{>3ML}/Rh(100) and Cu_{1.2ML}/Rh(100), respectively. Because of the relatively high initial Cu coverage of the Cu_{>3ML}/Rh(100)

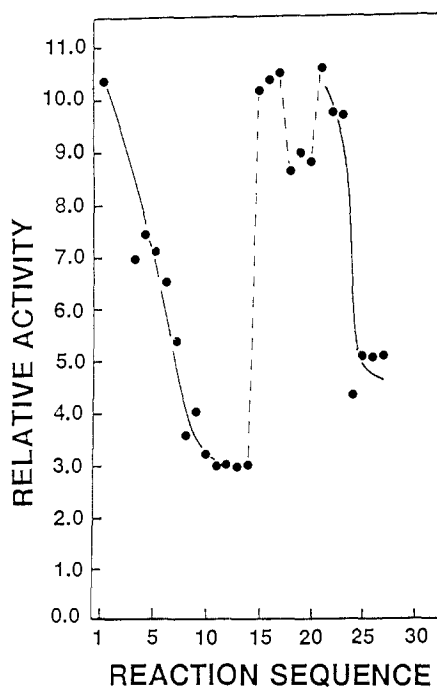


Fig. 2. Relative rates of CO_2 formation as a function of reaction time. $T = 455 \text{ K}$; $\text{CO}/\text{O}_2 = 2$; and $P_T = 10.0 \text{ Torr}$. The rates have been normalized to the TOF of 0.325 s^{-1} of Rh(100). The reaction time was 5 min in each sequence.

catalyst, a low initial catalytic activity was observed. However, as the Cu/Rh AES ratio falls, the catalytic activity first increases significantly, passes through a maximum, and then gradually decreases. There is a sharp initial decrease in the Cu/Rh Auger ratio and a concomitant increase in the O/Cu ratio. As the catalyst reaches its maximum activity, the Cu/Rh and O/Cu Auger ratios level toward constant values.

It should be noted that the Cu/Rh AES ratio at which the maximum catalytic activity is observed is virtually identical to that corresponding to the maximum activity of fig. 1. This Cu/Rh ratio of 0.55 corresponds to an Cu coverage of approximately 1.3 ML. At the onset of reaction, the Rh(100) surface is covered with a Cu overlayer of $> 3 \text{ ML}$. At this coverage the topmost layer of Cu is not significantly perturbed by the substrate Rh. Thus the initial activity of this surface is characteristic of Cu which is less than the corresponding activity of Rh(100). As the reaction proceeds, the Cu overlayer interacts with surface oxygen to form 3D CuO_x clusters. During the course of this clustering process, the activity of the catalyst climbs to a maximum and then attenuates.

Two factors are believed to contribute to the evolution of the activity for the multilayer Cu-covered Rh(100) surface. First, clustering of the $> 3 \text{ ML}$ Cu films necessarily will lead to the exposure of the first and second Cu layers. These

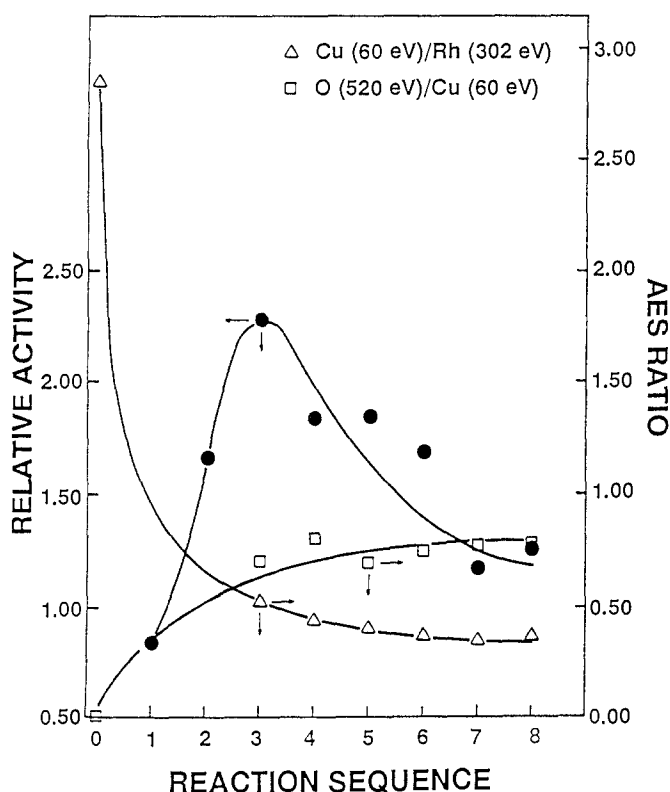


Fig. 3. Relative catalytic activity for CO_2 formation and surface composition determined by AES as functions of reaction time for a $\text{Cu}_{>3\text{ML}}/\text{Rh}(100)$ catalyst. $T = 455\text{ K}$; $\text{CO}/\text{O}_2 = 2$; and $P_T = 10.0\text{ Torr}$. The rates have been normalized to the TOF of 0.325 s^{-1} of $\text{Rh}(100)$. The reaction time was 5 min in each sequence.

have been shown to exhibit quite different CO chemisorptive properties, binding CO significantly more strongly than pure Cu [19]. Since the binding of CO is a critical parameter in the overall CO oxidation reaction scheme, the exposure of the first and second layers of Cu could play a key role in the enhanced kinetics of the reaction as a function of the clustering of the Cu. Secondly, the clustering process of the multilayer Cu films will necessarily produce a Cu/Rh interface with varying dimensions (morphologies). An optimum surface for CO oxidation can be envisioned by mixing Cu and Rh to optimize the surface CO coverage (strongly bound CO to Rh) and the surface oxygen coverage (strongly bound O(ads) to Cu). Combining these two properties could lead to more optimum coverages of CO and O(ads) on the Cu/Rh mixture compared to either Cu or Rh, and thus could reflect a more optimum catalytic surface for the reaction. However, as the reaction proceeds, a less appropriate Cu/Rh combination evolves with continued Cu clustering, and the overall activity falls below the optimum value. This latter explanation is considered to be more consequential than the first.

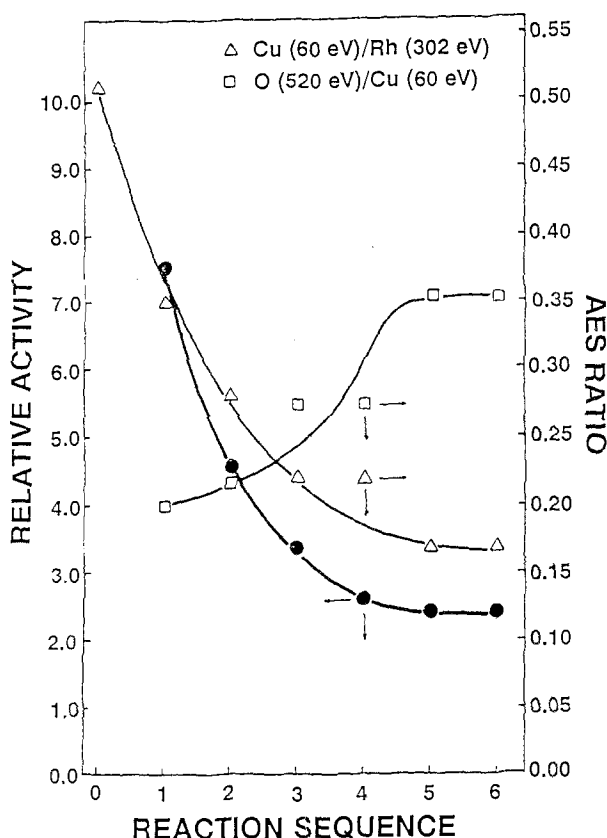


Fig. 4. Relative CO_2 formation rate and surface composition determined by AES as a function of the reaction time for a $\text{Cu}_{1.2\text{ML}}/\text{Rh}(100)$ catalyst. The rates have been normalized to the TOF of 0.325 s^{-1} of $\text{Rh}(100)$. The reaction time was 5 min in each sequence.

The evolution of the catalytic activity closely parallels the decrease in the Cu/Rh Auger ratio for the $\text{Cu}_{1.2\text{ML}}/\text{Rh}(100)$ catalyst. The Cu coverage of 1.2 ML is slightly less than the coverage which exhibits the maximum activity in fig. 1. In contrast to the $\text{Cu}_{>3\text{ML}}/\text{Rh}(100)$ catalyst, this surface does not exhibit a maximum in the catalytic activity as a function of reaction time since the initial Cu coverage is less than the optimum of fig. 1. However, similarly to the $\text{Cu}_{>3\text{ML}}/\text{Rh}(100)$ catalyst, a decrease in activity with reaction time is observed due to clustering of Cu.

Assuming that the attention of the catalytic activity arises due to the oxidizing reaction conditions, the use of a reactant gas mixture with a significantly higher CO/O_2 ratio should lead to a more stable catalyst surface. Therefore a reactant gas mixture of $\text{CO}/\text{O}_2 = 20$ was employed to investigate the effect of a more reducing environment on both the catalytic activity and the stability of the Cu overlayer. Results obtained by using this reaction mixture are compared in fig. 5 with those data obtained with a $\text{CO}/\text{O}_2 = 2$ mixture. As anticipated, the activity

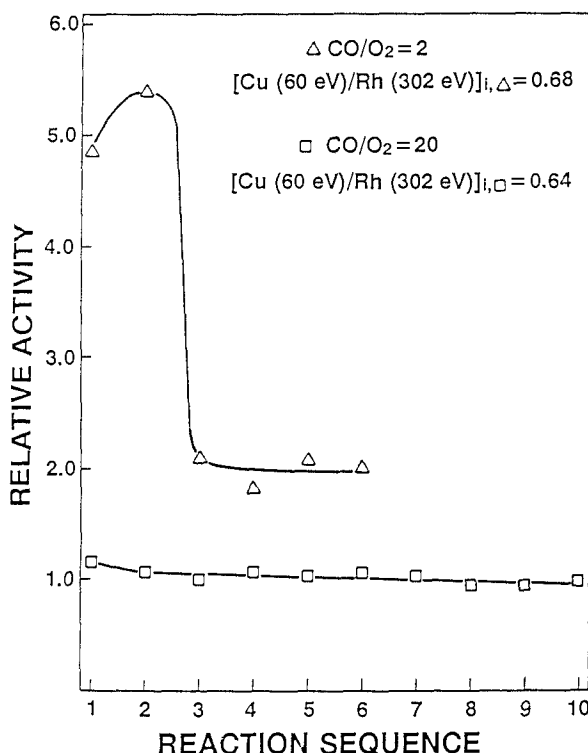


Fig. 5. The effect of reactant composition on the catalytic activity and surface composition. $T = 455$ K and $P_T = 10.0$ Torr. The rates have been normalized to the TOF of 0.325 s^{-1} of Rh(100). The reaction time was 5 min in each sequence.

observed for the $\text{CO}/\text{O}_2 = 20$ gas mixture is less than that found for the $\text{CO}/\text{O}_2 = 2$ mixture. On the other hand, the Cu/Rh catalyst is considerably more stable in the more reducing environment as indicated by the essentially constant Cu/Rh Auger ratio as a function of the reaction sequence. For example, after the tenth reaction sequence the Cu/Rh ratio is 0.45 compared to the initial value of 0.64. In contrast, there is a significant drop in the catalytic activity as a function of reaction sequence with the $\text{CO}/\text{O}_2 = 2$ reactant gas mixture. The activity is attenuated more than 50% after the first three reaction periods and the Cu/Rh Auger ratio is reduced to a value of 0.20 from the initial value of 0.68. These two sets of measurements indicated that oxidation of the Cu and thus the oxidizing character of the reactant gas mixture is primarily responsible for the changes in surface morphology as a function of reaction time.

In summary our results show that bimetallic Cu/Rh(100) catalysts are generally more active for CO oxidation than either the single metal component catalysts. A maximum in catalytic activity was observed at an initial Cu coverage of approximately 1.3 ML. Cu overlayers are not stable under reaction conditions

and cluster into 3D CuO_x clusters upon interaction with surface oxygen. The initial catalytic activity, the initial Cu/Rh Auger ratio, and an oxygen-free surface can be restored by annealing the Cu/Rh(100) surface to 750 K.

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