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Kinetics of the Reverse Water–Gas Shift Reaction over Cu(110)

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The reverse water–gas shift reaction ($CO_2 + H_2 \rightarrow H_2O + CO$) has been studied over a clean Cu(110) single-crystal model catalyst at temperatures between 573 and 723 K. The steady-state kinetic measurements were carried out at medium pressures (10–2000 Torr) in a microreactor after cleaning and characterization of the sample under UHV conditions. The H_2/CO_2-pressure ratios varied from 1000 : 1 to 1 : 10. The product buildup was monitored with a gas chromatograph (GC). The apparent activation energy is about 18 kcal/mol, and the reaction orders in H_2 and CO_2 depend strongly on the H_2/CO_2 ratio and temperature. The steady-state kinetics are compared favorably with the rates of elementary steps potentially involved in a "surface redox" reaction mechanism of the reverse and forward water–gas shift reaction involving the formation and removal of oxygen adatoms. Kinetic evidence that is tentatively attributed to a hydrogen-induced surface phase transition that affects the reaction rate, is also presented.

I. INTRODUCTION

The catalytic water–gas shift (WGS) reaction ($H_2O + CO \rightarrow CO_2 + H_2$) is of importance in hydrogen production and for future energy technologies. The so-called "low-temperature" Cu/ZnO catalysts are widely used. This reaction has been studied over both high-surface-area catalysts containing Cu and ZnO (*1*, *4–8*), and model catalysts based on Cu single crystals, which have very well-controlled surface cleanliness and geometric structure (*2*, *3*). Those studies showed that the kinetics over pure, single-crystal Cu(111) and Cu(110) are very similar to the kinetics over high-area Cu/ZnO, when compared on a "per Cu surface atom" basis (*2*, *3*). This indicates that metallic Cu provides the active site for catalysis (*2*, *3*).

The mechanism of the water–gas shift reaction is still not certain. Some authors support a "formate mechanism" whereby surface hydroxyls (OH_a) produced from dissociatively adsorbed H_2O combine with adsorbed CO (CO_a) to produce a surface formate intermediate ($HCOO_a$), which then decomposes to $\frac{1}{2}$ H_2 and CO_2 (*1*, *4–6*). Other authors (*2*, *3*, *7–9*) favor a "surface redox" or "oxygen adatom" mechanism, whereby H_2O dissociatively adsorbs to produce oxygen adatoms (O_a) and H_2, followed by the well-known reaction of CO with O_a to produce CO_2 (3 and references therein).

Perhaps the best evidence for this latter mechanism comes from the near equality in the rate of the dissociative adsorption of CO_2 to produce O_a and the rate of the reverse water–gas shift reaction (RWGS) at low conversion and at low CO_2/H_2 ratios, where the rate should be limited by dissociative CO_2 adsorption (if the surface redox mechanism is correct) (*10*). Unfortunately these two rates were measured on different types of catalysts: the rate of CO_2 dissociation was measured on a Cu(110) surface (*10*), while the RWGS catalytic kinetics were measured on high-area Cu/ZnO (*1*). The meaning of this favorable comparison in these rates is therefore subject to questions concerning possible electronic effects of ZnO and uncertainties associated with quantifying the metallic Cu surface area in the latter catalyst.

It is the goal of this paper to make a

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stronger comparison between these rates by providing kinetic data for the catalytic reverse water–gas shift reaction over a clean Cu(110) surface for *direct* comparison to the kinetics of CO_2 dissociation on this same sample's surface. As we will see, this comparison will still be complicated by the probable presence of a high coverage of hydrogen adatoms (H_a) under those catalytic conditions that ensure a rate which is first order in CO_2 pressure (and therefore possibly limited by CO_2 dissociation). Since H_a may alter the dissociative sticking probability of CO_2 at nearby sites, direct comparison with the sticking probability found on clean Cu(110) may not be valid, although the two rates are still found to be relatively similar. In any case, the current results are the first kinetics of the RWGS reaction on a verifiably clean Cu surface, and they provide compelling evidence to suggest that these kinetics are markedly effected by a surface phase transition, probably resulting from a buildup of the hydrogen surface coverage.

II. EXPERIMENTAL

The experiments were performed in a stainless-steel UHV chamber and an attached microreactor (vol = 36 ml), which are described in detail elsewhere (*3*, *11*). The sample heating wires were 0.005-in.-diameter tungsten, attached to more massive molybdenum blocks. This configuration was stable in the high H_2 pressures used here, whereas when tantalum was used for these wires or holder, it caused massive H_2 outgassing after reaction, and eventual deterioration of the wires. The sample could be transferred between the microreactor and the vacuum chamber rapidly (<20 s) and without exposure to air.

The Cu(110) crystal was cleaned by Ar^+ ion sputtering at 740 K. Annealing at 850 K resulted in a sharp (1 × 1) LEED pattern with low background intensity. Surface cleanliness was checked with AES. The reactants were research grade CO_2 and H_2 (99.999%). Their purity was checked by a gas chromatograph (GC).

In the kinetic measurements, the clean sample was transferred to the reactor at room temperature, followed by introduction of reactant gases. The total pressure, which was read by a capacitance-type manometer, never exceeded a total value of 2000 Torr. The sample was then rapidly heated (20 K/s) to reaction temperature. The rate of the RWGS reaction was analyzed by monitoring the buildup of CO product with a gas chromatograph using techniques described previously (*2*). The GC sensitivity was determined from known gas mixtures containing CO, CO_2, and H_2. The GC was equipped with a Carboseive S-IV column at 413 K and a thermal conductivity detector. Separation was accomplished in less than 3 min. In general, H_2O product was not monitored with the GC, but a few experiments using another column (Porapak Q) were performed to ensure that H_2O was also being produced in nearly 1 : 1 ratio with CO here.

The following experiment proved that the RWGS proceeded only at the front surface of the sample: H_2S, diluted in argon, was dosed to the front sample surface gradually at 500 K in the UHV chamber by using a directionally enhanced doser (*13*). The sulfur buildup on the surface was monitored by AES. The decrease of the RWGS activity correlated well with the sulfur coverage, as reported previously for the forward WGS reaction (*3*). The S-saturated surface showed no CO production via the RWGS reaction. The removal of most of the sulfur layer (~98%) by brief Ar^+ sputtering of the front Cu(110) surface restored the original RWGS activity. Heating the sample at reaction temperature in pure CO_2 or pure H_2 showed insignificant CO buildup. Therefore, CO displacement from the reactor walls or continuous CO_2 dissociation at the hot sample holder can be excluded as a source of CO product seen here.

III. RESULTS

Figure 1 shows examples of the CO buildup versus time for the reverse water–gas shift reaction ($H_2 + CO_2 \rightarrow CO + H_2O$) at 90 Torr H_2 and 850 Torr CO_2, at three different temperatures. The tempera-

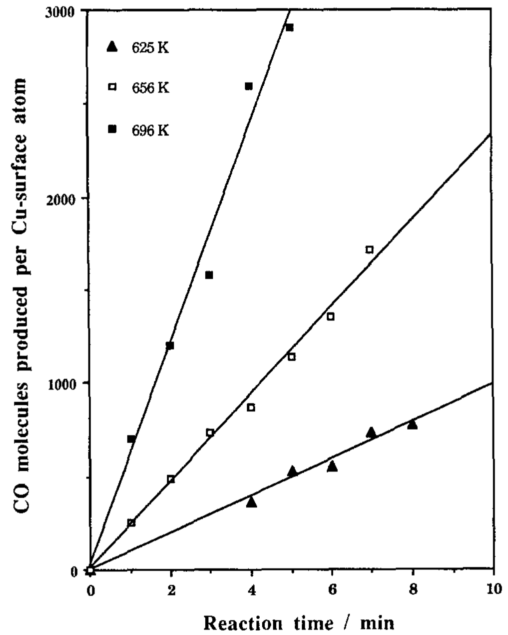

FIG. 1. The buildup with time of CO product due to the RWGS reaction under 90 Torr of H_2 and 850 Torr of CO_2 at 625, 656, and 696 K. The number of produced molecules is normalized here to the number of Cu atoms on the (110) surface (1.086×10^{15} atoms · cm^{-2}).

tures shown are the crystal temperatures. It was also shown in previous work that above approximately 20 Torr, the gas molecules hitting the surface are in thermal equilibrium with the sample, at least with respect to their rotational and translational temperatures (*14, 15*). (In the case of hydrogen adsorption from a Boltzmann distribution at ~600 K, it was also shown that vibrational temperature is relatively unimportant up to above 700 K (*14, 15*).) Due to the fact that there is a linear increase of product with time in Fig. 1, we typically determined the rates only by measuring the product buildup at a fixed time of 4 min. Under those conditions of low conversion the equilibrium lies far to the side of the products, and the reverse reaction is negligible. We report here, therefore, steady-state rates in the limit of low conversion. Note, however that many hundreds or even thousands of product molecules are produced per surface site during this measurement. Post-reaction analysis, performed by a fast transfer (~10 s) of the sample at reaction temperature from the microreactor to the UHV chamber followed by cooling, showed no carbon, oxygen, or other impurities in the AES spectra and still a sharp (1 × 1) LEED pattern characteristic of the clean Cu(110) surface.

Figure 2 shows an Arrhenius plot derived from RWGS rate data taken as a function of temperature at two sets of reactant partial pressures: P_{H_2} = 100 Torr, P_{CO_2} = 925 Torr, and P_{H_2} = 825 Torr, P_{CO_2} = 5 Torr. The slopes give apparent activation energies for the RWGS reaction of 16 ± 1.6 and 18 ± 2 kcal · mol^{-1}, respectively. Both values are nearly identical with the activation energy

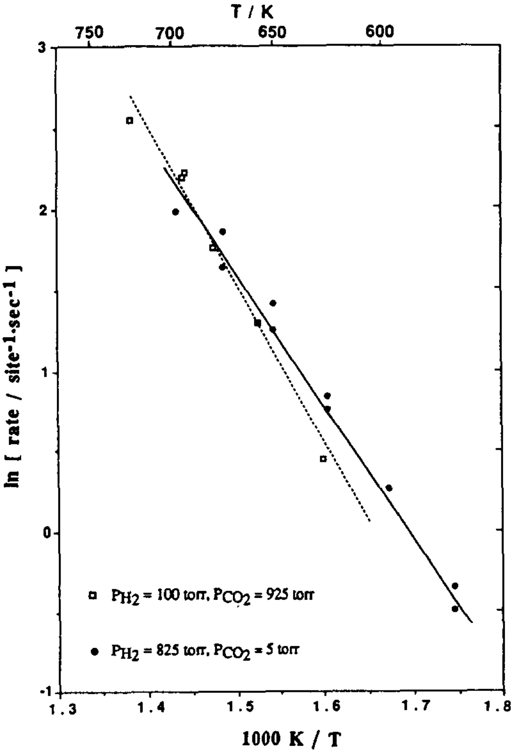

FIG. 2. The dependence upon temperature of the turnover frequencies of the RWGS reaction over Cu(110), in Arrhenius form, for two different reactant pressure conditions. The slopes of the best-fit curves show activation energies of 16 ± 1.6 kcal · mol^{-1} and 18 ± 2 kcal · mol^{-1}, respectively (95% conf. limit).

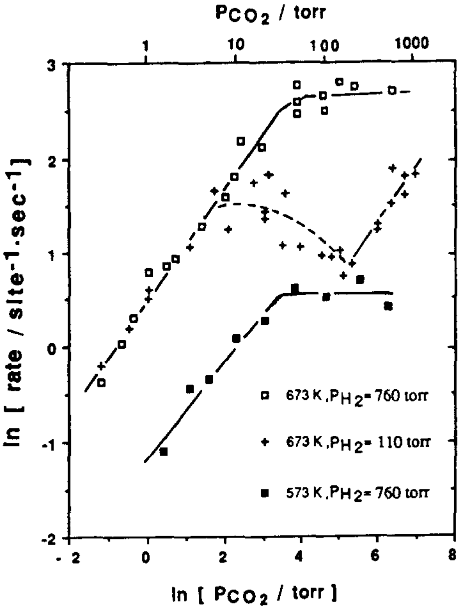

FIG. 3. Dependence of the rate of the RWGS reaction upon CO_2 partial pressure at several different fixed H_2 pressures and temperatures. One rate curve shows a curious minimum, which might be explained by a hydrogen-induced surface phase transition (see text for further details).

for CO_2 dissociative adsorption on Cu(110) (*10*). This suggests that the RWGS reaction rate here might be limited by CO_2 dissociation under these conditions, in which case the order with respect to CO_2 partial pressure should be near unity.

To test this, we measured the variation in the rate with CO_2 partial pressure at two fixed H_2 pressures and two fixed temperatures. The results are shown in Fig. 3. For low CO_2/H_2 ratios $(<\frac{1}{10})$, the rate increases strongly with CO_2 partial pressure (order in $P_{CO_2} \sim 0.6 \pm 0.05$). There is no difference in the rate between the two sets of H_2 partial pressures (open squares and crosses) in that region. Therefore, the order in H_2 pressure is nearly zero. At intermediate CO_2/H_2 pressure ratios (around 1 : 10 to 1 : 2) the rate becomes nearly independent in P_{CO_2} (zero order in P_{CO_2}). Under these conditions the RWGS rate depends strongly on the hydrogen partial pressure, as can be seen in Fig. 3 and is also shown below in more detail (Fig. 4).

When the CO_2/H_2 ratio at 673 K increases above unity as more CO_2 is added (see crosses in Fig. 3), the rate decreases slightly and, at even higher CO_2 pressures, increases again with CO_2 addition. At these highest CO_2 pressures and at low H_2 pressures, the order with respect to CO_2 is again very high ($\sim 0.7 \pm 0.1$). So again, and very unusually, the rate becomes nearly limited by the CO_2 flux to the surface. This unusual minimum in the reaction rate versus CO_2 pressure, which gives rise to two separate regions where the rate is nearly first order in CO_2, is discussed further below.

The dependences of the rate upon H_2 pressure at several different conditions of temperature and CO_2 pressure are shown in

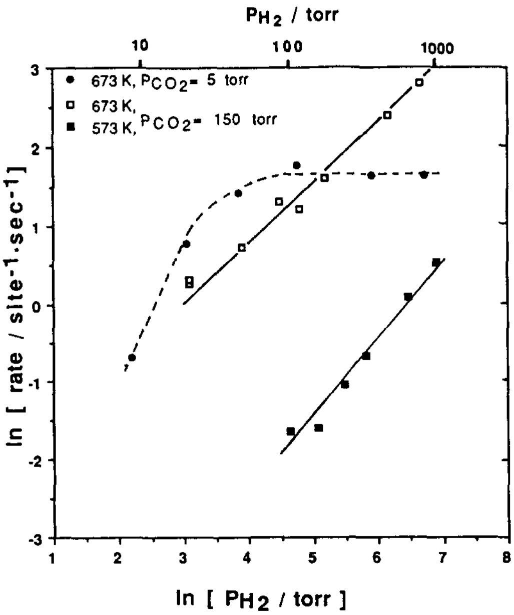

FIG. 4. The dependences of the rate of the RWGS reaction upon H_2 pressure at a fixed CO_2 pressure of 150 Torr at 673 and 573 K. The rate shows a high order in hydrogen ($n_{H_2} = 0.8$ and $n_{H_2} = 0.95$, respectively). The dashed curve shows the dependence of the rate upon H_2 pressure at $P_{CO_2} = 5$ Torr and 673 K. It shows that the rate is zero order in hydrogen when the H_2 pressure exceeds a value 100 Torr, but the rate is greater than first order in H_2 ($n_{H_2} \cong 2$) when the H_2 pressure is very low.

Fig. 4. As can be seen, the rate is close to first order in H_2 at moderate CO_2 pressures (150 Torr). For example, at 573 K the order with respect to H_2 (n_{H_2}) is 0.95 ± 0.1, and at 673 K n_{H_2} is 0.8 ± 0.08. However, at very low CO_2 pressures (5 Torr) and 673 K, the order in H_2 is zero provided the H_2 pressure exceeds about 50 Torr. Here, if the H_2 pressure is dropped below ~10 Torr, the order with respect to H_2 increases to about second order. Also not shown in Fig. 4 are a few measurements at P_{CO_2} = 400 Torr and 673 K that indicate that the order in H_2 is ~0.5 for P_{H_2} from 110 to 760 Torr (see Fig. 3).

IV. DISCUSSION

The present kinetics of the reverse water–gas shift reaction will be discussed in terms of the same surface redox or oxygen adatom mechanism previously used to successfully describe the kinetics of the forward water–gas shift over Cu(110) (*3*). This mechanism, in reverse form, is summarized as

$$CO_{2,g} \leftrightarrows CO_a + O_a \quad (1)$$

$$CO_a \leftrightarrows CO_g \quad (2)$$

$$H_{2,g} \leftrightarrows 2H_a \quad (3)$$

$$H_a + O_a \leftrightarrows OH_a \quad (4)$$

$$H_a + OH_a \rightarrow H_2O_a \quad (5)$$

$$H_2O_a \leftrightarrows H_2O_g, \quad (6)$$

where the subscript a refers to the adsorbed species. The energetics for these steps have all been approximately determined, and the rate constants for most of the steps are fairly well known (3, and references therein). These results have even been incorporated into a kinetic model that successfully simulates the forward WGS rates and the coverages of adsorbed species under a range of reaction conditions (*16*). It is still unclear whether step (4) occurs directly as an elementary step, or instead via the "water-catalyzed" sequence:

$$H_2O_a + O_a \leftrightarrows 2\,OH_a \quad (4a)$$

$$H_a + OH_a \leftrightarrows H_2O_a \quad (4b)$$

$$\text{Net: } H_a + O_a \leftrightarrows OH_a. \quad (4)$$

Certainly this sequence is rapid enough to explain the observed kinetics (*3*), but it may not be as rapid as some single, direct step (4).

The kinetics of the reverse reaction are clearly complicated under our reaction conditions in that different reagents can become rate limiting depending upon the reactant pressure ratio and temperature. In general the rate is strongly positive order in H_2 and low order (or even slightly negative order) in CO_2 at low to moderate H_2/CO_2 ratios. At very high H_2/CO_2 ratios (>10), the rate approaches zero order in H_2 and approaches first order in CO_2. A simple interpretation of these observations consistent with the surface redox mechanism is as follows. At low or moderate H_2/CO_2 ratios the rate is limited by dissociative hydrogen adsorption (step 3); but, at very high H_2/CO_2 ratios, the rate is limited by dissociative CO_2 adsorption (step 1). However, this switch in reaction orders requires a H_2/CO_2 ratio well in excess of unity. This is rather surprising within the surface redox mechanism, since the dissociative adsorption probability for H_2 ($\sim 10^{-5}$ at 673 K (*14, 15*)) is several orders of magnitude larger than the dissociative adsorption probability for CO_2 ($\sim 10^{-8}$ at 673 K (*10*)) at least on clean Cu(110). This difference would normally result in a switch in the rate-limiting step at H_2/CO_2 ratios well below unity.

Another observation inconsistent with such a simple interpretation is the unusual dependence of the rate upon CO_2 pressure at 673 K and 110 Torr H_2 (Fig. 3), where the rate again becomes highly positive order in CO_2 as the CO_2 pressure is increased *after* a region of CO_2 pressure where the rate actually decreases with CO_2 pressure. Such behavior is not common in catalysis, but it can be understood if we postulate some sort of surface structural or phase transition involving a change in reactivity with respect to CO_2, which is triggered by a change in the H_2/CO_2 ratio.

Insight into a possible origin for this phase transition comes from a simple consideration of the hydrogen coverages we expect under our reaction conditions. The activation energy for dissociative H_2 adsorption on clean Cu(110) is 14.3 ± 1.4 kcal/mol with a preexponential factor of about one per H_2 collision with the surface (*14, 15*). These values indicate that the rate of hydrogen adsorption $R_{ad}^{H_2}$ is about 2×10^{18} molecules $cm^{-2}\ s^{-1}$ at 673 K and $P_{H_2} = 110$ Torr, at least when the coverage of adsorbed species is low. This rate is a factor of about 1000 greater than the rate of RWGS at the same conditions and $P_{CO_2} = 100$ Torr, which is about 2×10^{15} molecules $cm^{-2}\ s^{-1}$ (Fig. 3). This immediately implies that the coverage of some species is very high, or that the rate of hydrogen desorption (step (3)) is comparable to the rate of hydrogen adsorption, or both. The rate of hydrogen desorption is given by

$$R_{des}^{H_2} = \nu_{des}^{H_2} \cdot \exp(-E_{des}^{H_2}/RT) \cdot \theta_H^2, \quad (7)$$

where θ_H is the hydrogen coverage, $\nu_{des}^{H_2}$ is about $1.09 \times 10^9\ s^{-1}$, and $E_{des}^{H_2}$ is about 13 ± 1 kcal/mol (*3, 17, 18*). Combining this with the rate constant for hydrogen adsorption given above in a second-order Langmuir adsorption isotherm allows us to calculate that the hydrogen coverage would be about 20% of saturation and the adsorption and desorption rates of H_2 would both be about 1.9×10^{18} molecules $cm^{-2}\ s^{-1}$ if H_2 adsorption and desorption were in rapid equilibrium over Cu(110) at $P_{H_2} = 100$ Torr and 673 K. These rates are much larger than the RWGS rate at $P_{CO_2} = 100$ Torr, which is about 2×10^{15} molecules $cm^{-2}\ s^{-1}$.

This simple calculation shows that the hydrogen coverage is a substantial fraction of a monolayer under such reaction conditions and that the surface hydrogen is in rapid equilibrium with the gas phase H_2, provided no other species are present on the catalyst surface in concentrations sufficient to poison H_2 adsorption. Since the heats of adsorption of CO_2, H_2O, and CO are all rather small (*19, 20*), the coverages of these molecular adsorbates is undoubtedly below a few percent of a monolayer at 673 K and at the partial pressures of these species present during our RWGS reaction (*3*). The only remaining species in the mechanism which could be at high coverage instead of H_a is O_a and it is known not to significantly inhibit H_2 adsorption up to $\theta_o = 0.4$ (*21*). Thus, the H_a coverage must be a substantial fraction of a monolayer and in rapid equilibrium with H_2 gas under the RWGS conditions stated above.

Also, the reaction of $2H_a$ with O_a to produce H_2O (steps 4–6) occurs with near unit probability once an H_2 molecule dissociatively adsorbs, for all oxygen coverages above about one-tenth monolayer at 673 K (*15, 21*). This indicates that the O_a coverage under reaction conditions must be below one percent of a monolayer since the dissociative adsorption rate of H_2 is several orders of magnitude faster than the rate of H_2O production (which equals the rate of RWGS), and the H_a coverage is very high. Neither case is consistent with a high coverage of O_a, given the efficiency of steps (4)–(6).

To summarize, unless some other species exist that are not currently known or considered, the coverages of all adsorbed species in the mechanism must be below a few percent of a monolayer under reaction conditions except for adsorbed hydrogen, which must be at a coverage of ~20% of a monolayer. This high hydrogen coverage may result in a well-known (1 × 2) "missing-row" reconstruction on Cu(110) (*22, 23*). Such a reconstruction offers a plausible mechanism for the unusual dependences of the rate on H_2 pressure and CO_2 pressure seen in the two curves of Fig. 3 at 673 K. What is most unusual about these curves is that the dependence of the rate upon H_2 pressure becomes *weaker* and its dependence upon CO_2 becomes *stronger* when the CO_2 pressure is increased (in the high CO_2 pressure regime). This can be understood based on a H_a-induced reconstruction to a surface phase of Cu(110) which is *more* reactive with respect to dissociative CO_2 adsorption. This more active phase is associated with higher hydrogen coverage. Since H_a can be removed both by recombinative desorption and by reaction with O_a, the H_a coverage will be to some small extent controlled by the RWGS reaction rate, with a higher rate leading to lower H_a coverage. Thus an increase in the CO_2 pressure at fixed P_{H_2}, which results in an increase in the rate, could also trigger the reconstruction of the surface from the more active (higher θ_H) phase to the less active (lower θ_H) phase. Surface phase transitions are well known to cause changes in surface reactivity (*25*). For example, the phase transition from the H-induced (1 × 3) reconstruction to the (1 × 2) reconstruction on Cu(110) decreases the reactivity of the surface for molecular adsorption of water (*24*).

This phase transition could explain the odd CO_2 pressure dependence in Fig. 3 at 673 K and 110 Torr H_2. Starting at low P_{CO_2}, the rate is nearly limited by the rate of dissociative CO_2 adsorption and therefore very high order in CO_2. Here the reaction is occurring on the high θ_H phase, which is more active for CO_2 dissociation. As P_{CO_2} increases, the rate increases and θ_H correspondingly decreases until θ_H drops below some critical coverage $\theta_{H,cr}$, where the surface reconstructs (or lifts the reconstruction) to the phase that is less active for CO_2 dissociation. Therefore the rate drops with increasing P_{CO_2} over some narrow range where the reconstruction takes place across the surface. After the reconstruction (or deconstruction) is completed, the rate should again increase nearly linearly with increasing CO_2 pressure, since the rate is nearly limited by CO_2 dissociation. This is indeed observed in the region of the highest CO_2 pressures, where the rate is again very high order in CO_2 pressure. Here, however, the reaction probability (per CO_2 collision) is lower than in the region of very low CO_2 pressure since now the reaction is proceeding on the low θ_H phase characterized by lower reactivity with respect to CO_2. We have postulated here that the necessary phase transition might be associated with the known H_a-induced (1 × 2) → (1 × 1) phase transition of Cu(110). However, it might also be changing from the (1 × 2) or the (1 × 1) to some other phase that is not observable under UHV conditions.

An appealing aspect of this mechanism is that the observed activation energies for RWGS under both conditions of Fig. 3 (where the rate is nearly limited by CO_2 pressure) is very close to the known activation energy of CO_2 dissociative adsorption on Cu(110) of 16 kcal/mol (*10*). The latter value was, unfortunately, measured in the absence of any H_a and at low but measurable coverages of O_a, so it might not be too directly comparable here, especially in the region of high H_2/CO_2 ratio. An even more appealing feature of this model is the fact that the absolute rate of dissociative adsorption per CO_2 collision (or reaction probability) measured on Cu(110) at low θ_o, which is about 1×10^{-8} at 673 K (*10*), is almost the same as the RWGS rate per CO_2 collision of about 2×10^{-8} measured in the low H_2/CO_2 pressure ratio regime of Fig. 3 (i.e., at 673 K and $P_{CO_2} > 100$ Torr), where the surface phase is in the less active phase characteristic of low θ_H. (This factor of two difference could easily be due entirely to various errors in measuring or absolute calibration of rates.)

We feel that this favorable comparison of activation energies and absolute rates per CO_2 collision over Cu(110) in this region also offers the best available evidence to date that the WGS reaction over Cu catalysts proceeds via the surface redox or oxygen adatom mechanism proposed above.

The phase transition suggested in Fig. 3 at 673 K and 110 Torr H_2 is not so obvious in the rate data at higher H_2 pressure or at lower temperature. It is not surprising that it is not seen distinctly below 800 Torr CO_2 at 760 Torr H_2 since a higher CO_2 pressure should be required to trigger this "active" → "less active" phase transition at higher H_2 pressure. It is perhaps not seen at lower temperatures since the CO_2/H_2 ratio needed to achieve the critical hydrogen coverage for this transition might obviously be temperature dependent. Of course, the critical hydrogen coverage itself might be temperature dependent.

According to the above model, the RWGS rate approaches zero order or slightly negative order in CO_2 pressure only because the changing CO_2/H_2 ratio changes the H_a coverage and thereby triggers an active → less active phase transition, and not because the coverage of any CO_2-derived species begins to saturate. Such CO_2-derived species might potentially have been O_a, $CO_{2,a}$, or a surface O–CO_2 complex related to surface carbonate. We argued above that the coverages of O_a and $CO_{2,a}$ must be below a few percent of a monolayer, and therefore too low to cause such kinetic changes. A surface carbonate or O–CO_2 complex, such as is easily observed on Ag surfaces (*26*), could not be produced on Cu(110) without added alkali (*19*), but it may also exist on Cu powder (*9*) or on Cu/ZnO catalysts (*27*). In the absence of any distinct evidence for such a species on Cu(110), we do not postulate a carbonate of any kinetic importance here.

Also, since the RWGS rate is, according to our model, largely controlled by the rate of CO_2 dissociative adsorption under all conditions examined here, the large positive orders with respect to H_2 seen at certain conditions is *not* because the rate is limited by H_2 adsorption, but instead because the H_2 pressure increases the H_a coverage, which in turn increases the surface reactivity with respect to CO_2. This nonlinear phenomenon easily explains the fact that the reaction is nearly *second* order in H_a at very low P_{H_2} (Fig. 4). The rate only becomes zero order in H_2 at very high H_2/CO_2 ratios, where, according to our model, the surface is already fully reconstructed to the more active phase.

We should emphasize that we present no direct evidence for the postulated H-induced phase transition occurring under our reaction conditions. Thus, this model to explain the kinetics is only a tentative one. It would be very interesting to probe the surface condition *in situ* during the reaction with some method that might be sensitive to such a reconstruction or to the H_a coverage. Other structural or compositional changes in the surface induced by changes in the CO_2/H_2 ratio might also prove to cause these unusual kinetic effects.

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Note Added in Proof. Taylor *et al.* [28] have recently shown that adsorbed formate ($HCOO_a$) can be produced on Cu(100) from high pressures of H_2 and CO_2. The decomposition rate of this species is, however, so fast [29] that its coverage should be very low under our reaction conditions, so it should not affect the rate of CO_2 dissociation here.

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