Research paper

Productivity and order versus the superficial behavior of the prox reaction on a copper-ceria catalyst Monte Carlo simulations

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ABSTRACT

Monte Carlo simulations for the productivity and order of the PROX/copper-ceria catalyst reaction with different superficial %Cu are made. The results are correlated with the behavior of the different surface species (CO, H, O, OH, vacancies) during the process. Among other results, an inversion is seen of the production of CO_2 with respect to that of H_2O with the increase of %Cu, a positive order for CO_2 with at low C_{CO}, and with C_{O2} if it is low, a positive order for H_2O with C_{O2} only if %Cu is high, and zero order with C_{H2} in all cases.

1. Introduction

Traditionally, the catalytic reaction of CO (CO/O_2 reaction), forming part of so-called three-way catalysts (TWCs) in automobiles, important because of the serious pollution problems, has used supported noble metals (Rh, Pt, Pd) [1]. Recently Cu has been used with good results [2], with CeO_2 as promoter related to a synergic effect of the system's redox properties. This has been of great interest in the preferential oxidation of CO (PROX reaction), which has gained renewed importance because of the growing interest in fuel cells due to their potential use in vehicles in place of internal combustion engines [3]. Monte Carlo simulations are a good way to study the link that there is between productivity and the behavior of the surface phases that coexist in a catalytic reaction. A good example of this is the PROX reaction, which will be studied in this paper.

It is interesting to mention a number of relevant works that have studied various aspects of these reactions in recent years. Semak et al. [4] studied the CO/O_2 reaction using a nanostructured copper-ceria catalyst when the O_2 is supplied from the gas phase, continuing the work of Martínez Arias on the same system [5], and in the case in which the O_2 is supplied from the gas and the bulk of the catalyst [6]. In relation to the present work there are also three aspects of the literature that should be mentioned: X-ray studies made by Polster et al. [7] and density functional

calculations developed by Wang et al. and the Martínez Arias group [8] helped us design the surface of the catalyst assuming that the support was identical to those of pure fluorite CeO_2. In relation to the mechanism of the reaction, it is necessary to mention the work of Martínez-Arias et al. [5] on the redox properties of the CO/O_2 reaction on copper-cerium catalysts, and that of Polster et al. [7] in the case of the PROX reaction. Furthermore, this work of Polster et al. [7] together with that of Marbán and Fuertes [9] and Ayastu et al. [10] provided experimental information on the PROX reaction on copper-ceria catalysts that was useful for the present work.

In a recent paper from our laboratory [11], a kinetic Monte Carlo simulation algorithm was developed for the PROX reaction on the nanostructured copper-ceria catalyst, confirming a series of published experimental results for this system and also giving a microscopic view of the process. For example, maximum CO_2 production at a temperature T was seen, with an increase at low T before water production appears, and a decrease at higher T when water production increases. A similar behavior of production is seen when the proportion of copper on the surface of the catalyst is varied, with a shift of the temperature corresponding to the maximum. As a continuation of our previous work, this last aspect is discussed in depth in the present paper, where we study the order of this reaction with respect to the various components of the gas phase and correlate it with the behavior of the species found on the surface of the catalyst. We have carried out this analysis by simulating a series of catalysts that have different proportions of surface copper.

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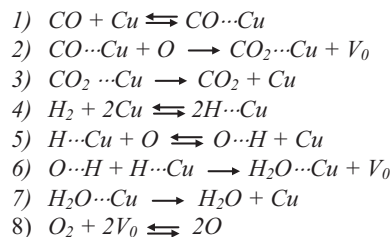
2. Monte Carlo simulation

The catalyst's surface was simulated as we had reported previously [11,12], assuming that it consists of the (1 1 1) crystal face, which is experimentally the most frequent one of cerium oxide CeO_2 and is shown in Fig. 1. As we have explained previously [12], on the surface we have modeled the localization of the copper atoms with a random distribution of these sites occupying all the holes or a fraction of those unoccupied by the cerium atoms exposed to the surface. This is the natural way of localizing these sites if the experiments and conclusions of Polster et al. [7] are considered: the methods of synthesis of the catalyst, e.g., co-precipitation to obtain a high degree of mixing between the CuO and CeO_2 phases, as well as its characterization. The choice of a random distribution of the Cu atoms also allows relating directly some results with the surface coverage.

Although in the literature we can find some experimental results for this reaction [7,9,10], the same is not true for the analysis of this system's mechanism. The mechanism used in this paper, which we adapted for use in the previous paper [11] to explore its consequences on the kinetic behavior of the system through MC simulations and is shown in Scheme 1, corresponds basically to an interesting general scheme for this reaction proposed by Polster et al. [7], who consider two irreversible reactions and six reversible reactions which allow them to make a mean field calculation of the kinetics equations. In the construction of the Monte Carlo of this paper we have assumed the additional approximations of considering steps (3) and (7) irreversible. These approximations are reasonable if low relative pressures of CO_2 and H_2O in the gas phase are considered as a result of the production. These approximations are usual for similar systems in the literature.

The simulation process begins by selecting an event of the mechanism (adsorption, reaction, or desorption) according to the probability of the event defined by

$$p_i = \frac{k_i}{\sum k_i}$$

where k_i is a function of the rate constant of step i of the mechanism. The other details of the kinetic MC simulation algorithm for the PROX reaction on a copper-ceria catalyst were reported previously [11]. The kinetics constants used were the same as those of the previous paper [11] and they are given below.

1) $CO + Cu \rightleftharpoons CO\cdots Cu$
2) $CO\cdots Cu + O \longrightarrow CO_2\cdots Cu + V_0$
3) $CO_2 \cdots Cu \longrightarrow CO_2 + Cu$
4) $H_2 + 2Cu \rightleftharpoons 2H\cdots Cu$
5) $H\cdots Cu + O \rightleftharpoons O\cdots H + Cu$
6) $O\cdots H + H\cdots Cu \longrightarrow H_2O\cdots Cu + V_0$
7) $H_2O\cdots Cu \longrightarrow H_2O + Cu$
8) $O_2 + 2V_0 \rightleftharpoons 2O$

Scheme 1. Mechanism of the PROX/copper-ceria catalyst reaction used in the simulations. CO···represents CO and H··· is H adsorbed on copper; Cu represents copper that can or cannot have an adsorbed particle; and V_0 is a vacant site on the surface.

The step's rate constants k_1, k_4, and k_8, that involve the adsorption of gas A, (where A can be CO, H_2, or O_2), were calculated from the expression of the kinetic theory of gases:

$$k_i = S_A\sigma(2\pi M_A RT)^{-1/2}P_A$$

where M_A is the molecular mass of A, the coefficient σ is the area occupied by one mole of active sites, P_A is the pressure of gas A, and T is the temperature. For the sticking coefficients of CO and O_2 use was made of those for Pt from reference [13] (S_{CO} = 1 and S_{O2} = 0.03), while the sticking coefficient of H_2 (S_{H2} = 0.01) was the result of a fitting with the experiment. Table 1 shows the frequency factors and activation energies of the rest of the rates constants assuming that the Arrhenius equation is valid. As indicated in the table, some of these parameters have been extracted from the literature and others have been adjusted using the experimental information published by Polster et al. [7] with the purpose of getting kinetic values, for example productivity, with reasonable orders of magnitude to analyze the system's microscopic behavior through Monte Carlo simulations.

3. Results and discussion

In this paper the order of the PROX reaction over a copper-ceria catalyst with respect to the gas phase species (CO, O_2, H_2) with different copper proportions (%Cu) has been determined by Monte Carlo, correlating those results with the behavior of the species on the catalyst's surface (CO, H, O, OH) and the vacancies in the lattice. As experimentalists well know, the order is in general a func-
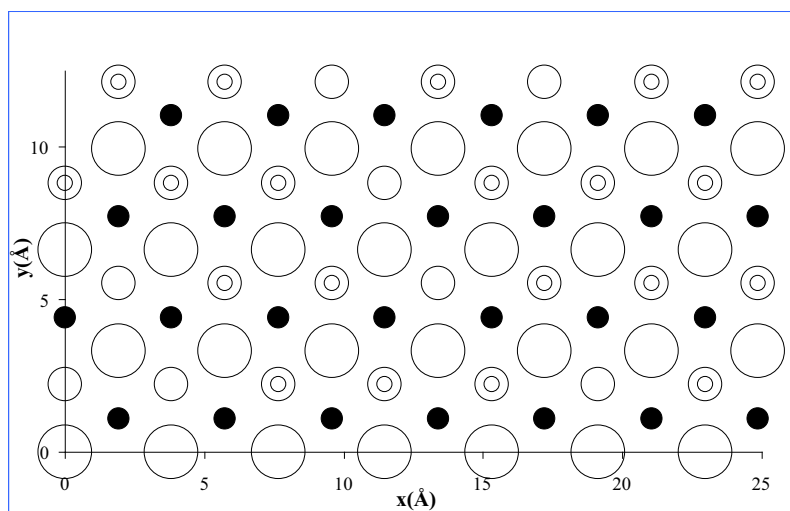

Fig. 1. Model of the catalyst's surface (face (1 1 1) of CeO_2) used in the Monte Carlo simulations: (○) oxygen, (●) cerium, (○) site that can contain copper; ◎ site that contains copper.

Table 1
Kinetics parameters used in the paper.

	Frequency factor (s^{-1})	Activation energy Ea (cal mol^{-1})
k_{-1}[a]	10^{13}	142.2
k_2[b]	6.69	13.3
k_3[a]	10^{13}	71.1
k_{-4}[b]	10^{13}	142.3
k_5[a]	$1.7*10^{10}$	50.6
k_{-5}[a]	$5.6*10^{11}$	102.1
k_6[b]	$3.5*10^8$	79.5
k_7[b]	10^{13}	58.6
k_{-8}[b]	10^{13}	146.4

[a] Ref. [13].
[b] Ajuste experimental.

tion of the concentrations interval of the gas phase. Here we have chosen a number of examples with intervals that we believe have some experimental interest, but they are also aimed at representing a general understanding of the phenomenon. The results are discussed here, and some representative examples are shown in the figures that follow.

If the temperature is sufficiently high, like that chosen for this work (515 K) and the gas phase concentrations are those that appear in Table 2, it is seen that the production of CO_2 (R_{CO2}) is much higher than that of water (R_{H2O}) if %Cu is low. This situation is reversed if %Cu increases. The increase of R_{H2O} with the subsequent decrease of R_{CO2} as %Cu increases can be explained because according to the reaction mechanism two neighboring copper

Table 2
Production of CO_2 and H_2O, and CO and H coverage versus the percentage of copper at 515 K and different gas phase concentrations $C_{H2} = 0.5$ $C_{CO} = 0.01$.

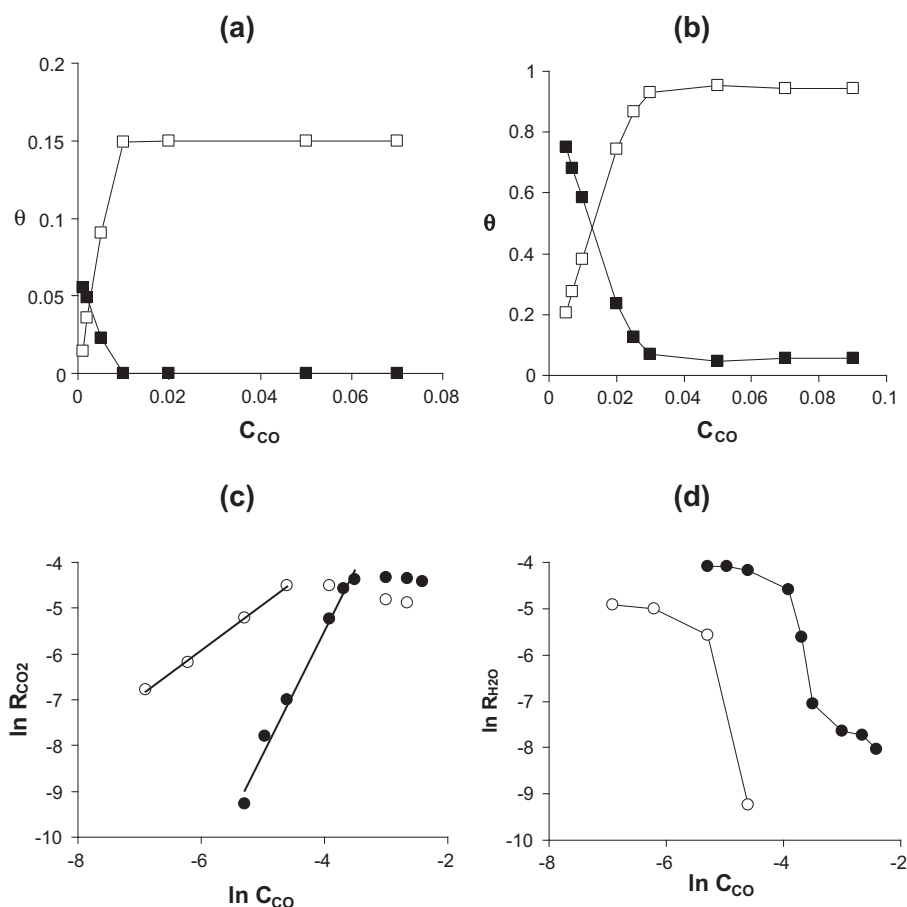| %Cu	R_{CO2}	R_{H2O}	θ_{CuCO}	θ_{CuH}	
15	0.011	0.0001	0.15	$2*10^{-4}$	$C_{O2} = 0.005$
36	0.0076	0.0068	0.26	0.07	
50	0.0052	0.0104	0.30	0.16	
100	0.0009	0.015	0.38	0.59	
15	0.013	0.0062			$C_{O2} = 0.01$
36	0.009	0.022			
50	0.007	0.027			
100	0.0016	0.032			

Fig. 2. Surface coverage, CO_2 and H_2O production as a function of CO concentration, C_{CO}, with fixed H_2 and O_2 concentrations $C_{H2} = 0.5$, $C_{O2} = 0.005$ at 515 K. (a) Surface coverage for 15% Cu θ_{CuCO}(□), θ_{CuH} (■). (b) The same as (a) for 100% Cu. (c) CO_2 production for 15% Cu(○), 100% Cu(●). (d) The same as in (c) for H_2O production.
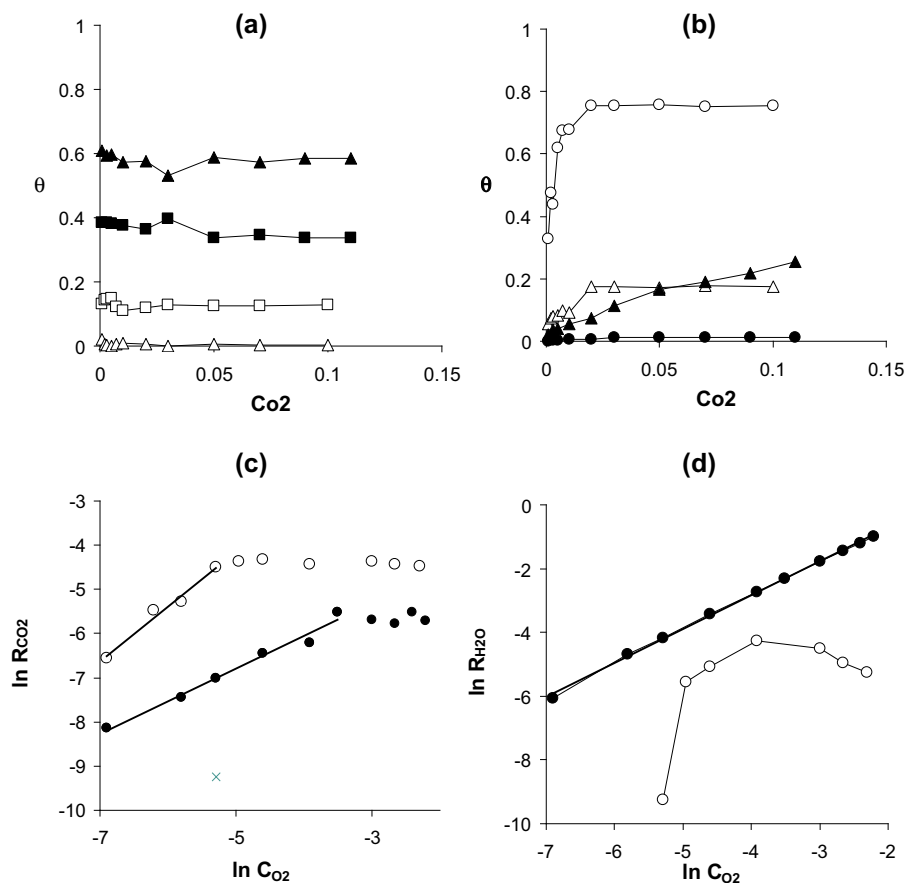
Fig. 3. Surface coverage, CO_2 and H_2O production as a function of O_2 concentration, C_{O2}, with fixed H_2 and CO concentrations $C_{H2} = 0.5$, $C_{CO} = 0.01$ at 515 K (a) surface coverage θ_{CuCO} (15% Cu($\square$), 100% Cu($\blacksquare$)), θ_{CuH} (15% Cu($\triangle$), 100% Cu($\blacktriangle$)). (b) Surface coverage θ_O (15% Cu($\bigcirc$), 100% Cu($\bullet$)), θ_{CuOH} (15% Cu($\triangle$), 100% Cu($\blacktriangle$)). (c) CO_2 production for 15% Cu ($\bigcirc$), 100% Cu($\bullet$). (d) The same as in (c) for H_2O production.

atoms are required on the surface for the dissociative adsorption of H_2 to take place, and only one copper atom for the adsorption of CO. This is reflected in the behavior of the coverage with the hydrogen and carbon monoxide surface species, whose corresponding inversion is shown with an example in Table 2, where it is seen that $\theta_{CuCO} \gg \theta_{CuH}$ for low %Cu and $\theta_{CuCO} < \theta_{CuH}$ for high %Cu.

If we include the effect of the variation of the concentration of gaseous CO, C_{CO}, it is seen that the curves corresponding to θ_{CuCO} and θ_{CuH} versus C_{CO} cross, and this is shown in Fig. 2 for two %Cu values. This means that for all %Cu, if C_{CO} is high the surface is poisoned with CO (even if the H_2 concentration is high) and R_{H2O} decreases until it vanishes. This is reflected in a positive reaction order for R_{CO2} until R_{H2O} is zero and the process does not depend on the later increase of C_{CO}. At the other extreme, for low C_{CO} values, CO_2 production decreases and R_{H2O} is independent of C_{CO}.

If we study the effects of the variation of the oxygen in the gas phase for different %Cu, various interesting situations are seen with various orders in different cases. Polster et al. [7] made a simplified analysis of his model using an adjustment that made it independent of temperature, finding an order close to zero for both R_{CO2} and R_{H2O} with oxygen concentration, C_{O2}. However, in that study he considered C_{O2} values greater than those of our work, so it is reasonable that production does not depend on C_{O2}. In the situation studied here, which is shown in Fig. 3, if % Cu is low (e.g., 15%) and C_{O2} is very small ($C_{O2} \to 0$), the surface

is sufficiently poisoned with CO for the small amounts of superficial hydrogen and oxygen to be unable to produce water ($R_{H2O} \to$ 0), and an positive reaction order is observed for R_{CO2} up to a C_{O2} above which the reaction order is equal to zero. If the %Cu is greater (e.g., 100%), a strong increase in the surface coverage with hydrogen is seen that results in a positive order of both R_{CO2} and R_{H2O} with C_{O2}.

The system's behavior with the hydrogen concentration C_{H2} in the gas phase is shown in Fig. 4, with a general reaction order close to zero in all the cases within the interval of C_{H2} values studied. This is explained by the high concentrations of C_{H2} with respect to C_{CO} and C_{O2}. However, these concentrations have been chosen because they correspond to magnitudes of interest for the experiment in the case of this reaction. For low C_{H2}, however, an increase in CO_2 production and a negative order of H_2 is seen for the production of CO_2 because the dissociation of H_2 allows a competition of the surface CO and H as shown by the case of 100% Cu.

Since in the literature there are only experimental data that provide one order of magnitude of the system's activity, the only way of making a Monte Carlo study of it is by determining a set of k_i that are approximately coherent with this order of magnitude. This inevitably limits the results of the simulation by considering in the study the catalytic surface through its geometry established in the simulation and not by its effect on the k_i constants. Therefore, in certain aspects the results are necessarily approximations in relation to some characteristics of the surface such as the percentage of copper in the catalyst, for example.
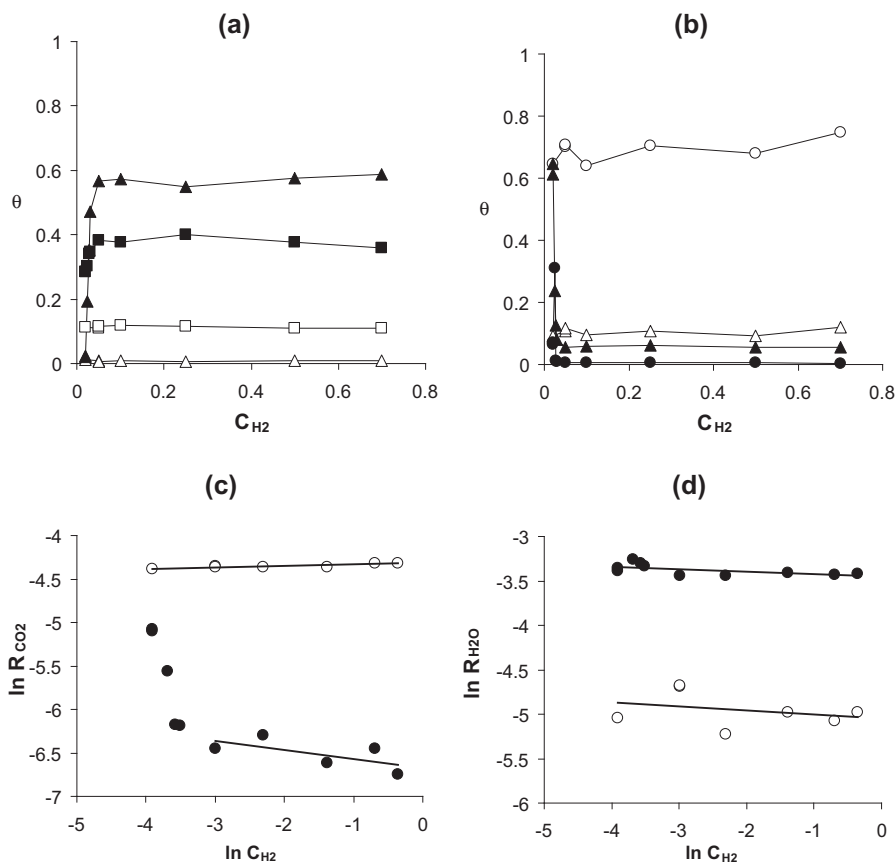
Fig. 4. Surface coverage, CO_2 and H_2O production as a function of H_2 concentration, C_{H2}, with fixed CO and O_2 concentrations $C_{CO} = 0.01$, $C_{O2} = 0.01$ at 515 K. (a) Surface coverage θ_{CuCO} (15% Cu($\square$), 100% Cu($\blacksquare$)), θ_{CuH} (15% Cu($\triangle$), 100% Cu($\blacktriangle$)). (b) Surface coverage θ_O (15% Cu($\bigcirc$), 100% Cu($\bullet$)), θ_{CuOH} (15% Cu($\triangle$), 100% Cu($\blacktriangle$)). (c) CO_2 production for 15% Cu($\bigcirc$), 100% Cu($\bullet$). (d) The same as in (c) for H_2O production.

4. Conclusions

(1) The reaction order, except in the elemental stages, is an empirical parameter which, without having a concrete physical meaning, constitutes a practical form which, even disregarding knowledge of the reaction mechanism, allows experimentalists to analyze their results through the behavior of the system with the reactants' interval and magnitude. In this case the reactants in the gas phase (CO, O_2, H_2) correspond to the PROX reaction over a copper-ceria catalyst, where it has also been possible to observe that the order of the catalytic experiment is directly related to the behavior of the surface species during the process. The most relevant results obtained in relation to the reaction order are the following:

(a) The order of CO with respect to the production of CO_2 is positive at low C_{CO}, turning to zero order if C_{CO} growth regardless of the CO reactant for both Cu percentages (15% and 100%). This is explained by the behavior of the surface species during the process that shows a competition between the surface CO and H until the surface is poisoned with CO.

(b) A positive O_2 order for the production of both CO_2 and H_2O if %Cu is high shows that H can compete with surface CO when there are sufficient neighboring Cu to allow the dissociation of the H_2 on the surface.

(c) If on the other hand the %Cu is low, so there are few neighboring Cu, a positive order for O_2 is found, which turns to zero order for high C_{O2} for the production of CO_2 when the surface is poisoned with oxygen. In this case no order is seen for O_2 for the production of H_2O.

(d) The order of H_2 is generally zero for the production of CO_2 and H_2O at both %Cu (15% and 100%), because C_{H2} was chosen high because this value is of interest in the experiment. However, if C_{H2} is sufficiently low and %Cu is high, a negative order of H_2 is seen for the production of CO_2 because the dissociation of H_2 allows a competition of the surface CO and H.

(2) An inversion of the production of CO_2 (R_{CO2}) with respect to the production of H_2O (R_{H2O}) with increasing %Cu ($R_{CO2} \gg R_{H2O}$ at low %Cu and $R_{CO2} \ll R_{H2O}$ for high %Cu) is obtained, because two neighboring Cu and only one CO are required for the dissociative adsorption of H_2. This inversion agrees with that of the surface CO and H species, leading to $\theta_{CuCO} \gg \theta_{CuH}$ for low %Cu and $\theta_{CuCO} < \theta_{CuH}$ for high %Cu.

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