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

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-

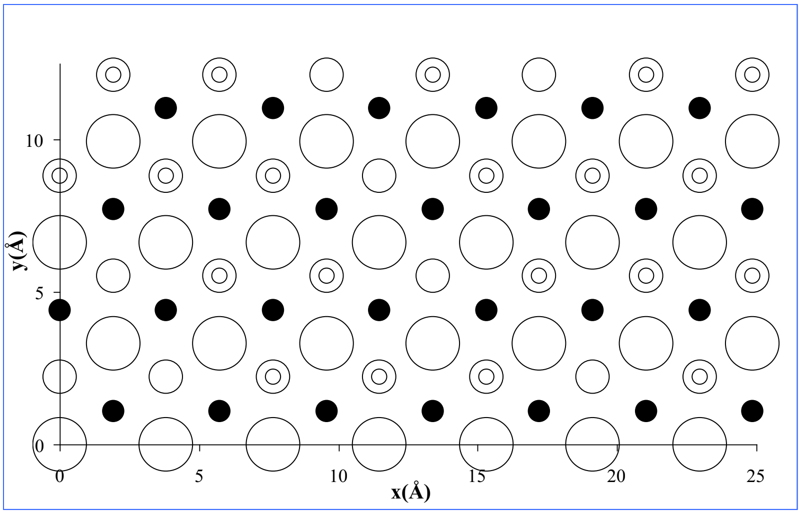

Fig. 1. Model of the catalyst's surface (face (1 1 1) of CeO_2) used in the Monte Carlo simulations: (○) oxygen, (●) cerium, (○) site that can contain copper; ◎ site that contains copper.