Catalysis Today 144 (2009) 324–333

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Catalytic oxidation of CO on CuO_x revisited: Impact of the surface state on the apparent kinetic parameters

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ARTICLE INFO

Article history:
Available online 23 January 2009

Keywords:
Catalytic oxidation of CO
Copper oxides
Defect active sites

ABSTRACT

Analysis of kinetic features of the copper oxides reduction by CO pulses as related to mechanism of CO catalytic oxidation by oxygen combined with monitoring the state of the surface by an electrochemical technique using a solid electrolyte—Pyrex glass and high resolution TEM data on the defect structure of CuO allowed us to suggest a partially "flexible" model of CuO surface. This model, with a due regard for the data of FTIR spectroscopy of adsorbed CO test molecules, assigns the most active surface sites able to coordinate highly reactive CO and O forms to clusters of Cu^+ cations located at outlets of extended defects (dislocations, twins). Variation of the number, size and structure of these clusters under the reaction medium effect allows explaining the difference between quasi-steady and true steady states of copper oxides in catalytic CO oxidation reaction as well as the difference between kinetic parameters of reaction estimated at quasi-steady and constant states of the surface following Boreskov's approach. Kinetic features of the reaction agree with the Langmuir–Hinshelwood reaction mechanism operating for clustered defect centers of CuO.

1. Introduction

Investigation of the kinetics and mechanism of catalytic CO oxidation on transition metal oxides, including copper oxides, has relatively long history [1–4]. They still attract significant interest [5], particularly due to the problem of hydrogen purification from CO impurities [6–8]. In most recent reviews the important role of defect sites in the surface chemistry of both metals [9] and oxides [10–12] is discussed. Specific features of the reaction mechanism are also intimately related to the structure of active sites at the atomic-molecular level. For example, Red-Ox Mars-van Krevelen (MVK) mechanism usually involves the formation and filling of anionic oxygen vacancies on the oxide surface. Langmuir–Hinshelwood (L–H) mechanism assumes that low-coordinated adjacent metal atoms forming metal–metal bonds are present in the adsorption layer [8,9].

However, experiments carried out on single crystals of metal oxides are very limited and cannot "distinguish the chemistry of defect sites as their population and variety are deliberately manipulated" [11]. This is largely related to the existing limitations in the sensitivity of modern physical methods that do not allow for determining the structure and electronic state of elements at nanoscopic level, especially at the background of bulk oxides with the same chemical composition [11,12]. Additional factors limiting the application of kinetic methods in investigating the chemistry of surface defects are, in our opinion, relatively rough estimates of the reactivity of oxide single crystals because the small geometric surface area considerably constrains the capabilities in differentiating the surface properties of single crystals, varying the concentration of defects and applying non-steady-state methods, especially with realistic concentrations of reagents (well-known "pressure gap" problem).

For highly dispersed copper oxides, some data on comparison of the rates of catalytic oxidation reactions with the rates of separate steps of reaction mechanism were published [13–15]. For Cu_2O, the rate of complete oxidation of 1-hexene was compared to that of the carbonate–carboxylate complexes decomposition [13]. An "associative" mechanism of CO oxidation on CuO was suggested by Boreskov and Marshneva [14] on the basis of much lower rates of the catalyst reduction by CO as compared with the rate of catalytic reaction, in general agreement with the earlier conclusions of Roiter [15] and Fesenko et al. [16] as well as the later results of Rozovskii et al. [17]. However, the absence of any information on the real/defect structure of studied samples of CuO (not speaking about any control of its variation under the reaction media and its component effect) results in contradictory conclusions about the detailed mechanism of this reaction.

In the current study we aimed to elucidate specific features in the chemistry of defect sites on oxide surfaces using several types

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doi:10.1016/j.cattod.2008.12.018

of bulk and SiO_2-supported copper oxide catalysts. The following approaches were used:

(A) Pulse techniques applied to finely dispersed oxides with high surface areas made it possible to introduce minimum perturbations to the state of the oxide surface while measuring the reaction kinetic parameters.
(B) The regularities of oxide reduction were first studied in detail in the pulse mode. This approach made it possible to analyze the dependence of catalytic activity on the phase composition and reduction degree of separate phases of Cu–O systems.
(C) The structures of extended defects in CuO were analyzed on the basis of high resolution transmission electron microscopic data and simplest models of active sites at their surface outlets.
(D) Specific features of the catalytic reaction kinetics in quasi-steady and true steady states of the copper oxide surface and the surface chemistry during pulse reduction were elucidated.
(E) The state of the surface was monitored by an electrochemical method using glass cation-conducting electrolyte [18]. The electrochemical methods of solid electrolyte potentiometry are rather informative in analyzing the surface properties of oxides under contact with reaction mixture, although cells based on oxide conducting electrolytes are used more widely [19].

2. Experimental

Several types of bulk copper oxides prepared by different methods were used in the study. "Nitrate" CuO was prepared by thermal decomposition of copper nitrates at 500 °C (specific surface area (SSA) = 0.40 m^2/g). "Wire" CuO (VEB Laborchemie Apolda) was prepared by oxidizing copper wire (SSA = 0.10 m^2/g). Cu_2O was synthesized from "nitrate" CuO by annealing in helium at 1000 °C (SSA = 0.15 m^2/g). Copper oxides with higher surface areas were used for non-steady-state experiments. "Hydroxide 1" CuO was prepared by precipitating from copper nitrate solution with NaOH followed by washing from sodium ions and calcination at 500 °C (SSA = 8.6 m^2/g). "Hydroxide 2" CuO was prepared by precipitating from copper nitrate solution with NaOH followed by washing from sodium ions and calcination at 500 °C under slightly different precipitation and drying conditions (SSA = 16.0 m^2/g). The concentration of impurities in the metal oxides did not exceed 0.1 wt.%. Supported CuO_x/SiO_2 (10 wt.% CuO) sample was prepared by impregnating A-300 aerosil (SSA = 300 m^2/g) with copper nitrate solution followed by calcination at 500 °C.

Kinetic studies were carried out in a pulse/flow catalytic installation in a glass reactor with a fluidized catalytic bed following the experimental procedures earlier described in detail [3,18,20]. Specific design of this kinetic installation equipped with several lines fed by gas streams of various compositions allowed us to supply into reactor the pulses of reagents with different compositions at a minimum (up to 1 s) time lag between pulses.

In the majority of experiments considered in this paper, the carbon imbalance was less than 10% rel. A bigger imbalance was observed in pulse experiments carried out at 25 °C (vide supra) due to readsorption of a part of CO_2 yielding carbonate–carboxylate surface complexes.

At temperatures exceeding 140 °C, continuous monitoring of the surface state of bulk oxides was carried out using an electrochemical method [3,18,21]. A thin wall of the working zone of specially designed Pyrex reactor served as a solid electrolyte, while a gold spiral contacting both the internal surface of the reactor wall and the powdered CuO catalyst (working electrode) served as catalytically/electrochemically non-active current collector. At the external reactor wall, Pt spiral covered with the Ag/AgO_x layer and purged by pure oxygen supplied into the shell surrounding the microreactor served as a reference electrode. From the measured values of the potential difference in this cell with a due regard for the asymmetry potential as described in details elsewhere [3], the oxide electrode potential E^* was estimated. This parameter is determined by the surface oxygen chemical potential (heat and entropy of adsorption) and Gibbs energy of oxide formation (Eq. (1)) [3,18,21]:

$$E* = \frac{1}{2F}[\mu O_{CuO_{1-\delta}} - 1/2\mu^0 O_2] - \frac{1}{2F}[\Delta G^0_{T\,CuO_{1-\delta}} - \Delta G^0_{T\,\text{“CuO”}}] + \Delta, \quad (1)$$

where F is the Faraday number, μ is the chemical potential, $\Delta G^0_{T\,CuO_{1-\delta}}$ and $\Delta G^0_{T\,\text{“CuO”}}$ are the standard thermodynamic potentials for the formation of a studied non-stoichiometric phase and a reference stoichiometric phase, respectively, and Δ is an increment characterizing the properties of copper cations incorporated into the surface layer of solid electrolyte and close to 0 for Cu–O system [3].

The rate of surface oxygen reduction by CO pulses was described by the kinetic equation $v = k p_{CO}^{0.5}(1-\theta)L$, where k is the reaction rate constant ($s^{-1}\,Pa^{-0.5}$), p_{CO} is CO partial pressure (Pa), θ is the surface reduction degree, and L is specific concentration of oxygen atoms in the monolayer (atoms/m^2). The diffusion flow rate of oxygen atoms from the bulk of the catalyst to the surface layer was characterized using equation $v_d = k_d \theta L$, where k_d is a constant (s^{-1}) [20].

A mathematical model of reactor with a fluidized catalyst bed was constructed assuming that the reaction takes place under ideal mixing conditions and reaction mixture follows the ideal gas law. Pressure and temperature in the reactor were assumed to be constant. Then, the mathematical model taking into account the balance of oxygen atoms on the surface and CO molecules in the gas phase would look as follows:

$$\frac{d\theta}{dt} = k_1 y^{0.5}(1-\theta) - k_d\theta, \quad (2)$$

$$\frac{dy}{dt} = \frac{Q}{V_R}(1-y) - k_1 y^{0.5}(1-\theta)\frac{LGS}{N_A V_R C_{CO,0}}, \quad (3)$$

$$p_{CO} = C_{CO} RT, \quad (4)$$

$$t = 0 : \theta = 0, y = 0. \quad (5)$$

Here $y = C_{CO}/C^0_{CO} = p_{CO}/p^0_{CO}$ is the molar fraction of CO in a pulse in the reactor, p^0_{CO}, p_{CO} are partial CO pressures at the reactor inlet and outlet, respectively, t is time, Q is the feed volume flow rate under experimental conditions (cm^3/s), V_R is the reactor volume (cm^3), $N_A = 6.023 \times 10^{23}$ is the Avogadro number (mol^{-1}), T is the reactor temperature (K), G is the catalyst weight, S is the catalyst specific surface area (m^2/g), and $k_1 = k p^{0.5}_{CO,0}$. This fractional CO order for CuO reduction was earlier revealed by Rozovskii and co-workers [22].

System (1)–(4) was numerically integrated with double precision using an explicit forth order Runge-Kutt-Merson with automatic choice of the step length. The acceptable error varied in the range of 10^{-8}–10^{-10}. The experiments and corresponding calculation were carried out using the following parameters: G = 0.5 g; S = 0.1 m^2/g; V_R = 1.7 cm^3; Q = 1.537 (cm^3/s); p^0_{CO} = 100 Pa and p^0_{CO} = 23 Pa; T = 458 K. The value of coefficient k_d = 0.014 s^{-1} was estimated from the reduction rate values at the minimum point (Fig. 1b). The average reaction rate constant k_1 was estimated without using any algorithm. At p^0_{CO} = 100 Pa, k_1 = 0.155 s^{-1}; at p^0_{CO} = 23 Pa, k_1 = 0.074 s^{-1}.