JOURNAL OF CATALYSIS **165,** 279–283 (1997)
ARTICLE NO. CA971528

LETTER TO THE EDITOR

Comment on "Carbon Monoxide Oxidation over Three Different Oxidation States of Copper: Metallic Copper, Copper (I) Oxide, and Copper (II) Oxide—A Surface Science and Kinetic Study" by G. G. Jernigan and G. A. Somorjai

Recently, Jernigan and Somorjai (1) have studied catalytic CO oxidation on thin films of metallic copper, copper (I) oxide, and copper (II) oxide grown on graphite using a high-pressure static batch reactor connected to a UHV chamber. The composition and oxidation state of copper were monitored by XPS and AES analysis. In the temperature range 200–350°C, the authors found the next order of activity $CuO < Cu_2O < Cu$, activation energy varying contrariwise. For all phases but CuO, CO oxidation was shown to be described with the Langmuir–Hinshelwood (LH) model. For copper (II) oxide, a redox cycle mechanism between CuO and Cu_2O was proposed, where the rate-limiting step is the reduction of CuO by CO. This conclusion was mainly inferred from the difference in the apparent activation energies, though the authors mentioned that variation in the number of the active centers due to effect of the reaction media might change activation energies as well.

Here, we pursue the authors suggestions with some independent data obtained earlier in our laboratory and published mainly in the Russian editions and conference proceedings (2–10). These relate to CO oxidation on the bulk powdered CuO_x samples in a broader temperature range (25–310°C) and with the oxidizing reaction mixtures, carried out in a pulse/flow setup with a vibrofluidized bed reactor (4). In these experiments, a pulse technique at relatively short contact times (a volume of pulse divided by a volume rate of He) ca 10 s allowed us to probe catalytic properties of the various Cu–O phases at a desired state of their surfaces set by a pretreatment. Besides, in the following discussion, we have used also the independent kinetic data of other authors (11–18) along with some data on the bulk and surface defect structure of CuO_x (7, 19–24). Our aim is to show that in analyzing the activity pattern of the copper-based catalysts in CO oxidation, we should take into account not only a mean stoichiometry of the surface layer, but also its defect structure/microheterogeneity. Further, for a partially flexible catalytic surface rearranging under the effect of a reaction mixture (and that is the case for the Cu–O system), even a mode of the activity estimation appear to be of importance when studying the mechanism of the reaction. Though these subtle points were briefly mentioned by the authors of (1), their significance for the Cu–O system (and heterogeneous catalysis in general) seems not to be fully appreciated.

1. PHASE COMPOSITION AND ACTIVE SITES DENSITY

The first question which requires comments is whether an order of activity of the different copper oxidation states found in (1) can depend upon the real (defect) structure of the samples. In our experiments, we have also found that the initial activity of a bare metallic copper surface layer formed on the cuprous oxide particles by a high-temperature reduction in CO was indeed higher than that of Cu_2O, rapidly falling down as the number of the oxidizing mixture pulses increases (5, 8). Hence, thus formed near-surface Cu–O metastable solid solution (or possibly some intermediate phases such as $Cu_{64}O$, Cu_8O, Cu_4O (25–28), is less active than Cu° in accordance with (1). Earlier, similar results were obtained by van Dillen *et al.* (11, 12) for bulk and/or supported copper oxide reduced by hydrogen. Recently, Szanyi, and Goodman (29) have also demonstrated a fall of the catalytic activity of a Cu (100) face due to its oxidation by a stoichiometric $CO + O_2$ mixture.

At temperatures lower than 300°C, a soft oxidation of Cu_2O is known to convert its surface layer into the cuprite-type solid solution $Cu_{2-x}O$ with O/Cu ratio approaching 0.7–1, phase transition into the monoclinic tenorite phase not occurring (5, 8, 30). We found that by such a treatment catalytic activity in CO oxidation of a coarse-powdered cuprous oxide synthesized by decomposition of a bulk CuO sample at 1000°C in a He flow was decreased (8). Hence, a stoichiometric Cu_2O phase is indeed more active than the oxidized ("CuO") cuprite phase. However, at 185°C, an initial (in the first pulse of the $1\%\ CO + 1\%\ O_2$ in He reaction mixture) activity of this stoichiometric cuprous

0021-9517/97 $25.00

oxide (ca 1×10^{17} molecules CO/m^2 s) was nearly two orders of magnitude lower than the highest level of the initial activity of tenorite samples pretreated in oxygen (ca 2×10^{19} molecules CO/m^2 s (6, 8)), specific activities of the latter varying within a 1.5 order of magnitude as dependent upon the method of preparation. Assuming that a true surface area of the oxidized copper film (CuO) used in (1) is ca 10 times higher than a geometric value, a level of the initial reaction rate ca 2×10^{18} molecules CO/m^2 s at the same conditions as we used can be derived, which falls reasonably well within the range of activities of our CuO samples. Moreover, the highest level of activity of our powdered tenorite samples at 185°C (5×10^{18} molecules CO/m^2 s) attained after 1 h of contact with the stream of the 1% CO + 1% O_2 in He reaction mixture (8) exceeds that found for the (100) face of copper (29) and extrapolated to the same concentrations (2×10^{18} molecules CO/m^2 s). All this implies that for copper oxide phase(s), the density of the active sites broadly varies and is related to surface defects, that was earlier suggested by Dillen *et al.* (11, 12). In fact, the authors of (1) mentioned this possibility though they were not able to measure either specific surface or site density for their model sample. Hence, stoichiometry of the surface layer or phase composition does not determine unequivocally catalytic activity of the Cu–O phases in CO oxidation due to an apparent structure sensitivity of this reaction.

We would like to stress that in our studies we have also revealed that for a copper–oxygen system a structure sensitivity manifests itself only at low/moderate temperatures, and for times of contact with a reaction mixture of ca hours. After a prolonged (hundreds of hours) treatment at high (ca 400–500°C) temperatures in the slightly oxidizing reaction mixtures, a true steady state of the CuO_x system in the reaction of CO oxidation was achieved which was found to be independent of the initial phase composition and/or defect structure. This state corresponds to a CuO_{1-x} phase with a high density of the cation and anion vacancies, while all extended defects appear to be annealed (8, 20). A pronounced fall of activity (up to 4×10^{16} molecules CO/m^2 s at 185°C and the reaction mixture composition 1% CO + 1% O_2 in He) was observed when achieving this steady state from both reduced and oxidized initial states. In this case, flexibility of the surface and bulk structures of all phases in the copper–oxygen system is apparent making the reaction of CO oxidation seemingly structure-insensitive; the reaction media effect washes out all the initial differences.

Hence, the conclusion of (1) is indeed valid though in strictly defined conditions and for certain structures of the surface layer. Broad variation of the specific catalytic activity of samples with the same phase composition and/or stoichiometry is due to a defect nature of the surface active centers which requires more detailed discussion.

2. NATURE OF THE ACTIVE SURFACE SITES AND THE APPARENT ACTIVATION ENERGIES

In their analysis of the dependence of the activation energies upon the copper oxidation state, authors of (1) explained the differences observed by the various rate-determining stages (different mechanism). Thus, for copper and cuprous oxide, a mechanism is thought to be of the LH type, while for copper (II) oxide a redox cycle is proposed. At least in part, this conclusion was supported by the fact that for CuO, a postreaction XPS analysis indicated invariance of the copper oxidation state at all temperatures; hence, a number of the active centers is thought to be temperature-independent. However, when the active center's density is small, this conclusion is not strictly valid since XPS is not sufficiently sensitive in this case. And, namely, such a situation is realized for the case of copper (II) oxide. In our experiments, we have found that high activation energy for CO oxidation on CuO is mainly due to an increase of the number of defect active centers with temperature that could be termed as a partial flexibility of the surface (3). To explain how it occurs, a nature of the surface defect centers of CuO should be first briefly described. Detailed TEM studies of the monoclinic CuO (tenorite) defect structure revealed such types of extended defects as polisynthetic twins, screw dislocations, incoherent grain boundaries to dominate in the particles of powdered samples (6, 19, 21). Their density was found to reasonably correlate with the specific catalytic activity thus suggesting active sites are located at outlets of such defects (20).

An analysis of the atomic structure of extended defects by a semiempirical interacting bond method supported by the data of IR spectroscopy of adsorbed CO showed their outlets are clusters of Cu+ ions having Cu–Cu bonds (7, 20, 21). Earlier, thermodynamic studies using high-temperature solid electrolyte cells suggested such clusters to be the predominant bulk defects for CuO (22). Clustering of the surface coordinatively unsaturated centers could be inferred from the coverage-dependent position of the adsorbed CO band (it is shifted from 2115 cm^{-1} to 2100 cm^{-1} in the course of CO pumping at room temperature (23)), that is, a typical feature of CO adsorption on the neighboring coordinatively unsaturated centers (24). In oxidizing conditions, these centers are covered by weakly bound forms of oxygen (Q_{des} is equal to 5–10 kcal/mol) easily removed even by pumping at ambient temperatures (7, 20). In such a way, Cu^+ sites for CO adsorption are created while all regular Cu^{2+} sites on the most developed planes of the (010) and (110) types are covered by the tightly bound bridged nonreactive forms of oxygen. For oxidized bulk CuO, inaccessibility of the regular Cu^{2+} ions to CO adsorption, even at 77 K was directly proved in our IR experiments (21). Hence, for CO and/or oxygen adsorption, it is not vital to remove a regular oxygen as was suggested in (1), since genetic surface defects of a reduced type already exist. Such cluster centers are characterized by CO complexes with ΔH of adsorption ca 20 kcal/mol (7). In a natural way, such cluster centers could coordinate both CO and O, thus ensuring their interaction in the adsorbed layer. Due to some variation of the properties of Cu^+ cations in the center of cluster and on its periphery, CO and oxygen adsorption could be noncompetitive (17).

At moderate temperatures, a weak reduction of the surface of CuO within homogeneity limits (without appearance of nuclei of any new phase) either via pretreatment in He or by feeding CO in He pulses was found to be confined to the vicinity of the outlets of extended defects (2, 3, 20). In such a process, oxygen is removed from the regular positions adjacent to a defect zone, so that reduced copper ions are then included in the extended surface defect. Hence, spreading of the reduced zone occurs accompanied by the development of the dislocation network (4, 10, 20). By such a weak reduction (ca 10–20% of the oxygen monolayer is removed), enhancement of the low-temperature catalytic activity of CuO on more than one order of magnitude was achieved (3, 10), which agrees with the results of (11, 12, 18).

In a general, for transition metal oxides including CuO, the activation energy of their reduction by CO is higher than the activation energy of the subsequent reoxidation by molecular oxygen (31). It means that for oxides in contact with oxidizing reaction mixtures, the surface becomes progressively more reduced with temperature. Due to specific features of the defect structure of CuO, for this oxide the number of active centers increases. In such a way, an apparent activation energy of the CO catalytic oxidation in the steady-state conditions can be enhanced. To prove this statement, it is sufficient to compare the activation energies of CO oxidation at the constant state of the surface set by a pretreatment (rates measured in a pulse regime) and those found in experiments with the steady-state surface (i.e., in the flow regime). In the first case, due to a sufficient pulse duration, all relaxations bound with adsorption of CO and oxygen could be neglected (32), so any possible differences in the activation energies could not be assigned to such trivial factors as a difference in the surface coverages. On the contrary, a pulse length is reasonably short not to change appreciably the surface stoichiometry (at temperatures lower than 185°C, it takes at least tens of minutes to reach a steady-state level of activity (8)). Indeed, for CuO in the former case (high temperature pretreatment in He), we have obtained $E_a \sim 13$ kcal/mol (nearly the same as for cuprous oxide and weakly oxidized copper (1)), while in the latter (flow of the same 1 : 1 mixture) E_a was close to that found in (1) for CuO, namely, 18–20 kcal/mol. A similar value of the apparent E_a ca 18–22 kcal/mol was also obtained by Choi and Vannice for alumina-supported Cu_2O in the flow of $CO + O_2$ mixture with an excess of oxygen (17). Hence, at a steady state of the surface, a number of the active centers for CuO as well as Cu_2O indeed appear to increase with temperature. A further evidence can also be drawn from the results of Choi and Vannice (17). Indeed, from the temperature dependence of the intensity of the IR band of CO adsorbed on the surface of their sample in the flow of $CO + O_2$ reaction mixture, they have estimated a heat of CO adsorption to be equal to 7.2 kcal/mol, that is, considerably lower than typical values for CO adsorption on Cu^+ centers (15–20 kcal/mol at low CO coverages, depending also upon the coordination environment of this cation (7, 33, 34)). It suggests that a number of Cu^+ centers accessible to CO adsorption increases with temperature, thus making the IR band intensity versus temperature dependence less steep. Other factors, such as the absence of the adsorption equilibrium at higher temperatures, could only accelerate a fall of intensity, thus increasing an apparent heat of adsorption. In agreement with a majority of the authors (12–16), we have not observed any effect of gas phase/adsorbed carbon dioxide on the reaction rate.

A general approach to kinetic analysis of the catalytic reactions proceeding on defect centers generated by the reaction media was formulated by Rozovskii as early as in 1967 (35). For CO oxidation on CuO considered here, a kinetic conjugation between the catalytic reaction and the process of the active center generation was first demonstrated by Rozovskii and co-workers in the isothermal unsteady-state experiments back in 1978 (36) and later discussed in detail in his monograph (37). Provided a defect's density is small, the steady-state apparent activation energy depends not only on the activation energy of the catalytic reaction by itself, but it includes, also, the activation energy required to create a surface defect (here to reduce surface with the activation energy ca 10 kcal/mol (31)), minus the activation energy of its "healing" (here to reoxidize the surface). For oxides, the activation energy of the latter stage is usually ca 1–2 kcal/mol, and so it can be neglected. As a result, we can obtain here a required surplus ca 8–10 kcal/mol. Hence, a high apparent activation energy for CuO and Cu_2O in the steady-state conditions can be semiquantitatively explained in the framework of the limited flexibility of their surface layer, i.e., its reversible rearrangement in the vicinity of the surface, extended defects as dependent upon the reaction conditions, thus influencing apparent kinetic parameters. In some way, authors of (1) are partially justified in their conclusion about the origin of such high activation energy for CuO, since it indeed includes the activation energy of CuO reduction. Moreover, a methodical aspect is worth commenting. To receive high activation energies, in the temperature range studied you should substantially change a density of the reduced active sites. So you can either start from the oxidized state of the surface and estimate the initial rates of CO oxidation within a rather big time interval of several minutes (1), or deal with a flow installations, oxidizing reaction mixture, and a (quasi)-steady state of the surface (3, 13, 17). In the case of operating with the stoichiometric mixtures and having a rather reduced state of the surface either set by a high-temperature vacuum pretreatment or obtained by a consecutive treatment with a stoichiometric $CO + O_2$ mixture at high temperatures using a static batch reactor, activation energies were found to be rather low, in the range of 6–9 kcal/mole (13–15), since in this case variation of the surface center's density with temperature is restricted.

3. MECHANISM OF CO OXIDATION

At temperatures lower than 100°C, the empirical reaction orders of oxygen and CO determined at the constant state of the surface (pulse regime) were found to be fractional, suggesting the LH type of mechanism (3). As the temperature is raised from 100 to 200°C, the empirical reaction order of CO increases from ca 0.5 to ca 1.0 due to CO desorption that complies with (1). Up to 100–150°C, carbonyl complexes were indeed observed on the CuO surface in $CO + O_2$ mixture (16, 38). Direct estimation of the rates of carbonyls oxidation by oxygen using in situ IR techniques proved these species to be true intermediates (16), which agrees well with the results of Choi and Vannice (17). Hence, there are no principal distinctions between the mechanism of the reaction of CO oxidation on all phases of the Cu–O system. At ambient temperatures, rates of CO_2 evolution under pulses of either CO or $CO + O_2$ were found to be equal, implying rather high coverage of the surface centers by adsorbed oxygen (39), due, probably, to a noncompetitive CO and oxygen adsorption (17).

Therefore, we have shown that stoichiometry of the surface layer or phase composition does not determine unequivocally the catalytic activity of the Cu–O phases in CO oxidation due to an apparent structure sensitivity of this reaction. For CuO, this reaction appears to proceed on small labile clusters of reduced Cu cations at the outlets of extended defects, whose rearrangement in the reaction media affects apparent kinetics. Here we have a clear case of a structure sensitivity, combined with a partial flexibility of the oxide surface, that seems to be very important from the fundamental point of view. In particular, enhanced apparent activation energies for CO oxidation on CuO were thus explained. Our data along with the independent results of other authors support the LH reaction mechanism of the CO oxidation reaction on CuO, as well as on the other oxidation states of copper, while CO and oxygen adsorption appear to be noncompetitive.

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Received October 17, 1995; revised August 12, 1996; accepted November 14, 1996

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