Journal of Thermal Analysis, Vol. 29 (1984) 655–663

HEATS AND KINETICS OF OXIDATION OF SMALL COPPER PARTICLES IN COPPER-CONTAINING CATALYSTS

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The r.t. interaction of oxygen with finely-divided copper in Cu/ZnO catalysts has been studied by gas-solid microcalorimetry. The oxidation is accompanied by the presence of a pseudo-equilibrium pressure, which increases as the reaction proceeds. Surface and several subsurface layers are involved, but a metallic core is always left.

The heat of reaction is the same for all samples and does not vary with the extent of reaction ($\Delta H = 181$ kJ mol $(1/2O_2)^{-1}$). The rate of reaction depends upon the pressure, and decreases dramatically to a point where oxidation stps and molecular oxygen is weakly chemisorbed. The overall process is interpreted by assuming that the rate-determining step is the surface dissociation of a molecular precursor onto Cu atoms.

Many heterogeneous catalysts consist of metal particles dospersed on an oxidic support of high surface area. The interaction of oxygen with these particles is relevant to catalysis for various reasons: some supported metals, such as copper and silver, are active in the partial oxidation of simple organic molecules by O_2 [1]; several methods for evaluation of the free metal surface area and based on the oxidation of the metal surface [2–7].

On the other hand, the oxidation of small metal particles is of interest per se, as they react with oxygen much more readily than do bulk specimens. Because of the high dispersion attained, such samples provide the opportunity to study the enhanced role of the surface in the oxidation and the possible influence of the support.

Copper is an essential component of mixed catalysts for methanol synthesis [8, 9] and CO shift reactions [10]. Since the pioneering work of Mott and Cabrera [11] and Rhodin [12], a great deal of research has been devoted to the oxidation of bulk copper [13]. Nevertheless, conflicting evidence exists about the mechanism of the process at low temperature, the influence of the oxygen pressure, and the growth of the oxidic phase [11–14].

More recently, the early stages of oxidation have been studied on single-crystal faces [15–21] or thin metal films [22]. Very few studies have been made of highly-dispersed supported copper, however [4, 5, 23, 24].

We have therefore investigated by microcalorimetry the room-temperature reaction of oxygen with Cu/ZnO catalysts at different copper loadings, as well as with pure metallic copper, in a previous investigation the reaction of N_2O with the same samples was described [6]. At room-temperature, N_2O was shown to involve only a fraction of the exposed surface (~ 60%) and to afford a reasonable calorimetric method for measurement of the area of the exposed copper [6, 7].

Experimental

The catalyst preparation and the experimental technique adopted have been described previously [6, 7, 10]. Cu/ZnO samples, obtained by decomposition of basic carbonates, were reduced to Cu/ZnO by H_2 at 483 K. The final reduction was carried out in the calorimetric cell itself [6].

The reduced catalysts, placed in a Calvet microcalorimeter kept at 303 K, were contacted with successive small doses of oxygen. During the adsorption of each dose, the oxygen pressure over the adsorbent was monitored and the following dose was admitted only when a constant pressure value has been attained and no variations were detectable in the calorimetric baseline.

The adsorption run was stopped when admission of an oxygen dose did not cause any appreciable evolution of heat. At this stage the sample was evacuated. The endothermic heat recorded, if any, measures the fraction of adsorbate reversibly held on the surface under the experimental conditions adopted.

The experiments were performed on samples of Cu/ZnO with a nominal Cu content of 3%, 15% or 30% and on microcrystalline Cu obtained by the same procedure. Prior to the interaction with oxygen, the samples were contacted with N_2O in order to measure the free copper area. The values obtained were 166, 74 and 87 m^2g^{-1} (Cu) respectively. On the assumption of a spherical shape for the particles and with the crude hypothesis of uniformity in size distribution, the average radii were calculated to be 2.05, 4.60 and 3.85 nm. Pure copper had a very low surface area, below 1 m^2g^{-1}. In some cases (3% and 30%) the reaction with oxygen was also studied on freash samples.

Results and discussion

From the very beginning each dose reacts to leave a constant oxygen pressure over the solid. Figures 1 and 2 illustrate for all samples examined the heat evolved as a function of the final oxygen pressure. Figure 1 relates to bare samples and Figure 2 to the N_2O-reacted samples. The corresponding uptake *vs.* pressure curves have a similar trend and are thus not reported. In both Figs 1 and 2 an almost linear dependence of the evolved heat upon oxygen pressure is observed up to a point (depending on the copper loading) where the oxidation stops abruptly, and only a weak adsorption of molecular oxygen occurs. Similar behaviour has recently been found for the reaction

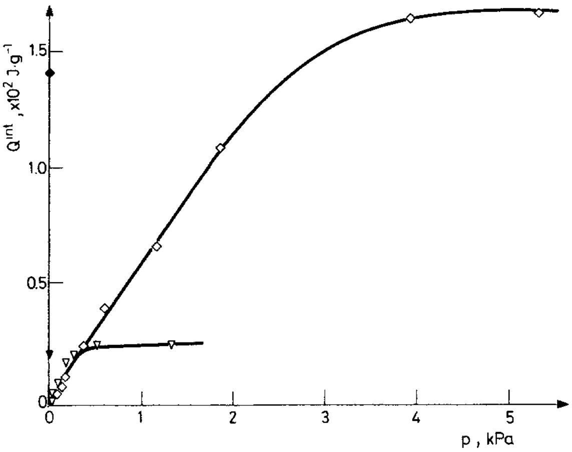

Fig. 1 Interaction of O_2 with Cu/ZnO catalysts. Heat evolved *vs.* pseudo-equilibrium pressure. ◇ 30% Cu, ▽ 3% Cu. Full points on the ordinate scale: evacuation

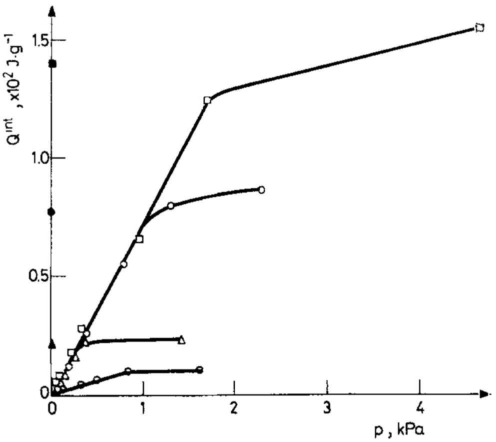

Fig. 2 Interaction of O_2 with Cu/ZnO catalysts previously contacted with N_2O. Heat evolved *vs.* pseudo-equilibrium pressure. □ 30% Cu, ○ 15% Cu, △ 3% Cu, ⊖ pure Cu. Full points on the ordinate scale: evacuation

of oxygen on iridium catalysts [24]. Upon evacuation (full points on the ordinate scale in Figs 1 and 2) the reversible fraction of oxygen turns out to be almost negligible, so that the final oxygen pressure for each dose must be considered pseudo-equilibrium, and not equilibrium ones.

Data concerning the total uptakes of N_2O, O_2 and O_2 after N_2O are collected in Table 1. Total O_2 uptakes indicate that the oxidation has gone far beyond the surface and has involved a substantial part of the bulk. The ratio between oxidized atoms and total copper content varies with the Cu loading. From the same data it is also inferred that the number of oxygen atoms which have reacted is the same in both the N_2O + + O_2 experiments and in the O_2 experiments alone, i.e. complementarity exists between N_2O and O_2. Accordingly, the data in Fig. 2 can be superimposed onto those in Fig. 1 by appropriate shifts of the origin, to take account of the fraction of the surface which has already reacted with N_2O. A noteworthy discrepancy, however, is that the N_2O reaction proceeds up to total consumption of the reactant, whereas the O_2 reaction, either in the presence or in the absence of N_2O preoxidation, is always characterized by a pseudo-equilibrium pressure.

Table 1 Uptakes in the oxidation of Cu/ZnO catalyst by O_2 and N_2O

	(1) O_2, mol $(\frac{1}{2}O_2)$ g^{-1}	(2) N_2O, mol N_2O g^{-1}	(3) O_2 after N_2O, mol $(\frac{1}{2}O_2)$ g^{-1}	2 + 3, mol $(\frac{1}{2}O_2)$ g^{-1}
Cu/ZnO (3% Cu)	140	19	126	145
Cu/ZnO (15% Cu)	–	45	355	400
Cu/ZnO (30% Cu)	906	113	830	936

In Fig. 3 the integral heat *vs.* oxygen uptake is reported for all samples studied. All experimental points fall on the same straight line passing through the origin, i.e. on the different samples the reaction occurs with the same energy (181 kJ per half mole

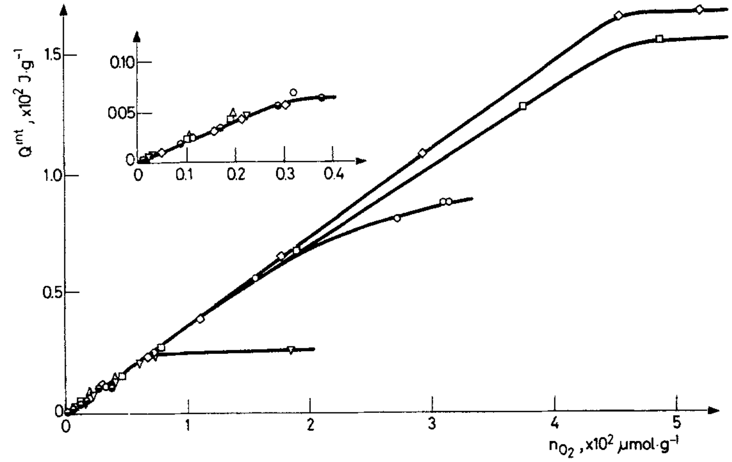

Fig. 3 Heat of interaction of O_2 *vs.* uptake on Cu/ZnO catalysts. ◇ 30% Cu, ▽ 3% Cu, □ 30% Cu + N_2O, ○ 15% Cu + N_2O, △ 3% Cu + N_2O, ⊖ pure Cu. Insert: expansion of the scale at low uptake values

of O_2). Careful inspection of the very first doses shows that the differential heat is slightly higher here; at the end of the interaction the differential heat drops abruptly below 40 kJ mol^{-1}. The data in Fig. 3 are in agreement with those reported by Stone and coworkers [25] and by Ostrowsky [23]. The constant heat of 181 kJ mol^{-1} $(1/2O_2)$ is close to the standard enthalpy of oxidation of Cu to Cu_2O ($\Delta H = -167.5$ kJ mol^{-1}). Cu_2O is in fact a thermodynamically stable compound at room-temperature and has indeed been found by many authors [19, 20, 22, 25]. We rule out the presence of any CuO phase, for in a parallel experiment followed by ESR the typical spectrum of Cu^{2+} has never shown up, even at the highest extent of reaction and after several days [6]. The difference between the two enthalpy values, however, is significant, and must probably be ascribed to the state of high subdivision of the copper in our samples. The decrease observed in the differential heat at the end of the reaction can probably be ascribed to the adsorption of O_2 in a molecular form onto the oxidic phase. In fact, a peak at 352 eV in the XPS spectra of similar copper systems after extensive O_2 reaction has been ascribed to adsorbed molecular oxygen [1, 26].

The observed increase in the extent of copper oxidation upon increase of the O_2 pressure is not related to a possible shift in the equilibrium

$$4\,Cu + O_2 \rightleftharpoons 2\,Cu_2O$$

the dissociation pressure of Cu_2O being extremely small (10^{-46} torr), and far below the range of pressure applied in our experiments. The effect of pressure is thus purely kinetic.

The kinetic role of the O_2 pressure is very substantial. When a dose is admitted onto the sample, the reaction proceeds at an observable rate, but the mere decrease in pressure due to the uptake of oxygen by the solid suffices to slow down the oxidation to below the threshold of detectability. The contact of a successive dose at a pressure higher than the previous one restarts the reaction.

Both the decrease in pressure and the rate of heat emission indicate that the kinetics of the reaction within a single dose are nearly first order. In fact, exponential decays of pressure are observed. Due to the slowness of the process, the deviation of the calorimeter is a measure of the rate of heat production, as the inertia of the instrument is in this case negligible with respect to the latter. Since the molar heats of reaction are constant, the deviation is also a measure of the rate of reaction. Nearly exponential decays of the instrument deviation are observed from the peak maximum onwards: this is the reason for the correlations between a whole set of thermokinetic parameters reported elsewhere [6, 7]. A first order of reaction was indeed observed by Ostrowsky [23] on porous metallic copper, and by Habraken et al. [16, 18] for the submonolayer oxidation of the 111 and 110 faces of Cu monocrystals.

However, the reaction slows down upon increase of the extent of the reaction itself. Typically, the first uptake reacts in less than one hour, whereas the final ones react over a period of ten hours. Thus, not only does the pressure play a marked role in the kinetics, but the apparent activation energy also seems to increase during the process. To illustrate semiquantitatively the kinetics of heat emission, Fig. 4 reports the half deviation time of the thermograms, $t_{1/2}$ (i.e. the time at which the deviation has attained half the value of the maximum), against different quantities, all of which are a measure of the extent of the reaction. The data in Fig. 4a and b refer to N_2O-pretreated samples: the data for bare samples are similar (when account is taken of the oxidation brought about by N_2O) and are therefore not reported. The data in Fig. 4c relate to all kinds of samples, including metallic copper. In Fig. 4a, $t_{1/2}$ values are plotted against the oxygen uptakes for unit copper content. A steady increase is observed in each case, but the slopes do not coincide. The final points [30% and 15%] show a lower $t_{1/2}$ than the preceding ones, because of the onset of a faster phenomenon (adsorption of molecular O_2) superimposed on the oxidation of the bulk.

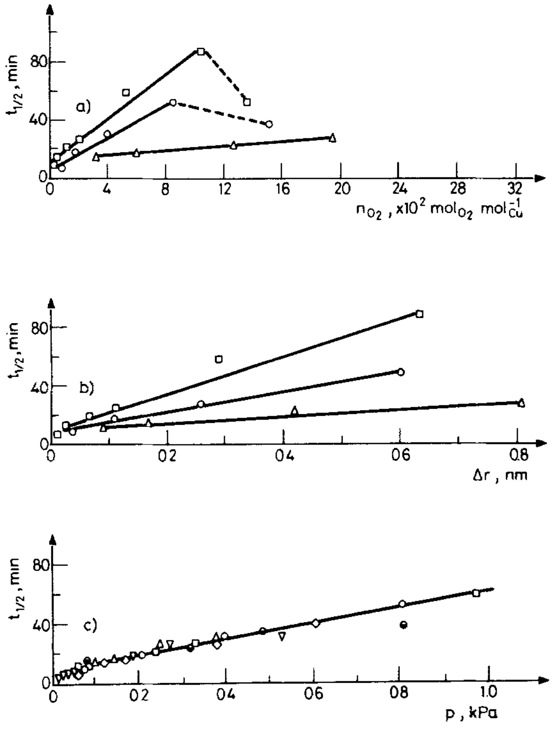

Fig. 4 Thermokinetics in the interaction of O_2 with Cu/ZnO catalysts. Half deviation time ($t_{1/2}$) as a function: (a) of uptakes for unit copper content, (b) of depth of penetration of the oxidation (Δr), (c) pseudo-equilibrium pressure. ◇ 30% Cu, ▽ 3% Cu, □ 30% Cu + N_2O, ○ 15% Cu + N_2O, △ 3% Cu + N_2O, ◉ pure Cu

According to the classical theories of metal oxidation [13], based on electronic and ionic currents through the oxidized layer, the depth of the oxidic phase is the major factor determining the rate of oxidation.

From the crude assumption that the particles of a sample all have the same spherical shape and size, and on the basis of the stoichiometry of the reaction, it can be shown that the depth of penetration Δr is

$$\Delta r = r[1 - (1 - 4n_{O_2})^{1/3}]$$

where r is the average radius and n_{O_2} the oxygen uptake per unit copper content. In fact, because of the stoichiometry, $4n_{O_2}$ is the fraction of Cu which has undergone oxidation, so that the corresponding volume per particle is

$$4n_{O_2} \cdot \frac{4}{3} \pi r^3$$

and the volume of the residual Cu core of a particle is

$$\frac{4}{3} \pi r^3 (1 - 4n_{O_2})$$

In Fig. 4b, $t_{1/2}$ values are plotted against Δr. Although the model assumed is obviously over-simplified, the kinetics of oxidation do not seem to be directly related to the depth of penetration. When (Fig. 4c) $t_{1/2}$ values are plotted as a function of the pseudo-equilibrium pressures instead (as those reported in Figs 1 and 2), all points from catalysts with different copper loadings and even those relating to metallic copper lie on the same linear poot. The explanation of Fig. 4c is not straightforward. We note, however, that on the basis of Fig. 4b the role of the diffusion across the oxide layer as the rate-determining step must probably be ruled out. An alternative hypothesis is that the surface dissociation of O_2 is the slowest step of the reaction. This is likely to occur via a molecular precursor, as hypothesized in the study of the early stages of oxidation of Cu monocrystals [16–20], following the scheme

$$O_{2(g)} \rightleftharpoons O_{2(a)} \xrightarrow{+4\,Cu} 2\,Cu_2O$$

In this case the concentration of the precursor is governed by the oxygen pressure and the centre of attack is assumed to be the defect sites [20]. These are likely to be relatively abundant on small particles. Afterwards, the reaction will proceed by incorporation of oxygen via a possible place-exchange mechanism between oxygen and copper [27] or via vacancy diffusion [28].

This mechanism provides new Cu atoms at the surface. However, surface Cu sites available for oxygen dissociation decrease during the course of the reaction, and consequently the rate decreases, as monitored by the increase of $t_{1/2}$. The reaction of each dose probably stops when the concentration of the precursor falls below a threshold value, corresponding to a pseudo-equilibrium pressure, as those reported in the abscissa scales of Figs 1, 2 and 4c. Because of the decrease in the number of Cu sites, the pseudo-equilibrium pressure corresponding to the threshold value of the precursor increases, and thus a correlation between $t_{1/2}$ and the psudo-equilibrium pressure is observed. When Cu sites are no longer available at the surface, the oxidation stops suddenly and oxygen is only adsorbed in a weak molecular form on the oxidic phase.

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Part of the experimental work was performed by Dr. P. Lauro while preparing his thesis. This research was supported by "M. P. I. Progetto nazionale e di rilevante interesse per lo sviluppo dell della ricerca — Gruppo 'Struttura e reattività delle superfici' "

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Zusammenfassung — Die Wechselwirkung von Sauerstoff bei Raumtemperatur mit feinverteiltem Kupfer in Cu/ZnO-Katalysatoren wurde mittels Gas-Festkörper-Mikrokalorimetrie untersucht. Bei der Oxydation herrscht ein Pseudogleichgewichtsdruck, der mit fortschreitender Reaktion ansteigt. An der Reaktion nehmen die Oberfläche und einige darunter liegende Schichten teil, der metallische Kern bleibt jedoch stets unberührt. Die Reaktionswärme ist bei allen Proben gleich und verändert sich nicht mit dem Grad der Reaktion ($\Delta H = 181$ kJ mol $(1/2O_2)^{-1}$). Die Reaktionsgeschwindingkeit hängt vom Druck ab und verringert sich drastisch bis zu einem Punkte, wo die Oxydation zum Stillstand kommt und Sauerstoff schwach chemisorbiert wird. Zur Interpretation des Gesamtprozesses wird angenommen, daß der geschwindigkeitsbestimmende Schritt die Dissoziation eines molekularen Präcursors in Cu-Atome ist.

Резюме — Методом газо-твердой микрокалориметрии было изучено при комнатной температуре враимодействие кислорода с мелко-раздробленной медью на Cu/ZnO катализаторах. Окисление сопровождается наличием псевдоравновесного давления, которое увеличивается по мере протекания реакции. В реакцию включались поверхностные и отдельные субповерхностные слои, но металлическое ядро всегда оставалось не тронутым. Теплота реакции для всех образцов была одинаковой и не изменялась на протяжении всей реакции ($\Delta H = 181$ кдж.моль. $(1/2O_2)^{-1}$). Скорость реакции зависила от давления и сильно уменьшалась до точки, где окисление прекращалось и молекулярный кислород является слегка хемисорбированным. Общий процесс окисления объяснен на основе предположения, что стадией, определяющей скорость реакции, является поверхностная диссоциация молекулярного предшественника на атомах меди.