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Aging of Cupric Oxide Supported on Activated Carbon

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The physicochemical changes occurring during the aging in a humid atmosphere of cupric oxide supported on activated carbon have been investigated by differential scanning calorimetry (DSC) and by X-ray diffraction and electron microscopy. In a freshly prepared sample copper is mainly present as amorphous CuO. The amount of amorphous CuO can be quantitatively determined by DSC using the exothermal reduction reaction of CuO to Cu_2O by the carbon support. Upon aging, the amount of amorphous CuO decreases, partly due to the formation of dispersed Cu(I) species and also because of crystallization of CuO.

INTRODUCTION

Activated carbons are extensively used for the purification of gases and liquids. In the case of toxic gases, the efficiency of carbons is increased by impregnation with chemicals such as metallic oxides.

Protection against hydrocyanic acid (HCN) and cyanogen chloride (CNCl) is achieved with activated carbon impregnated with Cu(II)/Cr(VI) species. However, after storage in a wet atmosphere, the efficiency rapidly decreases. Deitz *et al.* (*1*), using X-ray analysis and electron diffraction, found Cu^0, Cu_2O, CuO, and Cr_2O_3 in aged whetlerite samples. Berg *et al.* (*2, 3*) mentioned an increase of the crystallinity of the supported oxides.

The aging of Cu(II)/Cr(VI) systems supported on carbon is very complex. As a result, we have chosen to study initially only the supported cupric oxide. Changes in crystallinity of the supported oxide are known to result from long exposure to wet atmosphere but no satisfactory explanation is known as yet for the effect of short aging times on the copper oxide. Since the carbon support may act as a reducing agent it is possible that Cu^{II} is partially converted to Cu^{I}. This hypothesis is consistent with the fact that deposition of ammonium chromate over charcoal leads to a mixture of supported Cr^{VI} and Cr^{III} (*1*). In the present study supported copper oxide is characterized by its ability to be chemically reduced by the charcoal support. Since the reaction is exothermal the reduction can be followed by differential scanning calorimetry (DSC). The objective of the present work is to investigate by means of DSC the effect of aging in a wet atmosphere on copper oxide supported on charcoal. Physicochemical changes of the supported phase have been additionally determined by X-ray diffraction and transmission electron microscopy.

METHODS

Preparation of Samples and Conditions of Aging

The activated carbon (PICA) was prepared from a coconut charcoal (the ash content of the carbon support is 2% by weight). Deposition of cupric oxide was carried out by impregnation of the activated carbon (particle size between 1 and 1.6 mm) with an ammoniacal solution of basic cupric carbonate. For the deposition, 500 g of activated carbon were treated with 480 ml of an aqueous solution containing 240 ml of con-

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TABLE 1

Surface Areas and Micropore Volumes

Sample	Specific surface area (m^2/g)	Micropore volume (cm^3/g)
Activated carbon	889	0.34
Impregnated activated carbon	667	0.26

centrated ammonia, 82 g of ammonium carbonate, and 45 g of basic cupric carbonate. Under these conditions, the liquid phase was completely retained in the microporosity of the carbon. After drying at 390 K, the catalyst content, expressed as copper, was 4.8 wt%.

Aging was accomplished at 323 K in 90% relative humidity. Under these conditions the activated carbon adsorbs 30% by weight of water. Experimentally, aging was carried out as follows. The required amount of water was added to a solid sample and stirred in a confined atmosphere for 3 days. It was then stored in an oven at 323 K. The aging duration corresponds to the storage duration. Finally the sample was dried at 390 K for 20 h; the sample retained 6 to 7% water.

Analytical Techniques for Characterization of Samples

(a) Surface area and microporosity. After outgassing at 390 K under 0.13 Pa, carbon dioxide was adsorbed at 273 K. The micropore volume as well as the equivalent surface area were computed by the classical method of Dubinin (*4*) (Table 1). Surface areas and micropore volumes decrease on going from the original to the impregnated samples. Pores may be obstructed either by the metal oxide or by adsorbed water which is not totally desorbed during outgassing.

Three techniques were used for characterizing cupric oxide, namely (i) DSC, (ii) X-ray diffraction, and (iii) electron microscopy.

(i) Differential scanning calorimetry (DSC). A Mettler TA 3000 thermoanalyzer was used. Ten milligrams of finely ground material was introduced into a 40-μl aluminum pan covered with an aluminum cap; a small hole in the cap prevented overpressure during heat treatment. The reference was a similar but empty pan. Experiments were made under a flow of nitrogen. In order to minimize the endothermal effect due to desorption of water adsorbed on the cupric oxide and on the activated carbon, the sample was preheated at 453 K for 15 min in the DSC equipment. After cooling to room temperature enthalpic analysis was carried out between 298 and 770 K at 20 K/min heating rate. A preliminary study has shown that the pretreatment conditions do not affect the thermal pattern of the samples at higher temperature and optimize the removal of adsorbed water. Furthermore DSC runs carried out at heating rates between 10 and 25 K/min led to identical results.

(ii) X-Ray diffraction. Debye–Scherrer X-ray diffraction patterns have been recorded on powdered unaged and aged samples in order to identify the copper compounds present at the various stages of aging.

(iii) Electron microscopy. Observations by transmission were performed using a JEOL 100B electron microscope equipped with an EDAX attachment.

For TEM, the supported cupric oxide was embedded in an epoxy resin (Araldite D-HY 938 hardener from Ciba-Geigy). Thin sections were obtained with an L.K.B. Ultratome III microtome. The thickness of the section was between 30 and 100 nm.

RESULTS

Characterization of Supported Cupric Oxide by DSC and X-Ray Analysis

For unaged samples and for materials aged for less than 20 days, only two diffuse diffraction lines, corresponding to the (002)

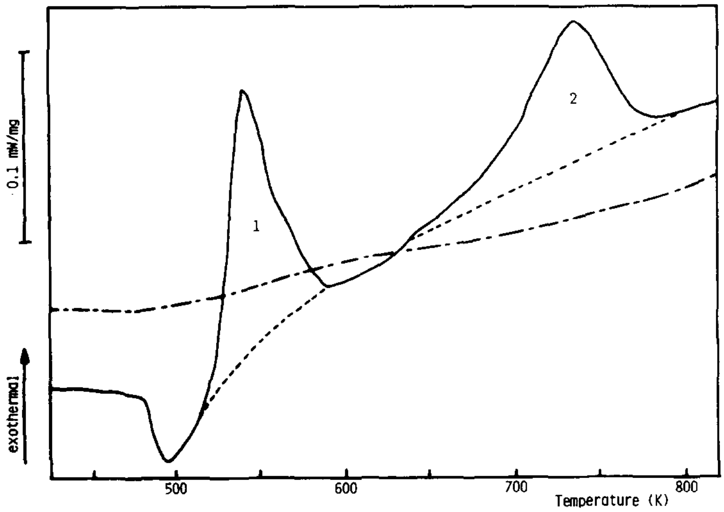

FIG. 1. DSC curve of an unaged CuO sample supported on carbon: (—) 1st run, (----) 2nd run.

and (10 *l*) reflections of the activated carbon are detectable. In particular no diffraction peak corresponding to a copper compound could be seen, which suggests a high dispersion of the copper oxide phase on the carbon support.

For a longer exposure time (20–40 days) two peaks corresponding to the most intense reflections of CuO $(\bar{1}11)$ and (111) appear in the Debye–Scherrer diffraction patterns. This fact suggests crystallite growth of supported cupric oxide.

Though samples aged for less than 20 days exhibit no X-ray line corresponding to copper derivatives, it is experimentally observed that even during that short period of aging the efficiency of the catalyst is decreasing. This aging does not correspond to a sintering of copper oxide on carbon. It might, however, result from the two following reactions:

$$CuO \rightarrow Cu_2O \quad (1)$$

$$Cu_2O \rightarrow Cu \quad (2)$$

It will be shown that DSC combined with X-ray analysis can clarify the mechanism involved.

Unaged impregnated samples. The DSC pattern of the initial sample (Fig. 1) exhibits three peaks, namely, an endothermal peak between 473 and 513 K attributed to water desorption and/or dehydration of amorphous cupric oxide, and two exothermal peaks at 513–593 and 673–793 K, respectively. A second heating cycle gives a flat DSC signal. Thus these latter peaks are associated with CuO, since activated carbon alone shows no noticeable thermal effects.

The transformation of supported CuO corresponding to the thermal effects in the DSC cell has been characterized by X-ray diffraction, the results of which are indicated in Table 2. By combining the results

TABLE 2

Copper Derivatives on an Unaged Sample as a Function of Heat Treatment under DSC Conditions

T (K)	Heat treatment conditions	Copper species (by X-ray analysis)
Room temperature	—	—
393	24 h	—
593	Heating rate 25 K/min	Cu_2O
723	Heating rate 25 K/min	Cu + traces of Cu_2O
823	Heating rate 25 K/min	Cu

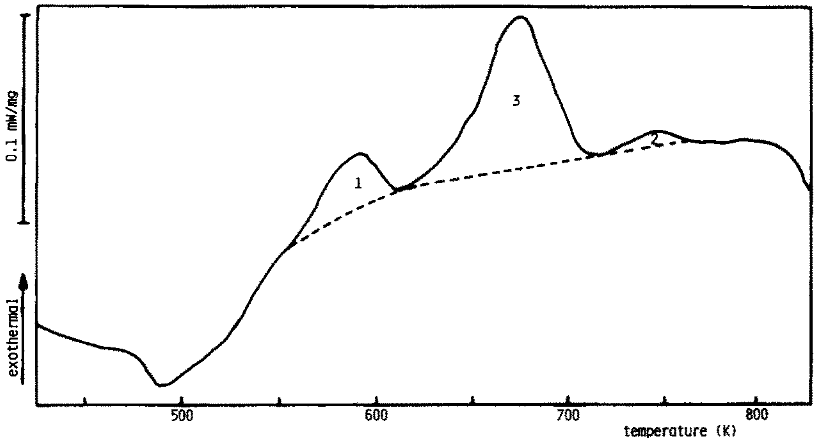

FIG. 2. DSC curve of a 25-day-aged CuO sample supported on carbon.

from Fig. 1 and Table 2, it is clear that the 513–593 K exothermal peak corresponds to the reduction of CuO to Cu_2O with the second (673–793 K) attributed to the further reduction of Cu_2O into metallic copper.

The reduction by the carbon of cupric oxide to cuprous oxide and copper may in general produce carbon monoxide and/or carbon dioxide. We have shown by infrared analysis that thermal treatment of supported cupric oxide at 720 K produces exclusively carbon dioxide.

The carbon dioxide evolved in the temperature interval corresponding to peak 1 corresponds stoichiometrically to

$$4\,CuO + C \rightarrow 2Cu_2O + CO_2 \qquad (3)$$

According to the thermodynamic data (5), the heat of reaction ΔH at 473 and 623 K is equal to −31.3 and −35.8 kJ/mole, respectively. Considering the small change in ΔH, an average value of −33.4 kJ/mole CuO has been taken. Thus the CuO content of the initial sample can be determined by measuring the heat corresponding to the first exothermal peak. The results obtained with three samples show that over 97% of the amount of cupric oxide supported on the carbon can be detected by DSC. Hence, DSC is well suited to the determination of CuO supported on carbon. It may be mentioned that the carbon dioxide evolved in the temperature interval corresponding to peak 1 is higher than the stoichiometric amount, due probably to the decomposition of oxygen surface complexes present on the carbon support. The measurement of the heat evolved in peak 2 which corresponds to the reduction of Cu_2O to metallic Cu is less reproducible. Therefore the quantitative analysis of this peak has not been further considered.

Aged samples. (a) Aging shorter than 18 days. The area of peak 1 of the DSC curve decreases with aging duration and suggests

TABLE 3

Copper Derivatives on a 25-Day-Aged Sample as a Function of Heat Treatment under DSC Conditions

T (K)	Heat treatment conditions	Copper species (by X-ray analysis)
Room temperature	—	CuO
393	24 h	CuO
593	Heating rate 25 K/min	CuO
723	Heating rate 25 K/min	Cu_2O
823	Heating rate 25 K/min	Cu

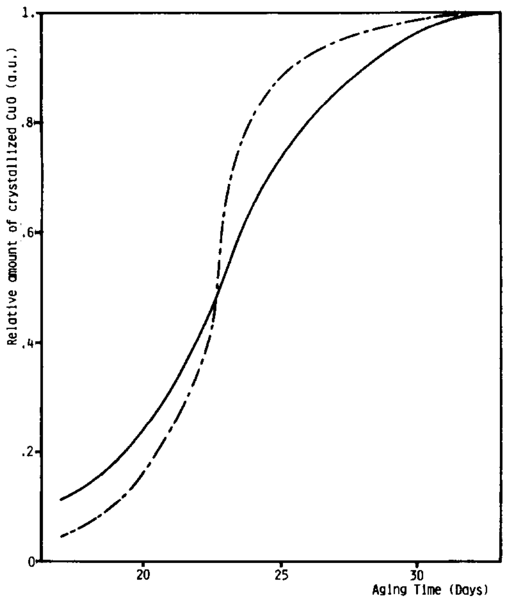

FIG. 3. Formation of crystallized CuO during aging as determined by DSC (—) and by X-ray diffraction (- - - -).

that the CuO content of the sample is decreasing.

(b) Aging between 18 and 40 days. A third exothermal peak appears in the DSC runs between 623 and 723 K with a maximum at ca. 680 K. Figure 2 shows the DSC curve corresponding to a sample aged for 25 days. It is seen that peaks 1 and 2 are much smaller than in the unaged sample. From X-ray analysis, peak 3 corresponds to the reduction of CuO detectable by X-ray diffraction, i.e., to well-crystallized CuO, as shown in Table 3. It is also observed that in these samples the reduction of Cu_2O to Cu occurs at a much higher temperature (820 K). The amount of crystallized CuO can be determined either by DSC (peak 3) or by X-ray diffraction. In Fig. 3, the amount of heat evolved (peak 3) is compared in arbitrary units to the intensity of the $(\bar{1}11)$ reflection of CuO for samples aged for various times. It is seen that a fairly good correlation exists between the energy corresponding to peak 3 and the intensity of the $(\bar{1}11)$ reflection of CuO.

(c) Aging between 40 and 60 days. When the duration of aging increases, peak 2 decreases and vanishes after 40 days. Simultaneously a new endothermal peak appears whose maximum is at 583 K (peak 4) (Fig. 4). For the same aging the two main diffraction peaks of CuO weakens and new reflections corresponding to spacings of 0.599, 0.506, and 0.369 nm appear; they correspond to basic cupric carbonate $CuCO_3 \cdot Cu(OH)_2$ which means that carbon dioxide is produced during aging. We have also verified by X-ray analysis that the endothermal DSC peak corresponds to the decomposition of the basic cupric carbonate into copper oxide.

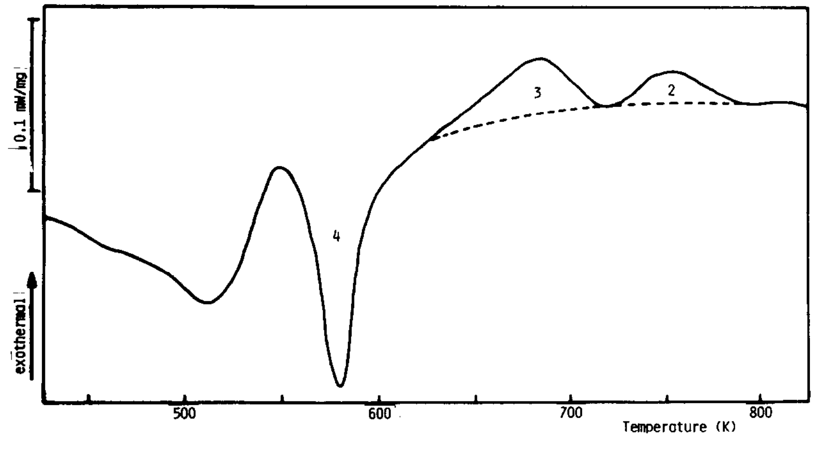

FIG. 4. DSC curve of a 40-day-aged CuO sample supported on carbon.

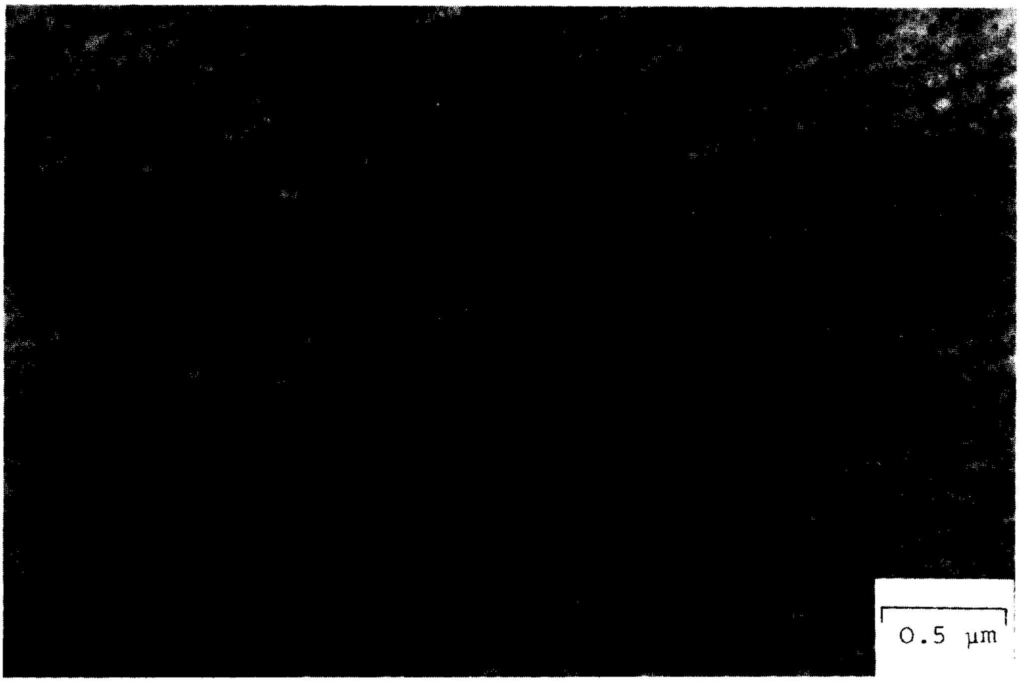

FIG. 5. Micrograph of a thin section of unaged sample.

Characterization of Supported Cupric Oxide by Electron Microscopy

Only a brief study has been made, but the observations confirm that in the initial sample CuO is well dispersed and cannot be separated from the background. On some micrographs, however, some 10 to 50-nm particles can be seen (Fig. 5): the dispersion is somewhat unhomogeneous. However, this fraction of CuO crystallites is very small since it gives no X-ray diffraction. The 25-day-aged samples exhibit particles with a bimodal distribution (5–20 and 50–100 nm), thus confirming crystallite growth upon aging (Fig. 6). Electron microdiffraction on the largest particles corroborates the X-ray observations as to the nature of the crystallites.

DISCUSSION

During the first period of aging (<18 days) no crystallized species can be observed by X-ray diffraction. It may be argued that the amount of crystallized CuO found by X-ray analysis is too small to be detected. However, the fact that both the DSC-detected reduction peak of the crystallized CuO (peak 3) and the intensity of the $\bar{1}11$ reflection of CuO show a sharp increase only after 20 days suggested another aging mode, i.e., aging is not a result of sintering of the initially dispersed cupric oxide in the first days of storage in a wet atmosphere.

At different stages of aging, the amount of CuO can be quantitatively determined by DSC (via the thermal effect of reaction 3). In Fig. 7, the percentage of amorphous and/or small CuO crystallites with respect to initial CuO content is plotted as a function of aging. Although the uncertainty of the measurements is somewhat high, it appears that the content of amorphous CuO steadily decreases upon aging and becomes negligible after 38 days.

From the thermal effect of the conversion of crystallized CuO into Cu_2O (cf. Fig. 3) as measured by DSC, it is possible to determine the amount of crystallized CuO present in the sample as a function of aging duration. Results are also plotted in Fig. 7.

FIG. 6. Micrograph of a thin section of a 25-day-aged sample.

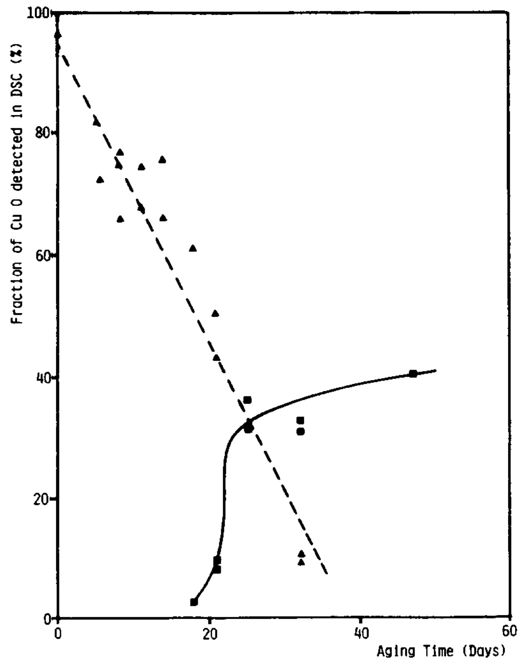

FIG. 7. Percentage of initial content of CuO detected in DSC as a function of aging time: (▲) peak 1, (■) peak 3.

On comparing the two curves of Fig. 7, it is clear that uncrystallized CuO is not quantitatively converted into crystallized CuO during aging. In particular, after 16 days aging about 40% of the amorphous CuO has disappeared with no formation of the crystallized variety. In addition after 30 days about 10% of the initially present CuO remains in the amorphous form and 40% is present in the crystallized form. Therefore about 50% of the initial CuO is no longer detectable by DSC.

To explain the discrepancies in the CuO mass balances, it can be assumed that a part of CuO is converted into Cu_2O in agreement with Deitz *et al.* (*1*). In order to substantiate this hypothesis unaged and aged samples have been reduced to metallic copper in H_2 at 393 K. The hydrogen consumptions for the unaged and the 25-day-aged samples are equal to 1.20 and 1.07 mmole H_2/g, respectively. The H_2 consumption for the unaged sample is higher than that corresponding to the reduction of CuO to Cu.

Nevertheless it is clear that after aging the supported copper species require less H_2 to be reduced to Cu. This result suggests that partial reduction of CuO has occurred during aging on the carbon support. Although the precise mechanism of reduction is not known detection of the formation of basic cupric carbonate after long aging times demonstrates that CO_2 has been produced. Therefore, the carbon support appears to be the reducing agent of Cu^{II} into Cu^{I}. Finally, since the rate of aging is strongly increased in the presence of water it can be assumed that the reduction of Cu^{II} occurs via adsorbed water in the micropores of the carbon support.

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