Aging of Cupric Oxide Supported on Activated Carbon

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Introduction

Copper and chromium oxides supported on activated carbons are efficient catalysts for the removal of toxic gases from the atmosphere. These materials are prepared by the impregnation of adsorbent charcoals with ammoniacal carbonate solution of copper (Cu(II)) and chromium (Cr(VI)) salts. Deitz et al. found that the activated carbon is not an inactive support since Cu(I) and Cr(III) species were detected in impregnated samples (1). Furthermore the efficiency of the catalytic system rapidly decreases when stored in a wet atmosphere. The aging of catalysts supported on carbon is presently not well understood and it is therefore worth to precise the physico-chemical changes of the catalysts upon storage. Since the Cu(II)/Cr(VI) system is a very complex one, we have choosen to study in a first approach the aging of supported cupric oxide. Considering the fact that the reduction of CuO by the carbon is exothermal there may be a possibility to follow the reduction reaction by differential scanning calorimetry (DSC). The objective of the present study is to investigate by means of DSC the aging of CuO supported on an activated carbon. More conventional techniques like X-ray diffraction and electron microscopy have also been used.

Experimental

An activated coconut charcoal has been impregnated in incipient wetness conditions with an ammoniacal solution of basic cupric carbonate and ammonium carbonate. After drying at 390 K the catalyst content expressed on a basis of metallic copper is 4.8 % by weight. The samples have been aged by storage at 323 K in 90 % relative humidity. After aging the samples are dried at 390 K for 20 hours and then kept in a dry atmosphere at room temperature. DSC measurements are carried out under flowing nitrogen in a thermoanalyser Mettler TA 3000. Enthalpic analysis is determined between 290 and 800 K at a heating rate of 20 K/min.

Results

Unaged impregnated Samples

The DSC pattern of the unaged sample exhibits three peaks as shown in Figure 1. The endothermal peek between 473 and 513 K is attributed to water desorption and/or dehydration of amorphous cupric oxide. Two exothermal peaks are respectively located at 513-593 K (peak 1) and at 673-793K(peak 2). These peaks are related to the supported copper oxide since no DSC signal can be seen with the activated carbon alone. X-ray diffraction diagrams have been recorded for the samples studied in DSC. The occurence of crystallized copper compounds is also indicated in Figure 1.

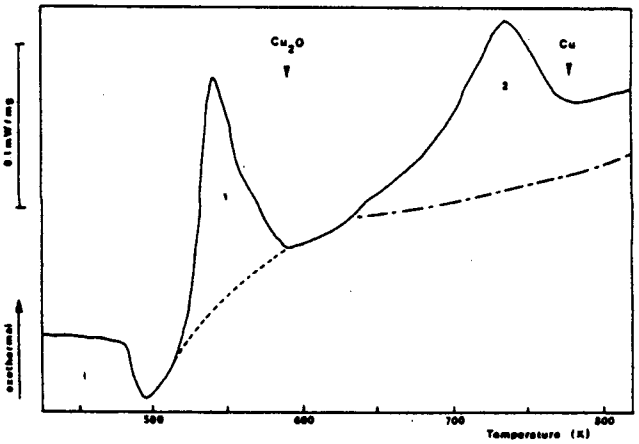

Figure 1. DSC curve of unaged CuO on carbon.

The results of DSC and X-ray diffraction indicate that peak 1 corresponds to the reduction of CuO into Cu_2O and peak 2 to the formation of metallic Cu. The reduction of the copper oxides by the carbon produces only CO_2. Therefore peak 1 of the DSC curve corresponds to the exothermal reaction :

$$CuO + \frac{1}{4} C \rightarrow \frac{1}{2} Cu_2O + \frac{1}{4} CO_2 + \Delta H \qquad (1)$$

The heat of reaction ΔH at 473 K and at 623 K is respectively equal to -31.3 and -35.8 kJ/mole CuO. Considering the small change of ΔH an average value of -33.4 kJ/mole CuO has been taken. The measurement of the heat release of peak 1 allows then to estimate the quantity of CuO according to reaction (1). Experimentally it was found that 97 % of the amount of CuO present on the activated carbon can be detected by DSC in the case of the unaged sample.

Aged impregnated samples

The area of peak 1 of the DSC curve is decreasing with aging duration which suggest that the amount of Cuo is decreasing. After 18 days of aging, CuO is found in the sample by X-ray diffraction. At the same time a third exothermal peak appears in DSC between 623 and 783 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. According to X-ray analysis peak 3 corresponds to the reduction of CuO detectable by X-ray diffraction, i.e. to well crystallized CuO as also shown in Figure 2. It is also observed that in these samples the reduction of Cu_2O into Cu occurs at much higher temperature (820 K).

When the duration of aging increases (40 days and more) basic cupric carbonate $CuCO_3$, $Cu(OH)_2$ is formed. Crystalline phases detected by X-ray diffraction are also found by electron microscopy.

Discussion and Conclusion

The combination of DSC and X-ray diffraction techniques clearly indicates that

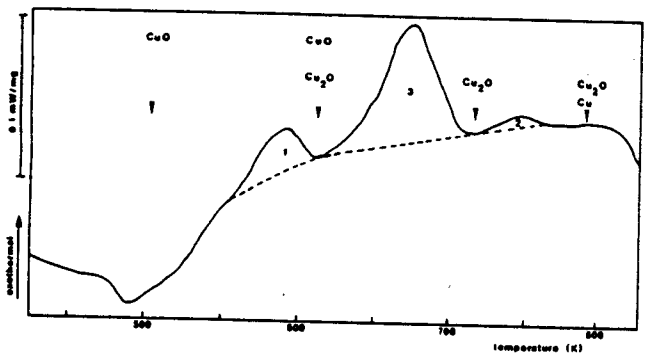

Figure 2. DSC curve of a 25 days aged CuO-carbon sample.

two types of CuO can be found on the carbon support : an amorphous and/or weakly crystallized one (peak 1 in DSC) not detected by X-ray and a crystallized one (peak 3 in DSC). It is therefore possible to determine the amount of both phases at different stage of aging. It appears that the amorphous CuO is not quantitatively converted into crystallized CuO during aging. Therefore sintering is not the only aging mechanism. There is a definite loss of CuO (about 50 % of the initial amount) during the first 25 days of aging. Hence the carbon support is not inactive toward CuO and causes its partial reduction in Cu(I) species.

References

1. V. Deitz, J. Robinson and E. Pozomiek, Carbon, 13, 181, 1975.