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SURFACE COPPER ENRICHMENT BY REDUCTION OF COPPER CHROMITE CATALYST EMPLOYED FOR CARBON MONOXIDE OXIDATION

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The effect of prereduction on CO oxidation activity of unsupported copper-chromite oxide catalysts was examined. Results were found to be in good agreement with two mechanisms for a surface copper enrichment due to CO prereduction which produced an activity increase in the copper-chromite catalyst.

1. Introduction

Synergistic or cooperative effects of two-metal based catalysts are some of the most fascinating aspects in catalysis research. These catalysts are generally composed of a main-active species and the so called promoter. Examples are the Co-Mo catalysts employed for hydrodesulphurization. Bi-Mo for ammoxidation, Cu-Zn for methanol synthesis, etc. [1,2]. In the case of Cu-Cr, the information regarding this catalyst system in connection with CO oxidation is scarce, even though this seems to be the most suitable combination for substituting precious metals employed as auto-emission control catalysts [3,4]. In previous reports on copper-chromite [5,6] it was suggested that the main active species for CO oxidation are copper cations and that the role of chromium is to protect copper

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from excessive reduction. It was also shown that activity was improved by prereducing the catalyst with CO, but there was no interpretation for that effect.

In the present work the nature of the active surface in copper-chromite catalysts employed for CO oxidation has been examined aiming to elucidate such a CO prereduction effect.

2. Experimental

Catalysts were prepared by evaporation (60 ° C) of mixed copper and chromium nitrate solutions using appropriate concentrations to obtain the desired Cr/(Cr + CU) weight ratios. After drying (100 ° C) the mixed nitrates were calcined by increasing the temperature at a rate of 100/h up to 500 ° C. This temperature was maintained overnight. After calcination the catalysts were in the form of fine powders.

The catalyst activity for CO oxidation was referred as the steady state CO conversion at 200 ° C. This was measured using a continuous flow reaction procedure as described in detail earlier [5]. Before reaction, samples were prereduced in-situ with pure CO at 300 ° C for 3 h. Otherwise the samples were treated with the reactant mixture (17% CO in air) for about 0.5 h during temperature increase from ambient to the reaction temperature (200 ° C).

Temperature Programmed Reduction (TPR) was carried out using apparatus and procedure as described previously [7]. A mixture of 20 vol.% of CO in He was employed as reducing gas.

X-ray photoelectronic spectra (XPS) of fresh and CO-pretreated samples were carried out with MgKα X-ray source using the 1s signal of carbon as reference. Samples were evacuated at 120 ° C overnight before the analyses. CO-pretreated samples were transferred to the analysis chamber without contact with air. Auger spectra (AES) were carried out in an all metal system with a cylindrical mirror analyzer using 5 μA and 3 keV for the primary beam. The analyses were carried out at glancing incidence in order to minimize the depth of beam penetration. Samples were handled under inert atmosphere most of the time and pre-evacuated thermically (200 ° C) before the analyses, signals at about 915 and 570 eV of Cu and Cr respectively were used for quantification employing the procedure described elsewhere [8]. Spectra were recorded at several points in repeated samples in order to check the reproducibility.

3. Results

3.1. CATALYTIC ACTIVITIES

Figure 1 shows that bimetallic catalysts increase in activity when pretreating with CO. Optimum catalyst composition for higher CO conversion corresponded

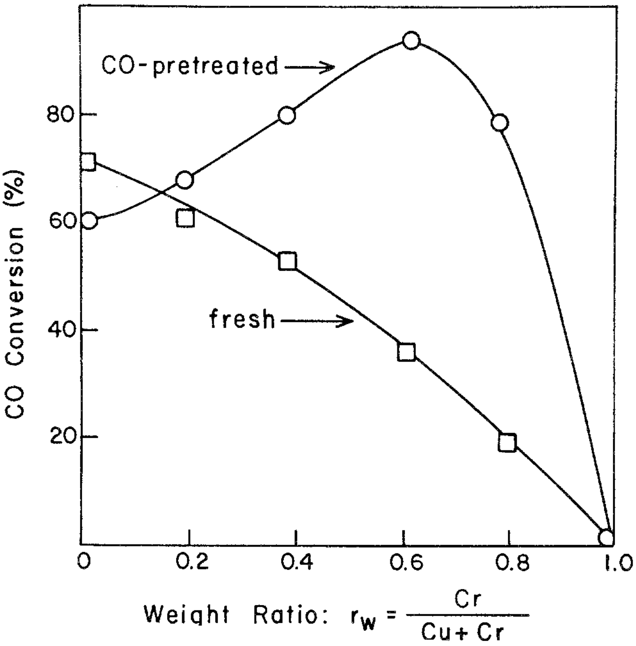

Fig. 1. Steady state catalytic activities. Sample weight: 50 mg, temperature: 200 ° C, flow: 180 sccm, 17 vol% CO.

to the stoichiometry of $CuCr_2O_4$ ($rw = 0.62$). However, in the absence of prereduction with CO, copper oxide ($rw = 0$) was found to be more active than the Cr containing catalysts.

CO pretreatment of CuO ($rw = 0$) produced an induction period of inactivity (not shown) as reported elsewhere [6], probably due to excessive reduction as suggested by TPR (see below)

3.2. XRD

X-ray diffraction analyses showed the presence of three crystalline phases (table 1). The CuO signal disappeared in samples with $rw = 0.62$. At this value, the intensity of the $CuCr_2O_4$ signal was maximum, although accompanied by weak signals of Cr_2O_3. The presence of Cr_2O_3, but not of CuO, in the sample with stoichiometry corresponding to $CuCr_2O_4$ ($rw = 0.62$) is probably the result of some amount of non-crystalline Cu, e.g. well dispersed or occupying point defects in the $CuCr_2O_4$ matrix. Also, peak intensity and breadth indicated the CuO phase was significantly more crystalline than both $CuCr_2O_4$ and Cr_2O_3.

3.3. TPR

Figure 2 shows a very intense TPR peak in CuO at 212 ° C which is indicative of an extensive reduction. Previous TPR of supported CuO employing same experimental condition reports a value of peak temperature of 185°C for 30% CuO supported on alumina [6], indicating that CuO is reduced easier when dispersed on alumina. A similar effect is found when Cr is added in small proportions (*rw* = 0.20 and 0.38), for which cases two peaks are found at temperatures smaller than 212°C.

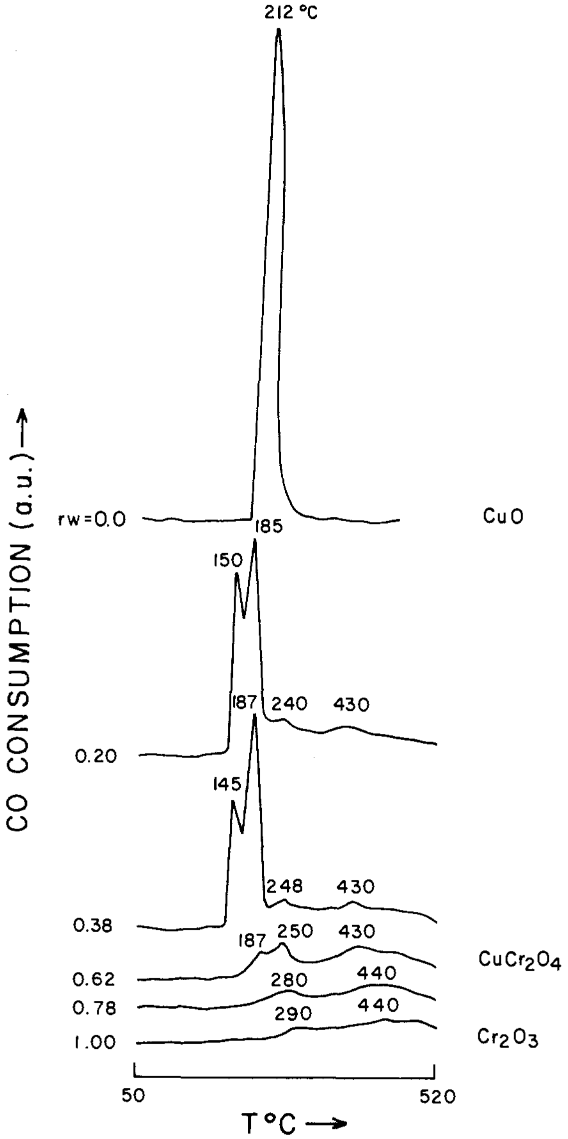

Fig. 2. TPR spectra. Reducing gas: 20% CO in He. Total flow: 50 sccm. Sample 20 mg diluted with 50 mg alumina.

Table 1
Surface area and X-ray data of the fresh catalysts

rw [a]	B.E.T. area (m^2/g)	XRD intensity of phases [b]		
		CuO	$CuCr_2O_4$	Cr_2O_3
0.00 (CuO)	0.5	100	0	0
0.20	1	5Q	15	3
0.38	1.5	35	25	3
0.62 ($CuCr_2O_4$)	2	0	60	8
0.78	2	0	15	30
1.00 (Cr_2O_3)	2.5	0	0	50

[a] $rw = Cr/(Cu + Cr)$; weight ratio.

[b] Intensities are relative to CuO peak located at $2\theta = 48.8°$ (XRD carried out using $CuK\alpha$).

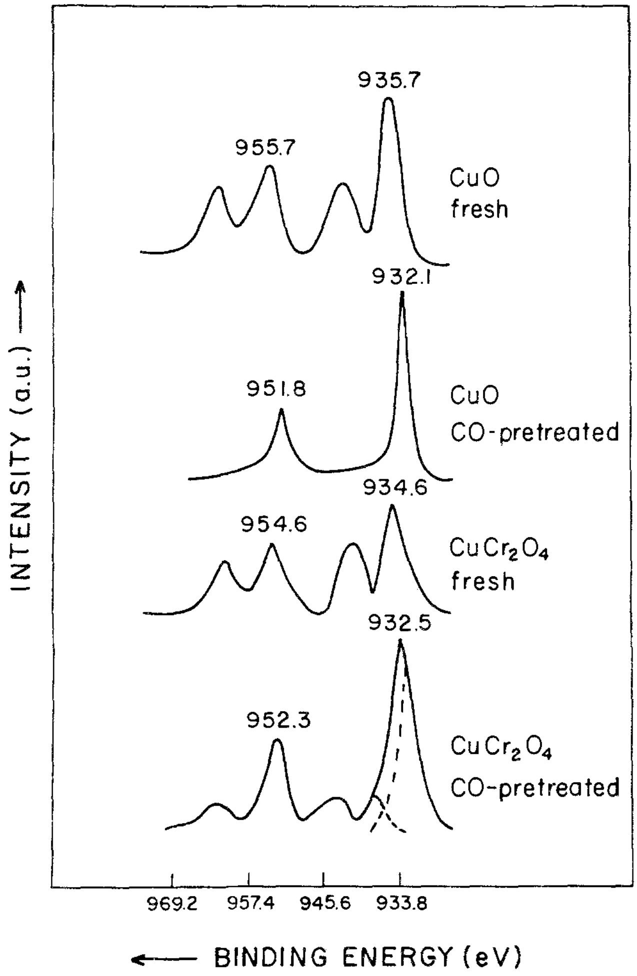

Fig. 3. XPS spectra in the copper 2p region.

3.4. XPS

Typical spectrum of Cu^{2+} was obtained for the fresh CuO sample (fig. 3). It is seen that after CO reduction the satellite signals completely disappeared and the Cu $2p_{3/2}$ peaks were shifted from 935.7 to 932.1 eV indicating that surface copper was in a reduced state [10]. Fresh $CuCr_2O_4$ also shows the Cu^{2+} signal, however, there is no indication of severe reduction as found in CuO as a result of the treatment with CO. Instead, peak deconvolution showed a composed signal of Cu^{2+} and Cu^{1+} and/or Cu^0 (it is not possible to differentiate them by XPS alone), suggesting partial reduction of the surface.

It was also recorded (not shown) the XPS in Cr 2p region of $CuCr_2O_4$ samples. Peaks at 576.1 and 585.9 eV which are typical of Cr^{3+} [11] were practically unchanged after CO reduction.

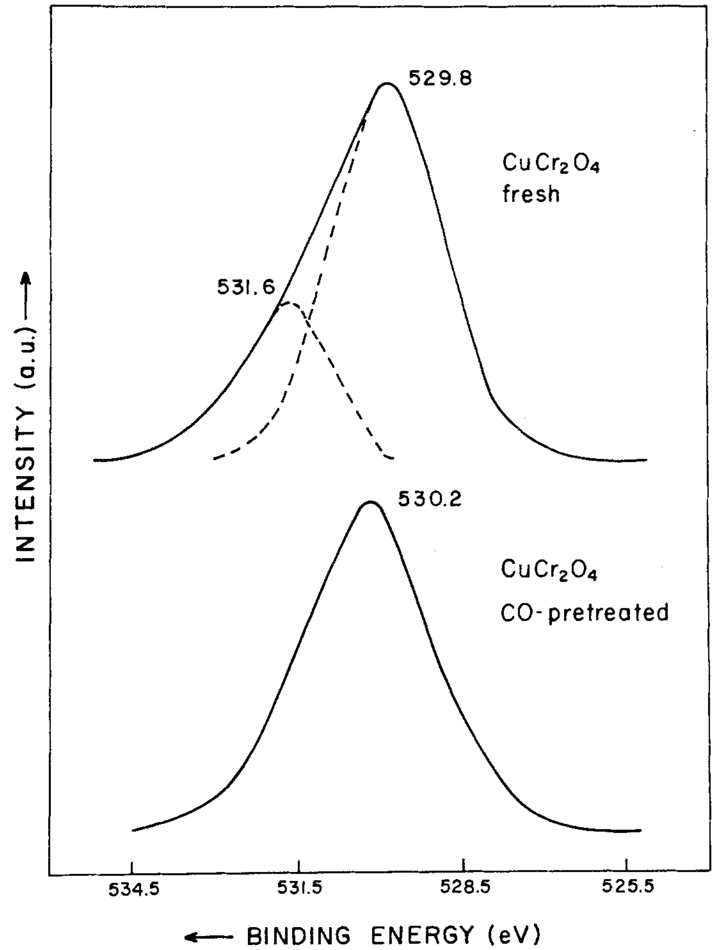

Fig. 4. XPS spectra in the oxygen 1s region.

Figure 4 shows the 1s signal of oxygen in $CuCr_2O_4$. Peak deconvolution suggests the presence of two types of surface oxygen in fresh $CuCr_2O_4$. It is also seen that the high binding energy oxygen disappeared after CO reduction.

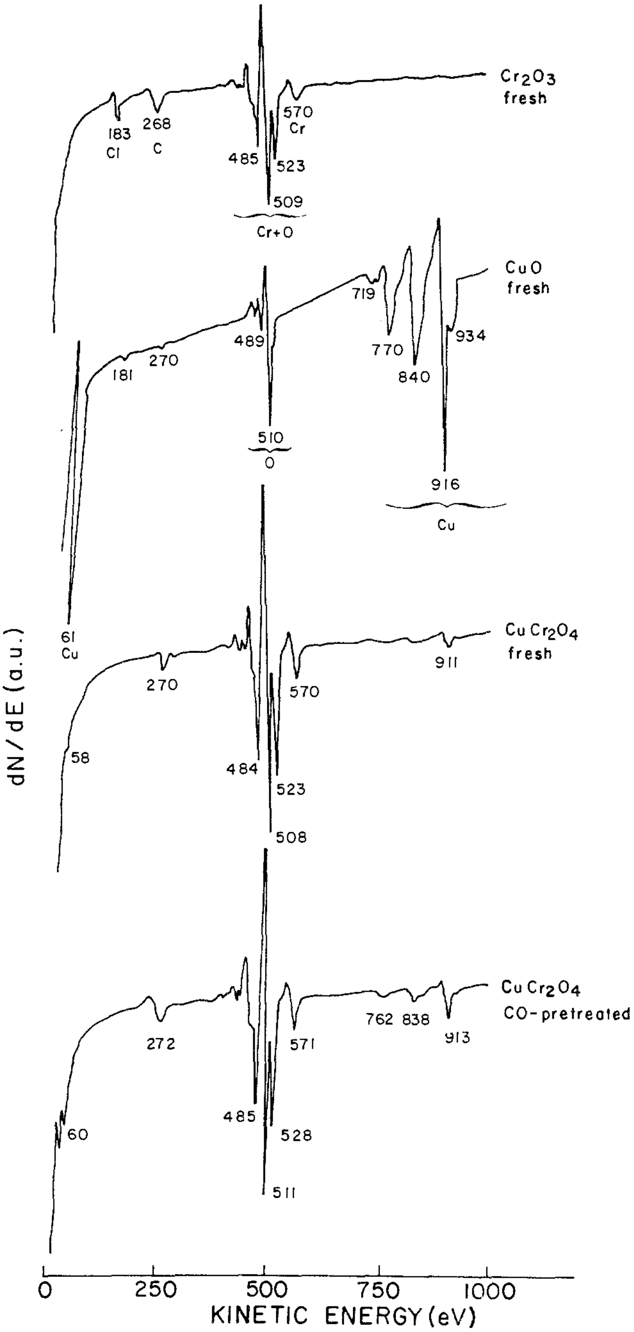

Fig. 5. AES spectra.

Table 2
Effect of CO pretreatment of $CuCr_2O_4$

$CuCr_2O_4$ sample	XCu [a]	Activity [b]	N° of turnover [c]
Fresh	0.11	0.38	0.25
CO-pretreated	0.27	0.95	0.26

[a] Surface atomic concentration: Cu/(Cu + Cr) determined by AES.
[b] Conversion of CO at 200 ° C (from fig. 1).
[c] Defined as: mol of CO converted/XCu.hour.

3.5. AES

Figure 5 shows typical Auger spectra of fresh and pretreated $CuCr_2O_4$ as well as fresh CuO and Cr_2O_3 catalysts. All samples presented contamination with carbon of unknown origin, which almost disappeared with the thermal evacuation. A close inspection of the signals indicated that surface concentration of Cu in $CuCr_2O_4$ was significantly smaller than the stoichiometric value (table 2). In addition, Co reduction of $CuCr_2O_4$ caused an increase in both surface Cu concentration and catalytic activity (table 2), strikingly producing almost the same number of turnover, with respect to Cu, in each case.

4. Discussion

The direct relation between surface Cu concentration and activity (table 2) confirms that Cu rather than Cr is the active species for CO oxidation on copper-chromite.

As reported previously for the alumina supported catalysts [6], the present unsupported $CuCr_2O_4$ is found to be more active than CuO, only if prereduction with CO is carried out. Also, TPR and XPS results confirm our previous finding indicating that the incorporation of Cr with Cu diminishes the extent of reduction of the oxide catalyst. However, the appearance of TPR signals at temperatures (e.g. 145–150 ° C) lower than that of CuO (212 ° C) suggests that the presence of Cr enhances initial Cu reducibility. The second peak at about 185–187 ° C in the Cu-Cr samples (which is greater at smaller *rw*: 0.20 and 0.28) could be associated to a phenomenon reported elsewhere [12] consisting in the formation of $Cu_2Cr_2O_4$ as a result of the reduction of well dispersed CuO (i.e. the first peak at 145–150 ° C) in the presence of $CuCr_2O_4$ (peak at 240–245 ° C). However, the peak assigned to well dispersed CuO (145–150 ° C) did disappear in sample with $rw = 0.62$, but that attributed to $Cu_2Cr_2O_4$ (187 ° C) did not, even though such phase was not detected by XRD. This could be the result of Cu occupying point defects in the $CuCr_2O_4$ matrix resembling an amorphous $Cu_2Cr_2O_4$ structure.

Hence, the detection by XRD of Cr_2O_3 but not of CuO in sample with $rw = 0.62$ (table 1).

Accordingly, one may speculate that to accomplish the reduction of $CuCr_2O_4$ with CO, a migration of the unstable Cu cations from the defective structure to the surface should occur explaining the increase in surface Cu concentration, and hence of activity, observed after prereduction with CO (table 2). The low surface concentration of Cu (table 2) relative to the overall Cu bulk concentration (i.e., $1 - rw$) probably acts as a driving force favouring the migration of Cu during reduction of $CuCr_2O_4$, similar to that occurring in other spinel structures (e.g. $CuAl_2O_4$), where Cu migrates to either bulk or surface after calcining or reducing repectively [13,14].

However, another process could be responsible for the enrichment phenomenon observed: the preferential generation of surface vacancies over Cu rather than over Cr. Supporting this, it is known that Cu cations tend to adsorb oxygen strongly forming a non-stoichiometric copper oxide at the surface [15,16]. Thus, CO prereduction should preferentially take that excess oxygen resulting in an increase in Cu exposure. This proposal correlated well with the results on XPS in the oxygen 1s region (fig. 4) i.e. the 1s electron of the non-stoichiometric oxygen has a binding energy approximately equal or higher than 531.6 eV. Nevertheless, Cu migration to the surface could also take place as a result of CO pretreatment, as discussed above, and it is not possible to elucidate from the present results whether both or only one of the two above proposed mechanisms predominate in the Cu-enrichment phenomenon observed.

5. Conclusions

It was confirmed that Cu is the active species for CO oxidation over copper-chromite, and that one of the roles of Cr is to favour initial catalyst reduction but limiting the extent of total reduction. The enhancement in activity produced by prereduction with CO of $CuCr_2O_4$ was attributed to an enrichment in Cu concentration at the spinel surface. Also, two types of oxygen were detected in $CuCr_2O_4$ one of which was removed from the surface by the prereduction. Two mechanisms for the Cu-enrichment phenomenon were proposed: migration of Cu from bulk to surface, and preferential generation of oxygen vacancies over Cu rather than over Cr.

Acknowledgements

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