Catalysis Letters 25 (1994) 29–36

Temperature programmed oxidation of Cu / ZnO catalysts with N_2O: an attempt for characterization of copper catalysts

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Received 12 April 1993; accepted 6 December 1993

For characterization of the surface structure of metallic copper formed on the support, temperature programmed oxidation (TPO) with N_2O was carried out over various Cu/ZnO catalysts. Four peaks of the N_2 formation (α, β, γ and δ) were observed at 223, 400, 545 and 600 K in the TPO runs. The average copper crystallite size estimated from the sum of the amount of α- and β-peaks agreed fairly with those determined by X-ray diffraction and transmission electron microscopy. It was concluded that α- and β-peaks resulted from the oxidation of metallic copper atoms on the steps, corners and/or defect sites, and on the flat sites of the surface of copper crystallites, respectively, while γ- and δ-peaks resulted from the bulk oxidation of copper.

Keywords: Temperature programmed oxidation; oxidation with N_2O; characterization of Cu/ZnO catalysts

1. Introduction

Oxidation of the surface of copper with N_2O

$$N_2O(g) + 2Cu_s \rightarrow (Cu{-}O{-}Cu)_s + N_2(g)\,,$$

where s denotes surface atoms, is a well-known method for measuring the metal surface area of supported copper catalysts [1–13]. By the use of ultraviolet photoelectron spectroscopy, Narita et al. previously confirmed that the metallic copper surface sites were transformed to monovalent copper by the oxidation with N_2O at temperatures below 373 K [6].

Habraken et al. carried out the decomposition of N_2O on Cu(111), Cu(110) and Cu(100) single crystals, finding great difference in the reactivity of these Cu surfaces to N_2O [14–16]. Hence, it is highly feasible to determine surface structures of metallic copper formed on the support by oxidation with N_2O.

In the present work, temperature programmed oxidation (TPO) with N_2O was carried out over various Cu/ZnO and unsupported Cu catalysts. We showed that structures of the surface copper sites were characterized by the use of this technique.

2. Experimental

Cu/ZnO catalysts having various molar ratios of Cu/Zn (Cu/Zn = 5/95, 10/90, 30/70, 50/50, 70/30, 90/10) were prepared by two methods. The catalysts with Cu/Zn ratios below 30/70 were prepared by coprecipitation of basic salts of copper and zinc from a solution of nitrates with a solution of sodium carbonate in a similar way to that employed by Herman et al. [17], whereas those with Cu/Zn ratios above 50/50 were prepared from copper and zinc nitrates and sodium bicarbonate by an inverse coprecipitation method similar to that employed by Porta et al. [18]. The precipitates were dried at 383 K overnight, and calcined in air at 623 K for 4 h. 1 g of the catalyst thus prepared was first reduced in a reactor in a stream containing 3 vol% of H_2 diluted with He at 483 K for 1 h. The temperature was then raised from 483 to 523 K stepwise by 10 K/h and finally kept at 523 K for 1 h in pure H_2. Details of the catalyst preparation were described elsewhere [19,20].

For comparison, experiments were also conducted over various unsupported Cu catalysts (denoted as Cu_A, Cu_B, Cu_C and Cu_D) which were prepared by different methods and subjected to different treatments prior to the TPO runs. Cu_A was prepared in the inverse coprecipitation method as mentioned above. The catalyst was calcined in air and subsequently reduced with H_2 as the Cu/ZnO catalysts. Cu_B was prepared by leaching Cu–Al alloy (50 wt% Cu) with an aqueous solution of NaOH at 323 K. Prior to the TPO runs the catalyst was reduced in a pure H_2 flow at 523 K for 1 h. Cu_C was prepared by reduction of Cu_B with H_2 at 773 K for 15 h. Cu_D was prepared by oxidation of Cu_B in a stream containing 2 vol% of N_2O at 773 K for 2 h and following reduction with H_2 at 773 K for 3 h.

TPO runs were carried out in a U-shaped flow reactor at a total flow rate of 100 cm^3-NTP/min. After the reduction of the catalysts in a H_2 flow, H_2 in the reactor was flushed with helium at 553 K for 20 min. The temperature of the catalyst was then lowered to 223 K. Thereafter, the catalyst was exposed to a stream containing 2 vol% of N_2O at 223 K. The temperature was raised up to 723 K at a heating rate of 3 K/min. Helium was used as a diluent. The effluent from the reactor was analyzed by gas chromatography.

Diffuse reflectance FT-IR spectra of adsorbed CO were recorded in He at room temperature with an infrared spectrophotometer (JASCO FT-IR-5M) to which a diffuse reflectance instrument was attached [20]. After the reduction with H_2 and the He treatment, the catalysts were exposed to a CO stream at room temperature for 15 min. Spectra of adsorbed CO were recorded after CO in the gas phase was flushed with He for 7 min.

The copper crystallite sizes of the reduced catalysts were determined by X-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD spectra of the catalysts were measured on a XRD diffractometer (Rigaku Denki ADP-301E) by using Ni filtered Cu Kα radiation. The average crystallite size of metallic copper was determined from the full width at half maximum of the Cu(111) peak by using the Scherrer equation. TEM measurements were carried out with an electron microscope (HITACHI H-800) at 200 kV.

3. Results and discussion

Fig. 1 illustrates a profile of N_2 formation in a TPO run over Cu/ZnO catalyst having Cu/Zn molar ratio of 30/70. On feeding the N_2O stream at 223 K, N_2 is instantly formed and then decreases rapidly with increasing temperature (α-N_2). One peak of the N_2 formation appears at 400 K (β-N_2). Above 450 K, the N_2 formation increases again more rapidly.

Fig. 2 shows the profiles of the N_2 formation between 453 and 700 K. Two peaks of the N_2 formation are seen at 545 and 600 K (γ- and δ-N_2). O_2 is evolved above 633 K. The partial pressure of O_2 in the effluent is a half that of N_2 evolved above 633 K, suggesting that N_2O decomposition, $N_2O \rightarrow N_2 + \frac{1}{2}O_2$, takes place. Based on these findings, we concluded that N_2O decomposed to N_2 and four types of oxygen species corresponding to the α-, β-, γ- and δ-N_2 formation were formed during the course of the TPO run. Henceforth, four types oxygen species were designated respectively as α-, β-, γ- and δ-oxygen.

When the TPO run was carried out over ZnO, a trace amount of N_2 was detected in the effluent above 650 K. The formation of N_2 was exceedingly slow as compared with that over Cu/ZnO. This strongly suggested that the N_2 formation proceeded at copper sites over Cu/ZnO.

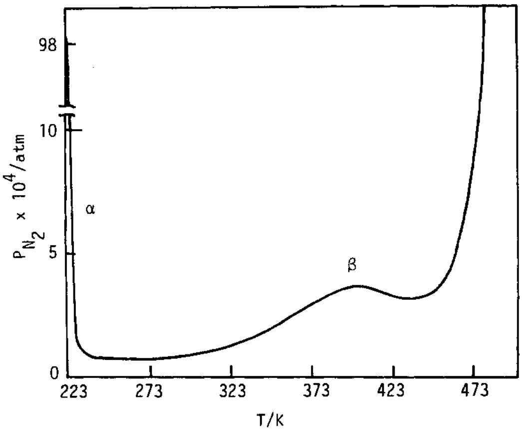

Fig. 1. A profile of the N_2 formation in the TPO run carried out over a Cu/ZnO catalyst (Cu/Zn = 20/70). The profile between 223 and 473 K is illustrated. Weight of the catalyst used was 1 g.

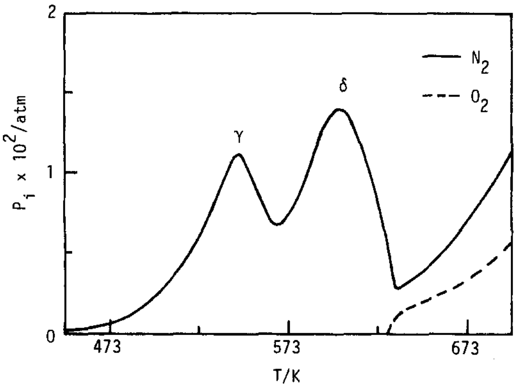

Fig. 2. A profile of the N_2 formation in the TPO run carried out over a Cu/ZnO catalyst (Cu/Zn = 30/70). The profile between 453 and 700 K is illustrated. Weight of the catalyst used was 0.5 g.

The sum of the amounts of α-, β- and γ-oxygen species was practically the same as that of δ-oxygen species, and the total amount of all of the oxygen species was in fair agreement with that of oxygen required for conversion of metallic copper to CuO. XRD measurements were carried out for the Cu/ZnO catalyst (Cu/Zn = 30/70) previously subjected to TPO to different temperatures where different stages of the oxidation of the catalyst were reached. In the XRD pattern of the catalyst oxidized to 400 K, where α- and β-oxygen species predominated, the peaks ascribed to metallic copper and zinc oxide were observed. This suggested that these oxygen species were formed on the surface and/or the sub-surface of the metallic copper crystallites. The XRD measurement revealed that the metallic copper converted to Cu_2O when the catalyst was oxidized up to 563 K. In the XRD pattern of the catalyst subjected to the TPO up to 630 K, the peaks ascribed to Cu_2O diminished, and those ascribed to CuO grew considerably. Therefore we concluded that γ- and δ-oxygen species were resulted from the oxidation of the bulk metallic Cu to Cu_2O and that of Cu_2O to CuO, respectively.

Similar TPO profiles were observed for the N_2 formation over other Cu/ZnO catalysts. The average crystallite sizes of metallic copper, $d(1)$ and $d(2)$, were estimated from the amount of α-oxygen species and the sum of those of α- and β-oxygen species, respectively, on the assumption that the number of copper atoms exposed per square meter of copper was 1.46×10^{19} atoms/m^2 [7] and that copper particles were spherical. In fig. 3, the estimated values are compared with those measured by XRD and TEM. Although the average crystallite size estimated by XRD for Cu/ZnO with Cu/Zn ratio of 50/50 is mismatched with the $d(1)$ value, the $d(2)$ values for other Cu/ZnO are substantially in agreement with the crystallite sizes measured by XRD and TEM.

Bartley et al. [11] and Luys et al. [12] claimed that sub-surface oxidation of copper occurred together with the surface oxidation in the course of the N_2O decompo-

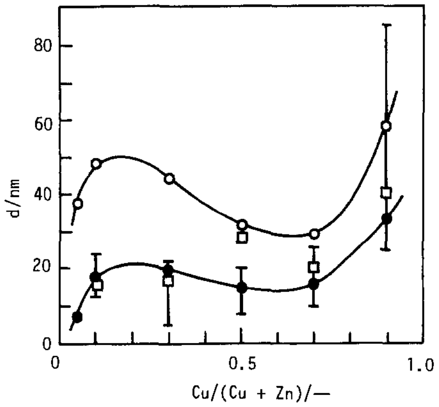

Fig. 3. Comparison of the average copper crystallite sizes, $d(1)$ and $d(2)$, of Cu/ZnO catalysts with those determined by XRD and TEM measurements. (○) $d(1)$, (●) $d(2)$, (□) determined by XRD. Bars represent the range of the diameters of the crystallites observed in transmission electron micrographs.

sition at 363 K. If β-oxygen species is formed by the sub-surface oxidation, the crystallite size estimated from the amount of α-oxygen species would correspond with those measured by XRD and TEM. However, this does not hold in the present experiments, suggesting that both of α- and β-oxygen species are formed on the surface of the copper crystallites.

In confirmation of this suggestion, similar experiments were carried out over unsupported Cu catalysts. In the TPO runs, all of the peaks ascribed to the formation of α-, β-, γ- and δ-oxygen species were observed. The surface areas, $S(1)$ and $S(2)$, were estimated from the amount of α-oxygen species and the sum of those of α- and β-oxygen species, respectively, and were compared with the BET surface areas (table 1). The values of $S(2)$ fairly agree with those of the BET surface areas. Therefore we concluded that both of α- and β-oxygen species were formed on the surface of the copper crystallites.

Table 1
The surface areas of the unsupported Cu catalysts estimated on the basis of the TPO runs and BET measurements

Catalyst	Amount of oxygen species [a]		Surface area (m^2/g)		
	α-oxygen	β-oxygen	$S(1)$ [b]	$S(2)$ [c]	BET
Cu_A	0.22	9.23	0.018	0.78	1.3
Cu_B	57.4	119.8	4.75	10.4	11.4
Cu_C	31.6	48.7	2.63	6.63	8.2
Cu_D	22.0	27.5	1.83	4.12	6.4

[a] In unit of μmol/g-cat.
[b] Estimated from the amount of α-oxygen species.
[c] Estimated from the sum of the amount of α- and β-oxygen species.

Scholten and Konvalinka [2], and Sengupta et al. [5] reported that bulk oxidation of copper crystallites with N_2O occurred at temperatures higher than 373 K, where the β-peak was observed. However, they carried out the oxidation for 12 h or more. Scholten and Konvalinka [2] showed that the bulk oxidation had an incubation time longer than 2 h at 413 K over a Cu/MgO catalyst. Under the present TPO conditions, the temperature was raised from 373 to 423 K for about 17 min. Hence, the contribution of the bulk oxidation to the β-peak was negligible in the TPO runs. On the other hand, Chinchen et al. [9] described that surface oxidation was completed at 333 K in the course of the frontal chromatography. However, with careful inspection of fig. 2 in ref. [9], it is shown that N_2 was still formed at slow rate after the break-through of N_2O. This slow evolution of N_2O would correspond to the β-peak in the present TPO runs.

In fig. 4 is plotted a ratio of the amount of α-oxygen species (V_α) to the sum of those of α- and β-oxygen species, ($V_\alpha + V_\beta$), against the Cu/(Cu + Zn) ratio. The ratio, $V_\alpha/(V_\alpha + V_\beta)$, increases with the increase of the Cu/(Cu + Zn) ratio up to 0.9.

Corresponding to the variation of $V_\alpha/(V_\alpha + V_\beta)$, infrared spectra of CO adsorbed on the catalysts varied by the catalyst composition (fig. 5). When CO was fed over the catalysts at room temperature and subsequently flushed with flowing helium, absorptions occur at 2100 and 2090 cm^{-1} along with that at 2195–2178 cm^{-1}. The absorption at 2195–2178 cm^{-1} is assigned to CO adsorbed on ZnO [21], whereas those at 2100 and 2090 cm^{-1} are assigned to CO adsorbed on metallic copper surface sites [22–25]. With the increase of the Cu content, the absorption at 2100 cm^{-1} increases in relative intensity to the absorption at 2090 cm^{-1}.

Pritchard and coworkers extensively studied the infrared spectra of CO adsorbed on various single crystal faces of copper [22–25]. The absorption occurred at 2079–2088 and 2070–2080 cm^{-1} respectively on Cu(100) and Cu(111) [22,23]. On Cu(211) and Cu(311) at low surface coverage, the infrared absorptions

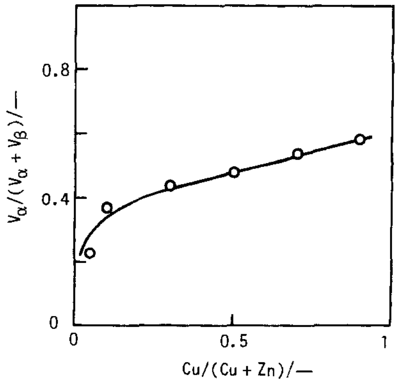

Fig. 4. $V_\alpha/(V_\alpha + V_\beta)$ versus catalyst composition.

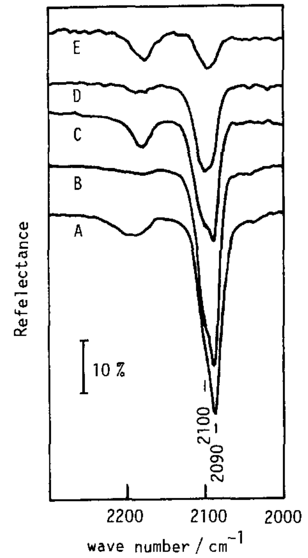

Fig. 5. IR spectra of CO adsorbed over various Cu/ZnO catalysts. Cu/Zn ratio: (A) 5/95, (B) 10/90, (C) 30/70, (D) 50/50 and (E) 70/30. CO was adsorbed at $P_{CO} = 10.1$ kPa and at room temperature. The spectra were recorded after CO in the gas phase was flushed with a He stream for 7 min.

of CO adsorbed were situated at 2100–2110 and 2088–2095 cm^{-1} [22]. These authors also showed that the infrared spectra of adsorbed CO exhibited two peaks at 2102–2106 and 2081–2090 cm^{-1} respectively on Cu(110) misorientated and Cu(100) misorientated [23,25]. They concluded that the absorption at 2110–2100 cm^{-1} arose from CO adsorbed at steps or defect sites [23,25]. Hence, the present variation of the spectra of CO strongly suggested that the fraction of the surface having steps or defect sites increased with the increased Cu/Zn ratio up to 90/10. Comparing the results in fig. 4 with those in fig. 5, we concluded that α- and β-oxygen species were formed on the metallic copper surface having steps, corners and/or defect sites and having flat sites, respectively.

At the present stage of the investigation, it is still unresolved why the surface fraction of steps, corners and/or defect sites increased with the increased Cu/Zn ratio up to 90/10. Klier and coworkers [26,27] studied the structures and the morphology of various Cu/ZnO catalysts by means of transmission electron microscopy, scanning transmission electron microscopy, microdiffraction and energy dispersive analysis. They showed that the morphology of the Cu and the ZnO components in reduced and oxidized states greatly varied by the Cu content. The variation of the morphology may cause the difference in the fraction of surface having steps, corners and/or defect sites.

The present results showed that the oxidation of metallic copper with N_2O was structure sensitive. The TPO with N_2O gave knowledge of the surface structures of copper containing catalysts.

Acknowledgement

The authors express their sincere thanks to Mr. Y. Nodasaka for the TEM measurements and for valuable discussions.

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