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Studies on the Chemical State of Cu during Methanol Synthesis

The conversion of synthesis gas to methanol is an important catalytic process (*1*). Two major catalyst systems, supported Pd and Cu/Zn catalysts, exhibit high activity and selectivity. Palladium supported on silica has been widely studied (*2–4*) and more recently, Hicks *et al.* (*5, 6*) observed an order of magnitude higher activity on lanthana-supported Pd. The industrial low-pressure catalysts, however, are all based on $CuO/ZnO/Al_2O_3$ or $CuO/ZnO/Cr_2O_3$ compositions. Herman *et al.* (*7*) studied these catalyst systems in great detail and suggest a Cu^+ solution in ZnO as active phase where Cu^+ nondissociatively chemisorbs and activates CO and ZnO activates H_2. In the range of 15 to 85% CuO in the catalyst, up to 16% Cu^+ became dissolved in the ZnO (*8*). Recently, however, Raney Cu–Zn catalysts have been shown to be very active methanol synthesis catalysts (*9*). The active component for these Raney catalysts was found to be metallic Cu with an activity maximum at 97 wt% Cu (*10*). The residual Zn in these catalysts provided a promotional effect to catalyst activity.

Obviously, more work is needed to elucidate the chemical state of the working catalyst surface. In this report XPS data are presented of a working $CuO/ZnO/Al_2O_3$ catalyst surface which show *metallic* Cu and ZnO. These data have been obtained with a system recently developed in our laboratories which permits a simultaneous study of catalyst performance and catalyst surface properties (*11*). This has been accomplished by coupling a pilot plant with a plug flow reactor to a minireactor which in turn is connected to a surface analysis instrument via a high-vacuum sample transfer system. The catalyst used was a commercial catalyst (C18HC, United Catalyst Inc.) with 43% CuO, 47% ZnO, and 10% Al_2O_3. The feed gas consisted of 73% H_2, 25% CO, and 2% CO_2. Treatment of the catalyst in this feed at 2 atm for 1 h at 250°C resulted in the quantitative conversion of all Cu^{2+} into Cu metal. Figure 1 compares the Cu 2*p* photoelectron and Cu ($L_3M_{45}M_{45}$) Auger lines (Al$K\alpha$ excitation, $h\nu = 1486.6$ eV) of an air-exposed catalyst surface and one after 3 h of methanol synthesis at 250°C. With those two lines Cu^{2+}, Cu^+, and Cu can easily be distinguished by XPS employing a so-called chemical state plot (CSP) with the Cu $2p_{3/2}$ binding energy on the abscissa (decreasing from left to right) and the Cu ($L_3M_{45}M_{45}$) kinetic energy on the ordinate as also shown in Fig. 1 (*12*). The diagonal lines representing the sum of $2p_{3/2}$ binding and $L_3M_{45}M_{45}$ kinetic energy indicate specific "Modified Auger Parameters" (Auger parameter plus photon energy) which are numbers useful in chemical identification (*12*). The position of Cu of the untreated catalyst in the CSP clearly identifies it as CuO. Copper electron energies have been referenced against C 1*s* at 284.6 eV and the experimental error in determining electron binding energies is ±0.15 eV. After synthesis gas conversion at 250°C only metallic Cu is seen on the catalyst surface. There was no further change in the chemical state of Cu upon many days on-stream. Ion beam bombardment of catalysts in order to remove the outer surface and to look for other Cu states (e.g., dissolved Cu^+ ions) in the ZnO matrix cannot be performed since ion bombardment leads to quick reduction of Cu_2O to metallic Cu.

The reducibility of Cu in both pure H_2 and CO was also studied as a function of temperature. Some of the data are compiled in the Cu CSP shown in Fig. 2. Treatment

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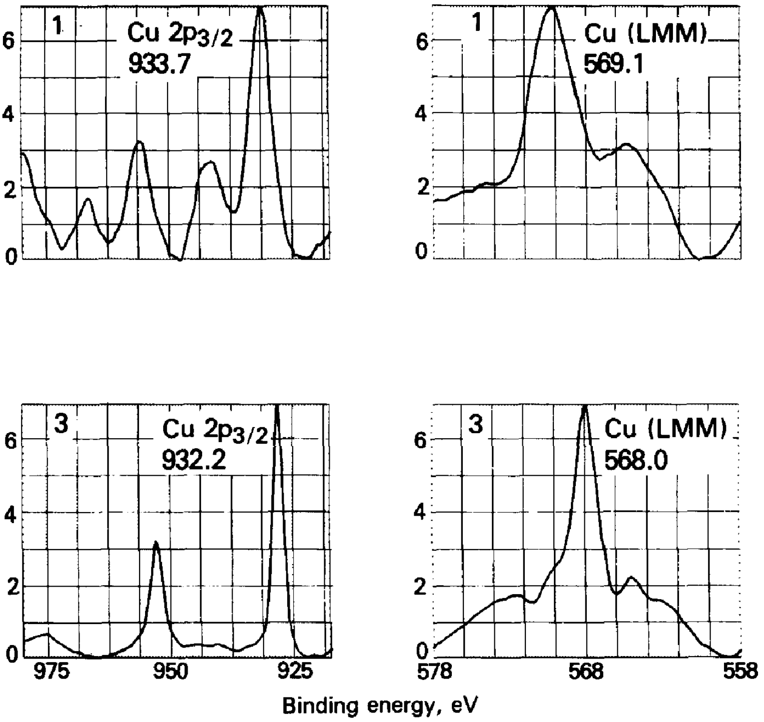
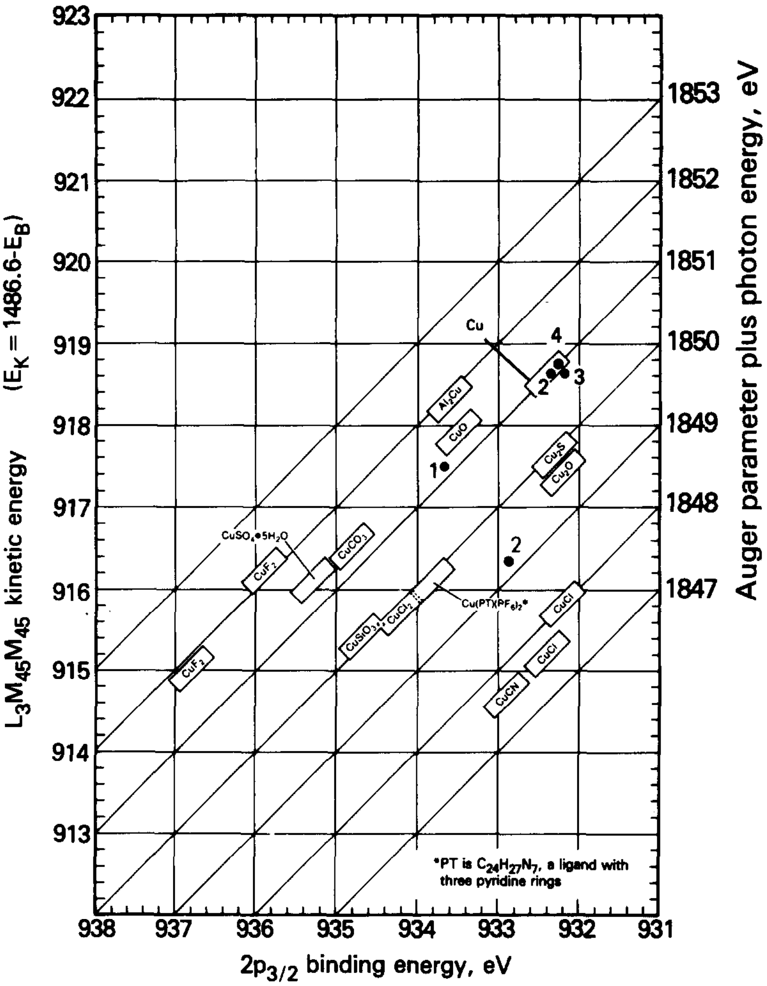


FIG. 1. Changes in Cu $2p$ and $Cu(L_3M_{45}M_{45})$ electron spectra during methanol synthesis. Synthesis gas: $H_2/CO/CO_2$ = 73/25/2, 2 atm. (1) As received, (2) 1 h 250°C, (3) 3 h 250°C, (4) 20 h 250°C.

in H_2 at temperatures as low as 50°C leads to a change in the chemical state of Cu which is due to reduction of Cu^{2+} into Cu^+. The decrease in the number of Cu^{2+} ions is clearly indicated in the Cu $2p$ spectra by decreasing satellite intensities. These satellites which have been attributed to shake-up transitions by ligand → metal $3d$ charge transfer (*13*) are very characteristic of Cu^{2+} compounds since this charge transfer cannot occur in Cu^+ compounds or in metallic Cu because of their completely filled $3d$ shells. The onset of CuO reduction at 50°C alludes to a catalytic effect since the reduction of pure CuO has been reported to proceed above 150°C (*14, 15*). At 100°C there is further reduction of Cu^{2+} into Cu^+ but no metallic Cu is yet formed. The position in the chemical state plot (Fig. 2) shows that the Cu^+ ions formed upon H_2 reduction are somewhat different from Cu^+ ions in Cu_2O. This observation could be indicative of a Cu^+/ZnO interaction. Since the position of the points is fairly close to the CuCl position, the Cl content of the sample was analyzed by XPS but no Cl could be detected. After about 5 h no further reduction is observed at 100°C. At this stage, Cu is predominantly present as Cu^+ accompanied by some Cu^{2+} as shown by the spectra in Fig. 3b.

Upon increasing the temperature to 250°C all Cu $2p$ satellite structure disappears indicative of complete reduction of Cu^{2+}. The Cu (LMM) Auger transition after 1 h of reduction exhibits two well-resolved peaks at 568.0 and 570.3 eV characteristic of metallic Cu and Cu^+, respectively (*16*) (Fig. 3c and data points 6 in Fig. 2). After 3 h at 250°C the conversion of Cu^+ into Cu metal is complete (Figs. 2, 3d). Vlaic *et al.* (*17*) studied the H_2 reduction of a $CuO/ZnO/Al_2O_3$ catalyst by XANES and EXAFS and also found highly dispersed metallic Cu and no Cu_2O. A recent XPS study by Okamoto *et al.* (*18*) also showed



*PT is $C_{24}H_{27}N_7$, a ligand with three pyridine rings

FIG. 1—*Continued.*

the formation of Cu metal upon 2-h reductions of both coprecipitated and impregnated CuO/ZnO catalysts in 1 atm of H_2 at 250°C. They observed, however, small quantities of Cu^+ in the coprecipitated catalysts.

The reduction of the same commercial methanol synthesis catalyst in pure CO is also illustrated in Fig. 2. These experiments were also performed *in situ*, however, in a static mode (catalyst was heated in 1 atm of CO). Interestingly, the reduction pattern closely parallels the one just described for H_2. At 100°C, Cu^{2+} ions are reduced to Cu^+ whereas at 250°C metallic Cu is formed. Major differences between H_2 and CO reduction are the different identities of the Cu^+ ions as evidenced by their different positions in the CSP (Fig. 2) as well as a considerable carbon buildup on the catalyst surface during CO reduction. This carbon buildup indicates CO dissociation on the catalyst surface. Barber *et al.* (*19*) found dissociative CO adsorption on metallic Cu above 100°C. At ambient and subambient temperatures CO adsorbs molecularly with metallic Cu (*20, 21*). Obviously, molecular CO adsorption on metallic Cu must also take place under methanol synthesis conditions (i.e., elevated temperatures, presence of H_2) since methanol is the main product with very little methane as byproduct and

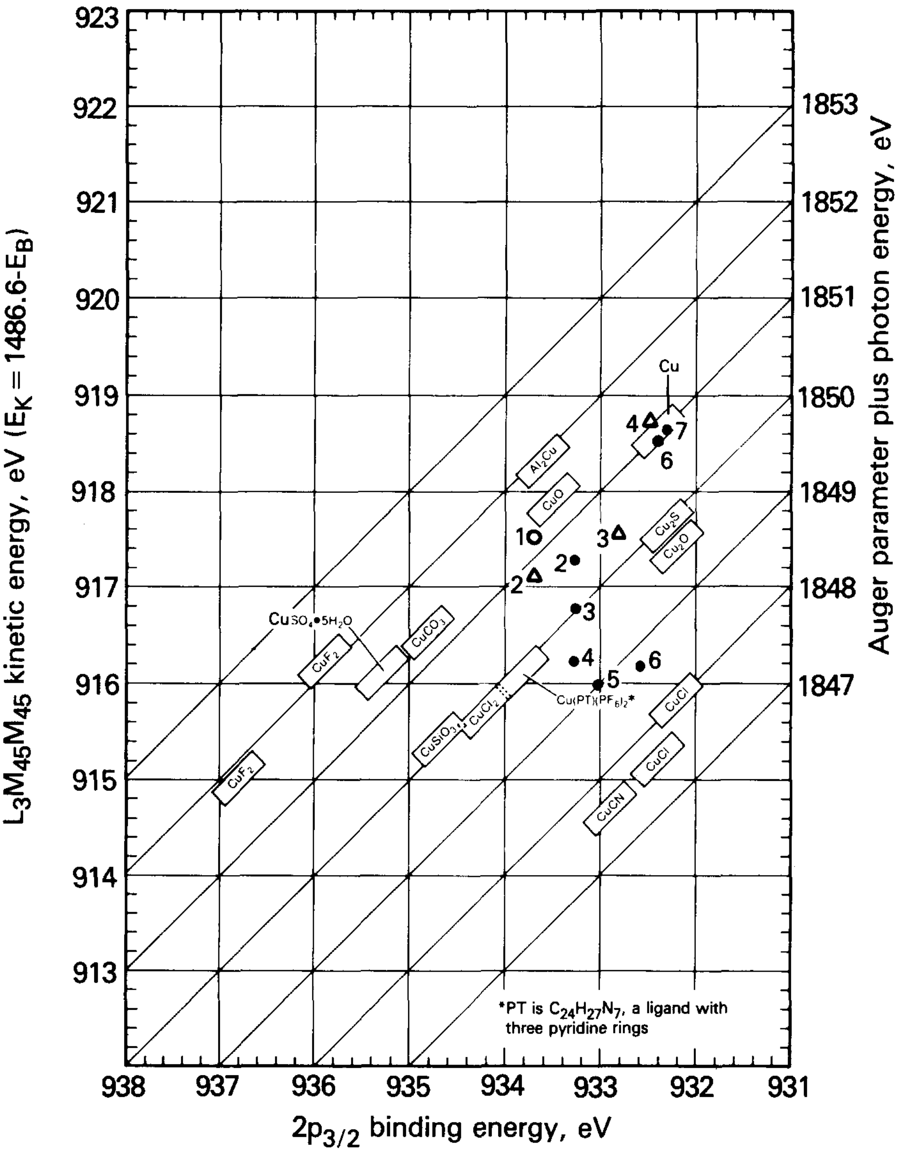


FIG. 2. Changes in the chemical state of Cu upon reduction in H_2 and CO. (1) As received (○). H_2 reduction (●): (2) 50°C, 1 h, (3) 100°C, 1h, (4) 100°C, 3h, (5) 100°C, 5 h, (6) 250°C, 1 h (contains CU + 1 and Cu), (7) 250°C, 3 h. CO reduction (△): (2) 100°C, 2 h, (3) 100°C, overnight, (4) 250°C, 3 h.

no detectable carbon buildup on the catalyst surface.

The reducibility of CuO by hydrogen in the presence of ZnO and ZnO/Al_2O_3 has also been investigated with temperature-programmed reduction (TPR). Figure 4 shows that complete reduction of CuO in CuO/ZnO/Al_2O_3 is achieved at a temperature 140°C lower than that for CuO alone, while CuO in CuO/ZnO reduces at about 50°C higher than CuO alone. In both cases the H_2 uptake as measured by a thermal conductivity cell, was equivalent to a reduction of 100% CuO, ±10%, relative to the pure CuO. While TPR temperatures cannot be easily translated to the static experiments performed in the XPS studies, the TPR profiles confirm that CuO can be

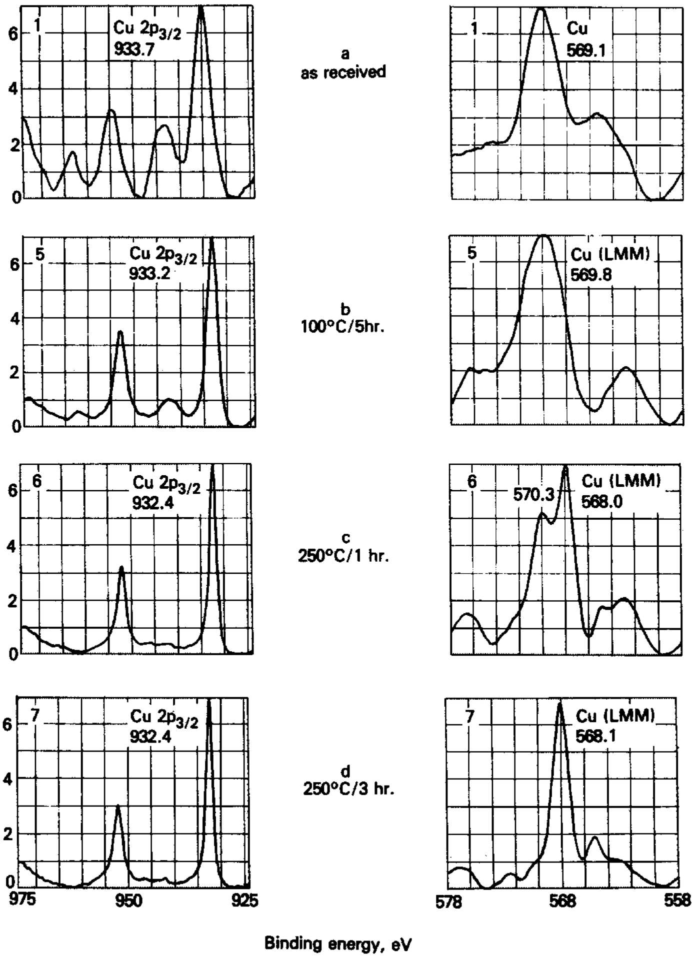


FIG. 3. Changes in Cu $2p$ and Cu($L_3M_{45}M_{45}$) electron spectra upon *in situ* reduction in H_2.

completely and easily reduced to metallic Cu in the presence of ZnO/Al_2O_3.

The difficulty in determining the minimum amount of Cu^+ that can be detected in the presence of Cu metal is illustrated by Fig. 5a which is an Auger electron spectrum of a clean Cu foil that has been repeatedly ion-bombarded and H_2-reduced at 400°C. It shows 3 satellite peaks (labeled A, B, and C) in addition to the main line at about 568.0 eV in agreement with other studies (*16, 22*). These satellites have been identified as L_3M_{45}–$M_{45}M_{45}M_{45}$ transitions, i.e., $L_3M_{45}M_{45}$ processes with spectator vacancies in the M_{45} shell (*23, 24*). Unfortunately, satellite B occurs at about 570.0 eV which is also the location of the Cu^+ main peak. Therefore, for any Cu^+ measurement in the presence of Cu metal, the satellite B component must be accounted for.

Figure 5b shows the same region obtained from the catalyst after 3 h methanol synthesis at 250°C. In addition to the main Cu ($L_3M_{45}M_{45}$) line at 568.0 eV and the 3 satellites there are 2 peaks at about 563 and 577 eV which are the Zn $L_2M_3M_{45}$ and $L_3M_3M_{45}$ Auger lines. A peak fit of the 2 peaks of interest (main line and satellite B) was done using the Physical Electronics Version 6 peak-fit routine assuming a linear background between the satellite A/main line and satellite B/satellite C valleys. The peak fit shows that 4% of the combined peak area belongs to satellite B. An identi-

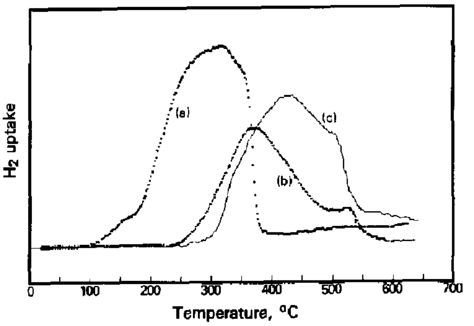


FIG. 4. Temperature-programmed reduction. Each sample was pretreated in dry air at 500°C for 1 h. Carrier gas: 5% H_2/Ar. Program rate: 20°C/min. (a) 0.05 g $CuO/ZnO/Al_2O_3$ (40/50/10), (b) 0.01 g CuO, (c) 0.05 g CuO/ZnO(40/60).

cal intensity of satellite B was obtained after reduction in pure H_2 at temperatures as high as 400°C. Therefore, this minimum satellite B intensity of 4% was used as base case corresponding to pure Cu metal. The discrepancy in satellite intensity between Cu foil and reduced catalyst is a particle size effect (*23*, *24*). Important for the discussion in this note is the fact that the intensity of B in the catalyst is lower than in the Cu foil. Thus, the presence of any residual Cu^+ in the catalyst surface can be excluded with high certianty.

After exposure of this reduced catalyst to laboratory air for 2 min spectrum 5c was recorded. It clearly exhibited increased intensity at 570 eV due to Cu^+ formation. A peak fit using identical parameters yielded a peak at 570 eV with 10.5% of the total intensity. Thus, approximately 6.5% Cu^+ are identified in the Cu metal/ZnO matrix. In many experiments with different times of air exposure it was established that despite experimental uncertainties due to the complex peak structure and the necessary peak-fit routine, as little as 2% Cu^+ in metallic Cu can be quantitatively determined.

Attempts to correlate CO conversion data with relative amounts of Cu^+ and Cu metal were not successful because the reduction of CuO to metallic Cu was completed at the onset of measurable CO conversion at about 130°C.

The chemical state of Zn during methanol synthesis is shown by the CSP in Fig. 6 (*25*). Zinc in the untreated catalyst occupies an area indicative of ZnO. Upon exposure to the $H_2/CO/CO_2$ feed, pure H_2 and pure CO at temperatures up to 250°C, only Zn^{2+} ions with $2p_{3/2}$ binding energies of 1022.0 ± 0.1 eV and $L_3M_{45}M_{45}$ kinetic energies of 987.8 ± 0.2 eV crowding a small area in the CSP were observed. These values are very close to numbers reported in the literature for pure ZnO (*26*, *27*) demonstrating that a ZnO surface is present during methanol synthesis.

In summary, we have found that the surface of a typical $CuO/ZnO/Al_2O_3$ methanol synthesis catalyst consists of metallic Cu and ZnO during actual reaction conditions. Because only very small amounts of Cu^+ (<2% of total Cu) could have gone undetected it is unlikely that Cu^+ could be the active Cu site on $CuO/ZnO/Al_2O_3$ catalyst

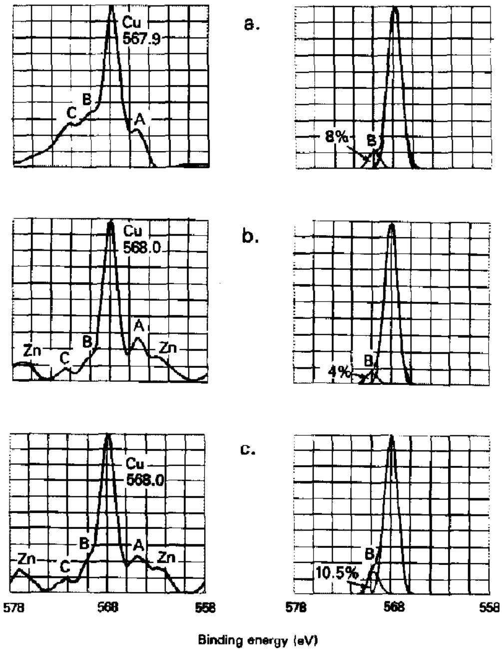


FIG. 5. Comparison of Cu (*LMM*) spectra and their partial peak fits for determination of Cu^+ in metallic Cu. (a) Clean Cu foil. (b) Catalyst, 250°C, $H_2/CO/CO_2$, 2 atm, 3 h. (c) Same as (b) plus 2 min air exposure.

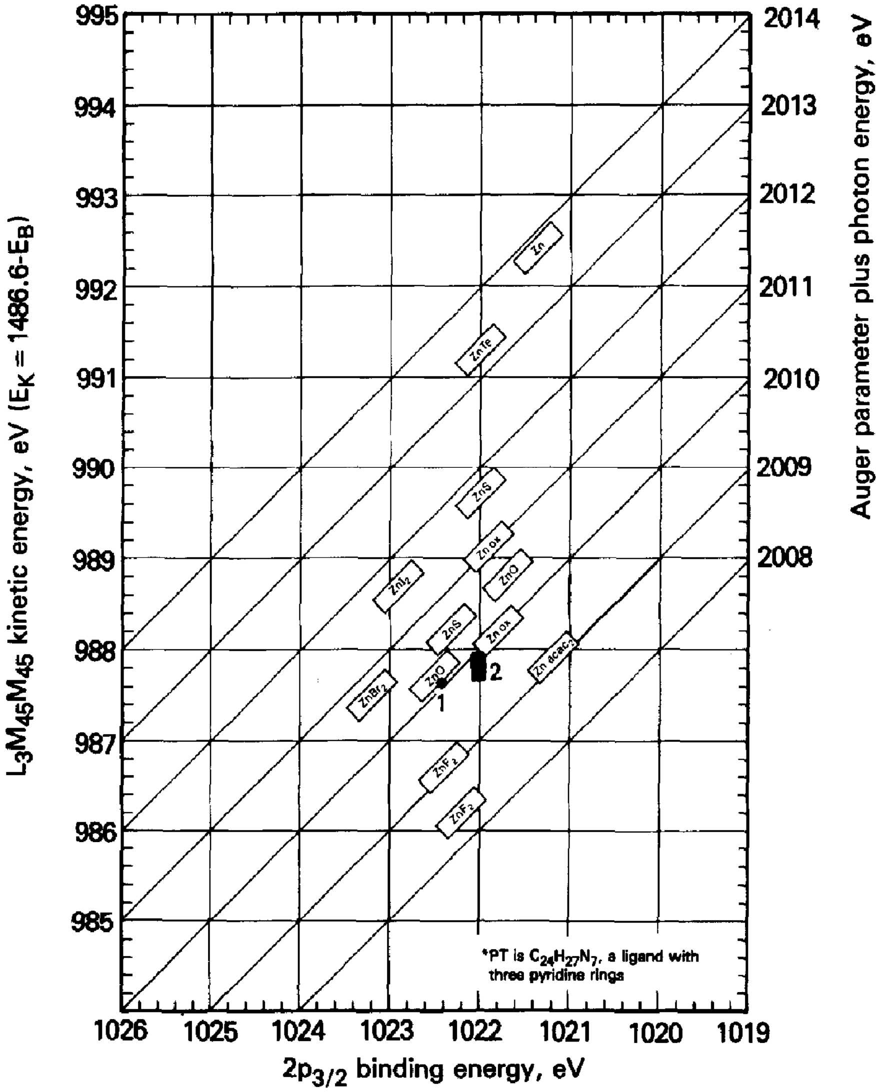


FIG. 6. Chemical state plot of Zn. (1) As received. (2) After treatment in feed, H_2, CO at temperatures up to 250°C.

surfaces. Our suggestion of metallic Cu as one of the active site in methanol synthesis is supported by the recent findings on Raney Cu.

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