

MECHANISM OF SYNERGISTIC CATALYSIS  
BY Cu-ZnO-M<sub>2</sub>O<sub>3</sub> CATALYSTS IN METHANOL SYNTHESIS\*\*

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ABSTRACT

Addition of a small amount of a trivalence-metal oxide M<sub>2</sub>O<sub>3</sub> (Sc<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, or V<sub>2</sub>O<sub>3</sub>), with ionic radius of M<sup>3+</sup> closer than that of Al<sup>3+</sup> to that of Zn<sup>2+</sup>, to methanol-synthesis copper-based catalyst Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> has been found to markedly enhance CO chemisorption and catalytic activity. Studies of XPS-Auger spectroscopy have shown that scandia-promoted catalyst, Cu-ZnO-Al<sub>2</sub>O<sub>3</sub>-Sc<sub>2</sub>O<sub>3</sub>, after activation treatment with H<sub>2</sub>-N<sub>2</sub> contained more Cu<sup>+</sup> than 3-component catalyst, Cu-ZnO-Al<sub>2</sub>O<sub>3</sub>, probably due to valence compensation for a small amount of dissolved Sc<sub>2</sub>O<sub>3</sub> in ZnO lattice by the formation of more Cu<sub>2</sub>O in the ZnO surface layer. Laser Raman peaks at 2103cm<sup>-1</sup> and 1602cm<sup>-1</sup> assignable to  $\nu_{C-O}$  of Cu-CO and  $\nu_{Cu-H}$  have been observed, respectively, with CO-N<sub>2</sub>/Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>-N<sub>2</sub>/Cu-ZnO-Al<sub>2</sub>O<sub>3</sub>, but no Raman peak in the spectral region of 1500 to 2400cm<sup>-1</sup> with pure ZnO similarly exposed to flowing CO-N<sub>2</sub> or to flowing H<sub>2</sub>-N<sub>2</sub> at 200°C and 150°C. Mechanism of the observed synergistic catalysis and reaction mechanism for methanol synthesis over Cu-ZnO-Al<sub>2</sub>O<sub>3</sub>(M<sub>2</sub>O<sub>3</sub>) catalysts have been proposed and discussed together with these experimental results.

INTRODUCTION

Catalysis by Cu-ZnO-Al<sub>2</sub>O<sub>3</sub>(or Cr<sub>2</sub>O<sub>3</sub>) catalysts in low-pressure methanol synthesis is known to be an outstanding example of synergistic catalysis. These catalysts are many orders of magnitude more active than any of the catalyst constituents under the reaction conditions of low-pressure methanol synthesis, thus synergistic catalytic effects of the metal and the oxide promoters are in evidence, and the active sites are probably located at the interfacial boundary of copper and ZnO. It has been postulated by Klier et al. (1,2) that these active sites contain Cu<sup>+</sup> on which coordination activation of CO by non-dissociative chemisorption can take place, and that heterolytic splitting of H<sub>2</sub> by dissociative chemisorption takes place on the ZnO constituent, as in the case of H<sub>2</sub> chemisorption on pure ZnO (3). Henrici-Olive and Olive (4) have also suggested the presence of Cu<sup>+</sup> in the working Cu-based catalyst, but they maintain that these Cu<sup>+</sup> ions can also chemisorb and activate H<sub>2</sub>. Recently, Li et al. (5) assigned an IR peak at 1660cm<sup>-1</sup> to the  $\nu_{Cu-H}$  of a Cu-H species on the H<sub>2</sub>-N<sub>2</sub>-treated Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> catalyst. However, Edwards and

\*\* This work was supported by a grant from the National Science Foundation of China.

Schrader (6) more recently assigned an IR peak at  $1663\text{cm}^{-1}$  to  $\nu_{\text{Zn-H}}$  rather than  $\nu_{\text{Cu-H}}$ , for hydrogen species chemisorbed on H<sub>2</sub>-N<sub>2</sub>-treated Cu-ZnO-Al<sub>2</sub>O<sub>3</sub>. Recently, Flesch et al. (7) showed by means of XPS-Auger spectroscopy that there is no conclusive evidence to confirm the presence of Cu<sup>+</sup> in their Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> catalyst; they pointed out that only very small amounts of Cu<sup>+</sup> (2% of total Cu) could have gone undetected in their XPS-Auger measurements. Thus, the presence or absence of Cu<sup>+</sup> at the interface of Cu-ZnO and the capability or incapability of these ions, if present, to chemisorb and activate hydrogen, as well as CO, are still a matter of debate. The role of Cu<sup>0</sup> present in excessive amounts (in commercial catalysts, for methanol synthesis Cu/Zn/Al=60/30/10, while for water-gas shift (WGS) reaction Cu/Zn/Al=30/60/10) is still left unexplained, so is the role of ZnO, besides chemisorption and activation of H<sub>2</sub> by heterolytic splitting; moreover, it appears that Al<sub>2</sub>O<sub>3</sub>, or Cr<sub>2</sub>O<sub>3</sub>, may be able to play more than just the role of a structural promoter. Finally, there is still some unresolved problem about the major reaction pathway (1,8) of methanol synthesis over this type of catalysts.

In present work, the effect of small amounts of M<sub>2</sub>O<sub>3</sub> (Sc<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, or V<sub>2</sub>O<sub>5</sub>) in Cu-ZnO-Al<sub>2</sub>O<sub>3</sub>-M<sub>2</sub>O<sub>3</sub>, with ionic radius of M<sup>3+</sup> closer than that of Al<sup>3+</sup> to that of Zn<sup>2+</sup>, on CO chemisorption, methanol synthesis activity, and Cu<sup>+</sup> concentration were investigated; laser Raman spectra of CO and H adspecies were taken for comparison with the known IR spectra. The results will be discussed in terms of coordination activation of H<sub>2</sub> and of CO on the copper site and partial stabilization of thermodynamically unfavorable oxygenated intermediates (HC=O) by dipole-charge interaction between the aldehydic C=O and Zn<sup>2+</sup>, and related to the reaction mechanism and the mechanism of the synergistic effects of the metal and oxide promoters.

## EXPERIMENTAL

### Catalyst preparation

Samples of Cu-ZnO-Al<sub>2</sub>O<sub>3</sub>-M<sub>2</sub>O<sub>3</sub> catalysts were prepared by known method of coprecipitation and activated by temperature-programmed heating for 16h upto 250°C in H<sub>2</sub> (5% in N<sub>2</sub>) stream, as recommended in the literature (1). The BET specific surface areas of these samples lied between 30 to 50m<sup>2</sup>/g, while that of 2-component catalyst Cu-ZnO (Cu/Zn=60/40) was about 10m<sup>2</sup>/g.

### Chemisorption measurements and catalytic activity evaluation

Chemisorption measurements for CO and H<sub>2</sub> on the catalysts was done by means of TPD-MS, TPD-TCD, as well as pulse chemisorption. Assays of catalyst activities were carried out at 230°C in a microreactor-CC combination, with s.v. of the syngas (H<sub>2</sub>/CO/CO<sub>2</sub>=66/28/6) 6000h<sup>-1</sup>.

### XPS-Auger determination of Cu<sup>0</sup>, Cu<sup>+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup>

The XPS-Auger measurements were done, using a VG Escalab Mark-II machine with Al-K<sub>α</sub> radiation (1486.6eV), 12.5kV high voltage and UHV (1x10<sup>-9</sup>Torr), taking the Zn(2p<sub>3/2</sub>) of Zn<sup>2+</sup> at 1022.0eV as reference (9). Prior to the measurements samples were activated by temperature-programmed heating in H<sub>2</sub> (5% in N<sub>2</sub>) stream for 15h upto 230°C, and then in the syngas stream for 1h at 230°C.

### LR spectroscopic characterization of H<sub>2</sub> and CO adspecies

LR spectra of chemisorbed species of H<sub>2</sub> and of CO were taken with a Spex Ramanlog-6 machine interfaced with a Datamate micro-processor. The intensity used of exciting laser beam (5145Å) was 50mW; slit width settings correspond to a resolution of 4cm<sup>-1</sup>. The controlled atmosphere cell was described elsewhere (10).

## RESULTS AND DISCUSSION

It can be seen from Table 1 that the presence of small amounts of Sc<sup>3+</sup> (optimum content: 2% atomic of the total metal ions) or Cr<sup>3+</sup>, or V<sup>3+</sup>, in the 4-component catalysts significantly enhanced the catalytic activities in comparison with the 3-component catalyst, Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>, the ratio of the observed activities being 362/374/231/161. The amount of CO chemisorbed on a Cu/ZnO/Sc<sub>2</sub>O<sub>3</sub> (Cu/Zn/Sc=60/39/1) was found from chemisorption isotherms to be about 46% larger than that chemisorbed on equal weight of a Cu-ZnO (Cu/Zn=60/40), and the catalytic activity about 57% higher.

Table 1 Effect of M<sub>2</sub>O<sub>3</sub> in catalyst systems on catalytic activity

No.	Cu-ZnO-Al <sub>2</sub> O <sub>3</sub> -M <sub>2</sub> O <sub>3</sub>				Methanol Yield		No.	Cu-ZnO-Al <sub>2</sub> O <sub>3</sub> -M <sub>2</sub> O <sub>3</sub> (M <sub>2</sub> )				Methanol Yield	
	Cu : Zn : Al : Sc				μm/hr.	g. cat		Cu : Zn : Al : Cr				μm/hr.	g. cat
1	60	40	0	0	133.0		7	60	30	8	2	374.1	
2	60	39	0	1	209.5		8	60	30	8	2	231.1	
3	60	38	0	2	111.4		9	60	30	8	2	191.2	
4	60	37	0	3	61.5		10	60	30	8	2	44.9	
5	60	30	8	0	161.3								
6	60	30	8	2	362.5								

The observed XPS-X-ray-induced Auger spectra for three catalysts, Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>, Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>/Sc<sub>2</sub>O<sub>3</sub>, and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>/Cr<sub>2</sub>O<sub>3</sub>, are shown in Fig. 1. The dominant spectral feature is two peaks at 567.5eV and 569.5eV. The peak at 567.5eV may reasonably be ascribed to Cu<sup>0</sup>(2p) (7). Since the intensity of the peak at 569.5eV is dramatically changed with different catalyst systems: as a weak shoulder for Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>, as a conspicuous shoulder for Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>/Sc<sub>2</sub>O<sub>3</sub>, and becoming a strong main peak for Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>/Cr<sub>2</sub>O<sub>3</sub>, this peak may not be one of sub-peaks of Cu<sup>0</sup>, although some sub-peaks of Cu<sup>0</sup> had been reported to appear in this spectral region (7). This peak (569.5eV) must be due to Auger peak of Cu<sup>+</sup>(2p). Further information in support of this assignment was obtained from the observation of the increase in intensity of the 569.5eV peak when a deeply-reduced catalyst sample, Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>, was exposed to increasing amounts of oxygen in small dosages (Fig. 2), indicating that parts of Cu<sup>0</sup> were re-oxidized to Cu<sup>+</sup>. Evidence of existence of Cu<sup>+</sup> on the catalyst surface was obtained also from the observed Cu(3p) peaks of the XPS of two catalysts, Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>/Sc<sub>2</sub>O<sub>3</sub>. As shown in Fig. 3, the XPS of both catalysts showed a shoulder peak at 76.7eV, which was in good agreement with the Cu<sup>+</sup>(3p) XPS peak of CuCl and of Cu<sub>2</sub>O at 76.8eV observed by Frost et al. (11). Moreover, Fig. 1 and Fig. 3 also showed that the Sc<sup>3+</sup>, or Cr<sup>3+</sup>, -containing catalyst system showed more pronounced Cu<sup>+</sup>(2p) XPS-Auger peak and Cu<sup>+</sup>(3p) XPS peak than the corresponding catalyst system containing neither Sc<sup>3+</sup> nor Cr<sup>3+</sup>, indicating that addition of small amounts of Sc<sup>3+</sup>, or Cr<sup>3+</sup>, to the catalyst systems significantly enhanced Cu<sup>+</sup> concentration on the catalyst surface. Investigation of Cu(2p) XPS-Auger spectra on the catalysts in varying degree of reduction showed that the intensity of Cu<sup>+</sup>(2p) peak was very dependent on the time of reduction. It is evident from the results showed in Fig. 4 that, as the Cu<sup>2+</sup>, Cu<sup>+</sup> reduction proceeded to form Cu<sup>0</sup>, the concentration of Cu<sup>+</sup> on the catalyst surface would pass through a maximum. After the reduction treatment, most of the copper was in the Cu<sup>0</sup>

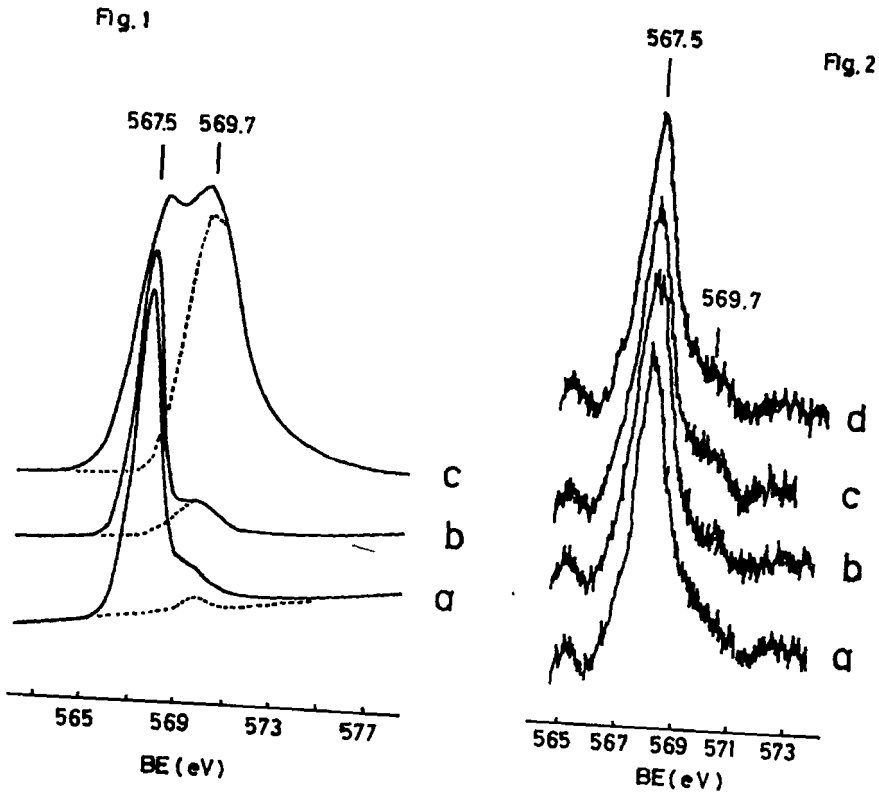


Fig. 1 XPS-Auger spectra of Catalysts: a) Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>,  
b) Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>/Sc<sub>2</sub>O<sub>3</sub>, c) Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>/Cr<sub>2</sub>O<sub>3</sub>, after reduction.

Fig. 2 XPS-Auger spectra of a) deeply-reduced catalyst Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>,  
followed by b) exposure to 3L O<sub>2</sub>, c) exposure to additional 9L O<sub>2</sub>,  
d) exposure again to additional 30L O<sub>2</sub>.

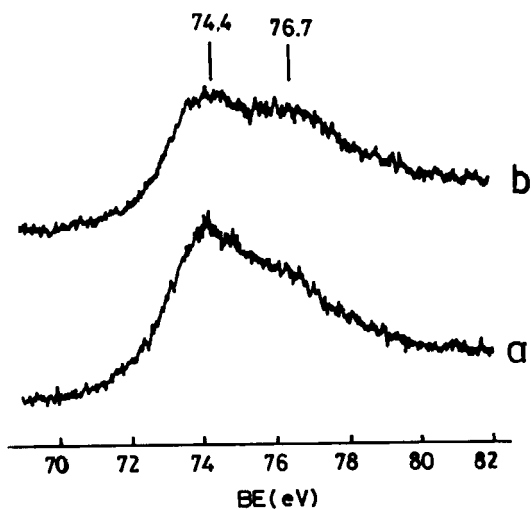


Fig. 3 XPS of Catalysts: a) Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> after reduction, b) Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>/Sc<sub>2</sub>O<sub>3</sub> after reduction.

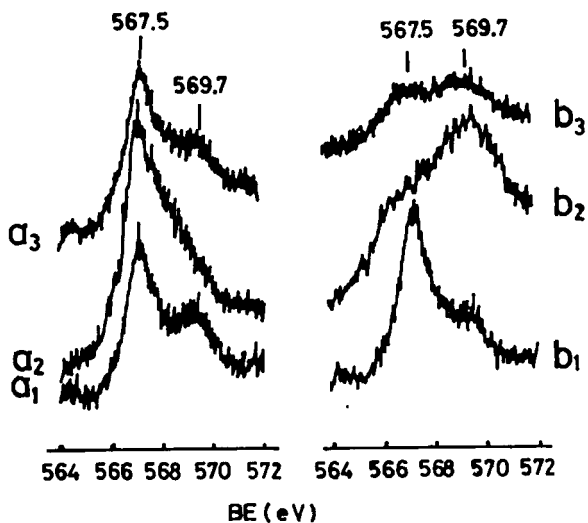


Fig. 4 XPS-Auger spectra of Catalysts: a) Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>/Sc<sub>2</sub>O<sub>3</sub>, b) Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>/Cr<sub>2</sub>O<sub>3</sub>, after reduction of: 1) 8h and 40min. 2) 11h and 40min. 3) 15h and 10min.

state, and only a small part of the copper was stabilized in Cu<sup>+</sup> state. Interestingly, the time when the Cu<sup>+</sup> concentration on the catalyst surface reached a maximum did not correspond to the time when catalytic activity for methanol synthesis reached the highest value. It is only after the Cu<sup>+</sup> concentration on surface had passed through the maximum and enough amounts of Cu<sup>0</sup> had been formed that the catalysts demonstrated high activity. This together with the observation that there is an optimum dosage of Sc<sup>3+</sup> and the known experimental fact (1) that the low pressure methanol synthesis requires a larger proportion of Cu<sup>0</sup> than the corresponding WGS catalyst probably implies that, besides Cu<sup>+</sup>, Zn<sup>2+</sup> and Cu<sup>0</sup> are also essential constituents of the active sites for methanol synthesis and that these constituents synergistically play important roles in the catalytic cycle.

The more pronounced promoter action of Sc<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> in comparison with that of Al<sub>2</sub>O<sub>3</sub> may be due to higher solubilities of these oxides in ZnO lattice since the ionic radii (12) of Sc<sup>3+</sup> (0.73Å) and Cr<sup>3+</sup> (0.63Å) are closer to that of Zn<sup>2+</sup> (0.74Å) than that of Al<sup>3+</sup> (0.51Å) is. Note that the ionic radius of V<sup>3+</sup> (0.74Å) is practically the same as that of Zn<sup>2+</sup>, but for some unknown reason the observed promoter effect of vanadium oxide was only mediocre; a check of the actual valence state of V<sup>n+</sup> in ZnO lattice thus appears to be of interest. Solution of an amount of the M<sub>2</sub>O<sub>3</sub> oxides in ZnO lattice will result in the formation of cationic vacancies unless it is compensated by solution of equimolar amount of M<sub>2</sub>O, but Cu<sub>2</sub>O apparently does not dissolve in appreciable amount in ZnO lattice because of the much larger ionic radius of Cu<sup>+</sup> (0.96Å). Thus the Schottky defects in the form of cationic vacancies due to dissolved M<sub>2</sub>O<sub>3</sub> in ZnO lattice will diffuse to the surface of ZnO, where Cu<sup>+</sup> can be better accommodated and stabilized, thus forming a Cu<sup>+</sup>-rich surface layer of -Cu<sup>+</sup>-O<sup>2-</sup>--Zn<sup>2+</sup>--O<sup>2-</sup>- to achieve valence and charge compensation for subsurface layers of -M<sup>3+</sup>--O<sup>2-</sup>--Zn<sup>2+</sup>--O<sup>2-</sup>-. These Cu<sup>+</sup>--O<sup>2-</sup>--Zn<sup>2+</sup>--O<sup>2-</sup>- may be the active site for CO chemisorption and activation. On the surface of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>/Cr<sub>2</sub>O<sub>3</sub> catalyst, unusually high concentration of Cu<sup>+</sup> may result not only from this valence-compensation effect due to dissolved Cr<sup>3+</sup>, but also from the probable formation of some CuCrO<sub>2</sub>, as in the case of Cu/Cr<sub>2</sub>O<sub>3</sub> (Cu/Cr=0.7) catalyst reported by Monnier (13).

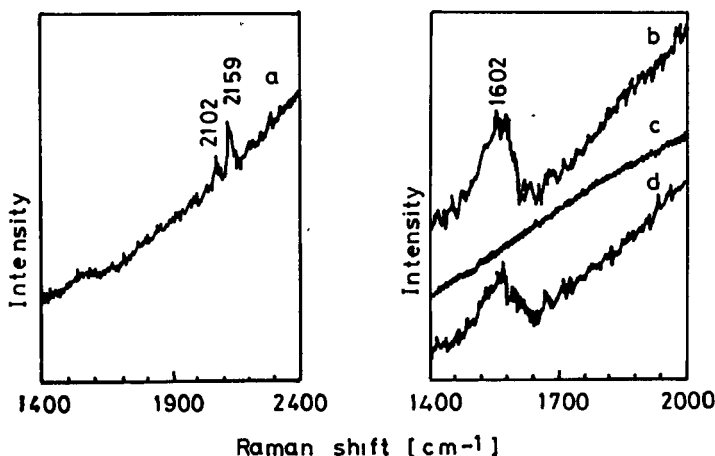
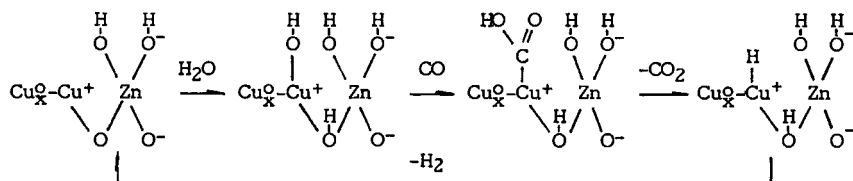


Fig. 5 Raman spectra of chemisorbed species of: a) CO, b) H<sub>2</sub> on prerduced Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>, c) H<sub>2</sub> on ZnO/Al<sub>2</sub>O<sub>3</sub>, d) H<sub>2</sub> on CuO in reduction process.

Raman spectra of chemisorbed species of hydrogen and of CO on these catalysts are shown in Fig. 5. Raman peaks at 2103cm<sup>-1</sup> and 1602cm<sup>-1</sup> were observed with Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>/Sc<sub>2</sub>O<sub>3</sub> (2 atomic% Sc), exposed, respectively, to flowing CO-N<sub>2</sub> at 150°C and to flowing H<sub>2</sub>-N<sub>2</sub>(5:95v/v) at 150-230°C and atmospheric pressure for 16h. The 1602cm<sup>-1</sup> peak decreased in intensity after 40-50 scans with 50mW laser beam, probably indicating laser-induced reduction of Cu<sup>+</sup>. The peak at 1602cm<sup>-1</sup> was also observed with pure CuO similarly exposed to flowing H<sub>2</sub>-N<sub>2</sub>(5:95v/v), but no Raman peak in the spectral region of 1500-2400cm<sup>-1</sup> with pure ZnO similarly exposed to flowing CO-N<sub>2</sub> and to flowing H<sub>2</sub>-N<sub>2</sub>(5:95v/v). Thus the amount of chemisorbed CO on ZnO appeared to be too small and the polarizability of Zn<sup>2+</sup> too low for the Zn<sup>2+</sup>-CO and Zn<sup>2+</sup>-H to be detected by laser Raman spectroscopy, and the Raman peaks at 2103cm<sup>-1</sup>(w) and 1602cm<sup>-1</sup>(s, br.) observed with CO (in N<sub>2</sub>)/Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>(5% in N<sub>2</sub>)/Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> could therefore be assigned to  $\nu_{C-O}$  of Cu<sup>+</sup>-CO and  $\nu_{Cu-H}$  of H (on Cu<sub>x</sub><sup>0</sup>-Cu<sup>+</sup>). The amount of H seemed to be considerably larger than that of CO, indicating that H might migrate from Cu<sup>+</sup> to contiguous, amorphous copper, Cu<sub>x</sub><sup>0</sup>.

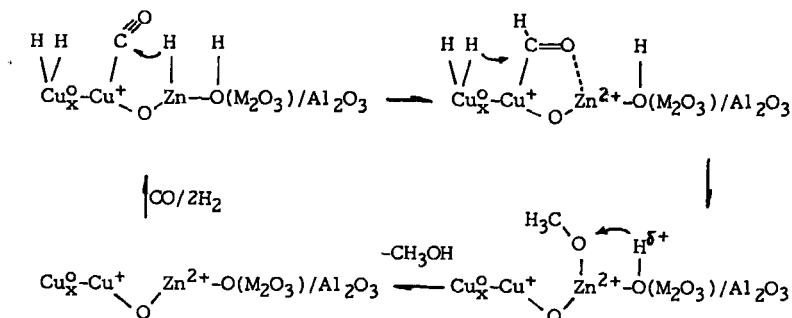
Based upon these experimental facts and other informations reported in the literature (1,2), a mechanism of synergistic catalysis and a model of active site may be proposed as follows: Solution of a small amount of Sc<sub>2</sub>O<sub>3</sub>, or Cr<sub>2</sub>O<sub>3</sub>, in ZnO lattice may induce, via valence compensation, the formation of equivalent amount of Cu<sub>2</sub>O in ZnO surface layer. There may be an optimum proportion of Cu<sup>+</sup> and Zn<sup>2+</sup> ions in ZnO surface layer for synergistic catalysis. Cu<sub>x</sub><sup>0</sup> grown epitaxially (or in amorphous form) from ZnO crystalites may be linked to the interfacial Cu<sup>+</sup> through metal-metal bonding, as in the case of Ag-Ag bonding in Ag<sub>2</sub>F and of Cs-Cs bonding in Cs<sub>3</sub>O. Thus each Cu<sup>+</sup> may actually carry less than a unit of positive charge. This partial-cationic site may have a stronger affinity toward CO than a Cu<sup>0</sup> site, but will not weaken the C≡O triple-bond as much upon chemisorption. Besides heterolytic splitting of H<sub>2</sub> known to occur by chemisorption on ZnO, dissociative chemisorption of H<sub>2</sub> may be also take place via coordination activation of H<sub>2</sub> on Cu<sub>x</sub><sup>0</sup>-Cu<sup>+</sup>, or via heterolytic splitting of H<sub>2</sub> on Cu<sup>+</sup>-O<sup>2-</sup>. The crucial first step of hydrogenation of CO coordinated on Cu<sup>+</sup> to form the highly unstable formyl intermediate, HC=O, may be assisted by dipole-charge interaction between the HC=O ( $\mu \approx 2.8$  debyes) and an adjacent Zn<sup>2+</sup> (at about 3Å internuclear distance from the Cu<sup>+</sup>); further hydrogenation gives CH<sub>3</sub>O coordinated on Zn<sup>2+</sup>; which subsequently picks up a protonic hydrogen from an adjacent OH to form CH<sub>3</sub>OH. Thus Cu<sub>x</sub><sup>0</sup>-Cu<sup>+</sup> plays the dual role of coordination activation of CO by non-dissociative chemisorption on Cu<sup>+</sup> and of dissociative chemisorption of H<sub>2</sub> on Cu<sub>x</sub><sup>0</sup>-Cu<sup>+</sup> to form 2 H, which might migrate from Cu<sup>+</sup> to contiguous Cu<sub>x</sub><sup>0</sup>; and the ZnO plays the dual role of dissociative chemisorption of H<sub>2</sub> to form H-Zn-O-H and partial stabilization of the highly unstable formyl intermediate (HC=O) by dipole-charge interaction to lower the activation energy. It is known (14) that small amount of water vapor in the syngas feed can exert some promotional effect on methanol synthesis over the Cu-ZnO-based catalysts, and larger amount beyond 1-2% will inhibit it, while the WGS reaction is not inhibited by water vapor over such Cu-ZnO-based catalysts. Thus, over such catalysts, WGS reaction probably takes place by such a reaction pathway, i.e., via Cu<sup>+</sup>-COOH or Cu<sup>+</sup>-OOCH



intermediate; no ZnO site is required for the activation of H<sub>2</sub> by heterolytic splitting and no inhibition by H<sub>2</sub>O is observed.

## CONCLUSION

The actual catalyst with chemisorbed  $\underline{\text{CO}}$  and  $\underline{\text{H}}$  and the synergistic catalysis may be expressed symbolically as follows:



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