

Letter

Selective Enhancement of Surface Cu^+ Species in $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ Catalyst by Nitrous Oxide Decomposition

C. SIVARAJ, B. MAHIPAL REDDY and P. KANTA RAO

Catalysis Section, Regional Research Laboratory, Hyderabad 500 007 (India)

(Received March 1, 1988; accepted April 6, 1988)

The structure and reactivity of $\text{CuO}/\text{Cr}_2\text{O}_3$, CuO/ZnO and $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalysts are currently the subject of numerous investigations, especially with respect to methanol synthesis [1 - 3]. Monovalent copper in these catalysts has been proposed to be the active centre for the synthesis of methanol from CO and H_2 at low temperature and pressure. Herman *et al.* [4], on the basis of diffuse reflectance spectroscopy, proposed that Cu^+ dissolved in the ZnO lattice is the catalytically active species for methanol synthesis. Apai *et al.* [5], using X-ray photoelectron spectroscopy, have shown a direct correlation between the amount of stable surface Cu^+ and the activity for methanol formation. Having established the fact of a Cu^+ species responsible for methanol synthesis activity, in this communication we report a novel method for selective enhancement of the Cu^+ species in $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst via nitrous oxide decomposition. The active Cu^+ species is estimated quantitatively by a double isotherm CO chemisorption technique.

The $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalysts with various copper loadings were prepared by the deposition-precipitation technique using urea as hydrolysing agent. In a typical experiment ~20 g γ -alumina fine powder was suspended in a solution containing the required amounts of $\text{Cu}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$ and urea. The resulting mixture was heated to 90 °C with constant stirring. After precipitation was complete, the resulting solids were filtered, dried at 110 °C and finally calcined at 400 °C for 24 h. A standard volumetric high vacuum system with the facility for reducing the samples *in situ* by flowing hydrogen was used for CO chemisorption and N_2O decomposition study. The standard procedure employed was reduction of the catalyst sample for 5 h at 250 °C, followed by evacuation for 2 h (10^{-6} torr vacuum) at the same temperature prior to N_2O decomposition and/or CO chemisorption. Nitrous oxide decomposition was carried out at 90 °C for 5 h and then evacuated for 2 h at the same temperature. Before introduction of CO, the system was further evacuated for 1 h at the temperature of chemisorption (25 °C). Introducing purified CO (Matheson, 99.9%), the first adsorption isotherm (I) representing the sum of physisorbed (reversibly adsorbed) and

chemisorbed (irreversibly adsorbed) CO was determined. The physisorbed CO was then removed by evacuating for 1 h at the same temperature. Immediately afterwards, a second isotherm (II) representing only the physisorbed CO was generated. This second isotherm corresponds to the physisorbed CO, and the difference between I and II corresponds to the chemisorbed CO.

The CO adsorption isotherms before and after N_2O decomposition on a typical catalyst are shown in Fig. 1. It appears from Fig. 1 that the physisorbed and chemisorbed CO can be determined more precisely and accurately via this double isotherm method. The physisorbed CO corresponds to metallic Cu species, whereas the chemisorbed CO is specific to Cu^+ species on the catalyst surface [3]. The physisorbed and chemisorbed quantities of CO on various catalysts are shown in Fig. 2. It can be noted from Fig. 2 that the amount of physisorbed CO is more (Fig. 2A) compared to the chemisorbed one, on the prerduced catalysts. Upon N_2O decomposition, a reversing phenomena can be seen and a considerable enhancement in Cu^+ concentration, as reflected by chemisorbed CO, can also be noted from Fig. 2B. An important point here is that practically no adsorption, neither

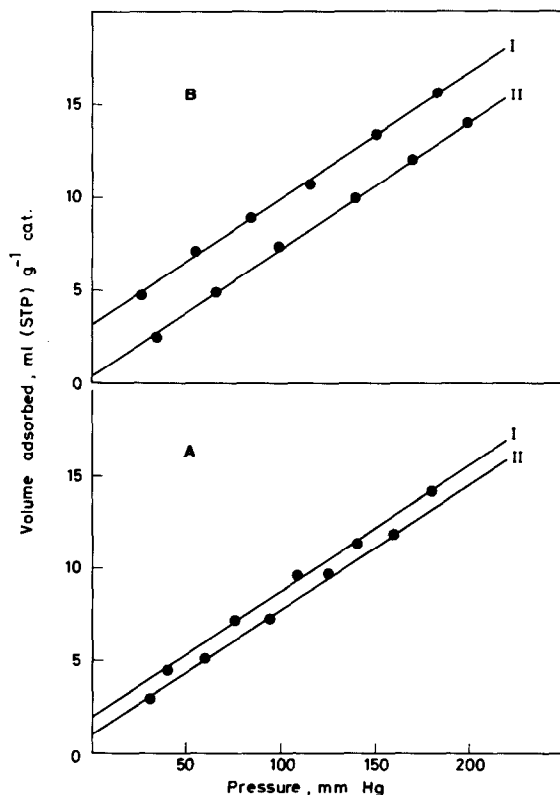


Fig. 1. CO adsorption isotherms at 25 °C on a typical $CuO/ZnO/Al_2O_3$ catalyst: A, after H_2 reduction; B, after H_2 reduction followed by N_2O decomposition.

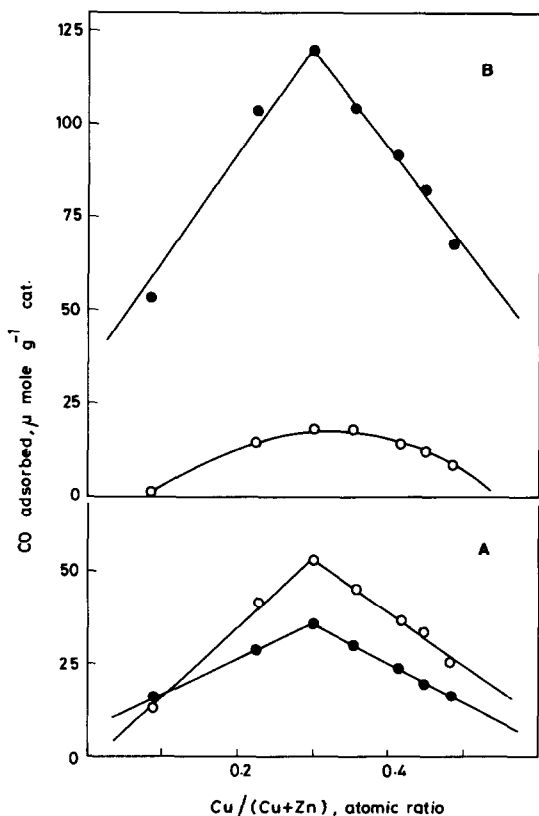


Fig. 2. CO uptakes at 25 °C as a function of catalyst composition: ●, irreversible; ○, reversible; A, after H₂ reduction; B, after H₂ reduction and followed by N₂O decomposition.

physical nor chemical, is observed on unreduced catalysts, which clearly demonstrates that Cu²⁺ species is totally inactive for CO adsorption. Another important observation to be noted from Fig. 2 is that the volume of physisorbed as well as chemisorbed CO increases as a function of Cu/(Cu + Zn) and reaches a maximum at a ratio of 0.3, after which it decreases sharply with further copper loading. Very interestingly, this optimum composition corresponds to a Cu:Zn atomic ratio of 3:7, at which a maximum activity for methanol synthesis was reported [3].

The reduced CuO/ZnO/Al₂O₃ catalyst consists of copper essentially as Cu⁰ and a lesser amount of Cu⁺ species under the conditions employed in this study. Due to its high concentration, the Cu⁰ species is partially inaccessible to the physisorbed (weakly adsorbed) CO. Hence, the total uptakes before and after N₂O decomposition are not equal on various catalysts. Nitrous oxide decomposition converts the Cu⁰ species to a Cu⁺ species which can hold CO more strongly. In conclusion, it is possible to enhance Cu⁺ species on CuO/ZnO/Al₂O₃ catalysts three- or four-fold using N₂O decomposition.

Acknowledgement

We thank CSIR, India for the award of a research fellowship to C.S.

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