Response to Comment on “Active sites for CO₂ hydrogenation to methanol on Cu/ZnO catalysts”

Shyam Kattel,¹ Pedro J. Ramírez,² Jingguang G. Chen,¹,³ José A. Rodríguez,¹,⁴ Ping Liu¹,⁴*

In their Comment on the our recent Report, Nakamura et al. argue that our x-ray photoelectron spectroscopy (XPS) analysis was affected by the presence of formate species on the catalyst surface. This argument is not valid because the reactant gases were evacuated at temperatures from 525 to 575 kelvin, conditions under which formate is not stable on the catalyst surface. An analysis of the XPS results obtained after exposing zinc oxide/copper (111) [ZnO/Cu(111)] surfaces to hydrogen (H₂) and mixtures of carbon dioxide (CO₂)/H₂ show an absence of carbon (C) 1s signal, no asymmetries in the oxygen (O) 1s peak, and a Zn:O intensity close to 1:1. Thus, the most active phase of these catalysts contained a ZnO-Cu interface.

In our recent paper, the combined experimental and theoretical results identified the ZnO-Cu interface as the most likely active sites for CO₂ conversion to methanol (1). The Comment by Nakamura et al. raised the possibility that our x-ray photoelectron spectroscopy (XPS) results could also be interpreted as metallic Zn bonded to formate species (2). As described below, based on the absence of C 1s features, the 1:1 atomic ratio for ZnO in XPS, and Zn LMM Auger features (Fig. 1), our results are fully consistent with the presence of ZnO instead of metallic Zn.

The main motivation for our detailed study of the properties of ZnO/Cu(111) and ZnO/Cu/ZnO(0001) for the conversion of CO₂ to methanol was related to recent studies by Lunkenbein et al. (3) in which transmission electron microscopy (TEM) was used to identify the active phase of a Cu/ZnO/Al₂O₃ catalyst. They found a ZnO overlayer on top of the Cu particles (3). Such an inverse oxide-metal configuration was in agreement with the high activity found for CeO₂/Cu(III) catalysts during methanol synthesis (4, 5).

Thus, we decided to investigate the performance of ZnO/Cu(111) as a catalyst. We noted two articles published by Fujitani et al. in which the importance of ZnO or a ZnOₓ-Cu interface during methanol synthesis was highlighted (6, 7). However, we did not prepare our model ZnO/Cu(111) and ZnO/Cu/ZnO(0001) catalysts in the same way that Fujitani et al. did. We generated ZnO/Cu(111) and ZnO/Cu/ZnO(0001) by vapor deposition of Zn in a background atmosphere rich in O₂. Our method produced ZnO/CuOₓ/ZnO(0001) systems that quickly transformed into ZnO/Cu(111) and ZnO/Cu/ZnO(0001) upon reaction with hydrogen.

We did not observe any C 1s signal in XPS, as expected, and the position of the Zn 2p½ core level, Zn LMM Auger, and the O/Zn ratio were consistent with the presence of ZnO clusters or aggregates. When several of these systems were exposed to 20 atm of H₂ between 525 and 575 K, we did not observe any substantial shift in the Zn 2p½ core level in XPS or change in the Zn LMM Auger features, indicating that the ZnO

Fig. 1. Characterization of the catalysts by XPS and Auger spectroscopies. (A and B) C 1s (A) and O 1s (B) XPS spectra collected after performing the hydrogenation of CO₂ on ZnO/Cu(111) catalysts. T = 550 K, P_Cu = 4.5 atm, P_CO₂ (partial pressure of CO₂) = 0.5 atm. Before recording the spectra, the gases were pumped out from the microreactor while holding the sample at 550 K. The corresponding Zn 2p½/2 XPS spectra are shown in figure S2 of (1). (C) Zn LMM Auger spectra acquired before and after performing the reaction on a Cu(111) surface precovered ~20% by ZnO. (D) (Black triangles) Variation of the Zn 2p½/2 XPS signal for a plain Zn/Cu(111) surface; θ_Cu = 0.22 monolayer (ML), heated from 300 to 600 K under ultrahigh vacuum conditions. The sample was held for 30 s at each temperature. (Black squares) Corresponding variation of the Zn 2p½/2 XPS signal of a Zn/Cu(111) surface; θ_Cu = 0.21 ML after exposure to 0.5 atm of CO₂ at 300 K in a reaction cell. Initially, a small attenuation of the Zn signal is seen due to the deposition of O adatoms.
was not being reduced to metallic zinc on the catalysts (1). Furthermore, in our postreaction surface analysis with XPS [figure S2 in (1)], the gases were evacuated from the reactor at temperatures between 525 and 575 K. At these high temperatures, formate would not survive on a metal-oxide surface once the reaction mixture of CO2 and H2 was removed from gas phase (5, 8). In our postreaction XPS analysis (Fig. 1, A and B), we observed neither C 1s signal nor asymmetries in the O 1s peak. The relative intensity of the C 1s and O 1s signals was far below the value expected for adsorbed formate species. Thus, our postreaction measurements did not reveal the presence of formate on the catalyst surface. The ZnO clusters or aggregates deposited before reaction were still present on the catalyst, and they had the typical Zn LMM line shape (Fig. 1C) expected for the oxide (9).

Fujitani et al. started their studies using ZnCu or ZnCu(111) alloys (6, 7). We also performed experiments with Zn/Cu(111) surfaces and found that under ultrahigh vacuum conditions, Zn had a tendency to migrate deep into the copper substrate (Fig. 1D) at the typical temperatures used for methanol synthesis (500 to 600 K). Interaction with CO2 oxidized the Zn, increasing its stability and residence time on the surface (Fig. 1D) (1). In our studies, the deposition of Zn on Cu(111) produced alloys that were more active than plain Cu(111), but these samples were not stable under reaction conditions and transformed into ZnO/ Cu(111), as predicted by theoretical calculations. Fujitani et al. observed a similar transformation but only at high coverages of Zn. Although it is difficult to understand why the Zn to ZnO transformation would not occur at low coverages of Zn, the difference could be a consequence of the way in which the ZnCu alloys were prepared in each study and the temperature of exposure to the reactant gases. In any case, the increase in catalytic activity that we observed upon adding small amounts of ZnO to Cu(111)—reaction rates of 25 to 90 times higher (1)—was much greater than that reported by Fujitani et al., where the reaction rate was 11 times greater (6, 7). In our opinion, this difference in the rate enhancement further demonstrates the importance of having a ZnO-Cu interface. Our theoretical studies, based on combining density functional theory and kinetic Monte Carlo simulations, indicate that formate bonded to Zn in a ZnCu alloy is not a very active species when compared with formate present at a ZnO-Cu interface (1). For these systems, the catalytic activity increased in the following sequence: Cu < ZnCu < ZnO-Cu. The importance of the ZnO-Cu interface is also consistent with observations from other active catalysts for the conversion of CO2 to methanol. For example, in catalytic systems that have an activity or selectivity or both much greater than that of Cu-ZnO, the active phase also consists of an oxide or a metal-oxide interface [Pt/ CeO2/TiO2 (4), In2O3/ ZrO2 (10), MnOx-CoOy (11)].

REFERENCES
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