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

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Kattel et al. (Reports, 24 March 2017, p. 1296) report that a zinc on copper (Zn/Cu) surface undergoes oxidation to zinc oxide/copper (ZnO/Cu) during carbon dioxide (CO₂) hydrogenation to methanol and conclude that the Cu-ZnO interface is the active site for methanol synthesis. Similar experiments conducted two decades ago by Fujitani and Nakamura et al. demonstrated that Zn is attached to formate rather than being fully oxidized.

The industrial synthesis of methanol is conducted over Cu/Zn/Al-based catalysts. It is commonly accepted that Cu is the active metal and that a synergetic interaction with Zn promotes the synthesis. However, the nature of the catalytic active site has been the subject of an intense debate for decades. In the 1990s, the surface science approach was adopted to examine how methanol is formed on metallic Cu single-crystal surfaces (1–3). Moreover, Nakamura et al. (4) demonstrated the promotional effect of adding Zn to Cu surfaces. The experimental work reported by Kattel et al. (5) resembles this latter work but concludes that the synergistic effect between Cu and ZnO refers to sites at the interface between ZnO and Cu, at the edges of ZnO overlaysing Cu surfaces, or both. This conclusion also differs from many later experimental and theoretical studies that demonstrate that metallic Zn in the Cu surface represents the surface site responsible for the promoted synthesis of methanol (1, 6–9).

It is appropriate to address the present discrepancy because the conclusions made by Kattel et al. leave the field with the wrong impression. The x-ray photoelectron spectroscopy (XPS) analysis reported by Kattel et al. is deficient compared with the seminal studies by Fujitani and Nakamura, including (1, 4, 6, 10). In the following, we describe how the work by Kattel et al. (5) is in fact fully consistent with the first XPS studies (4) and how more elaborate XPS analyses (1, 6, 10) substantiate the conclusion that Zn, and not ZnO, in Cu surfaces acts as the promoted site for methanol synthesis.

Kattel et al. studied methanol synthesis until steady-state rates were reached at 4.5 bar of a 1:9 = CO₂:H₂ gas mixture at temperatures of 525, 550, and 575 K over Zn and ZnO–deposited Cu(111) surfaces, prepared by evaporating Zn in the absence or presence of oxygen on the Cu surface. After the reaction, the high-pressure reaction cell was evacuated and the single-crystal specimen was transferred to an ultrahigh vacuum chamber for XPS analysis. These results allowed for an evaluation of the methanol synthesis activity as a function of the Zn coverage as shown in figure 1A of the report by Kattel et al. and are similar to data established at 3.6 times higher pressure in the work by Fujitani and Nakamura (1, 10) (Fig. 1A). This agreement shows the relevance of comparing the different studies.

To address the oxidation state of Zn, Kattel et al. limit the XPS analysis to the Zn 2p₃/₂ line. Specifically, Kattel et al. report that the binding energy for the Zn 2p₃/₂ line is stable during an activity test for the ZnO/Cu(111) samples and moves from ~1021.2 eV to 1021.6 eV for the Zn/Cu(111) sample. From these results, it is concluded that Zn is present as ZnO during synthesis. Whereas the shift of the oxidation state is consistent with the observations made by Nakamura and Fujitani (4), as also acknowledged and cited by Kattel et al., the interpretation of the XPS line shift is unfortunately insufficient and misleading, as realized by Fujitani and Nakamura in their subsequent work (1, 6, 10).

It was discovered that the evacuation temperature is crucial for the state of Zn, and at high temperatures (523 K), oxygen may form by decomposition of formate intermediates under evacuation and eventually oxidize Zn (4). Fujitani and Nakamura switched to an evacuation temperature of 373 K in their later work (1, 6, 10). Kattel et al. do not specify this important detail of the sample temperature during evacuation of the high-pressure cell before examination by XPS, except for commenting that a procedure was followed as in (4). On a similar note, Kattel et al. did not perform any investigations of the Zn L₃M₄.5M₄.5 Auger lines, the C 1s, O 1s lines, or of the presence of formate. It is therefore impossible to judge properly whether their detection of the Zn 2p₃/₂ line is related to the methanol synthesis, the decompositions of intermediates during evacuation, or to the sample transfer conditions.

Furthermore, in their very detailed studies, Fujitani and Nakamura (1, 6, 10) provided

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Fig. 1. Methanol synthesis activity and postreaction oxygen coverage of Zn/Cu(111). Turnover frequencies (TOFs) for methanol formation (A) and the coverage of ZnO-oxygen and formate-oxygen (B) as a function of the Zn coverage (θ_Zn) on a Zn/Cu(111) model catalyst. The activity was measured at 523 K, and 18 bar of H₂/CO₂ = 3. The sample was cooled to 373 K and evacuated before XPS analysis. The coverage of ZnO-oxygen and formate-oxygen were obtained from the O 1s XPS peaks at 530.4 and ~532 eV on the postreaction Zn/Cu(111) surface, respectively. The ratio θ_{O/ZnO}/θ_{C/HCOO} were determined to be 2. Reprinted from (10).
additional quantitative analysis of the O 1s and C 1s lines. This analysis shows that at low Zn coverages (qZn ≤ 0.15 monolayers), the main fraction of the oxygen (~80%) is bonded to Zn in the form of formate, whereas only at higher Zn coverages is the main fraction of the oxygen bonded to Zn in ZnO (see Figs. 1B and 2). The qO, HCOO/qC, HCOO ratio was 2, consistent with the assigned C and O XPS peaks originating from HCOO.

Obviously, XPS has some limitations to its sensitivity with respect to oxidation state determination unless the carbon and oxygen signals are studied simultaneously. Several subsequent studies have reported evidence of oxidation state change of Zn by Auger electron spectroscopy analysis using the Zn Auger line, while the Zn XPS 2p3/2 line is much less sensitive (8, 11, 12). These data combined with specific surface area measurements using hydrogen and oxygen capacity further suggest that Zn does not exist solely as ZnO (8). Kattel et al. also state that they exposed the ZnO/Cu(111) to 20 bar hydrogen under reaction conditions and that no change in the ZnO was observed. Unfortunately, no reference experiments on the Zn/Cu(III) were reported, just as no spectra of the Zn L3M4.5M4.5 Auger line, Zn XPS 2p3/2, O 1s, or the C 1s line were presented in evidence for any of the cases. Thus, although the measurements obtained by Kattel et al. agree with the earlier report (4), more elaborate studies subsequently found that the conclusion made by such measurements was incorrect and that Zn is present in a metallic form bound to formate and not in the form of ZnO (1, 6, 10).

REFERENCES AND NOTES

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