

Revealing the role of parallel reaction pathways during CO₂ hydrogenation to methanol over Cu-ZrO₂ and Cu-ZnO catalysts at low pressure

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Highlights

- Cu-ZnO and Cu-ZrO₂ follow two-site kinetics: (1) H₂ adsorption at Cu (2) CO₂ activation by support.
- Similar apparent activation energies for methanol synthesis over Cu-ZnO and Cu-ZrO₂.
- Lower energy barrier for reverse water gas shift pathway on Cu-ZrO₂, linked to bicarbonate species.

1. Introduction

Both Cu-ZnO and Cu-ZrO₂ catalysts enable hydrogenation of CO₂ to methanol (MeOH) and facilitate the reverse water gas shift (RWGS) to by-produce CO. Elucidating the mechanisms, and kinetics, at low pressure is pertinent to utilising low-pressure CO₂ sources, *e.g.* coupling MeOH synthesis with sorbents for direct air capture; however, prior studies have often worked at high pressure (≥ 50 bar) to align with incumbent industrial MeOH production, leaving low-pressure (1-10 bar) operations underexplored. In prior work [1], we confirmed a formate pathway to MeOH over Cu-ZnO, whilst Cu-ZrO₂ evolved both formate and bicarbonate intermediates, as also reported at high pressure [2]. However, the pathway of bicarbonates to methanol remains uncertain [2], especially under low pressure. Here, we extend our mechanistic investigation to derive kinetic models, utilising steady-state operation and thermal cycling to probe the transient behaviour of the identified surface species. Interactions between Cu and ZnO or ZrO₂ are then studied with near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS).

2. Methods

A 0.2 g batch of CuO-ZnO or CuO-ZrO₂, prepared by coprecipitation [1], was loaded between upper (4.0 g) and lower beds (2.5 g) beds of SiC within a packed bed reactor. Heating tape (Watlow) and a thermocouple in the upper bed of SiC were used to control the operating temperature; a second thermocouple recorded the temperature within the catalyst bed. Catalysts were reduced *in situ* at 250°C under 5vol% H₂ (in N₂), followed by MeOH synthesis from 10vol% CO₂ and 90vol% H₂, with outlet gas sent to an infrared analyser (FTIR Multigas2030, MKS). The reactor was cooled from 250, 230, 210 to 190°C, reaching a steady state at each temperature. For thermal cycling, the temperature was sinusoidally oscillated about 230°C, with an amplitude of 10°C over a period of 10 min.

For NAP-XPS (SPECS), catalyst powder (~10 mg) was embedded within tantalum foil, which was spot-welded to a sample stub. The sample was scanned under ultra-high vacuum (UHV) conditions, followed by transfer into the NAP-cell, allowing for the introduction of gases, and control of temperature using a filament heater. Reduction behaviour of the catalyst, at 250°C, was tracked under 3 mbar of H₂, followed by 90vol% H₂ and 10vol% CO₂, still at 3 mbar and 250°C; the H₂/CO₂ ratio was then decreased to 3. Finally, 0.3 mbar H₂O vapour was introduced *via* a leak valve, holding H₂/CO₂ in a ratio 3:1 at 2.9 mbar.

3. Results and discussion

Experiments aiming at steady-state operation, between 190 and 250°C, yielded the Arrhenius plot shown in **Fig. 1a**, demonstrating similar apparent activation energies, E_a^{app} , for MeOH synthesis over Cu-ZnO and Cu-ZrO₂. The E_a^{app} for the RWGS was lower over Cu-ZrO₂, despite improved selectivity towards methanol – potentially connected to bicarbonates forming carboxyl (COOH) species that lead to MeOH over Cu-ZrO₂ [2]. The obtained kinetics were incorporated into a two-site Langmuir-Hinshelwood (L-H) model, proposing Cu sites as responsible for dissociative H₂ adsorption, with the support material for CO₂ activation. The model accorded well with the transient behaviour of Cu-ZrO₂ during thermal

cycling (**Fig. 1c**) but slightly over-predicted the rate of MeOH formation over Cu-ZnO when increasing temperature (**Fig. 1b**). For comparison, a single-site model [3], derived at 50 bar, overestimated MeOH formation rate by ~100 times, failing to capture transient responses during thermal cycling.

During NAP-XPS, the Cu 2p and Cu LMM showed reduction of surface Cu(II) to Cu(I) when exposing CuO-ZnO to H₂ (**Fig. 2a,b**), with further reduction to Cu(0) under 90vol% H₂ and 10vol% CO₂. The Zn 2p_{3/2} shifted up by 0.4 eV (**Fig. 2c**), and a shoulder emerged at 992 eV in the Zn LMM (**Fig. 2d**), showing partial reduction of Zn(II) – potentially alongside Cu-Zn alloying [4]. For CuO-ZrO₂, surface Cu(II) reduced fully to Cu(0) under H₂ (**Fig. 2e,f**). Under H₂, the Zr 3d_{5/2} shifted from 181.5 to 182.2 eV (**Fig. 2g**), indicating Zr(III) oxidation to Zr(IV) [5], arising from changing Zr coordination as oxygen was removed from CuO-ZrO₂ [6]. For both catalysts, the surface oxidation states showed no further change under the 3:1 H₂ + CO₂ mixture or after the introduction of H₂O.

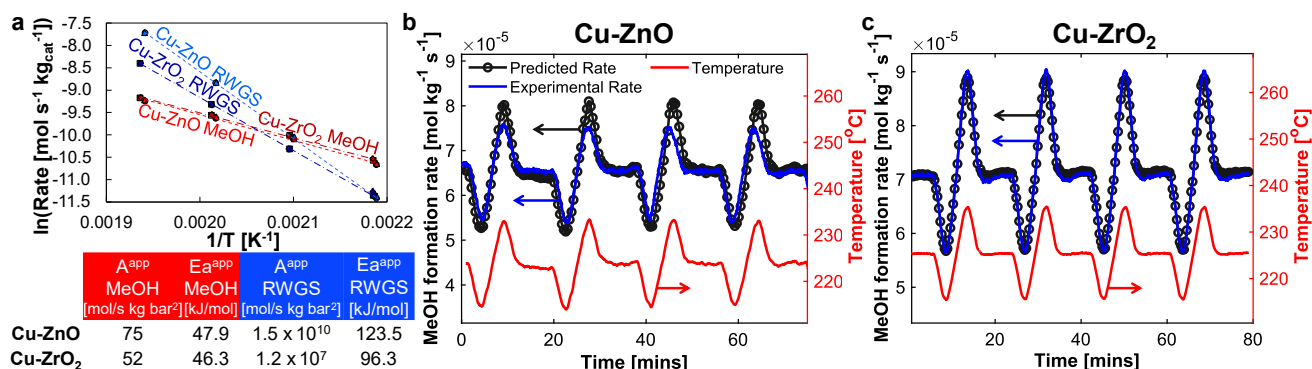


Figure 1. (a) Arrhenius plot of MeOH synthesis and RWGS over Cu-ZnO and Cu-ZrO₂. (b, c) The variation in the rate of MeOH synthesis (blue) during thermal cycling (red) over (b) Cu-ZnO and (c) Cu-ZrO₂. The predicted rate, using a two-site Langmuir-Hinshelwood (L-H) model is overlaid (in black with circular markers).

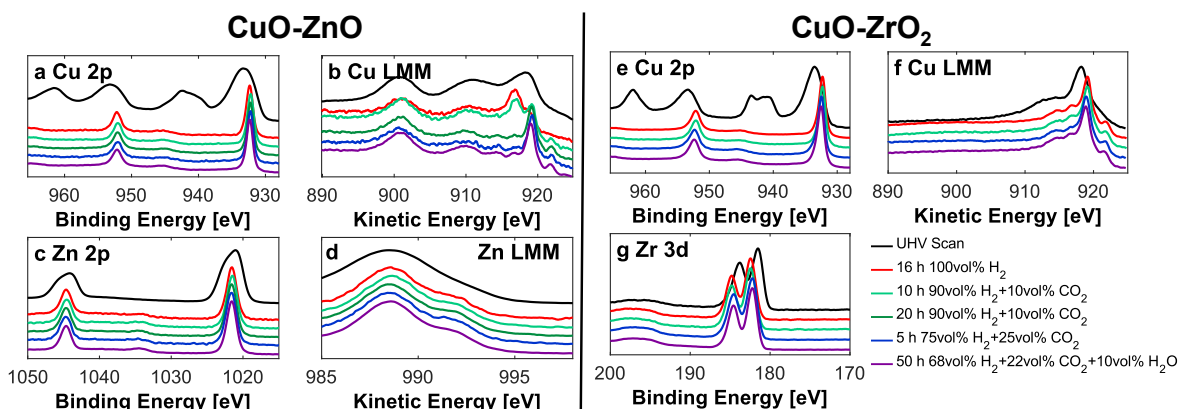


Figure 2. Spectra acquired under UHV-XPS (black), followed by NAP-XPS under H₂ (red), 90vol% H₂ + 10vol% CO₂ (green), 75vol% H₂ + 25vol% CO₂ (blue), and then with the introduction of 10vol% H₂O (purple). Over CuO-ZnO: (a) Cu 2p, (b) Cu LMM, (c) Zn 2p, (d) Zn LMM. Over CuO-ZrO₂: (e) Cu 2p, (f) Cu LMM, (g) Zr 3d.

4. Conclusions

Methanol synthesis over Cu-ZnO and Cu-ZrO₂ at low pressure follows a two-site L-H mechanism, emphasising the copper-support interaction, which NAP-XPS shows is not deactivated by oxidation when supporting CO₂ hydrogenation. Future work will develop refined kinetic models, incorporating temperature-programmed desorption (TPD) to fully describe the reaction pathways over each catalyst.

References

- [1] G.J. Fulham, W. Liu, X. Wu, E.J. Marek *Chem. Eng. J.* 147732 (2023)
- [2] K. Larmier, W.C. Liao, S. Tada, E. Kam *et al. Angew. Chem. Int. Ed.* 56(9) (2017)
- [3] K.V. Bussche, G.F. Froment. *J. Catal.* 161(1) (1996)
- [4] S. Kuld, C. Conradsen, P.G. Moses, I. Chorkendorff, J. Sehested *Angew. Chem. Int. Ed.* 53(23) (2014)
- [5] S. Tsunekawa, K. Asami, S. Ito, T. Sugimoto *Appl. Surf. Sci.* 252(5) (2005)
- [6] S. Kamari, A.N. Alexandrova, P. Sautet *J. Am. Chem. Soc.* 145(48) (2023)

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