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Stable Amorphous Georgeite as a Precursor to a High Activity Catalyst

Simon A. Kondrat^{1*}, Peter P. Wells², P. Jakob B. Wagner³, Christopher J. Kiely⁴, Gordon J. Kelly⁵, Matthew J. Rosseinsky⁶ and Graham J. Hutchings^{1*}

¹ Cardiff Catalysis Institute, Cardiff University, Park Place, Cardiff, CF10 3AT, U.K., ² UK Catalysis Hub, Research Complex at Harwell, Harwell, OX11 0FA, U.K., ³ Technical University of Denmark, Fysikvej 307, DK-2800 Kgs, Denmark, ⁴ Department of Materials Science and Engineering, Lehigh University, 5 East Packer Avenue, Bethlehem, PA 18015, U.S.A. ⁵ Johnson Matthey, PO Box 1, Belasis Avenue, Cleveland, TS23 1LB, U.K., ⁶ University of Liverpool, Crown Street, Liverpool, L69 7ZD, U.K.

*kondratSA@cardiff.ac.uk, Hutch@cardiff.ac.uk

Introduction

Cu/ZnO/Al₂O₃ catalysts have been used are well known catalysts for methanol synthesis variety and low temperature water gas shift reaction, which are important for the production of chemical intermediates. These catalysts are conventionally prepared by co-precipitation of metal nitrate salts with sodium carbonate to produce copper and zinc hydroxycarbonate phases, with are then calcined and reduced *in situ* to form the active Cu/ZnO/Al₂O₃. [1] Precursor phases strongly influences the activity of the final catalyst with zincian malachite being the desired phase. [1] Its preparation by co-precipitation involves the transient formation of amorphous georgeite [2], which then transforms rapidly to crystalline malachite. The inability to synthesize stable georgeite, or even to find mineralogical examples of georgeite with high purity, has led to it being largely ignored. Here we report the preparation of a stable georgeite precursor phase using a supercritical CO₂ anti-solvent (SAS) precipitation method. This synthetic georgeite is a precursor to highly active methanol synthesis and LTS catalysts that display in the latter case superior stability to comparable catalysts prepared from crystalline malachite.

Materials and Methods

Well-known catalyst precursors, such as zincian malachite were prepared by the conventional co-precipitation, using nitrate salts, Na₂CO₃ at 65 °C and pH 9. The zincian georgeite was produced using the SAS anti-solvent method. Briefly, solutions of copper and zinc salts were precipitated into supercritical carbon dioxide at 100-150 bar and 40-60 °C. The recovered precipitates from both preparation routes were dried and calcined. Prior to catalyst testing or copper surface area analysis the calcined CuO/ZnO was reduced *in-situ* with dilute hydrogen.

Results and Discussion

FT-IR and XRD confirmed that the SAS prepared material was analogous to the mineral georgeite. Advanced characterization by X-ray absorption spectroscopy (XAS) and X-ray pair distribution function analysis (PDF) demonstrated that zincian georgeite is highly amorphous with structural order being smaller than a single unit cell of conventionally prepared malachite. Calcination of the zincian georgeite sample resulted in a well-mixed matrix of nano-crystalline CuO and ZnO, compared to the larger crystallites observed from calcination of the zincian malachite sample. Environmental Transmission electron microscopy

and *in situ* XRD-XAS show that micro-structure of the active reduced Cu/ZnO catalyst is dependent on the catalyst precursors structure. Zincian georgeite derived catalysts were found to have small Cu crystallites dispersed in a highly disordered ZnO matrix, whereas the zincian malachite sample had defined crystalline ZnO interspersed amongst Cu particles. The greater Cu-ZnO interface in the georgeite derived catalyst resulted in high initial activity for methanol synthesis for syn-gas and exceptional stability in the LTS reaction (Figure 1).

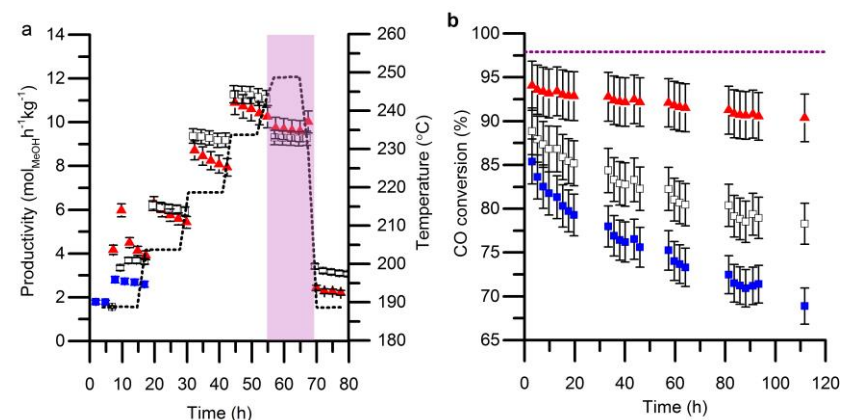


Figure 1. Catalyst test results: (a) Mass normalized time-on-line methanol productivity; (b) CO conversion for LTS reaction time-on-line (...) represents maximum equilibrium conversion). Key: (---) shows representative methanol synthesis reactor bed temperature; (▲) zincian georgeite; (■) co-precipitated zincian malachite (□) industrial standards (methanol synthesis catalyst wt% is CuO:ZnO:Al₂O₃ = 60:30:10, LTS catalyst wt% is CuO:ZnO:Al₂O₃ = 50:33:17).

Significance

Our findings highlight the value of advanced synthesis methods in accessing unusual mineral phases, and show that there is room for exploring improvements to established industrial catalysts. The high activity of the zincian georgeite catalyst can be explained by a strong metal support interaction between Cu and ZnO, facilitated by the small ZnO particle size and high dispersion of Cu, which is in agreement with recent theoretical studies [3]

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