

Analyzing surface intermediate stoichiometry using the transient kinetic analysis (TKA) approach for methanol synthesis on a Cu/ γ -alumina catalyst

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Introduction

A novel apparatus is employed at Pacific Northwest National Laboratory in a study of methanol synthesis enabling the collection of time resolved information of both *in-situ* surface intermediates and gas phase species via a transmission FTIR probe of a grid-support powder catalyst, as well as reactor effluent analysis using mass spectrometric detection, both with a high time resolution of under 10 seconds [1]. This is the basis for a powerful experimental tool enabling catalytic reaction mechanisms and kinetic parameters to be determined using a transient kinetic analysis (TKA) approach (e.g., transmission FTIR-MS-TKA technique).

Materials and Methods

The experimental methodology has been previously published [1]. In this study a 10 wt.% Cu/ γ -alumina catalyst was prepared by incipient wetness from Cu(NO₃)₂ and calcined in a zero-air stream at 623 K. XPS was used to confirm a purity of CuO/alumina in excess of 99%. *In-situ* reduction with H₂ was performed prior to use as part of the experiments. High purity reagent gases (99.99+%) were used throughout.

Results and Discussion

Figure 2 shows the type of data that can be provided with this FTIR-MS-TKA apparatus in methanol synthesis, in this case during a CO₂/H₂ reaction over a Cu/alumina catalyst. Shown are (a) *in situ* (operando) FTIR spectra of species adsorbed on the catalyst surface and on the pure alumina support, and (b) transient methanol mass spectrometer signals from the reactor effluent during gas-feed switching from pure H₂ to a H₂ / CO₂ mixture. The 453 K result is seen to yield a ~100 s transient 'spike' suggesting the reduced catalyst prior to switching to a H₂/CO₂ reagent feed results in enhanced transient catalytic activity, possibly through additional active catalyst vacancies. In addition to methanol, we also observed CO and H₂O as products with the mass spectrometer when feeding H₂ / CO₂, as expected from the reported rate of reverse water-gas shift over Cu [2,3] (which is much faster than methanol synthesis).

In additional work as part of this study, surface formate is formed from a steady-state H₂+CO₂ reagent flow on the catalyst at ~473 K and is then titrated with H₂ yielding CO₂, CO, H₂O, methanol, and/or HCHO products. Integration of the transient mass spectrometric signals enables the composition of the surface species to be determined and a mass balance calculation

to be performed, thus identifying the C:O:H surface molar ratio under steady-state reaction conditions. In addition, we have also co-fed small gas concentrations of CO, formic acid and formaldehyde to observe their effect on methanol synthesis. The information delivered assist further understanding of the surface concentrations present in methanol synthesis for this catalyst.

Significance

This studies purpose is to elucidate the reaction mechanisms and rate-determining steps for methanol reforming so as to *optimize catalytic processes* for the production of clean hydrogen for use in fuel cells.

Figure 1. (a) Steady-state FTIR spectra of species adsorbed on a Cu / γ -Al₂O₃ catalyst surface under CO₂+H₂ feed (red) and on Cu-free γ -Al₂O₃ under pure CO₂ (black). The IR bands can be assigned to aluminum-bound formate (AF), aluminum-bound carbonate (AC), or copper formate (CuF) species. (b) Transient methanol production rate (mass spectrometer signal) over Cu / γ -Al₂O₃ at various temperatures when the feed is switched from pure H₂ to 3:1 H₂:CO₂ at 2.5 bar.

References

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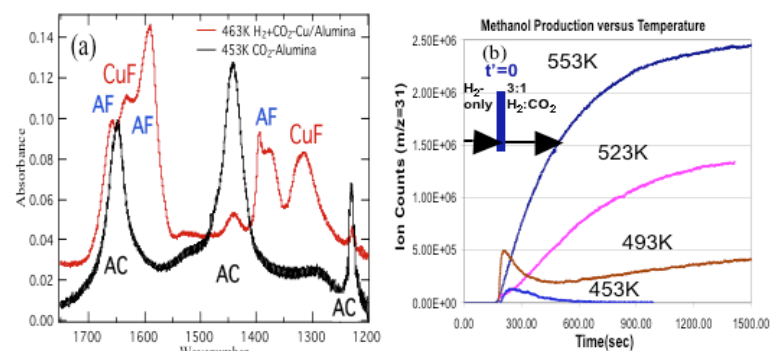


Figure 1