A transient kinetic analysis (TKA) study of methanol synthesis on a Cu/γ-alumina catalyst employing in-situ transmission FTIR and MS detection

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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 inicipient wetness from $Cu(NO_3)_2$ 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 H_2 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 CO_2/H_2 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) the transient FTIR signal for Cu-bound adsorbed formate as it is titrated (hydrogenated) with H_2 (initiated by a rapid gas switching). This data shows the ability to monitor adsorbate transients in FTIR with high sensitivity. This decay is fit with a lifetime of 670 s (black curve), but time resolution of ~1 s has been proven in such measurements with adsorbed species that are formed or removed more rapidly. In addition to methanol, we also observed CO and H_2O as products with the mass spectrometer when feeding H_2 / CO_2, 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 H_2+CO_2 reagent flow on a Cu/γ-alumina catalyst at ~473 K and its importance as an intermediate in methanol synthesis is examined. Below 453 K significant Cu-formate IR absorption signal is seen, whereas at the higher temperatures of 453-553 K methanol production is observed. Two transient processes are thus investigated: 1. Starting from reduced Cu surface under steady H_2 input a gas switch to constant flow of H_2+CO_2 (forming methanol) is performed; 2. Second, the reverse gas switch from H_2+CO_2 to H_2-only (e.g., formate titration) is performed. The former yielded a slow build-up of catalyst activity for methanol synthesis at temperatures higher than 493 K whereas the latter resulted in surface formate titration and gas phase products that may include methanol, CO and HCHO.

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-Al_2O_3 catalyst surface under CO_2+H_2 feed (red) and on Cu-free γ-Al_2O_3 under pure CO_2 (black). The IR bands can be assigned to aluminum-bound formate (AF), aluminum-bound carbonate (AC), or copper formate (CuF) species. (b) Transient FTIR signal of copper-bound adsorbed formate (CuF) during its transient hydrogenation at 353 K. The CuF was prepared at times <1000 s using a feed of 3:1 H_2:CO_2 at 2.5 bar total pressure.

References

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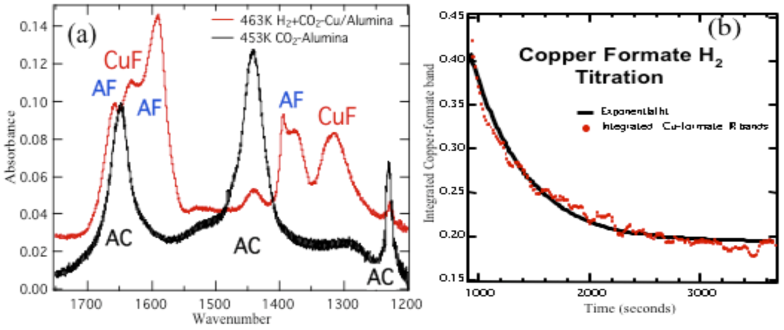

Figure 1