

MS-IR STUDIES OF SURFACE FORMATE REACTIVITY UNDER METHANOL SYNTHESIS CONDITIONS ON Cu/SiO₂

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Introduction

Methanol formation / reformation and water gas shift are of current interest as catalytic processes in possible future hydrogen energy systems [1]. Previous studies have examined the reactivity of formate as a proposed intermediate on copper single crystals as well as on supported copper catalysts. Nevertheless, the reaction channel from formate to methanol is still unproven. Our recent work [2] has shown that, over the temperature range 100-240°C, hydrogen at pressures up to 6 bar has little or no effect on the lifetime of formate on a Cu/SiO₂ catalyst, and that little or no methanol is produced during the decomposition of formate under the same exposure conditions. For further understanding of the reactivities of the possible surface intermediates, simultaneous *in-situ* information at reaction steady state (H₂+CO₂) is performed in this study. Using dynamic isotope switching, the lifetimes of the surface formate pool on Cu/SiO₂ under steady state reaction conditions were measured and compared to those seen in previous reported transient situations in hydrogen and inert atmospheres.

Materials and Methods

The experimental methodology has been previously published [3]. Experiments were performed at 140°C – 160°C. These lower temperatures yield both precise measurements of the IR response, as well as measurable product formation rates. In the experiment, the Cu/SiO₂ catalyst was first exposed to D₂/¹³CO₂ to reach steady-state, then switched to D₂ + ¹²CO₂ to obtain an isotopic transient (SSITKA) by monitoring the replacement of ¹³C isotopic species on the catalyst and in the gas phase with ¹²C species. Once ¹²C steady-state is achieved, the gas composition is changed again to a non-catalytic mixture (usually D₂:Ar) and the decay of the surface intermediates and product concentrations monitored. We also obtain the steady-state catalytic rates from the MS data. D₂ rather than H₂ was used to minimize feature overlap in both MS and FTIR results.

Results and Discussions

DCOO lifetimes under steady state catalytic conditions in CO₂:D₂ atmospheres were measured by ¹²C – ¹³C isotope transients (SSITKA) (fig 1). The values range from 220s at 160°C to 660s at 140°C. These times are 2-3 times shorter than those observed for formate decay under non-catalytic conditions in D₂ or Ar atmospheres [2]. Fits to the Arrhenius expression yield parameters for the isotope transients of $A = 7.5 (\pm 0.8) \times 10^7 \text{ s}^{-1}$, $E_A = 84.8 (\pm 2.7) \text{ kJ mol}^{-1}$, while values for the decomposition in D₂:Ar are $A = 2.3 (\pm 0.9) \times 10^{10} \text{ s}^{-1}$, $E_A = 108.3 (\pm 9.8) \text{ kJ mol}^{-1}$.

Analyzing the MS results shows that the catalytic rates of reverse water gas shift (RWGS) and methanol synthesis are too low to influence the formate lifetime at steady state. Therefore the shorter life time under reactions conditions arises from increased rates of decomposition of formate to D₂ and CO₂. The isotope transient in the methanol product is substantially slower (by 400-500 s) than that in the formate. The additional delay on the surface is attributed in part to readsorption of methanol on the catalyst, thus obscuring the mechanistic link between formate and methanol.

Significance

Simultaneous measurements of both the surface adsorbates and the gaseous products provide unique opportunities to understand the mechanisms of heterogeneous catalytic reactions.

Reference

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- [2] Y. Yang, C.A. Mims, R.S. Disselkamp, D. Mei, J.H. Kwak, J. Szanyi, C.H.F. Peden, C.T. Campbell, Catal. Lett., **125**, 201 (2008).
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Figure 1: IR intensities of ¹³C and ¹²C adsorbed isotopomers of DCOO during the SSITKA isotopic transient described in the text. Reaction conditions: 6 bar total pressure D₂:CO₂ = 3:1. Solid symbols are for D¹²COO, open symbols are for D¹³COO; triangles (red) = 160°C, circles (magenta) = 150°C, diamonds (blue) = 140°C.

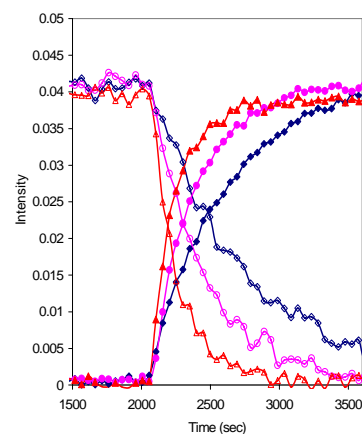


Figure 1