

The Role of Water in Methanol Synthesis on Copper Catalysts

C. A. Mims^{1*}, Y. Yang² and C.H.F. Peden²

¹University of Toronto, Toronto, Ontario M5S3E5 (Canada)

²Institute for Interfacial Catalysis, Pacific Northwest National Laboratory, Richland Washington, 99352 (USA)

*charles.mims@utoronto.ca

Introduction

Step-wise hydrogenation of formate to methanol is thought to be the dominant reaction pathway for methanol production on copper catalysts [1-3]. Monolayer amounts of copper bound formate species are visible by IR spectroscopy under low temperature (140-200°C) reaction conditions, however methanol has yet to be seen in the reaction of copper-bound formate species under high pressure hydrogen conditions [4,5]. In recent studies of formate reactivity on copper catalysts, we have observed that formate lifetimes under reaction conditions in H₂/CO₂ are substantially shorter than in “titration” experiments in H₂ or Ar at the same temperature and pressure. The only significant difference between the two environments is the presence of small amounts of H₂O and CO, simultaneously produced in the reverse water gas shift (RWGS) reaction. Here we present results which show that the presence of water is critical to the hydrogenation of formate to methanol on copper.

Materials and Methods

The apparatus, described previously [5], consists of a high pressure (10 bar) flow cell fitted with IR transparent windows. A small fraction (5-10%) of the 30-50 mg catalyst charge is held in a mesh between the windows for IR analysis while mass spectrometry is performed simultaneously on the product gas. The results in this study were obtained by (1) establishing a steady state surface adlayer and reactivity in 6 bar H₂:CO₂ (3:1) followed by (2) measuring the reactivity of the surface adlayer under various gas atmospheres including hydrogen and water vapor. Water is introduced by syringe pump into a separate gas stream which can be switched to the reactor when desired. The catalyst (10% Cu/SiO₂) was pretreated before each experiment in flowing hydrogen at 200°C. The use of H,D stable isotope variants allows better mass spectral sensitivities and also provides tracer information regarding the origin of the hydrogen in the methanol product.

Results and Discussion

Figure 1 shows the results of three such experiments at 140°C. In all three, steady state was reached prior to the switch to the “titration” gas at t = 0. The IR intensities of the symmetric O-C(D)-O formate band at 1330 cm⁻¹ are shown in panel a and the methanol MS traces at 34 m/e (CD₃O⁺) are shown in panel b. In the control experiment in dry Ar (labeled 1), the IR intensity decreases with a time constant of about 2000s as a result of decomposition back to D₂ and CO₂ - no evidence of methanol is seen in the MS trace in panel b. A similar result is seen when Ar is replaced with 6 bar dry D₂ (labeled 2), although a slight increase in the m/e 34 signal is seen. In a third experiment (labeled 3) D₂ mixed with 0.07% water (D₂O) vapor is introduced after 10 minutes in dry Ar. This water feed rate is similar to the water production rate from RWGS during steady state catalysis. The introduction of moist D₂ causes a marked increase in the

disappearance rate of the surface formate (panel a) while at the same time methanol is

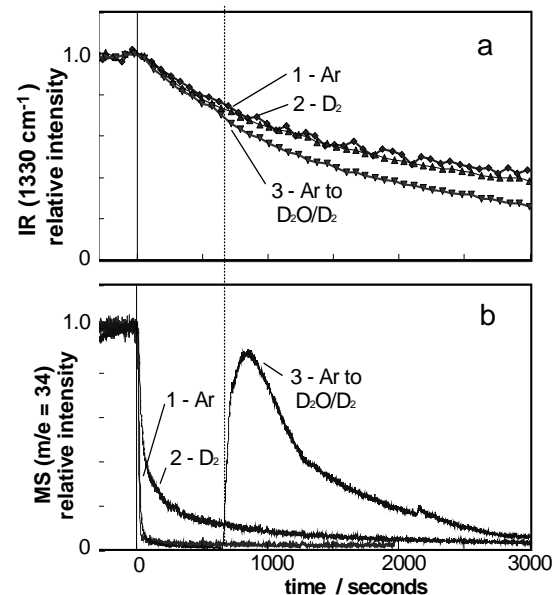


Figure 1. Formate IR intensities (panel a) and m/e 34 MS intensities (panel b) during exposure to various gas atmospheres (T = 140°C, pressure = 6 bar)

Significance

Adsorbed species derived from water are critical for the production of methanol from adsorbed formate species on copper - a fact not included in current microkinetic models. The role of CO₂ and simultaneous water-gas-shift activity in commercial methanol synthesis [6] are undoubtedly related to this phenomenon.

References

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produced at rates which are similar to the steady state catalytic rates (panel b). The increased formate loss is quantitatively equal to the integrated methanol product and corresponds to 8 mol% of the steady state formate adlayer. Further data reveal that both water and hydrogen are required to produce methanol - no methanol is from D₂O : Ar mixtures. Experiments with various H,D isotopic content in the titration gas show that the hydrogen in the methanol arises both from pre-titration surface reservoirs and the reactant gas.