A TPR XANES and XRD study of transition metal promoted Fe-based Fischer-Tropsch catalysts

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Introduction

Fischer-Tropsch (FT) synthesis is being widely studied as a means of converting coal, biomass, and stranded natural gas to liquid fuels. In particular, the promotion of Fe-based catalysts with transition metals has been investigated as a means of increasing activity and selectivity.

The work described by Lohitharn et al. [1] have reported significant differences in the CO conversion rates of Fe-based transition metal-promoted catalysts with a mol. based formula 95Fe/5 Me/5 Cu/17 SiO_2 (Me = Cr, Mn, Zr, Mo, W) and 100 Fe/5 Cu/17 SiO_2. They found significant improvements in CO conversion and C_1-C_8 FTS activity (relative to the unpromoted catalyst) with Mn, Zr, Cr-promotion, However W and Mo showed little to no improvement.

Here, we report the results of a study designed to investigate the changes in the local environment of Fe and its reducibility caused by the transition metal-promotion.

Materials and Methods

A 2:1 ratio of H_2:CO was used for an in-situ TPR (temperature-programmed reduction) XANES (X-ray absorption near-edge structure) experiment from 25°C to 350°C, ramped at a rate of 2°C/min, with the residual gas analyzed. The TPR XANES experiments used an in-situ Lytle cell [2] with a Variac and (PID) temperature controller to ramp the temperature at the DCM beamline at the J. Bennett Johnston Sr., Center for Advanced Microstructures and Devices (CAMD). The body of the Lytle cell was purged in He and water-cooled. Each XANES scan took approximately 12 min, allowing 25°C intervals. The catalyst synthesis is described elsewhere [1]; with approximately 0.02g of catalyst diluted in approximately 0.02g amorphous SiO_2, with syngas flow rates of ~30 cc/min. Athena [3] was used in the data reduction and least-squares fitting of the data with standards to semi-quantitatively show phase speciation (Fe_2O_3, Fe_3O_4, θ-Fe_3C) as a function of temperature.

Results and Discussion

The data show that there is an effect of the reducibility of the catalysts based on the transition metal used to promote the catalyst. However, there was no CO or H_2 conversion until the XANES showed some reduction of the catalyst, implying that the active catalyst is a reduced form of Fe (likely the carbide phase). The XRD shows amorphous Fe_2O_3 in the calcined catalyst, therefore the changes in the XANES spectra correspond to phase changes of $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow$ θ-Fe_3C, which is consistent with the literature [4]. Figure 1 clearly shows the reduction of Fe by changes in the pre-edge peak (~7.112 KeV) and the main absorption peak shape, consistent with reduction of Fe.

Significance

This work is one of the few reported studies in which in-situ XANES has been carried out at FT reaction conditions. The results clearly show the structural effects of both reduction and reaction conditions on the Zr-promoted Fe catalyst.

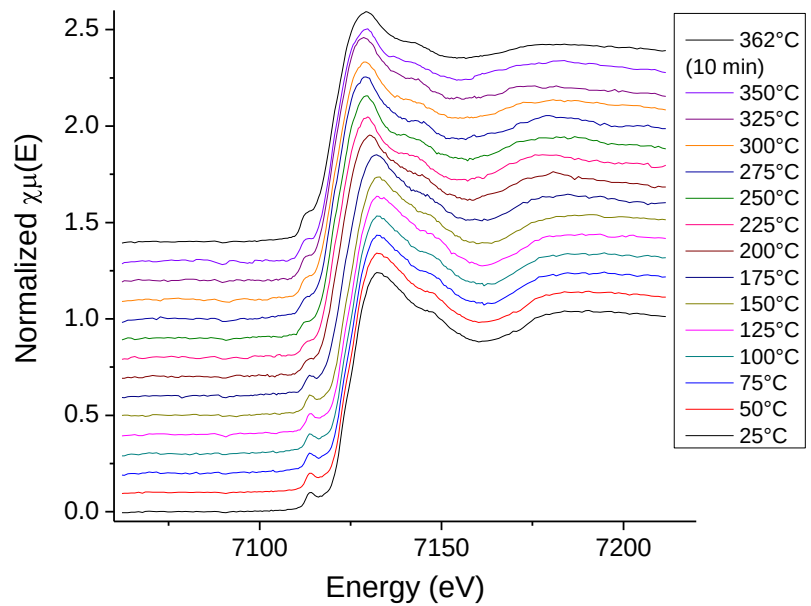

Figure 1. 95Fe5Zr XANES of a 2:1 H_2:CO ratio syngas TPR from 25°C to 362°C.

References

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