# Adsorption/Dissociation of CO on Polycrystalline Fe

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## Introduction

Fischer-Tropsch synthesis (FTS) on Fe catalysts has been practiced commercially for more than 70 years. Reaction kinetics and mechanisms of FTS have been extensively studied, and substantial work has focused on unraveling the elementary steps. A mechanism for CO hydrogenation on metal carbide surfaces was proposed first by Fischer and Tropsch in 1926 [1]. In the carbide mechanism, CO is dissociated and forms a surface metal carbide which is further hydrogenated to $CH_x$ monomer. Eidus and Anderson et. al. [2] proposed a mechanism involving an adsorbed hydroxyl carbine or enol, M=CH(OH), which was thought to undergo further hydrogenation to produce a methylene group, which in turn could polymerize to hydrocarbon chain. A third mechanistic path was proposed by Pichler et. al. in the 1970's [3] involving insertion of CO into the metal-carbon bond of an adsorbed alkyl species. Experimental and theoretical evidence supports to some extent all three mechanisms.

Our work focuses generally on development of a microkinetic model for Fe catalyzed FTS and more specifically on adsorption and dissociation of CO on polycrystalline Fe. Much of the previous experimental and theoretical work has addressed energetics and kinetics of CO adsorption and dissociation on single crystal Fe, two the most basic steps in FTS. However, reliable data describing energetics and kinetics of CO adsorption and dissociation on promoted and unpromoted polycrystalline Fe surfaces in the presence of surface hydrogen is scarce and yet needed for the development of commercially-relevant microkinetic models.

## Materials and Methods

Unsupported Fe FT catalysts with/without K and/or Pt were prepared by co-precipitation of $Fe(NO_3)_3 \cdot 9H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ in aqueous solution with total cation concentrations of 1 M with aqueous-phase $NH_4OH$ according to the relation $[NH_4OH] = 3.2 \ [M^{3+}]$. The $NH_4OH$ solution was added dropwise to the stirred solution of $Fe(NO_3)_3$ and $Al(NO_3)_3$ at 70°C at a pH of 8-9 over an interval of 2 h, during which time a brown precipitate was formed, following which the slurry was stirred for another 30 min at 70°C. The precipitate was filtered, washed with demineralized water, and dried at 110°C overnight, followed by reduction in 10% $H_2$ at 500°C. Temperature programmed desorption (TPD and TGA) was used to study CO adsorption and dissociation after CO adsorption at temperatures ranging from 298 to 423 K and following 10 minutes exposure to $H_2$ and CO at 398 to 448 K.

## Results and Discussion

Two desorption peaks, associated with molecularly-adsorbed CO and dissociated CO were typically observed in CO-TPD spectra at 400-450 K and 800-850 K respectively (Fig. 1). Temperature of desorption (hence binding energy) increases while intensity decreases for molecularly adsorbed CO while binding energy decreases and intensity increases for dissociated CO with increasing adsorption temperature. Similar TPD spectra were obtained for K- and Pt-promoted Fe. The quantitative analysis of these data provides heats of adsorption

and kinetics of CO adsorption and dissociation on polycrystalline Fe as a function of adsorption temperature, coverage, and promoter. Table 1 compares the heat of CO adsorption on unsupported, polycrystalline Fe from this work with calculated values for SC Fe.

**Table 1. CO Heat of Adsorption on SC and PC Fe**

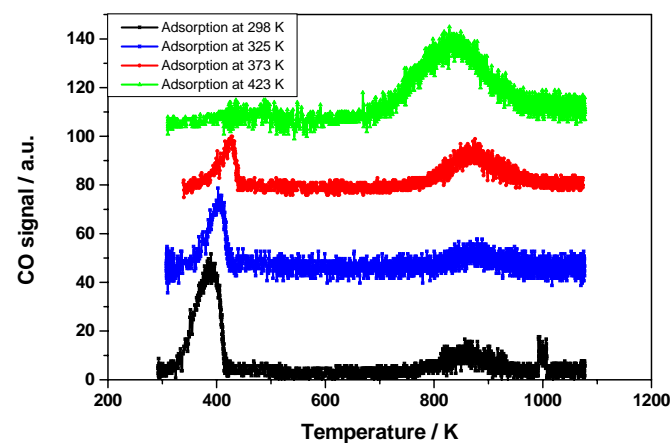|  | Heat of Adsorption (kJ/mol) | Reference |
|---|---|---|
| SC Fe, Calculated | 140~200 | 4 |
| Fe(100), Experimental | 100 ± 5 | 5 |
| PC Fe, Experimental | 100 | This work |



**Figure 1.** CO-TPD spectra on 99% Fe samples at different adsorption temperatures

## Significance

Need is evident for reliable, relevant kinetic parameters for microkinetic modeling of CO adsorption and dissociation on promoted and unpromoted polycrystalline Fe.

## References

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