

# Selective Adsorption of Manganese onto Cobalt for Optimized Mn/Co/TiO<sub>2</sub> Fischer-Tropsch Catalysts

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## Introduction

By controlling the charging parameters of the hydroxyl groups on an oxide support via pH, Regalbuto et al. have shown that a metal complex can be strongly adsorbed on to the oxide surface with high dispersion [1]. Schwarz proposed years ago that one could utilize these electrostatic interactions to direct the adsorption of a metal onto the precursor oxide phase of a supported metal catalyst rather than the support to achieve selective adsorption [2]. Application of this technique can be very beneficial in promoted metal catalysts where intimate contact between the active metal and promoter oxide is of fundamental importance.

Manganese promoted Cobalt Fischer-Tropsch (FT) catalysts have been shown to have higher CO conversion and enhanced selectivity towards C<sub>5+</sub> hydrocarbon chains especially when the MnO particles are in close interaction with the Co<sup>0</sup>, inducing an electronic promotion effect [3]. Until now, controlled intimate contact between the Co<sup>0</sup> and MnO particles has proven difficult to achieve. This current work applies the theory of selective adsorption to the synthesis of Mn/Co/TiO<sub>2</sub> FT catalysts by driving the manganese on to the supported Co<sub>3</sub>O<sub>4</sub> phase to achieve systematic catalyst preparation for reaction.

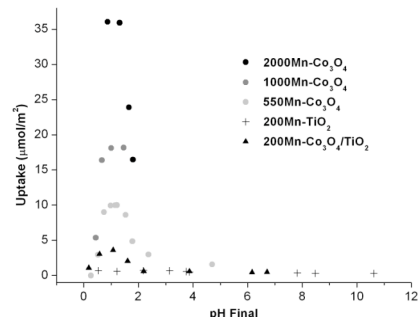
## Materials and Methods

Cobalt nitrate was deposited onto the TiO<sub>2</sub> support (Degussa P-25) via homogeneous deposition precipitation using urea as the precipitation agent [4]. Filtered samples were dried overnight and calcined at 400°C for 4 h. The resulting material was suspended in solutions containing various amounts KMnO<sub>4</sub> adjusted to pH 1 for optimal uptake of the [MnO<sub>4</sub>]<sup>-</sup> precursor and subsequently calcined. Uptake and [MnO<sub>4</sub>]<sup>-</sup> stability were monitored with Inductively Coupled Plasma (ICP) Spectrometry and UV-Visible Spectroscopy. Samples were characterized by X-ray Diffraction, Temperature Programmed Reduction (TPR), and X-ray Photoelectron Spectroscopy (XPS). Catalytic performance for the FT reaction was monitored at 1 bar, 220°C and H<sub>2</sub>/CO = 2 after reduction in H<sub>2</sub> at 350°C for 2 h.

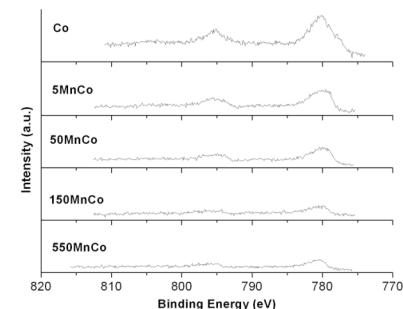
## Results and Discussion

Figure 1 reveals the ICP results of the [MnO<sub>4</sub>]<sup>-</sup> adsorption on pure Co<sub>3</sub>O<sub>4</sub>, TiO<sub>2</sub> and supported Co<sub>3</sub>O<sub>4</sub>/TiO<sub>2</sub>. The [MnO<sub>4</sub>]<sup>-</sup> readily adsorbed to the pure and supported Co<sub>3</sub>O<sub>4</sub> while negligible amounts adsorbed on the TiO<sub>2</sub>. The difference in adsorption behavior may be ascribed to the difference in the density of positively charged hydroxyl groups on the oxide surface as the Co<sub>3</sub>O<sub>4</sub> being far greater than that of TiO<sub>2</sub>. While the preliminary adsorption of [MnO<sub>4</sub>]<sup>-</sup> appears electrostatic, a redox reaction on the surface of the Co<sub>3</sub>O<sub>4</sub> may also contribute to deposition of MnO<sub>2</sub>. UV-Vis spectra agreed with the ICP results showing the disappearance

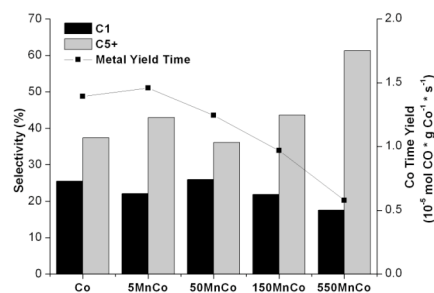
of the [MnO<sub>4</sub>]<sup>-</sup> fingerprint for both the pure and supported Co<sub>3</sub>O<sub>4</sub> in less than an hour while the spectra remained virtually stable even after 24 hr of contact with TiO<sub>2</sub> alone. TPR results confirm that as manganese content is increased, reduction of the Co<sub>3</sub>O<sub>4</sub> is hampered [3]. A decrease in the Co 2p peak is observed with increasing manganese loadings in XPS results seen in Figure 2 as the manganese covers the Co<sub>3</sub>O<sub>4</sub>. As can be seen in the catalytic results in Figure 3, small additions of manganese favorably affect both the activity and selectivity in the FT reaction.



**Figure 1:** [MnO<sub>4</sub>]<sup>-</sup> uptake on Co<sub>3</sub>O<sub>4</sub>, TiO<sub>2</sub> and supported Co<sub>3</sub>O<sub>4</sub>/TiO<sub>2</sub> vs. pH.



**Figure 2:** Co 2p XPS spectra with increasing manganese loading.



**Figure 3:** Influence of manganese loading on activity and selectivity in the FT reaction.

## Significance

Close contact between the active and promoter elements is often of vital importance to the catalyst's performance. However, current synthesis methods often lead to inconsistent and random distribution of the promoter over the catalyst surface. Systematic preparation of promoted catalysts can lead to an improved understanding of the active site ultimately resulting in improved catalyst activity and selectivity. Our work with Mn promoted Cobalt catalysts is one example where the technique of electrostatic adsorption can improve catalyst formulation and usage of promoting agents.

## References

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