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Z-Contrast Imaging and EELS study of Mn/Co/TiO_2 Fischer-Tropsch Catalysts

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Co-based Fischer-Tropsch (FT) catalysts have drawn increasing attention due to their ability to convert natural gas into high quality diesel fuels. Mn is used as a promoter in Co-based FT catalysts, which results in an increased activity and selectivity of the catalysts (Figure 5). Previous studies have utilized homogeneous deposition precipitation and incipient wetness impregnation to synthesize Mn/Co/TiO_2 catalysts resulting in an indiscriminate coating of Co and TiO_2 with Mn. In this study, we use the strong electrostatic adsorption (SEA) method that relies on the pH-value of the metal salt solution to control the electrostatic force between the support and the solution to enhance the Mn particle adsorption on Co catalysts, in order to increase the Mn loading on the Co surface. [1-3]

Co-based catalysts with different Mn loading amount (up to 3.43 wt%) are synthesized by using SEA, followed by calcinations at 400˚C, and a subsequent reduction at 350˚C in H_2. In this study, transmission electron microscope (TEM), as well as Z-contrast imaging in combination with electron energy-loss spectroscopy (EELS) is used to analyze the unreduced and reduced Mn/Co/TiO_2 FT catalysts. The atomic and electronic structures of both catalysts are compared to the changes in the catalysts reactivity and selectivity.

Figure 1 shows the TEM images of the unreduced and reduced FT-catalysts. While the unreduced catalysts do not show any metal particles smaller than 10 nm (Figure 1a), CoO particles with less than 6 nm diameters are seen on the TiO_2 support in the reduced catalysts (Figure 1b). In Figure 2, elemental mapping shows that after calcinations, the Co-particles are Co_3O_4 and the Mn prefers to accumulate in the vicinity of the Co_3O_4 particles rather than on the TiO_2 support. During the reduction process, the Co_3O_4 particles are reduced to CoO and the elemental mapping shows that Mn now accumulates at the CoO-TiO_2 interface for CoO particles larger than 20 nm (Figure 3) and less than 6 nm (Figure 4) in diameter. FT reaction measurements (Figure 5) clearly show that the presence of Mn results in an increased activity and selectivity, but the atomic scale mechanism for this enhancement remains unclear.

In this presentation, we will examine the influence of the Mn promoter on the atomic and electronic structures of the Co-based FT catalysts as a function of Mn loading and correlate this with the changes in the FT reaction. Further, we will utilize in-situ reduction in the microscope column to study the changes in the catalysts morphology and examine the role of Mn in inhibiting the complete reduction of the CoO_x nano-clusters. [4]

References

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Fig. 1

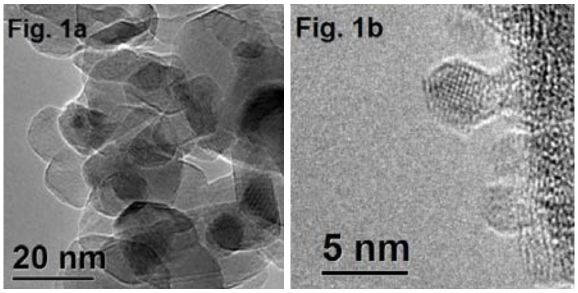

Figure 1: TEM images of Mn/Co/TiO_2 catalysts, (a) unreduced sample, (b) reduced sample.

Fig. 2

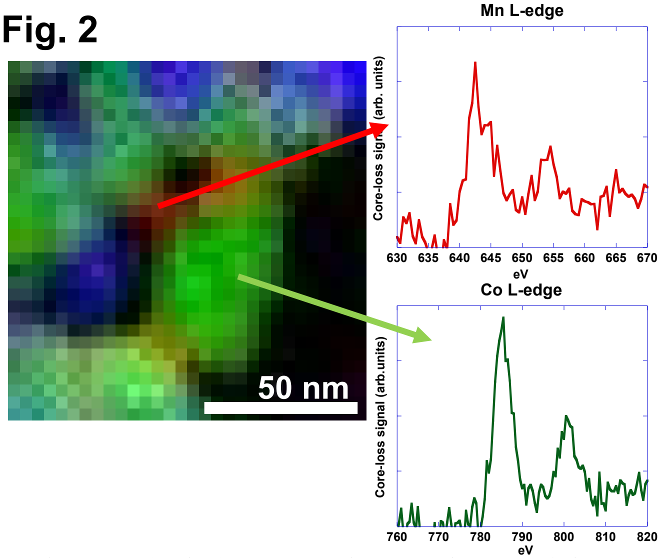

Figure 2 (color): EELS elemental map of the unreduced Mn/Co/TiO_2 catalysts. Red represents Mn, green represents Co and blue represents Ti.

Fig. 3

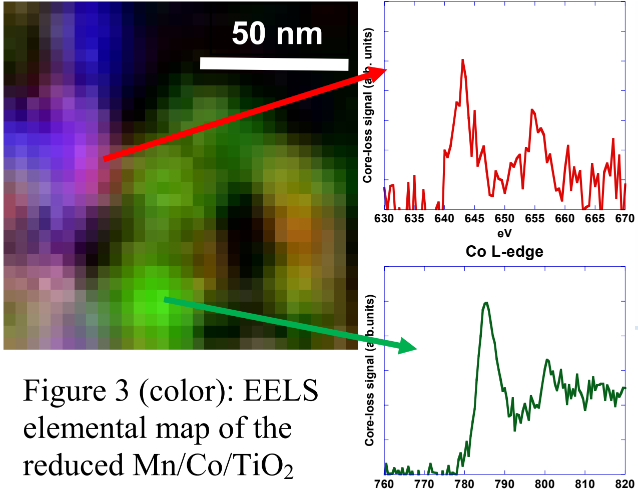

Figure 3 (color): EELS elemental map of the reduced Mn/Co/TiO_2 catalysts.

Fig. 4

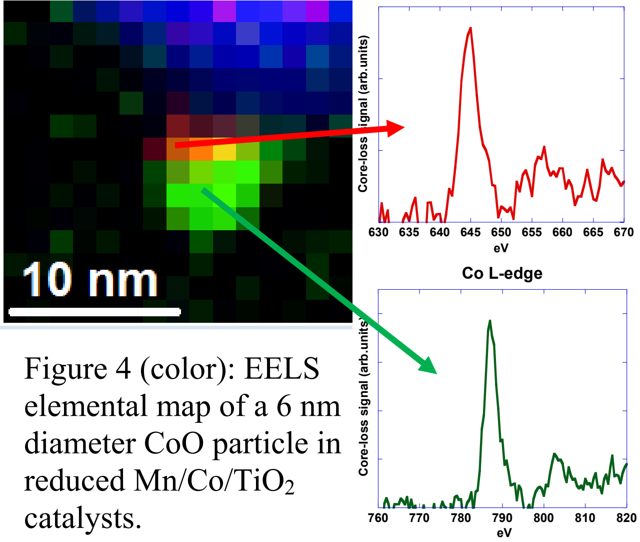

Figure 4 (color): EELS elemental map of a 6 nm diameter CoO particle in reduced Mn/Co/TiO_2 catalysts.

Fig. 5

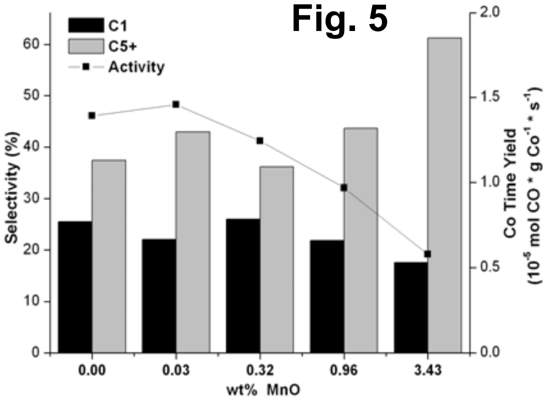

Figure 5: Influence of manganese loading on activity and selectivity in the FT reaction. C1 represents methane production which is not wanted. C5+ represents hydrocarbon chains production which is wanted.