Unraveling the Structure of Mn-Promoted Co/TiO$_2$ Fischer-Tropsch Catalysts by In Situ X-Ray Absorption Spectroscopy

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Abstract. Combination of in situ X-ray absorption spectroscopy (XAFS) at the Co and Mn K-edges with electron microscopy (STEM-EELS) has allowed to unravel the complex structure of a series of unpromoted and Mn promoted TiO$_2$-supported cobalt Fischer-Tropsch catalysts prepared by homogeneous deposition precipitation (HDP), both in their calcined and reduced states. After calcination the catalysts are generally composed of large Co$_3$O$_4$ aggregates (13-20 nm) and a MnO$_2$-type phase that is either dispersed on the TiO$_2$ surface or, for the major part, covering the Co$_3$O$_4$ particles. Additionally Mn is also forming a spinel-type Co$_{3-x}$Mn$_x$O$_4$ solid solution at the surface of the Co$_3$O$_4$ particles. In pure Co or when small amount of this spinel-type phase are formed during calcination, reduction in H$_2$ at 350 °C produces Co^0 particles of variable sizes (3.5-15 nm) otherwise Co reduction is limited to the Co^{2+} state. Manganese that exists entirely in a Mn^{2+} state in the reduced catalysts is forming (1) a highly dispersed Ti$_2$MnO$_4$-type phase at the TiO$_2$ surface, (2) a less dispersed MnO phase close to the cobalt particles that coexists with (3) a rock salt-type Mn$_{1-x}$Co$_x$O solid solution. Similarly, large amount of spinel solid solution in the calcined state favors the formation of Mn$_{1-x}$Co$_x$O-type solid solution during reduction showing that one of the main roles of the Mn promoter is to limit Co reducibility.

Keywords: EXAFS, XANES, STEM-EELS, Fischer-Tropsch, Catalysis, Cobalt, Manganese, Titanate.
PACS: 61.10.Ht   X-ray absorption spectroscopy: EXAFS, NEXAFS, XANES, etc.; 68.37.Lp Transmission electron microscopy (TEM) (including STEM, HRTEM, etc.); 61.43.-j Disordered solids; 82.45.Jn Surface structure, reactivity and catalysis.

INTRODUCTION

Fischer-Tropsch technology, in which high molecular weight hydrocarbons are synthesized by catalytic hydrogenation of CO using Co-based catalysts [1], is to play a major role in the expected shift from crude oil to natural gas (GTL) and biomass (BTL) as feedstocks for chemical industries. Although the use of manganese as promoter for these catalysts has been reported a few times in the open as well as in the patent literature [2], the exact role of manganese and its influence on the cobalt active site composition remains largely unclear. In order to get a better understanding of the physico-chemical and catalytic properties of TiO$_2$-supported Co-based Co/Mn/TiO$_2$ catalysts, and more specifically the role played by manganese, a full characterization of a series of catalysts in the calcined and the reduced state have been achieved by *in situ* X-ray absorption spectroscopy (XAS) at the Co and Mn K-edges and STEM-EELS.

EXPERIMENTAL

Three catalysts have been investigated (Table 1). Pure cobalt H-Co was synthesized by a homogeneous deposition precipitation (HDP) method using aqueous solutions of Co(NO$_3$)$_2$.6H$_2$O and calcination in air at 400 °C for 4 h. Part of uncalcined H-Co was

TABLE 1. Catalysts composition and preparation method.

Catalysts	Preparation method	Co wt%	Mn wt%
H-Co	HDP Co	7.5	0
H-CoMn-S	HDP Co + IWI Mn Surf.	7.5	2
H-CoMn-V	HDP [Co+Mn] Volume	7.8	4

subsequently loaded with manganese by incipient wetness impregnation (IWI) using aqueous solutions of Mn(NO$_3$)$_2$.4H$_2$O followed by the same calcination as described above, to obtain H-CoMn-S (Mn at Surface). A third catalyst H-CoMn-V (Mn in volume),

was prepared with the same procedure as for H-Co but starting with a mixture of Co and Mn precursors.

STEM-EELS (scanning transmission electron energy loss spectroscopy) measurements of H-CoMn-S and H-CoMn-V before and after reduction in H_2 at 350 °C and passivation in CO_2 were performed in Orsay, France with a 100 keV STEM instrument (VG HB 501) equipped with a field emission source and a parallel Gatan 666 EELS spectrometer (0.5 eV energy resolution and sub-nanometer spatial resolution).

X-ray absorption data were collected on DUBBLE (ESRF, Grenoble, France), operating under beam conditions of 6 GeV, 200 mA using a Si (111) double-crystal monochromator. XAS signals were measured *in situ* at the Co and Mn K-edge, before (room temperature) and after a 2 h reduction in H_2 at 350 °C (reduction temperature), in transmission (Co) and fluorescence (Mn) mode using a 9-channel Ge detector. Data reduction and EXAFS refinements (k^3 weighting) were performed using respectively the programs EXBROOK and EXCURV98. Phase shifts and backscattering factors were calculated ab initio using Hedin-Lundqvist potentials.

RESULTS AND DISCUSSION

Calcined Catalysts

In agreement with XRD results [3], phase-corrected Fourier transforms (FT's) at the Co K-edge of the three calcined catalysts (Figure 1) present all peaks very similar to those of Co_3O_4. The peak broadening points out the nanocrystalline character of this phase in all the catalysts (aggregates of 13-20 nm). EXAFS results show however a slight increase of Co-O distances from 1.91 Å in H-Co to 1.93 Å in H-CoMn-V [3].

FT's at the Mn K-edge of the two Mn-promoted calcined catalysts exhibit two peaks corresponding, respectively, to an O and a Mn shell. EXAFS results in Table 2 show that both catalysts present slightly longer bonds distances than in MnO_2 suggesting that in addition to a MnO_2-type phase, part of the Mn is forming another phase. This is further confirmed by

TABLE 2. EXAFS results at the Mn K-edge for the calcined catalysts along with αMnO_2 crystallographic data.

Catalysts	R (Å) Mn-O	O C.N.	$2\sigma^2$ (Å^2)	R (Å) Mn-Mn	Mn C.N.	$2\sigma^2$ (Å^2)
H-CoMn-S	1.91	5.7	0.007	2.87	4.2	0.01
H-CoMn-V	1.91	4.2	0.007	2.89	4.7	0.01
MnO_2	1.88	6.0	-	2.88	4.0	-

the lower number of O neighbors (5.7 to 4.2) in the catalysts compared to 6 in MnO_2. These results, together with XRD results [3] showing a shift of the

Co_3O_4 reflections towards small angles, as well as the STEM-EELS measurements [4] indicating a very close interaction between Co and Mn, point towards the formation in both catalysts of a cubic spinel solid solution $Co_{3-x}Mn_xO_4$ (with x = 0.9 in H-CoMn-V) [3].
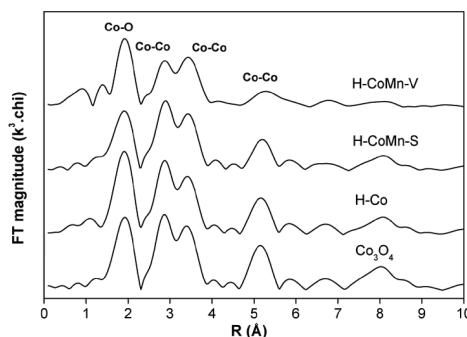

FIGURE 1. Phase-corrected Fourier transforms of the EXAFS at Co K-edge for the calcined catalysts and Co_3O_4.
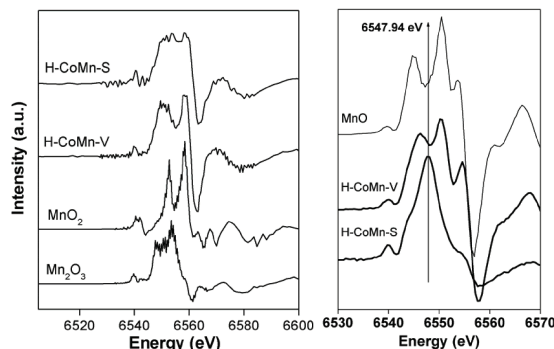

FIGURE 2. First derivative of the XANES of calcined (left) and reduced (right) H-CoMn-S and H-CoMn-V and reference compounds.

Combination of these two phases would result in the slight increase of the Mn-O and Co-O bond distances observed particularly in H-CoMn-V. These findings are also supported by the XANES analysis (Figure 2) showing that the edge position corresponds to a mixture of Mn^{4+} and Mn^{3+} in both calcined catalysts.

Reduced Catalysts

EXAFS results at Co K-edge show that the reduction of $Co_3O_4/Co_{3-x}Mn_xO_4$ phases in H-Co and H-CoMn-S results in formation of Co^0 particles with sizes of 3.5 and 3.5-15 nm, respectively [3], whereas in H-CoMn-V Co reduction is limited to Co^{2+}.

A comparison of the edge positions (Figure 2) of the Mn K-edge XANES first derivatives of the reduced catalysts with MnO reveals the reduction of the Mn^{4+} and Mn^{3+} mixture into Mn^{2+}. EXAFS analysis (Table 3) shows however, that the Mn-O distance in the catalysts differs significantly from the

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typical distance in bulk MnO. Mn-O bond distance varies from 2.20 Å in MnO to 2.15 in H-CoMn-V and 2.07 Å in H-CoMn-S. This decrease, particularly in H-CoMn-S, is likely due to the formation during reduction of a highly dispersed Ti_2MnO_4 phase with Mn in tetrahedral coordination. In contrast, in H-CoMn-V, Mn features

TABLE 3. EXAFS results at the Mn K-edge for the catalysts reduced at 350 °C along with MnO and Ti_2MnO_4 cryst. data.

Catalysts	R (Å) Mn-O	O C.N.	$2\sigma^2$ (Å^2)	R (Å) Mn-Mn	Mn C.N.	$2\sigma^2$ (Å^2)
H-CoMn-S	2.07	5.2	0.07	2.98	4.3	0.03
H-CoMn-V	2.15	5.6	0.02	3.07	11.9	0.03
MnO	2.20	6.0	-	3.14	12	-
Ti_2MnO_4	2.02	4.0	-	3.72	4.0	-

nearly an octahedral coordination with longer Mn-O distances (2.15 Å). Additionally, a second Mn shell with 11.6 atoms at 3.07 Å has been obtained. Although these Mn-O and Mn-Mn distances are similar to those of bulk MnO (2.20 and 3.14 Å), they are significantly shorter. These results combined with those of XAFS at Co K-edge that showed the presence of a pure Co^{2+} phase and the occurrence of longer Co-O and Co-Co
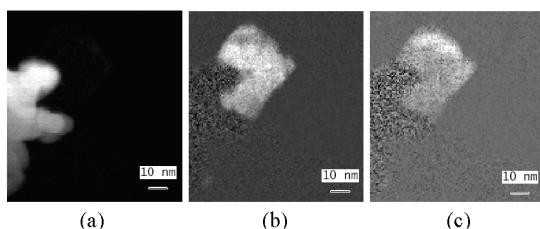

FIGURE 3. Grayscale EELS Ti (a), Co (b) and Mn (c) L-edges chemical maps of reduced and passivated H-CoMn-V.

bonds than in CoO, strongly suggest the existence of a rock salt-type $Mn_{1-x}Co_xO$ solid solution [3]. XAFS results are further confirmed by STEM-EELS in H-CoMn-V (Figure 3) that shows the formation of a bulk mixed Co/Mn/O phase.

A plausible model describing the evolution of the structures during the reduction at 350 °C is given in Figure 4. Before reduction, Mn-promoted catalysts mainly consist of Co_3O_4 particles covered up by a variable amount of spinel-type $Co_{3-x}Mn_xO_4$ solid solution and some MnO_2 phase. In H-CoMn-S, reduction transforms Co_3O_4 into Co^0 particles while Mn is migrating towards the TiO_2 support to form a highly dispersed Ti_2MnO_4 phase and a less dispersed $Co_xMn_{1-x}O$ solid solution that remains close to the metal particles. In H-CoMn-V, the large amount of bulk spinel solid solution $Co_{2.1}Mn_{0.9}O_4$ formed during calcination limits both the migration of Mn and the reduction of Co oxide to the formation of a $Mn_{1-x}Co_xO$ phase.
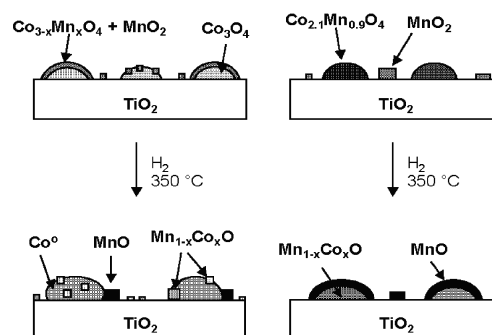

FIGURE 4. Schematic representation of the composition of H-CoMn-S (left) and H-CoMn-V (right) before and after the reduction treatment.

One of the major roles of the Mn promoter is then hampering the reducibility of Co and limiting the spreading of this phase over the support, giving bigger Co^0 particles that are more catalytically active. Similarly by forming $Mn_{1-x}Co_xO$ in the vicinity of the Co^0 particles, Mn may also improve the C_{5+} selectivity of these catalysts [3,4].

CONCLUSION

The combination of *in situ* XAFS with STEM-EELS has proved to be a powerful technique to investigate the complex structural changes occurring in Mn-promoted Co/TiO_2 Fischer-Tropsch catalysts during the reduction phase. It has allowed unraveling the role of Mn and will certainly contribute to a better understanding of the promotion effect in other catalyst systems.

ACKNOWLEDGMENTS

REFERENCES

1. M. E. Dry, *Catal. Today* **71**, 227 (2002).
2. M. F. Goes, P. J. M. Rek, D. Schaddenhorst, J.-P. Lange, J.J.C. Geerlings, and H. Oosterbeek, US Patent No. 5981608 (1999).
3. F. Morales, D. Grandjean, A. Mens, F. M. F. de Groot, and B. M. Weckhuysen, *J. Phys. Chem. B* **110**, 8626-8639 (2006).
4. F. Morales, D. Grandjean, F. M. F. de Groot, O. Stephan, and B. M. Weckhuysen, *Phys. Chem. Chem. Phys.* **4**, 568-572 (2005).