New Insights into the Water-Gas Shift Reaction over Bulk Cr_2O_3*Fe_2O_3 Mixed Oxide Catalysts: A Combined *Operando* Raman-IR-XAS-MS Investigation

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Introduction and Objectives

The bulk chromia-iron mixed oxide catalyst is the primary catalyst for the high temperature (310-450°C) water-gas shift (WGS) reaction for the production of hydrogen and carbon dioxide from steam and carbon monoxide.[1] Although few *in situ* characterization studies have been reported in the literature, the magnetite (Fe_3O_4) phase is present in activated and reduced catalysts recovered from WGS reactors.[2-6] The commercial lifetime of pure magnetite catalysts is limited because of thermal sintering and chromium oxide addition, 8-12% Cr_2O_3, has been found to stabilize the surface area and extend the catalyst life to 2-5 years.[2-6] Despite numerous characterization studies, the role of the chromia promoter is still not completely understood. Edwards *et al.*[3] have found, from XRD and STEM-EDX studies that Cr^{+3} exists in solid solution within the Fe_3O_4 phase as an inverse spinel lattice and that discrete Cr_2O_3 grains are not detected. Similar conclusions were reached from by Robbins *et al.*[4], Newsome *et al.*[5] and Pereira *et al.*[6] from XRD and Mössbauer spectroscopy characterization. Both STEM-EDX and XPS surface analysis by Edwards *et al.*[3] and bulk and XPS surface characterization by Pereira *et al.*[6] revealed that the surface of the Fe_3O_4 catalyst was highly enriched in chromium oxide concentration, but the nature of chromium oxide at the surface could not be determined with these bulk characterization methods. Furthermore, regardless of preparation method, all Cr-doped catalysts were found to be surface enriched in chromium oxide.[5] Recently, *in situ* EXAFS[11] and Mössbauer[12] studies have confirmed that Cr^{+3} is the active chromium oxidation state and Fe_3O_4 is the active iron oxide phase, respectively.

The absence of fundamental *in situ* and *operando* spectroscopic studies of the bulk Cr_2O_3*Fe_2O_3 WGS shift catalyst during the WGS reaction in the catalysis literature has hindered the development of molecular level insights about the catalytic active sites, surface reaction intermediates and the reaction mechanism.[1-10] In order to address the state of the iron oxide catalyst under reaction conditions, the role of the chromia promo-

ter, and the nature of the catalytic active site, *in situ* and *operando* Raman, IR, and XAS spectroscopic studies under reaction conditions were undertaken in the present investigation.

Results and Conclusions

The *operando* Raman spectroscopy studies during WGS, given in Figure 1, confirm that crystalline Fe_3O_4 is the active bulk phase in Cr-doped samples, which forms an amorphous phase for unpromoted Fe_2O_3, and that crystalline Cr_2O_3 NPs are not present. The corresponding *Operando* IR spectroscopy measurements revealed that dioxo surface $(O=)_2CrO_2$ species are also present under oxidizing conditions and become reduced during the WGS reaction. IR measurements also revealed that no surface reaction intermediates are present, even when the reaction is performed at its temperature limit of ~225°C. *Operando* XANES measurements of the Cr K-edge confirm the reduction of Cr^{+6} (dioxo species) to Cr^{+3} at steady-state. The EXAFS Fe K-edge data reveals that the Cr-doped samples stabilize as Fe_3O_4 under steady-state WGS reaction conditions, while unpromoted Fe_2O_3 is active as an amorphous phase consisting mostly of Fe metal and some indistinguishable oxidized state (2+ or 3+). Insights into the WGS reaction mechanism and catalytic active site will be discussed on the basis of these observed phenomena.

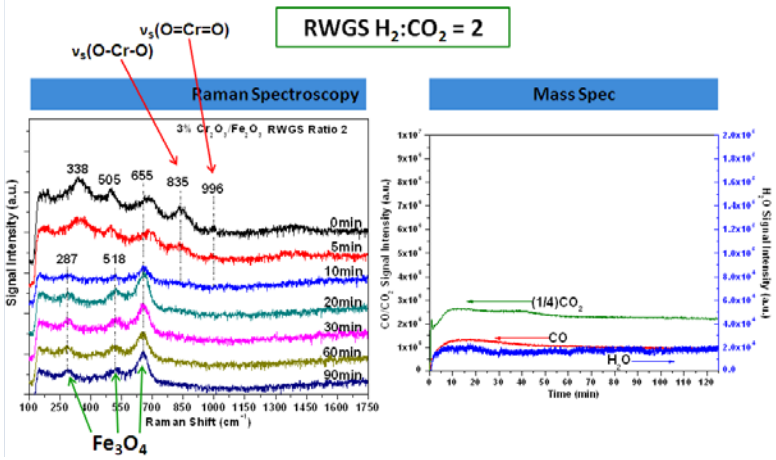

Figure 1. *Operando* Raman spectroscopy of 3% CrO_3/Fe_2O_3 during Reverse-WGS conditions.

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