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

Christopher Keturakis[a], Marco Daturi[b] and Israel E. Wachs[a]
[a]*Operando* Molecular Spectroscopy and Catalysis Laboratory, Chemical Engineering Department, Lehigh University, Bethlehem, PA 18015 USA
[b]Laboratoire Catalyse et Spectrochimie, ENSICAEN,
Université de Caen, CNRS, 6 Bd Maréchal Juin, F-14050 Caen Cedex, France

The high temperature water-gas shift (WGS) reaction is commercially conducted over bulk Cr_2O_3*Fe_2O_3 (~10% CrO_3) catalysts. Much is known about the bulk properties of this catalytic system: the active catalyst consists of the Fe_3O_4 phase and Cr^{+3} cations are dissolved in the Fe_3O_4 lattice. A separate phase of Cr_2O_3 nanoparticles (NPs) has never been found and the only thing known about the surface of this catalyst system is that it is enriched with chromium. The objective of this investigation is to learn more about the bulk and surface aspects of this important catalyst system during WGS reaction conditions, which has never been reported, by employing Raman and IR operando spectroscopy investigations. The operando Raman spectroscopy studies during WGS confirm that Fe_3O_4 is the active phase and that crystalline Cr_2O_3 NPs are not present. The corresponding IR spectroscopy measurements revealed that dioxo surface $(O=)_2CrO_2$ species are also present under oxidizing conditions that become reduced during WGS reaction. The surface CrOx species enhance the reaction rate and are intimately involved in the formation of surface formate intermediates. These studies strongly suggest that it is the surface CrO_x species that are the catalytic active sites for the high temperature WGS reaction and that the Fe_3O_4 phase just serves as a support for the chromium oxide sites.

Rational design of catalysts, Reaction Path Analysis, Hydrogen production.

Introduction

The bulk chromia promoted iron 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

$$H_2O + CO \leftrightarrow H_2 + CO_2 \quad (1)$$

steam and carbon monoxide.[1] Although *in situ* characterization studies have not 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 addition 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 characterization methods. Furthermore, regardless of preparation method, all Cr-doped catalysts were found to be surface enriched in chromium oxide.[5]

Much ambiguity also exists about the mechanism of the high temperature WGS reaction over bulk chromia promoted iron oxide catalysts. The two key reaction mechanisms often discussed in the literature are the associative and regenerative mechanisms.[1] The associative mechanism involves the reaction proceeding via a surface reaction intermediate that is represented by Eqn. 2.

$$CO + H_2O \rightarrow (\text{intermediate}) \rightarrow CO_2 + H_2 \quad (2)$$

Surface formate (HCOO) is the most commonly invoked intermediate[1] for the water-gas shift reaction, however, no *recent* studies exist for the support or opposition of a surface intermediate over the Cr_2O_3*Fe_2O_3 catalyst. The regenerative mechanism involves a two-step cyclic redox process of the catalytic active site (*) represented by Eqns. 3 and 4.

$$H_2O + * \rightarrow H_2 + O^* \quad (3)$$
$$CO + O^* \rightarrow CO_2 + * \quad (4)$$

This mechanism is most easily visualized as the “splitting” of water to produce hydrogen and leaving an atomic oxygen atom on the catalyst for oxidation of the catalyst surface in the first step. In the second step, carbon monoxide reduces the catalyst surface and reacts with the atomic oxygen to produce carbon dioxide, which returns the catalyst surface to its original oxidation state.

The absence of fundamental *in situ* and *operando* spectroscopic studies of the 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 addition, and the nature of the catalytic active site, *in situ* and *operando* Raman and IR molecular spectroscopic studies were undertaken in the present investigation.

In Situ IR & Raman Spectroscopy of bulk α-Fe_2O_3 and supported CrO_3/Fe_2O_3 Catalysts

The *in situ* IR spectra of the dehydrated supported 1-9% CrO_3/Fe_2O_3 catalysts along with the α-Fe_2O_3 support under oxidizing conditions are shown in Figure 1. The IR M=O vibrational region exhibits a strong band at 1008 cm^{-1} along with a weaker band at 980 cm^{-1} and a shoulder at 993 cm^{-1}. These bands have been assigned to ν_{as}(Cr=O) and ν_s(Cr=O) vibrations, respectively, of a surface dioxo $(O=)_2CrO_2$ species.[11] The weak IR band at 1037 cm^{-1} is assigned to the ν_s(Cr=O) vibration of surface monoxo $(O=)CrO_4$ species,[11] while the band at 1025 cm^{-1} is assigned to a surface Fe=O group[12]. The titration of the α-Fe_2O_3 surface hydroxyls with increasing chromia loading is reflected in the FT-IR spectra (not shown), revealing that surface $(O=)_2CrO_2$ species react with surface Fe-OH species. At 3% CrO_3/Fe_2O_3 loading, the surface hydroxyls at 3690 cm^{-1} are completely titrated indicating monolayer surface $(O=)_2CrO_2$ coverage has been reached.

The corresponding *in situ* Raman spectra (not shown) of the supported CrO_3/Fe_2O_3 catalysts as well as the α-Fe_2O_3 support are dominated by the vibrations of the α-Fe_2O_3 support. Raman bands from surface Cr=O vibrations at ~1000 cm^{-1} are not detected against the stronger signal from the α-Fe_2O_3 support. The absence of a Raman band at ~550 cm^{-1}, corresponding to crystalline α-Cr_2O_3 nanoparticles (NPs),[11] which gives rise to strong Raman bands, above monolayer surface coverage suggests α-Cr_2O_3 (Cr^{+3}) dissolution into the iso-structural α-Fe_2O_3 support. Formation of the α-$Fe_{2-x}Cr_xO_3$ solid solution has been previously reported.[3-6]

Operando IR & Raman Spectroscopy during the WGS/*Reverse*-WGS Reaction

The *operando* FT-IR spectra (not shown) reveal that the surface $(O=)_2CrO_2$ species become reduced during the WGS reaction at 400 °C. The surface $(O=)_2CrO_2$ species, however, reappear upon catalyst reoxidation. The lower IR intensity of the surface $(O=)_2CrO_2$ species in the reoxidized catalysts indicates that a portion of the surface $(O=)_2CrO_2$ species dissolved in the α-Fe_2O_3 support during the reducing WGS reaction conditions. Surface reaction intermediates were not detected by FT-IR spectroscopy at this high temperature, which may be related to their low concentration and/or their short life-time.

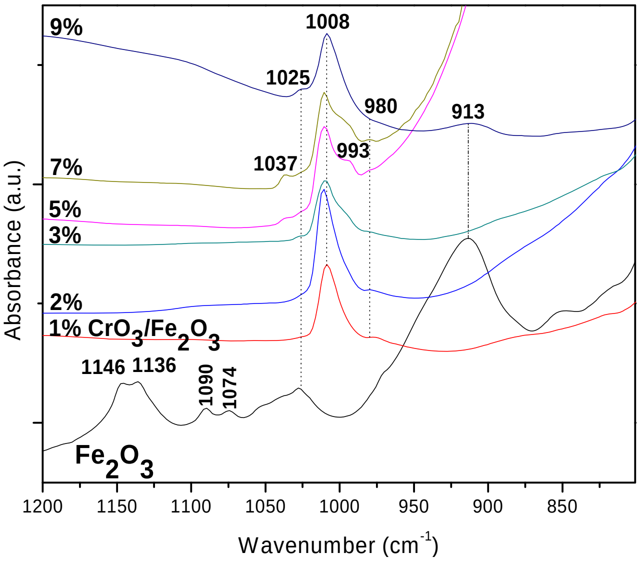

Figure 1

The *operando* Raman spectra (not shown) during the *reverse*-WGS reaction were measured as a function of reaction temperature to determine the nature of the starting α-Fe_2O_3 support, with and without the chromia promoter. The Raman bands of crystalline α-Fe_2O_3 disappear after 10 minutes of reaction indicating reduction of the α-Fe_2O_3 phase and/or its transformation to a disordered phase by the net reducing environment of the WGS reaction. The α-Fe_2O_3 Raman bands, however, reappear as the catalyst temperature is lowered to room temperature, but are accompanied by a new strong Raman band at ~647 cm^{-1} originating from the bulk Fe_3O_4 phase.[13]

For the supported 3% CrO_3/Fe_2O_3 and 9% catalysts, reduction of the α-Fe_2O_3 Raman bands also takes place within 10 minutes exposure to the reverse-WGS reaction at 400 °C and are replaced with the Raman band of Fe_3O_4 at ~648 (s), 487 (w) and 415 (w) cm^{-1}. The catalysts are active for the reverse-WGS both during the induction period with the amorphous structure as well as the transformation period with Fe_3O_4. Consequently, the iron oxide bulk phase is not a critical parameter during the WGS reaction. The Cr-free iron oxide catalyst is virtually inactive as the reaction temperature is decreased to 300 °C, but the Cr-promoted iron oxide catalysts are active down to 200 °C. These results suggest that surface CrO_x is the catalytic active site.

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