Cr-free High-Temperature Water-Gas Shift Catalysts

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Contributor: Sagar Sourav , Israel E. Wachs

Replacement of *toxic* Cr in the industrial Fe-oxide based High-Temperature Water-Gas Shift (HT-WGS) catalysts has been the focus of intense research in the past decades. In the current manuscript, we examine the promotion effect of Ca, Ni, Co and Ge as possible Cr substituents, and Ca and Ni are found to improve catalysts performance relative to Cr promotion. The current study, besides finding two promising Cr substitutes (Ca and Ni) for the HT-WGS reaction catalyst, also emphasizes on the qualities a promoter must possess to become a suitable substitution of Cr. The remarkable performance of Ca and Ni promoters are related to their ability to stabilize the surface area of the respective catalysts by making partial or complete solid solution with the bulk Fe-oxide phase and by promoting highly redox Cu^0-FeO_x interfacial sites on the catalyst surface. The poorer performance exhibited by Co and Ge promoters is related to the lack of their ability to promote the highly active Cu^0-FeO_x interfacial sites along with inability of Co to stabilize the surface area. All the promoters follow a redox type mechanism for the HT-WGS reaction.

HT-WGS Fe oxide-based catalysts Cr-free catalysts structure-function relationship

1. Introduction

The water-gas shift (WGS) reaction converts CO in the presence of H_2O into CO_2 and H_2, which allows controlling the H_2 to CO ratio for the synthesis of NH_3 and CH_3OH, production of synthetic fuels, etc. [1][2] Due to the reversible and exothermic nature of the WGS reaction (Equation (1)), the reaction is industrially performed in several stages with different catalysts to attain greater CO equilibrium conversions [3][4]. The low-temperature water gas shift (LT-WGS) reaction is performed at ~190–250 °C with copper-zinc-oxide based catalysts and the high-temperature water gas shift (HT-WGS) reaction is performed at ~350–450 °C with iron oxide-based catalysts. Recently, there has been an increasing interest in medium-temperature water gas shift (MT-WGS) catalysts and sulfur tolerant catalysts.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H = -40.6\ kJ/mol \qquad (1)$$

2. Background

Industrial HT-WGS catalysts mostly contain Fe oxide (~80–90% by bulk weight) with Cu and Cr oxides added as promoters for improved activity [4]. Unfortunately, the hexavalent Cr (VI) present in the catalyst is a significant carcinogen [5] and has been the topic of intense research over the past decades in order to find Cr-free HT-WGS catalysts. A thorough understanding of the structures and roles of various metal oxides present in Cu/Cr–Fe oxide catalysts, however, is needed for the rational design of an environmentally friendly Cr-free catalyst for the HT-WGS reaction. In this regard, detailed *in situ* and *operando* spectroscopy studies have been undertaken to gain this information, along with the identification and determination of the catalytic active site(s) and structure-function relationship for the Cu/Cr–Fe oxide-based HT-WGS catalysts. A brief summary of these studies is given in the main publication: https://www.mdpi.com/2073-4344/10/3/305.

3. Approach

The summary of the Cu–Cr–Fe oxide WGS catalyst system suggests that ideal substitutes for the toxic Cr promoter should possess the following properties: (i) be able to stabilize the surface area of Fe_3O_4 against excessive thermal and mechanical sintering, (ii) form a solid solution with the Fe_3O_4 bulk lattice to inhibit over-reduction of iron oxide, and (iii) not interfere with the formation of highly active FeO_x-Cu interfacial sites.

4. Designing and Testing of Cr-free Catalysts

In the present investigation, the oxides of Ca, Co, Ni, and Ge in Cu were examined as promoters of Cr-free Fe oxide catalysts for an HT-WGS reaction since these oxides form solid solutions with the Fe_3O_4 bulk lattice. Although these metals have been previously investigated, the present study is unique because (i) experiments were conducted on catalysts activated under the WGS or r-WGS reaction conditions to accommodate the dynamic nature of the catalyst structure and (ii) without exposure to air that could oxidize and change the pyrophoric catalyst. In addition, unique characterization (e.g., High Sensitivity Low Energy Ion Scattering (HS-LEIS) Spectroscopy to determine the elemental composition of the outermost surface layers) and chemical probe reactions (CO- Temperature Programmed Reduction (TPR) and CO+H_2O-Temperature Programmed Surface Reaction (TPSR) experiments to gain insight into the number of catalytic active sites, surface redox ability, reaction mechanism, and TOF values) were undertaken to gain a fundamental understanding of the functioning of non-Cr promoters in the Cu–Fe oxide HT-WGS catalytic system.

5. Summary of Experimental Findings

A series of Cu-promoted and Cr-free Fe-oxide based catalysts were synthesized by a two-step co-precipitation, followed by the incipient-wetness impregnation method to test the performance of the Cr-free promoters for an HT-WGS reaction. The HS-LEIS surface analysis characterization and CO-TPR, CO+H_2O TPSR, and SS-WGS activity experiments were conducted to understand the catalyst structure, nature of the active site, structure-function relationship, and the HT-WGS reaction mechanism. It was found that both Ca and Ni promote the formation of highly active FeO_x-Cu interfacial areas and exhibit better SS-WGS activity, compared to the 3Cu8CrFe catalyst.

The Co and Ge promoters, however, lack the ability to promote the FeO_x-Cu interface and perform poorly for the HT-WGS reaction. These activity findings are related to the ability of the promoters to form solid solutions with Fe_3O_4 support (Cr, Ni, and Ca). Promoters that do not stabilize the Fe_3O_4 surface area (Co), do not dissolve in the Fe_3O_4 lattice (Ge), are surface enriched, and minimize the formation of FeO_x-Cu interfacial sites. This suggests that FeO_x-Cu interfacial sites are active sites for 3Cu8MFe catalysts. The role of FeO_x-Cu interfacial sites was further elaborated upon by correlating the redox ability with SS-WGS performance. Consequently, both redox ability and SS-WGS performance follow the same trend: 3Cu8CaFe > 3Cu8NiFe ≥ 3Cu8CrFe > 3Cu8CoFe >> 3Cu8GeFe. This trend reveals that both Ca and Ni can be utilized as substitutes for the toxic Cr promoter in the HT-WGS catalyst. Furthermore, all the catalysts follow the redox-type reaction mechanism for the HT-WGS reaction. For detailed experimental findings, interested readers are redirected to the published article (https://www.mdpi.com/2073-4344/10/3/305).

6. Conclusions

This entry found that Ca and Ni promoters improve catalyst performance relative to promotion with Cr for the HT-WGS reaction. The HS-LEIS surface analysis data demonstrate that Ge tend to segregate on the surface, while Ca, Ni, Co, and Cr form complete or partial solid solutions in the Fe_3O_4 bulk lattice. The corresponding number of catalytic active redox sites and WGS activity values of the catalysts were determined with CO-TPR, CO+H_2O-TPSR, and SS-WGS studies, respectively. The poorer HT-WGS performances of the Ge and Co promoters are related to the presence of surface Ge and Co that inhibits catalyst redox ability, with the Co also not stabilizing the surface area of the Fe_3O_4 support. The Ni promoter uniformly disperses the Cu nanoparticles on the catalyst surface and increases the number of FeO_x-Cu interfacial redox sites. The Ca promoter on the catalyst surface, however, enhances the activity of the FeO_x-Cu interfacial redox sites. The CO+H_2O TPSR results reveal that the redox ability of the active sites follows the SS-WGS performance of the catalysts and show the following trend: 3Cu8CaFe > 3Cu8NiFe ≥ 3Cu8CrFe > 3Cu8CoFe >> 3Cu8GeFe. Furthermore, all the catalysts followed a redox-type reaction mechanism for the HT-WGS reaction.

References

1. Ridler, D.E.; Twigg, M.V. Catalyst Handbook, 2nd ed.; CRC Press: Boca Raton, FL, USA, 1996. [Google Scholar]
2. Satterfield, C.N. Heterogeneous Catalysis in Industrial Practice, 2nd ed.; McGraw Hill Book Co.: New York, NY, USA, 1991.
3. Newsome, D.S. The Water-Gas Shift Reaction. Catal. Rev. 1980, 21, 275–318. [Google Scholar] [CrossRef]
4. Ratnasamy, C.; Wagner, J.P. Water Gas Shift Catalysis. Catal. Rev. 2009, 51, 325–440.

5. Chinchen, G.C.; Logan, R.H.; Spencer, M.S. Water-Gas Shift Reaction over an Iron Oxide/Chromium Oxide Catalyst.: II: Stability of Activity. Appl. Catal. 1984, 12, 89–96.

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