

# High-Temperature Water-Gas Shift Reaction over Cr-Free Fe-Al Catalysts Promoted with First Row Transition Metals

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## Introduction

Hydrogen generation technologies have become increasingly important due to recent attention focusing on fuel cells. The water-gas shift reaction, which is performed in two stages as high- and low-temperature shift, is of central significance to produce high-purity hydrogen. Generally, the high-temperature water-gas shift reaction (HTS) is conducted on Fe-Cr catalysts. However, these catalytic systems possess many drawbacks such as low activity at low temperatures, sintering of magnetite ( $\text{Fe}_3\text{O}_4$ ), and a pyrophoric nature. Moreover, the use of Cr poses additional complications due to harmful effects of  $\text{Cr}^{6+}$  on human health. Thus, development of Cr-free catalytic systems is necessary. Also, it is apparent that innovative chromium-free iron-based catalysts that can overcome those drawbacks would have a significant impact on widespread applications of fuel cell systems. Araujo and Rangel [1] investigated the catalytic performance of Al-doped Fe-based catalyst with small amounts of copper (%wt Cu  $\approx$  3) in the HTS reaction. The aluminium and copper-doped catalysts showed similar catalytic activity compared to the commercial Fe-Cr catalyst at 350 °C and  $\text{H}_2\text{O}/\text{CO} = 0.4$ . Costa et al. [2] subsequently examined the use of thorium instead of chromium in iron- and copper-based catalysts for the HTS reaction. It was found that the thorium and copper-doped catalyst was more active than the commercial Fe-Cr catalyst at  $\text{H}_2\text{O}/\text{CO} = 0.6$  and 370 °C. Its high activity was attributed to an increase in surface area by thorium.

In this work, chromium-free iron-based catalysts promoted with first row transition metals have been studied for the high-temperature water-gas shift reaction. The effects of synthesis variables and reaction parameters on catalytic reaction performance have been examined. Structural and surface characterization of Fe-based catalysts promoted with first row transition metals is also performed to correlate catalyst performance and characteristics.

## Experimental

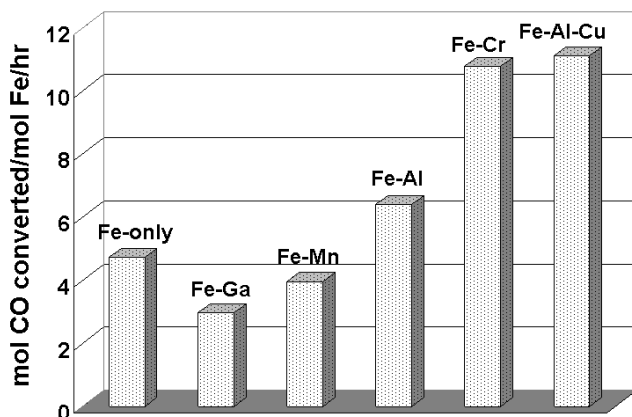
Catalysts were prepared using a coprecipitation method. All metal precursors (Aldrich) used were in nitrate form. Ammonium hydroxide (29.63 vol%, Fisher Scientific) was used as the precipitating agent. The synthesis parameters examined include choice of textural and structural promoters, Fe/promoter molar ratio, pH of precipitation medium, calcination/reduction temperatures, and reducing atmosphere. The dry samples were ground to a fine powder and were calcined under air at 450 °C (ramp rate = 2.5 °C/min) for 4 h. The catalysts promoted with first row transition metals were synthesized by a coprecipitation-impregnation method.

Catalyst characterization was performed using BET surface area and pore size distribution measurements, X-ray diffraction (XRD), temperature-programmed desorption/reduction (TPD/TPR), X-ray photoelectron spectroscopy (XPS), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS).

The steady-state reaction experiments were performed using a fixed-bed flow stainless steel reactor (1/4 in. OD). The reaction conditions were as follows: 400 °C, 1 atm, CO/H<sub>2</sub>O/N<sub>2</sub> = 1:1:8, GHSV = 9,500 h<sup>-1</sup>. Prior to the reaction, catalysts were reduced *in situ* under 20% H<sub>2</sub>/N<sub>2</sub> (50 cm<sup>3</sup>/min) at 350 °C for 2 h. The feed and effluent were analyzed on-line using an automated Shimadzu GC-14A equipped with FID and TCD detectors. Separations were performed under Ar using 2 columns: Porapak Q (12 ft x 1/8 in. SS, 80/100 mesh) and molecular sieve 13X (5 ft x 1/8 in. SS, 60/80 mesh). Carbon and hydrogen balances maintained close to 100% (±5%). Reaction data were taken after the steady state was reached. The catalytic activity is defined as moles of CO converted per moles of Fe present per hour.

## Results and Discussion

It is believed that the function of chromium in commercial HTS formulations is to stabilize magnetite from sintering, thus enhancing the activity and stability of iron catalysts [4,5]. In this study, aluminium, manganese, and gallium were chosen as potential replacements for chromium. The Fe/promoter molar ratio was kept constant at 10.



**Fig. 1** Reaction comparison of various Fe-based catalysts in the HTS reaction [Reaction conditions: 400 °C, 1 atm, CO/H<sub>2</sub>O/N<sub>2</sub> = 1:1:8, GHSV = 9,500 h<sup>-1</sup>, *in situ* reduction under 20% H<sub>2</sub>/N<sub>2</sub> at 350 °C, 2 h].

As shown in Fig. 1, Fe-Al catalysts showed an improvement in WGS activity compared to Fe-only catalysts. On the other hand, the addition of Mn or Ga caused a decrease in WGS activity. Although Fe-Al catalysts were not able to match the WGS activity of Fe-Cr catalysts, reaction results have suggested that aluminium could be a potential chromium replacement. To examine a potential use of aluminium as a stabilizer, Fe-Al catalysts promoted with copper (Fe/Cu = 20) were subsequently synthesized.

The presence of Cu in Fe-Al catalysts resulted in an enhancement of WGS activity. More importantly, Fe-Al-Cu catalysts not only matched the activity of Fe-Cr catalysts, but surpassed them. It is indicated that formulations of highly active and chromium-free iron-based catalysts can be achieved by adding both aluminium and copper.

The Al- and Cr-promoted catalysts calcined at 450 °C exhibit higher surface area than the Fe-only catalyst. This could be due to the presence of aluminium or chromium preventing hematite from sintering during calcination. *In situ* XRD results indicate that the addition of Al or Cr helps improve the magnetite sintering resistance, leading to smaller crystallite sizes of magnetite. TPR results suggests that the addition of Cr or Al helps stabilize magnetite and prevents its further reduction to inactive FeO and metallic Fe. The presence of Cu facilitates the formation of magnetite, leading to a significant improvement in WGS activity.

## Conclusion

Various chromium-free iron-based catalyst were synthesized and tested in the HTS reaction at 400 °C and  $H_2O/CO = 1$ . The presence of aluminium in Fe-based catalysts shows an improvement in sintering resistance of magnetite, suggesting that aluminium is a potential chromium replacement. Promotion with Cu of Fe-Al catalysts further enhances WGS activity significantly. *In situ* XRD and TPR results indicate that the catalytic activity of Fe-based catalysts is strongly related to magnetite crystallite size and catalyst reducibility.

## Acknowledgement

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## References

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