

## Design of Modified Ferrite-Based Shift Catalysts for Ultra High Temperature Membrane Reactor Applications

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### Introduction

The water-gas-shift (WGS) reaction is a key step in fuel processing to generate H<sub>2</sub>. The application of membrane reactors to WGS reaction will improve the reaction efficiency through shifting the chemical equilibrium toward the product side, there by reaching complete conversion [1]. Conventionally iron-chrome catalyst is employed in HT-WGS processes [2]. An interesting feature of magnetite is the possibility to replace iron by other metals while maintaining the spinel structure. The interest for preparation of substituted ferrites is generated by the fact that such materials have unique physico-chemical properties different from the parent compound. The physico-chemical properties of the modified ferrites are strongly dependent on the site, nature and amount of metal incorporated in the structure. For optimum design and efficient utilization of catalysts require a thorough understanding of the surface structure and surface chemistry of the catalyst material [3].

### Materials and Methods

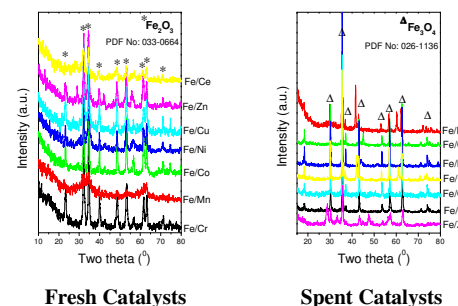
The selected iron-based mixed oxides Fe<sub>2</sub>O<sub>3</sub>/MO<sub>x</sub> [M = Cr, Mn, Co, Ni, Cu, Zn, & Ce] (10:1 atomic ratio) were prepared by co-precipitation route by employing ultra-high dilute solutions. The BET surface area and pore size distribution (PSD) measurements were performed on a Micromeritics ASAP 2010. Powder X-ray diffraction (XRD) patterns were recorded on a Phillips Xpert diffractometer. The H<sub>2</sub>-TPR experiments were performed on Micromeritics Autochem 2910. For Raman analysis DILOR XY spectrometer was employed.

### Results and Discussion

The modified ferrite-based inverse spinels were obtained by doping iron oxide with various transition/non-transition and inner transition metals [M = Cr, Mn, Co, Ni, Cu, Zn, & Ce] in situ during synthesis. The catalytic surface was selectively functionalized to attract CO (weak base), repel CO<sub>2</sub> (weak acid) and retain water molecules. As shown in Figure 1. XRD measurements proved the existence of Fe<sub>2</sub>O<sub>3</sub> type phases in the freshly prepared catalysts, which are pre-requisite for the active Fe<sub>3</sub>O<sub>4</sub> inverse spinel phase; Fe<sub>3</sub>O<sub>4</sub> type phases, were observed in the spent catalysts. The increase of the lattice parameter upon M<sup>II</sup> (foreign cation) substitution suggest the incorporation of M<sup>II</sup> into the spinel structure (Table 1.). H<sub>2</sub>-TPR was used to investigate the effect of M<sup>II</sup> addition on the reduction behavior of the ferrite-based catalysts. Narrow PSD was observed for all the samples, specifically Fe/Cr and Fe/Ce samples exhibit pore diameter of 76.9 and 77.3 Å respectively. Preliminary Raman characterization gave insight into the existence of Fe<sub>3</sub>O<sub>4</sub> type phase in the spent catalysts, thus supporting the XRD analysis. The WGS tests were performed in H<sub>2</sub> lean and exceedingly H<sub>2</sub>O-rich, CO<sub>2</sub>-rich environments to mimic membrane reactor (MR) conditions. WGS activity was tested as function of operating temperature between 400 to 550 °C. An increase in WGS activity was

observed as reaction temperature was raised, with maximum activity observed at 550 °C, interestingly this coincides with the temperature for the favorable operation of silicalite membranes. High WGS activity (% CO conversion) was observed in single pass. Among all the systems studied Fe/Ce system is found to be very promising. These results are supported by intensive characterization studies. Additionally, sulfur-tolerance of the above catalysts under WGS conditions was tested, preliminary studies on some of the samples, are encouraging, further studies are under way which is will be subsequently presented at the 20<sup>th</sup> NACS.

**Figure 1.** XRD patterns of both fresh and spent catalysts.



**Table 1:** Crystallite size, cell parameter, and cell volume from XRD measurements.

Catalyst	Fresh <sup>a</sup>				Spent <sup>d</sup>		
	D <sub>XRD</sub> <sup>f</sup> [nm]	'a' (Å)	'c' (Å)	Cell vol. (Å <sup>3</sup> )	D <sub>XRD</sub> <sup>f</sup> [nm]	'a' (Å)	Cell vol. (Å <sup>3</sup> )
Fe/Cr	12.5	6.65	12.673	485.35	23.7	8.357	584.27
Fe/Mn	10.1	nd	nd	nd	34.2	nd	nd
Standard	na	5.036 <sup>b</sup>	13.749 <sup>b</sup>	301.93	na	8.0903 <sup>d</sup>	529.53 <sup>d</sup>
Fe/Co	16.3	6.66	12.667	486.57	34.2	8.38	588.48
Fe/Ni	11.8	6.7	12.615	490.42	44.4	8.368	586.37
Fe/Cu	10.1	6.65	12.626	483.55	34.2	8.357	584.27
Fe/Zn	10.7	6.74	12.605	495.90	44.4	8.403	592.7
Fe/Ce	7.1	6.7	12.716	494.35	18.2	8.334	578.0

<sup>a</sup>Fe<sub>2</sub>O<sub>3</sub>: (33-0664) Hexagonal crystal symmetry

<sup>b</sup>Fe<sub>3</sub>O<sub>4</sub>: (26-1136) Cubic crystal symmetry

<sup>f</sup>Crystallite size from XRD using Scherrer equation

nd: not determined

na: not applicable

### Significance

Development of modified ferrite-based catalysts for ultra high temperature MR applications.

### References

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