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Water Gas Shift Reaction over Magnetite-based Catalysts in Membrane Reactor Conditions

J. Dufour, C. Martos, A. Ruiz, Department of Chemical and Energy Technology, ESCET, Universidad Rey Juan Carlos, Spain

1 Introduction

The water gas shift (WGS) reaction is used in many industrial processes for hydrogen production to enhance the hydrogen generation and to reduce the carbon monoxide content to the appropriate value for fuel cell applications. This is a reversible and exothermic reaction and it is usually carried out in two stages to maximize CO conversion. The first step is performed at high temperatures (320-420 °C) under favorable kinetic conditions, using a Fe₃O₄-Cr₂O₃ based catalyst. The second one takes place at low temperatures (200-250 °C) to favor thermodynamic conditions with a catalysts based on Cu/ZnO/Al₂O₃ [1]. An alternative to this process is the use of a hydrogen permeable membrane in the reactor that allows carrying out the reaction in a single stage. In this type of reactor, an equilibrium shift is produced by the removal of hydrogen from the reaction mixture leading to an increase of the CO conversion. This allows operating at lower H₂O/CO ratios without suffering thermodynamic constraints. The catalytic systems used for palladium membrane reactors are those for high temperature WGS since temperatures lower than 300 °C leads to membrane degradation. However, CO₂ concentration will reach high levels into the reactor due to permeation of the H₂ through the membrane, producing the inhibition of the reaction rate over conventional catalysts. For this reason, they should be modified to operate in the extreme conditions imposed by membrane reactors [2].

The high temperature WGS catalysts contain iron oxide structurally promoted with chromium oxide (8-14 wt %). The active phase of the catalysts is magnetite (Fe₃O₄). This iron oxide forms an inverse spinel cubic structure with tetrahedral positions occupied by Fe³⁺ and the octahedral ones by equal amounts of Fe³⁺ and Fe²⁺. The activity of magnetite in WGS reaction is related to the rapid electron hopping between Fe³⁺↔Fe²⁺ redox couple. The active phase loses activity under reaction conditions due to the reduction in surface area by thermal sintering [3-4]. Therefore, chromium oxide is usually added to magnetite as structural stabilizer. The conventional catalysts based on Fe-Cr have environmental and safety concerns since they can contain about 2 % wt. of toxic Cr⁶⁺ compounds. For this reason, the replacement of chromium by other promoters such as V, Th, Ga, Al, Mo and Mn has been recently studied [5-7].

Additionally, several authors have been developing new catalysts formulations to improve their performance in membrane reactors. Lund suggested that the inhibition of the catalysts by carbon dioxide could be reduced by decreasing the magnetite surface oxygen bond strength. Promotion of magnetite based catalysts with metals such as Cu or Ce could produce a decrease of the reduction temperatures of the material which is indicative of the weakening of surface oxygen bonds [8]. In this context the aim of this work is to prepare new
formulations of magnetite-based catalysts doped with different metals. The replacement of Cr by Mo was studied and the role of Cu and Ce as promoters in membrane reactor conditions was evaluated.

2 Experimental

Oxidation-precipitation method was used to prepare the catalysts, obtaining four different formulations: FeCrCu, FeMoCu, FeCrCe and FeMoCe. Additionally, FeCr and FeMo catalysts were prepared to compare them with the promoted materials. Initially, an aqueous solution of metal salts was prepared with Fe/Cr or Fe/Mo ratios of 12.2 (wt.) and with an appropriate Fe/promoter ratio to obtain solids with 2 % (wt.) of Cu or 1 % (wt.) of Ce. FeCl₂, CrCl₃, (NH₄)₆Mo₇O₂₄, CuCl₂ and CeCl₃ were the precursors used to prepare the catalysts. The solution was heated up to 70 °C and stirred at 300 r.p.m. Next, ferrous ions were oxidized bubbling air into the system. Simultaneously, alkali was added drop-wise adjusting pH to 7 until the end of reaction. The solid was recovered by filtration and washed out with water to remove ions. Finally, the samples were dried at 70 °C overnight.

X-ray powder diffraction (XRD) patterns of the catalysts were obtained on a Philips X-Pert diffractometer using CuKα radiation. The data were recorded in the 2θ range from 10° to 70°. Average crystallite sizes were calculated by applying the Scherrer equation. X-ray fluorescence (XRF) spectrometer Philips MagiX was used to determine Fe/promoter ratios. Temperature programmed reduction (TPR) was performed in a Micromeritics Autochem 2910 instrument. The sample (50 mg) was heated up from 323 to 1173 K (heating rate 10 K/min) under a hydrogen–argon mixture (10 % H₂) with a flowrate of 40 ml/min. Specific surface areas of samples were calculated from N₂ adsorption–desorption isotherms at 77 K that were measured on a Quantachrome NOVA 4000 instrument. Transmission electron microscopy (TEM) micrographs were obtained on a Philips Tecnai-20 electron microscope operating at 200 kV and equipped with an energy dispersive X-ray (EDX) spectrometer.

The performance of catalysts was tested in a fixed bed stainless steel reactor (i. d. = 9 mm) under isothermal conditions (380 °C), 10 bar and GHSV = 10000 h⁻¹. All experiments were carried out using 1 g of catalysts. A feeding gas composition of 68.7 % N₂, 18.8 % CO and 12.5 % CO₂ was used and a low steam/CO molar ratio (H₂O/CO = 2) was introduced into the reactor to simulate the membrane reactor conditions. The product stream was analyzed by gas chromatography in a Varian CP-4900 Micro GC.

3 Results and Discussion

Table 1 shows Fe/promoters ratios of the synthesized catalyst measured by XRF. Metal contents for all the samples were near to the theoretical ones. A lower incorporation of Mo was detected as compared to FeCr materials. This fact could be explained by the value of pH used during the synthesis procedure. In the case of Cr³⁺, chromium hydroxide precipitation occurs at pH 5. However, the precipitation of the solid phase in the case of Mo⁶⁺ happens at low pH (pH <5) and soluble species are predominant in the solution at pH 7. Comparing Cu with Ce, a lower content of the last metal was detected because its precipitation takes places at pH 8.
Table 1: XRF results of the catalysts prepared.

<table>
<thead>
<tr>
<th>Sample</th>
<th>XRF (wt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe/Cr</td>
</tr>
<tr>
<td>FeCrCu</td>
<td>12.8</td>
</tr>
<tr>
<td>FeMoCu</td>
<td>--</td>
</tr>
<tr>
<td>FeCrCe</td>
<td>12.4</td>
</tr>
<tr>
<td>FeMoCe</td>
<td>--</td>
</tr>
</tbody>
</table>

XRD analyses were performed to study the iron oxide phases present in the catalysts. Figure 1 shows the results obtained by this technique. Magnetite was the only crystalline phase detected for all the samples. Cr, Mo, Cu or Ce separate phases did not appear in the diffractograms.

Lattice parameters (a₀) were calculated from the highest intensity lines to study the incorporation of promoters into the magnetite lattice. These results are shown in Table 2. All the samples exhibited values slightly lower than that theoretical for magnetite (0.8397 nm). This fact could be explained by the existence of small amounts of maghemite (γ-Fe₂O₃), especially on the surface of the particles. The addition of Cr to the catalysts did not produce any variation of the lattice parameter, compared to a magnetite prepared by the oxidation-precipitation method (a₀ = 0.8365 nm). In the case of Mo, a contraction of the lattice parameter was detected for FeMo sample. Addition of Cu to FeCr materials did not affect the lattice parameter but in the case of FeMo materials this metal produced an expansion of the unit cell. Finally, promotion with Ce did not change the lattice parameters on a large extent. These results suggested that for the catalysts based on FeCr, promoters were not...
incorporated into magnetite lattice. In the case of catalysts based on FeMo, Mo and Cu were incorporated in the lattice of the iron oxide.

Table 2: Characterization results of the samples prepared.

<table>
<thead>
<tr>
<th>Sample</th>
<th>XRD a0 (nm)</th>
<th>Dc (nm)</th>
<th>Ads.-Des. N2 SBET (m²/g)</th>
<th>TPR1</th>
<th>TPR2</th>
<th>TPR3</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCr</td>
<td>0.8368</td>
<td>22</td>
<td>107</td>
<td>301</td>
<td>565</td>
<td>614</td>
</tr>
<tr>
<td>FeCrCu</td>
<td>0.8370</td>
<td>19</td>
<td>109</td>
<td>223</td>
<td>485</td>
<td>618</td>
</tr>
<tr>
<td>FeCrCe</td>
<td>0.8374</td>
<td>29</td>
<td>121</td>
<td>306</td>
<td>528</td>
<td>626</td>
</tr>
<tr>
<td>FeMo</td>
<td>0.8357</td>
<td>28</td>
<td>32</td>
<td>373</td>
<td>603</td>
<td>763</td>
</tr>
<tr>
<td>FeMoCu</td>
<td>0.8377</td>
<td>19</td>
<td>74</td>
<td>220</td>
<td>513</td>
<td>663</td>
</tr>
<tr>
<td>FeMoCe</td>
<td>0.8362</td>
<td>25</td>
<td>46</td>
<td>332</td>
<td>578</td>
<td>727</td>
</tr>
</tbody>
</table>

The results obtained in this study were confirmed by TEM analysis. Figure 2 shows TEM micrographs obtained for the promoted samples. The materials were composed of spherical particles with sizes in the range of 20-100 nm. The results obtained by energy dispersive X-ray indicated that FeCr materials were composed of magnetite crystals surrounded by smaller high chromium and copper or cerium containing particles. However, this fine phase was not detected in the case of FeMo catalysts and EDX analysis showed that there was not a considerable variation in the metal contents in different crystals. This suggested that in these catalysts Mo and Cu were incorporated into the magnetite lattice.

Figure 2: TEM micrographs obtained from promoted samples.

Crystallite sizes and BET surface areas obtained from N2 adsorption-desorption isotherms are also shown in Table 2. The replacement of Cr by Mo produced a decrease in the BET surface area as a consequence of the larger crystallite size of FeMo sample and the absence
of small particles around magnetite crystals. Addition of copper did not modify BET surface area for FeCr material but produced an increase of this parameter in the case of FeMo catalysts. This could be related to the differences in copper incorporation for both samples. When the catalysts were doped with Ce a slightly increase in the BET surface areas was detected. In the case of FeCr materials, the addition of Ce produced larger crystallite size that could be explained by the deposition of cerium compounds over the magnetite crystals.

Redox properties of the catalyst were evaluated by TPR. The reduction temperatures obtained from these analyses are shown in Table 2. There were three main reduction peaks in the samples analyzed. The lower temperature peak (TPR1) was attributed to the reduction of Fe$^{3+}$ species to Fe$_3$O$_4$. When the catalyst contained Cr$^{6+}$ or Cu$^{2+}$, the reduction of these metals also happened at this temperature. The second peak (TPR2) corresponded to the reduction of Fe$_3$O$_4$ to FeO and to the partial reduction of Mo$^{6+}$. The last peak (TPR3) was due to the reduction of FeO to metallic iron, CeO$_2$ to CeO$_{2-x}$ and MoO$_{3-x}$ to Mo. Replacement of Cr by Mo produced an increase of the reduction temperatures probably because of the lower BET surface areas and the larger crystallite sizes of FeMo materials. Addition of Cu to FeCr and FeMo catalysts improved the reducibility of the samples. This decrease of the reduction temperatures could indicate the weakening of surface oxygen bonds in magnetite that could lead to a lower inhibition by carbon dioxide. Promotion with Ce did not change the reduction temperatures of the samples on a large extent, probably because that metal was not incorporated into magnetite lattice. These results suggested that Ce would not improve the performance of the catalysts in membrane reaction conditions.

Figure 3 shows the results obtained from the catalytic tests. A decrease of the catalytic activity was detected for non-promoted samples when Cr was replaced by Mo. This could be explained by the lower specific surface area of FeMo material. As expected by TPR results, addition of copper produced an increase of the CO conversion for FeCr and FeMo catalysts. This increase of the activity was higher for FeMo materials, probably because copper was incorporated into magnetite lattice for that sample, modifying the degree of covalency of Fe$^{3+}$↔Fe$^{2+}$ redox couple. This activity of FeMoCu sample is higher than that obtained for FeCrCu material. When Ce was added to the materials, an increase of the catalytic activity was not observed but higher hydrogen selectivity was obtained for the samples. These results agree with those obtained by TPR analysis, confirming that there is a relationship between the reducibility and the catalytic activity.
Figure 3: Catalytic activity results in WGS reaction.

4 Conclusions

Replacement of Cr by Mo in high temperature WGS catalysts decreased the reducibility and the catalytic activity of the samples. Addition of Cu to FeMo catalysts increased the reducibility and the CO conversion, suggesting the weakening of surface oxygen bonds in magnetite that improved the catalytic performance in membrane reactor conditions. Promoting with Ce did not change the redox properties and the catalytic activity of the material although higher hydrogen selectivity was obtained.
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