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# Comparative study of selective CO oxidation over Pt-Co-M/Al<sub>2</sub>O<sub>3</sub> catalysts (M=Ce, Mg, Mn, Zr, Fe) in hydrogen-rich streams: effects of a second promoter

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The selective CO oxidation over Pt-Co/Al<sub>2</sub>O<sub>3</sub> catalyst in hydrogen-rich streams was studied in the presence of Ce, Mg, Mn, Zr, and Fe as the second promoters. The catalysts were prepared using incipient wetness co-impregnation, and tested in a microflow reaction system. The effects of the second promoter were investigated in near 100% CO conversion conditions both in the absence and presence of CO<sub>2</sub> and H<sub>2</sub>O in the feed. 100% CO conversion was obtained with the addition of each second promoter at 110 °C while Pt-Co/Al<sub>2</sub>O<sub>3</sub> catalyst had 96%-98% CO conversion. It was also found that changing the Pt ratio from 1.4 wt.% to 0.7 wt.% at 110 °C did not have any significant effects on catalysts containing Ce, Mg, or Mn, and it had negative effects in the case of Fe and Zr. The CO conversion decreased for all the catalysts in the presence of 25% CO<sub>2</sub> in the feed as expected, and recovered fully or significantly with the addition of 10% H<sub>2</sub>O. The addition of Ce, Mg, and Mn as the second promoter also improved the performance 2%-3% compared to Pt-Co/Al<sub>2</sub>O<sub>3</sub> catalysts in the presence of CO and H<sub>2</sub>O. The increase in the reaction temperature to 130 °C decreased the CO conversion over all the catalysts.

**Key Words:** Selective CO oxidation, promoted Pt catalysts, Pt-Co/Al<sub>2</sub>O<sub>3</sub> catalyst, fuel cell, fuel processor.

## Introduction

Fuel cells have been subject to increasing attention in recent years due to their high energy efficiency and the low environmental impact compared to the fossil fuel applications.<sup>1,2</sup> Among several fuel cell types, the

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proton exchange membrane fuel cell (PEMFC) seems to be a promising choice for transportation vehicles and residential power generation.<sup>2-4</sup>

One of the main requirements for PEMFC is CO-free hydrogen since the Pt-anode is deactivated if the CO content of the feed is over 10 ppm.<sup>5,6</sup> Consequently, CO removal becomes an important task considering that the hydrogen produced from hydrocarbons by autothermal reforming, steam reforming, or partial oxidation contains large amounts of CO (5%-15%).<sup>2</sup> Then the bulk CO is removed by water-gas shift (WGS) reactions leading a typical gas composition of 40-75 vol% H<sub>2</sub>, 15-25 vol% CO<sub>2</sub>, 0-20 vol% N<sub>2</sub>, and 1 vol% CO.<sup>7</sup> Since this amount of CO has deteriorating effects on fuel cell performance, another process followed by the WGS step is needed to eliminate the remaining CO just before the entrance of the fuel cell. Preferential catalytic CO oxidation (PROX) is considered one of the most feasible alternative among the various proposed methods.<sup>7-9</sup> In this method, O<sub>2</sub> should be added to the feed stream to preferentially oxidize CO in a well balanced CO/O<sub>2</sub> ratio so that undesired oxidation of the hydrogen is avoided.<sup>8-10</sup> Hence a good PROX catalyst should exhibit (a) high CO oxidation activity between the operating temperature of the WGS process (200-270 °C) and PEMFC (80-100 °C), (b) high selectivity towards CO, and (c) resistance to CO<sub>2</sub> and H<sub>2</sub>O in order to sustain stability.<sup>11</sup>

Pt/Al<sub>2</sub>O<sub>3</sub> was first proposed as an effective catalyst for selective CO oxidation by Cohn in 1963.<sup>12</sup> Many supported noble metal catalysts were proposed for PROX since then, and platinum (usually over Al<sub>2</sub>O<sub>3</sub> support) is the most studied noble metal for this purpose.<sup>2,3,5-10,12-14</sup> The catalytic properties of Pt as well as of the other noble metals are usually enhanced with the addition of a promoter such as Ce, Fe, Co, Ni, Mn, Mg, and K.<sup>5,6,10,13-22</sup>

We have studied the preferential CO oxidation over Pt-Co-Ce/Al<sub>2</sub>O<sub>3</sub> and Pt-Co-Ce/MgO catalytic systems and found that Co and Ce promote the CO oxidation better if they are used together.<sup>23,24</sup> In the present study, we examined the performance of various metal oxides as the second promoter instead of Ce for the selective CO oxidation over Pt-Co/Al<sub>2</sub>O<sub>3</sub> catalyst to test the possibility of further improving the catalytic performance.

## Experimental

### Catalyst preparation

The catalysts were prepared using incipient to wetness co-impregnation. The 250-355 μm commercial γ-alumina was used as support, and it was calcined at 450 °C for 2 h in air prior to impregnation. The metal precursors were dissolved in de-ionized water, the amount of which was determined from the difference of dry and water saturated alumina. Then 5 g of Al<sub>2</sub>O<sub>3</sub> was mixed using an ultrasonic mixer under vacuum during the impregnation process for 30 min and the metal precursor solution was pumped at a rate of 5 cm<sup>3</sup>/min using a MasterFlex computerized-drive peristaltic pump. The slurry was mixed under vacuum for 90 min in order to obtain uniform distribution of the precursor solution. At the end of the impregnation process, the catalyst was dried in an electric oven at 105 °C for 16 h, and calcined at the conditions given in the Table.

**Table.** Calcination and reduction conditions.

Catalyst	Calcination	Reduction	Conditions
Pt-Co/Al <sub>2</sub> O <sub>3</sub>		2 h at 400 °C	
Pt-Co-Ce/Al <sub>2</sub> O <sub>3</sub>	2 h at 400 °C	2 h at 400 °C	
Pt-Co-Mg/Al <sub>2</sub> O <sub>3</sub>	4 h at 400 °C		in H <sub>2</sub> flow
Pt-Co-Fe/Al <sub>2</sub> O <sub>3</sub>	2 h at 300 °C		
Pt-Co-Zr/Al <sub>2</sub> O <sub>3</sub>	2 h at 400 °C		
Pt-Co-Mn/Al <sub>2</sub> O <sub>3</sub>	5 h at 400 °C	2 h at 400 °C	in 50% H <sub>2</sub> + 50% He flow

## Activity measurements

The catalytic activity measurements were performed in a microreactor flow system. The catalysts were reduced as the procedure given in the Table prior to activity tests. The flow rates of the gases were controlled by Brooks 5850E mass flow controllers. A Jasco PU-2080Plus HPLC pump was used for the water addition. The water was evaporated with pre-heated reactant mixture (150 °C) before entering the reactor. A Shimaden FP-21 type programmable controller was used to control the temperature of the reactor. The product gas stream was analyzed using a Hiden HPR-20 QIC mass spectrometer equipped with a personal computer and MAssoft software. In all experiments 0.25 g of catalyst and 100 mL/min gas flow rate were used.

## Results and discussion

The 1.4 wt.% Pt-1.25 wt.% Co-1.25 wt.% Ce/Al<sub>2</sub>O<sub>3</sub>, catalyst which was investigated in our previous study, was used as the starting point.<sup>23</sup> Ce was replaced with the other alternatives and the resulting catalysts were tested at various conditions. A Pt-Co/Al<sub>2</sub>O<sub>3</sub> catalyst was also prepared and tested for comparison. The percent conversion and selectivity, which were defined as follows, were used to compare the performances of the catalysts:

$$CO \text{ conversion (\%)} = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}} \times 100 \quad (1)$$

$$O_2 \text{ conversion (\%)} = \frac{[O_2]_{in} - [O_2]_{out}}{[O_2]_{in}} \times 100 \quad (2)$$

$$\text{Selectivity Towards } CO(\%) = \frac{0.5 \times ([CO]_{in} - [CO]_{out})}{[O_2]_{in} - [O_2]_{out}} \times 100 \quad (3)$$

### Performance of 1.4 wt.% Pt catalyst at 110 °C in the absence of CO<sub>2</sub> and H<sub>2</sub>O

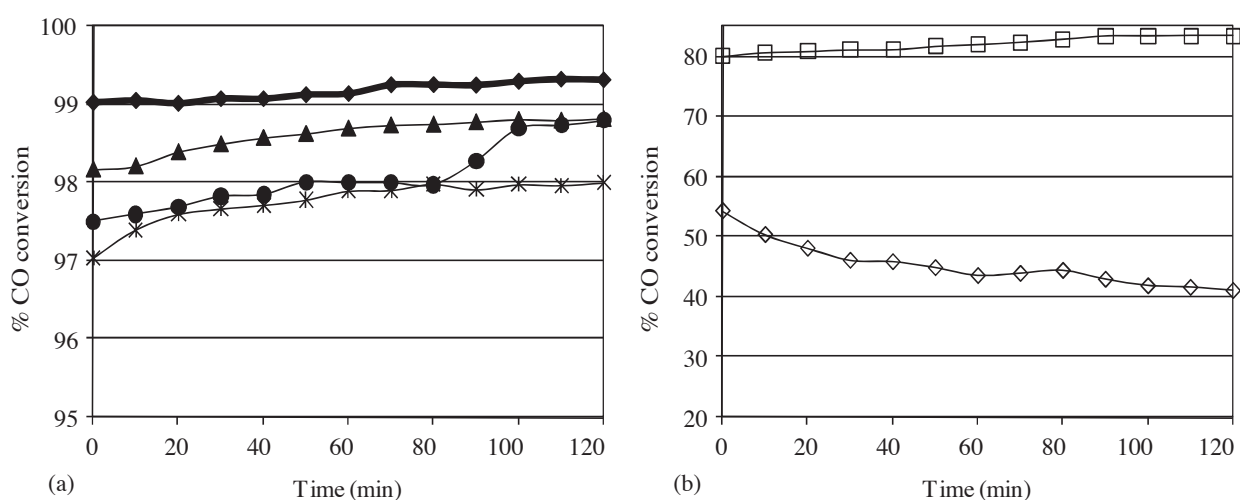
All the catalysts were tested in the absence of CO<sub>2</sub> and H<sub>2</sub>O at 110 °C, which was the most suitable temperature for 1.4 wt.% Pt-1.25 wt.% Co-1.25 wt.% Ce/Al<sub>2</sub>O<sub>3</sub> catalyst in our previous study.<sup>23</sup> The CO conversion over Pt-Co/Al<sub>2</sub>O<sub>3</sub> was about 96%-98%, which was very close to the 100% conversion value reported by Suh et al.

for a Co promoted Pt/Al<sub>2</sub>O<sub>3</sub> catalyst.<sup>20</sup> All the remaining 5 catalysts gave 100% conversion up to 120 min on stream, indicating that all the second promoters improved catalytic activity.

Although the results obtained at 110 °C are quite satisfactory as far as the objective of CO elimination is concerned, they do not allow a comparison of the performances of second promoter alternatives. Moreover, these results may also arise from the presence of excess Pt. Hence the Pt content of new catalysts was decreased to 0.7 wt.% while keeping all the promoter concentrations constant, and these catalysts were also tested at 110 °C.

### 3.2 Performance of 0.7 wt.% Pt catalyst at 110 °C in the absence of CO<sub>2</sub> and H<sub>2</sub>O

The CO conversion decreased with decreasing Pt content in all catalysts to some extent as expected. The decrease was minor (from 100% to 97%-99%) for the catalysts containing Ce, Mg, and Mn while Pt-Co/Al<sub>2</sub>O<sub>3</sub> catalyst was not affected much, and it became the best performing catalyst (Figure 1a). O<sub>2</sub> conversion remained 100% in all those cases.



**Figure 1.** The CO conversion in the absence of CO<sub>2</sub> and H<sub>2</sub>O at 110 °C for catalysts containing 0.7 wt.% Pt; CO 1.0%, O<sub>2</sub> 1.0%, H<sub>2</sub> 60.0%, He balance in feed, F/W = 24,000 cm<sup>3</sup>/(g h). Pt-Co/Al<sub>2</sub>O<sub>3</sub> (♦), Pt-Co-Ce/Al<sub>2</sub>O<sub>3</sub> (▲), Pt-Co-Mg/Al<sub>2</sub>O<sub>3</sub> (\*), and Pt-Co-Mn/Al<sub>2</sub>O<sub>3</sub> (●) in Figure 1a; Pt-Co-Fe/Al<sub>2</sub>O<sub>3</sub> (□) and Pt-Co-Zr/Al<sub>2</sub>O<sub>3</sub> (◇) in Figure 1b.

Pt-Co-Fe/Al<sub>2</sub>O<sub>3</sub> lost significant activity with the decreasing Pt content, and the CO conversion dropped from 100% to about 80% (Figure 1b). Liu et al. reported that Fe prefers to interact with Pt rather than alumina in the impregnation process.<sup>5</sup> Thus Fe may be blocking the Pt-Co interaction easier with 0.7 wt.% Pt than that with 1.4 wt.% and resulting lower CO conversion. It should be also noted that O<sub>2</sub> conversion was still 100%, indicating that the selectivity shifted towards H<sub>2</sub> oxidation.

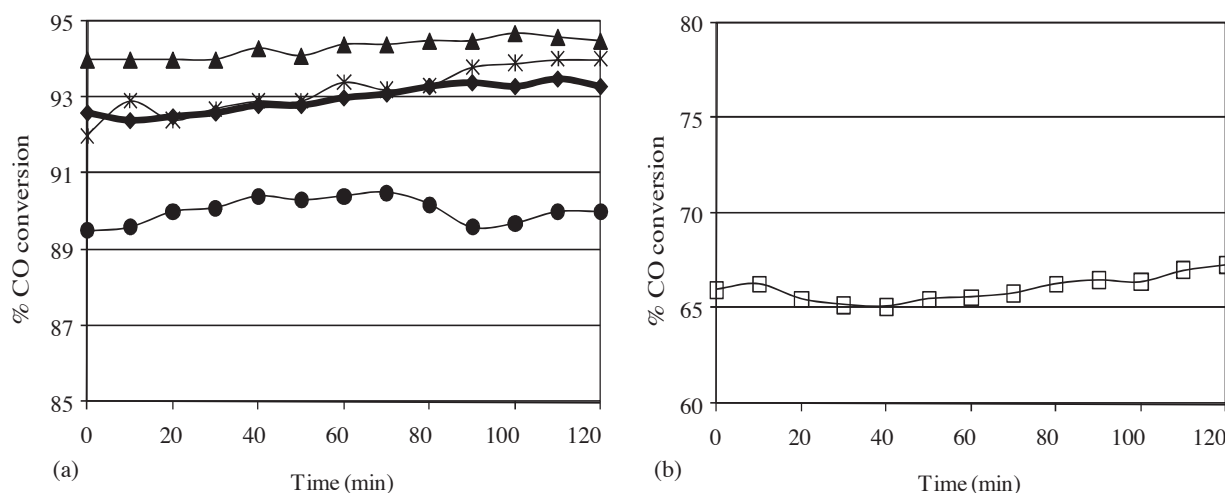
The decrease in CO conversion was quite pronounced for Pt-Co-Zr/Al<sub>2</sub>O<sub>3</sub> with nearly 50% (Figure 1b). O<sub>2</sub> conversion also dropped to about 50%. Hence Zr was not included in the remaining part of the study since it is obviously not a good alternative as a second promoter.

### Performance of 0.7 wt.% Pt catalyst at 110 °C in the presence of CO<sub>2</sub>

In real conditions, the hydrogen stream from WGS unit will contain 15%-25% CO<sub>2</sub>, which may affect the performance of the PROX catalyst through the reverse water gas shift reaction, which produces CO and consumes H<sub>2</sub>.<sup>7</sup> Hence the performances of 0.7 wt.% Pt containing catalysts were also tested in the presence of 25% CO<sub>2</sub> at 110 °C.

As expected, the CO conversion dropped for all catalysts including Pt-Co/Al<sub>2</sub>O<sub>3</sub> with about a 7% decrease (Figure 2) although Ko et al. did not report any activity loss for this catalyst with the addition of CO<sub>2</sub>.<sup>13</sup> Pt-Co-Ce/Al<sub>2</sub>O<sub>3</sub> was the catalyst least affected by the presence of CO<sub>2</sub>, with a 4% decrease in CO conversion. The CO conversion dropped about 6%-8% for catalysts containing Mg and Mn, indicating some significant water gas shift activity. This activity loss for Pt-Co-Mg/Al<sub>2</sub>O<sub>3</sub> was quite small compared to the 23% decrease reported by Cho et al. for Pt-Mg/Al<sub>2</sub>O<sub>3</sub> catalyst with the addition of 20% CO<sub>2</sub> at 100 °C in the presence of 1.0% CO, 0.75% O<sub>2</sub>, 65% H<sub>2</sub>, and the rest He.<sup>3</sup>

Pt-Co-Fe/Al<sub>2</sub>O<sub>3</sub> seems to have the most pronounced activity loss (about 15%) as presented in Figure 2b. Kotobuki et al., on the other hand, reported that CO<sub>2</sub> addition to the gas stream does not significantly affect the CO oxidation on Pt-Fe/Mordenite, suggesting that Fe support interaction may play a significant role in CO oxidation.<sup>10</sup>



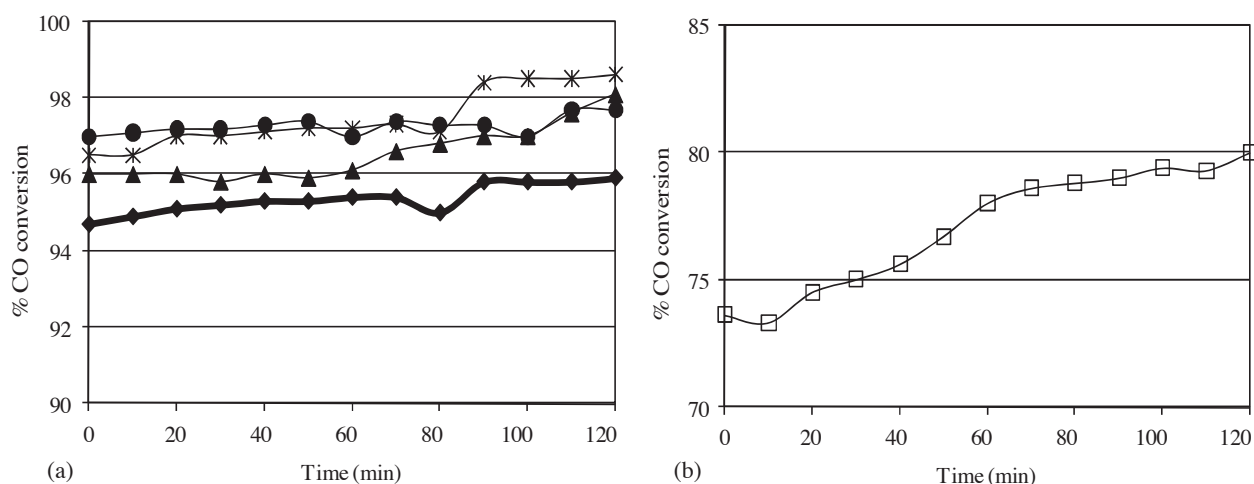
**Figure 2.** The CO conversion in the presence of CO<sub>2</sub> at 110 °C for catalysts containing 0.7 wt.% Pt; CO 1.0%, O<sub>2</sub> 1.0%, H<sub>2</sub> 60.0%, CO<sub>2</sub> 25.0%, He balance in feed, F/W = 24,000 cm<sup>3</sup>/(g h). Pt-Co/Al<sub>2</sub>O<sub>3</sub> (♦), Pt-Co-Ce/Al<sub>2</sub>O<sub>3</sub> (▲), Pt-Co-Mg/Al<sub>2</sub>O<sub>3</sub> (\*), and Pt-Co-Mn/Al<sub>2</sub>O<sub>3</sub> (●) in Figure 2a; Pt-Co-Fe/Al<sub>2</sub>O<sub>3</sub> (□) in Figure 2b.

O<sub>2</sub> conversion, however, was 100% for all cases including catalyst containing Fe. Apparently the presence of CO<sub>2</sub> did not affect the H<sub>2</sub> oxidation activity of any catalyst. It should be also noted that only the presence of Ce as the second promoter enhanced CO oxidation (about 94%-95%) slightly compared to Pt-Co/Al<sub>2</sub>O<sub>3</sub> (about 92%-93%) while the effects of the other second promoter were insignificant or negative.

### Performance of 0.7 wt.% Pt catalyst at 110 °C in the presence of CO<sub>2</sub> and H<sub>2</sub>O

Next, the effects of 10% water vapor, which is the expected level in the actual feed stream after the WGS unit, was investigated at 110 °C by adjusting the balance helium accordingly and keeping all the other parameters at the same values discussed in the previous section.

The water addition improved the CO conversion on all catalysts from 2% to 17% depending on the type of second promoter (Figure 3). Although none of the catalysts exhibited 100% CO conversion in the presence of water vapor, the inverse effects of CO seem to be balanced by the water to a great extent since the conversion levels were very close to the value obtained in the absence of both water and CO<sub>2</sub>. O<sub>2</sub> conversion, on the other hand, was 100% in all cases.



**Figure 3.** The CO conversion in the presence of CO<sub>2</sub> and H<sub>2</sub>O at 110 °C for catalysts containing 0.7 wt.% Pt; CO 1.0%, O<sub>2</sub> 1.0%, H<sub>2</sub> 60.0%, CO<sub>2</sub> 25.0%, H<sub>2</sub>O 10.0%, He balance in feed, F/W = 24,000 cm<sup>3</sup>/(g h). Pt-Co/Al<sub>2</sub>O<sub>3</sub> (♦), Pt-Co-Ce/Al<sub>2</sub>O<sub>3</sub> (▲), Pt-Co-Mg/Al<sub>2</sub>O<sub>3</sub> (\*), and Pt-Co-Mn/Al<sub>2</sub>O<sub>3</sub> (●) in Figure 3a; Pt-Co-Fe/Al<sub>2</sub>O<sub>3</sub> (□) in Figure 3b.

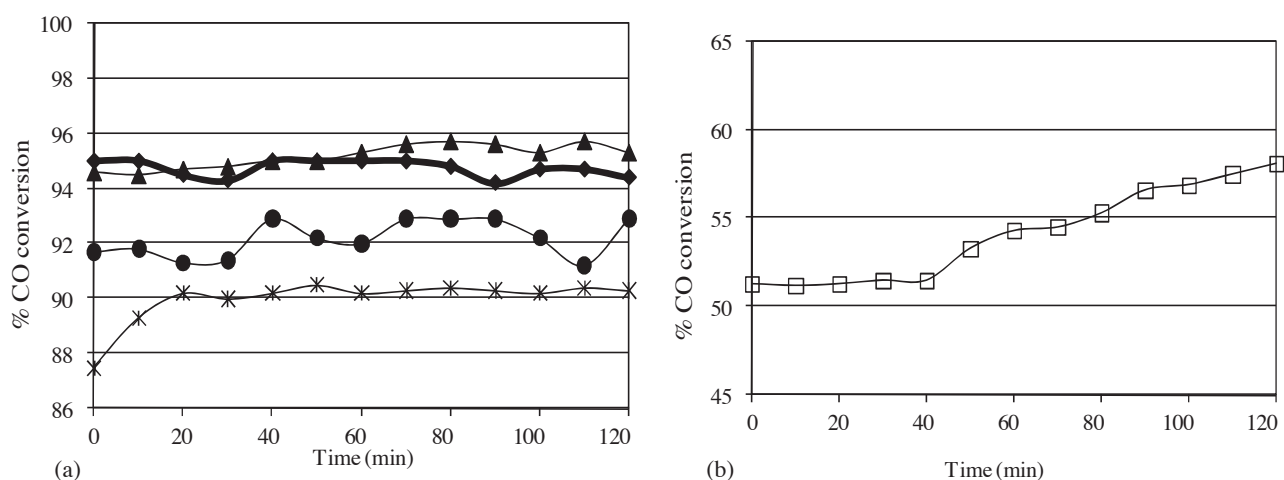
The CO conversion increased with increasing time on stream for all the catalysts as a good sign of stability. Ce, Mg, and Mn also seem to enhance CO oxidation slightly considering that they gave 2%-3% higher CO conversion than Pt-Co/Al<sub>2</sub>O<sub>3</sub> alone. The performance of catalyst containing Fe was quite low compared to the others although CO conversion over this catalyst was also significantly increased with the addition of water (Figure 3b).

The positive impact of water vapor can be partially attributed to the increasing water gas shift activity while another explanation may be the formation of OH groups on the surface facilitating CO removal.<sup>25</sup> This is supported by the results reported by İnce et al. for Pt-Co-Ce/Al<sub>2</sub>O<sub>3</sub>.<sup>22</sup> However, according to Ayastuy et al., 5% water vapor addition to MnO<sub>x</sub>/Pt/Al<sub>2</sub>O<sub>3</sub> has no significant effect on CO conversion over the catalyst containing less than 2 wt.% Mn and the water vapor shows a detrimental effect on conversion with the increasing Mn content in the catalyst.<sup>6</sup> On the other hand, Cho et al. found that the addition of 2% water vapor to feed stream increased the CO conversion from 94.6% (with 20% CO<sub>2</sub>) to 98.0% for Pt-Mg/Al<sub>2</sub>O<sub>3</sub> while increasing the amount of water vapor further had a negative effect. They reported that, for example, the addition of 10% water vapor decreased the CO conversion to 87.9% under the same conditions.<sup>3</sup>

### Performance of 0.7 wt.% Pt catalyst at 130 °C in the presence of CO<sub>2</sub> and H<sub>2</sub>O

Although the addition of Ce, Mg, and Mn as the second promoter seemed to improve the activity in some levels in the actual feed conditions (in the presence of CO<sub>2</sub> and water), as discussed in the previous section, the conversions were still not yet sufficient for fuel cell applications. Hence all the catalysts (with 0.7 wt.% Pt) were also tested at 130 °C to examine the possibility of having 100% CO conversion.

However, CO conversion decreased in all cases to some extent as given in Figure 4. Pt-Co-Ce/Al<sub>2</sub>O<sub>3</sub> seems to be least affected by this change in the reaction temperature, with about 2%-3% activity loss, while the CO conversion dropped about 8%-9% and 5%-6% for catalysts containing Mg and Mn, respectively. Again catalyst containing Fe was affected most considering that the activity loss reached to almost 20% (Figure 4b).



**Figure 4.** The CO conversion in the presence of CO<sub>2</sub> and H<sub>2</sub>O at 130 °C for catalysts containing 0.7 wt.% Pt; CO 1.0%, O<sub>2</sub> 1.0%, H<sub>2</sub> 60.0%, CO<sub>2</sub> 25.0%, H<sub>2</sub>O 10.0%, He balance in feed, F/W = 24,000 cm<sup>3</sup>/(g h). Pt-Co/Al<sub>2</sub>O<sub>3</sub> (◆), Pt-Co-Ce/Al<sub>2</sub>O<sub>3</sub> (▲), Pt-Co-Mg/Al<sub>2</sub>O<sub>3</sub> (\*), and Pt-Co-Mn/Al<sub>2</sub>O<sub>3</sub> (●) in Figure 4a; Pt-Co-Fe/Al<sub>2</sub>O<sub>3</sub> (□) in Figure 4b.

The negative effects of the high temperatures on CO conversion were also reported for some other Pt-M/support systems (where M represents the promoters such as Co, Ce, Mg, and Mn) tested at various conditions.<sup>3,6,14,20</sup> This may be attributed to the possible reverse water gas shift activity at higher temperatures as well as to the increase in H<sub>2</sub> oxidation considering that the O<sub>2</sub> conversion was still 100%.

### Performance of 1.0 wt.% Pt -1.25 wt.% Co, and 1.25 wt.% Mg containing catalyst at 110 °C in the presence of CO<sub>2</sub> and H<sub>2</sub>O

Finally Pt wt.% was increased to 1.0% for the catalyst containing Mg, which was one of the best performing catalysts, to test the possibility of obtaining full CO conversion, and the sample was tested at 110 °C in the presence of CO<sub>2</sub> and H<sub>2</sub>O. Indeed, 100% CO conversion was achieved at all times on stream up to 120 min. O<sub>2</sub> conversion was also 100% in all measurements.

To sum up, it can be concluded that the use of Mg, Mn, and Ce as the second promoter enhanced the performance of Pt-Co-/Al<sub>2</sub>O<sub>3</sub> about 2%-3% at 110 °C in a realistic feed containing CO<sub>2</sub> and H<sub>2</sub>O. Although



this improvement is relatively small, it may be important near to 100% conversion level considering that full conversion of CO is required in fuel cell applications. The use of these promoters may also help to reduce the precious metal content of the catalyst and reduce the cost. The use of Fe and Zr as the second promoter, on the other hand, negatively affected the CO conversion. It was also found that further increases in temperature from 110 to 130 °C decreased CO conversion.

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