Comparison in Dimethyl Ether Steam Reforming of Conventional Cu-ZnO-Al₂O₃ and Supported Pt Metal Catalysts

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The catalytic performance of platinum based catalysts supported on CeO₂/Al₂O₃ (with different proportion of both oxides) was compared to the conventional Cu-ZnO-Al₂O₃ (CZA) catalyst for methanol steam reforming (MeOH-SR), which is the second stage in the dimethyl ether steam reforming (SRD) process for obtaining H₂. The catalytic performances of Pt based catalysts were notably influenced by the addition of CeO₂ to the support: a higher content of CeO₂ improved the catalyst activity and selectivity to H₂, and limited to some extent CO and CH₄ formation. At low temperatures (below 350 ºC), the copper based CZA catalyst provided the best results in MeOH-SR, but at high temperature (350-500 ºC) Pt/CeO₂ and CZA showed similar catalytic performance. Consequently, Pt/CeO₂ can be envisioned as a proper metallic function to be used in the bifunctional catalyst for SRD together with γ-Al₂O₃ acid function, which requires temperatures above 350 ºC for attaining high conversion in dimethyl ether hydrolysis.

1. Introduction

Hydrogen is a suitable fuel to meet the increasing demand of energy as it may be produced from renewable sources (Hočevar and Summers, 2008). Hydrogen fuel cell, which transforms chemical energy into electrical energy by consuming hydrogen and oxidant, is presented as an efficient and environmentally friendly power generator for both mobile and stationary use (Sieniutycz and Póswiata, 2011). Nevertheless, hydrogen is difficult to handle and store, and therefore, a hydrogen vector needs to be used. Methanol is an excellent raw material for on-board H₂ production for proton exchange membrane (PEM) fuel cells, as it can be easily and selectively converted into an H₂-rich gas at low temperature (150 – 300 ºC) by steam reforming (Sa et al., 2010), but due to its toxicity and corrosiveness there is interest in the use of alternative H₂ vectors. Amongst them, dimethyl ether (DME) is an alternative of growing interest, since it is relatively inert, non-corrosive, non-carcinogenic, it can be stored and handled as liquefied petroleum gas (LPG) and, consequently, it is more readily used in fuel cells (Semelsberger et al., 2006). Moreover, DME can be synthesized from biomass resources (bio-DME), via the ‘syn gas’ obtained from biomass gasification (Higo and Dowaki, 2010), and consequently, the DME synthesis by co-feeding CO₂ with syngas in a single reaction step is considered a key process for both CO₂ sequestration and the viability of lignocellulosic biomass gasification (Bulushev and Ross, 2011).

The steam reforming of DME (SRD) proceeds over bifunctional catalysts, via hydrolysis of DME (over an acid function), followed by MeOH-SR (over a metallic function). Additionally, other reactions take place which decrease H₂ production, such as reverse water gas shift (r-WGS), MeOH/DME decomposition and methanation reactions that must be avoided by employing the appropriate catalysts and operating conditions. The Cu/ZnO/Al₂O₃ (CZA) formulation has been extensively used in literature as a catalyst for the MeOH-SR (Sá et al., 2010), but it suffers from sintering at relatively low temperature of 300 ºC which is
a handicap for i) its use as metallic function in DME-SR together with γ-Al₂O₃ as acid function (as the latter requires T>350 ºC for high activity in DME hydrolysis) and ii) the regeneration of the bifunctional catalyst by coke combustion (which requires temperature above 500 ºC). Catalysts based on noble metals, such as Pd and Pt, have also been used in MeOH-SR, and can also act as metallic functions alternative to CZA for SRD because they present some advantages such as higher thermal stability and long-term stability (Sá et al, 2010). Noble metals supported on different ionic oxides such as Al₂O₃ and CeO₂ have been studied and found promising in the reforming of DME (Fukunaga et al., 2008) and other oxygenated compounds such as ethanol (Palma et al., 2012).

This work is focused on the viability of Pt based catalysts (with Al₂O₃, CeO₂ and mixed Al₂O₃/CeO₂ supports) as metallic functions for the bifunctional catalysts in SRD, by comparing their behavior in the MeOH-SR reaction (second step in SRD process) with that corresponding to a commercial CZA catalyst.

2. Experimental

2.1 Catalyst preparation and characterization

The following supports were used for the preparation of the supported Pt catalysts: Al₂O₃ (provided by Axens), CeO₂ (provided by Solvay) and three mixed oxides of Al₂O₃(80 % wt)-CeO₂(20 % wt), Al₂O₃(20 % wt)-CeO₂(80 % wt) and Ce₅₂Zr₅₂O₂(90 % wt)-Al₂O₃(10 % wt) denoted as Al(80)Ce(20), Al(20)Ce(80) and CeZrAl, respectively. Al(80)Ce(20) mixed support was prepared by wet impregnation of Al₂O₃ support with cerium nitrate Ce(NO₃)₃.6H₂O while Al(20)Ce(80) and CeZrAl were synthesized by the sol-gel method with aluminium isopropoxide, Al[OCH(CH₃)₂]₃, and commercial CeO₂ or Ce₀.₅Zr₀.₅O₂. After preparation all the supports were calcined at 800 ºC, in order to obtain the alpha phase of the Al₂O₃ for 5 h in a muffle oven Nabetherm Controller P3 30. The 1 wt. % of platinum was deposited on each support by wet impregnation, using H₂PtCl₆ as precursor salt (Gauthard et al., 2003). The Pt catalysts were calcined at 600 ºC for 4 h in air and pre-reduced in H₂ at 500 ºC for 1 h. The conventional CZA commercial catalyst employed in this study was provided by Süd Chemie.

The catalysts were characterized employing different techniques. Specific surface area and pore volume measurements were determined by N₂ physisorption in a TriStar Micromeritics volumetric device after degassing of the samples at 250 ºC during 4 h. The metallic species liable to reduction and the temperature triggering the reduction were determined by temperature programmed reduction (TPR) from room temperature to 1050 ºC at a rate of 5 ºC/min in a gas mixture of 1% H₂ in Ar (30 cm³ min⁻¹) using an AutoChem 2920 from Micromeritics. Prior to TPR, the sample was oxidised with pure O₂ from room temperature to 500 ºC (1h) at a rate of 10 ºC min⁻¹. Platinum content in the catalyst was determined by ICP-OES using a Perkin Elmer Optima 2000 DV. Prior to the analyses, the samples were mineralized with a mixture of nitric and chloridric acids. The metallic dispersion and the metal crystallite size of Pt based catalysts were determined by H₂ chemisorption in an own designed chromatographic device, while the same parameters for CZA catalyst were determined by N₂O pulsed chemisorption in a Micromeritics AutoChem 2920 coupled to a Balzers Intruments Omnistar mass spectrometer. Metal particle size was calculated as indicated in Eq(1).

\[
d(\text{nm}) = 5 \cdot 10^{-5} \frac{M}{\rho \cdot D \cdot S} \tag{1}
\]

where M and ρ are the molar mass (g mol⁻¹) and density (g cm⁻³) of the metal, D is the metal dispersion and S is the surface developed by one mole of metal (m² mol⁻¹).

2.2 Catalytic tests

Figure 1 shows the scheme of the reaction and analysis device, which was already described elsewhere (Rijo Gomes et al (2011). The MeOH-SR reaction was carried out in a quartz tubular continuous flow reactor (L=330 mm; Ø₅=12 mm). Methanol and water were injected with a Gilson 305 pump and preheated up to 200 ºC before entering the reaction zone. The reaction products passed through a condenser working at 0 ºC in order to trap the remaining water and methanol and then gaseous products were analyzed every ten minutes in two gas chromatographs connected on line; a Varian 3800 GC employing a 5A molecular sieve and H₂ as carrier gas was used for detecting CO, CO₂ and CH₄ and a Varian 3900 employing a 13X molecular sieve and Ar as carrier gas for detecting H₂. Liquid products (MeOH and H₂O) were collected every hour, weighted in a balance and measured in an HPLC pump employing H₂SO₄ as eluent. The catalytic tests were carried out at atmospheric pressure, under increasing temperature steps from 200 ºC to 500 ºC, space time of 0.13 g cat.h.gMeOH⁻¹ and steam/MeOH ratio of 1.3. The catalytic bed consisted of 0.2 g of the catalyst and 0.2 g of an inert (SiC). Prior to the reaction, the catalyst was reduced in situ with pure H₂ (100 cm³ min⁻¹) at the first reaction step temperature (200 ºC) for 1 h.
The reaction indices employed to quantify the catalytic activity are MeOH conversion, $X_{\text{MeOH}}$, and yield of products ($H_2$, CO and CH4), $Y_i$, defined by Eq(2) and Eq(3), respectively:

$$X_{\text{MeOH}} = \frac{F_{\text{MeOH,0}} - F_{\text{MeOH,}}}{F_{\text{MeOH,0}}} \times 100$$  \hspace{1cm} (2)

$$Y_i = \frac{F_i}{F_{\text{MeOH}}} \times 100$$  \hspace{1cm} (3)

where $F_{\text{MeOH,0}}$ and $F_{\text{MeOH}}$ are the molar flow rate of the MeOH at the inlet and the outlet respectively; $F_i$ is the molar flow rate of product $i$ at the outlet and $\nu_i$ is the stoichiometric coefficient for $i$.

**Figure 1: Scheme of the reaction equipment**

## Results

### 3.1 Catalyst characterization

Table 1 shows the values of specific surface area and average pore volume for CZA catalyst, for the different supports and for the Pt based catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Specific Surface (m$^2$ g$^{-1}$)</th>
<th>Pore Volume (cm$^3$ g$^{-1}$)</th>
<th>Pore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZA</td>
<td>83</td>
<td>0.35</td>
<td>155</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>184</td>
<td>0.49</td>
<td>108</td>
</tr>
<tr>
<td>$\text{Pt}/\text{Al}_2\text{O}_3$</td>
<td>180</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al(80)Ce(20)</td>
<td>103</td>
<td>0.32</td>
<td>124</td>
</tr>
<tr>
<td>Pt/Al(80)Ce(20)</td>
<td>83</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CeZrAl</td>
<td>66</td>
<td>0.2</td>
<td>125</td>
</tr>
<tr>
<td>Pt/CeZrAl</td>
<td>44</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al(20)Ce(80)</td>
<td>34</td>
<td>0.07</td>
<td>76</td>
</tr>
<tr>
<td>Pt/Al(20)Ce(80)</td>
<td>25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>256</td>
<td>0.17</td>
<td>147</td>
</tr>
<tr>
<td>Pt/CeO$_2$</td>
<td>221</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

All the supports are mesoporous solids, as their average pore size is comprised between 20 and 500 Å. The commercial CeO$_2$ support shows higher specific surface area than $\text{Al}_2\text{O}_3$. For all $\text{Al}_2\text{O}_3$-CeO$_2$ supports, prepared by impregnation and by the sol-gel method, an increase in the CeO$_2$ content implies a decrease in both specific surface area and the pore volume. The noticeable higher surface area and pore volume of CeO$_2$ support compared to the rest of CeO$_2$ containing supports could be due to the fact that this commercial support was not calcined at 800 ºC as was the rest of supports. The addition of platinum to all
the supports involves a decrease in the specific surface area. The metallic properties of the catalysts are summarized in Table 2. Metallic content for CZA catalyst is much higher than for platinum based catalysts, and consequently it shows lower metallic dispersion and higher particle size. It is observed that supported platinum catalysts with high content of CeO2 in the support (≥80 wt%) have dispersion values around 35% with metallic particle size of 30 Å. As the content of CeO2 in the support diminishes the dispersion of platinum is enhanced and smaller particle sizes are obtained (with values of 77% and 12 Å, respectively, for 20 wt% CeO2 in the support), which could be attributable to the higher surface area of the support.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Metal content (ICP) (%)</th>
<th>Metal dispersion (%)</th>
<th>Metal particle size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZA</td>
<td>45</td>
<td>12</td>
<td>86</td>
</tr>
<tr>
<td>Pt/Al2O3</td>
<td>0.66</td>
<td>67</td>
<td>14</td>
</tr>
<tr>
<td>Pt/Al(80)Ce(20)</td>
<td>1.33</td>
<td>77</td>
<td>12</td>
</tr>
<tr>
<td>Pt/CeZrAl</td>
<td>1.04</td>
<td>50</td>
<td>19</td>
</tr>
<tr>
<td>Pt/Ce(80)Al(20)</td>
<td>0.96</td>
<td>31</td>
<td>30</td>
</tr>
<tr>
<td>Pt/CeO2</td>
<td>1.15</td>
<td>36</td>
<td>27</td>
</tr>
</tbody>
</table>

The TPR profile of CZA metallic function contains a peak with a maximum at 190 ºC corresponding to the reduction of Cu2+ to Cu0 (Agrell et al., 2003). Figure 2 shows TPR profiles (graph a) and the evolution of the reduction temperature with CeO2 content (graph b) for the Pt based catalysts. In the TPR profiles of the catalysts with CeO2 in the support, two temperature domains can be distinguished. In the first one (T<350 ºC) the reduction is due to the reduction of PtOx and superficial CeO2 whose reduction at low temperature is promoted by the Pt interaction with the support (Mi lone et al. 2006), while the second one (T>350 ºC) is due to the reduction of the bulk CeO2 (Sedjame et al, 2014). As it is observed in Figure 2.b, in the first reduction domain, the reduction temperature is in general lower for catalysts with higher content of CeO2.

Figure 2: TPR profiles (graph a) and evolution of the reduction temperature with CeO2 content (graph b) for the Pt based catalysts.

### 3.2 Catalytic performance

The evolution with temperature of the methanol conversion and H2 yield for the different catalysts are shown in Figure 3.

These results show that CZA catalyst is highly active at low temperature for MeOH-SR (Kurr et al., 2008), and complete MeOH conversion and maximum H2 yield (100%) are achieved at 300 ºC. Above this temperature MeOH decomposition and reverse WGS reactions take place, which favor CO formation and slightly decrease H2 yield.

At low temperature, the Pt based catalysts show much lower MeOH conversion and H2 yield than CZA catalyst (Sá et al., 2010). Both reaction indices increase noticeable with temperature and total conversion (Figure 3a) and H2 yield of around 100 % (Figure 3b) are reached just with the Pt/CeO2 catalyst, but at higher temperature than that required with CZA catalyst. Moreover, high yields of by-products CO and CH4 (especially the former) are obtained with the Pt catalysts even at low temperature (Fukunaga et al., 2008),
especially with that supported on Al$_2$O$_3$, which is consistent with other results of literature that conclude that methanol decomposition is promoted over this type of catalysts (Imamura et al., 1999). The addition of ceria to the Al$_2$O$_3$ support slightly increases MeOH conversion and H$_2$ yield, suppresses to a great extent methanation reactions and significantly decreases CO formation, which can be explained by the high activity of CeO$_2$ for WGS reaction (Roh et al., 2012). These effects are accentuated as the amount of ceria in the support is increased. The best results in MeOH-SR with Pt based catalysts are obtained with Pt supported on commercial CeO$_2$, which shows almost the same catalytic performance at 400 °C than CZA catalyst.

Figure 3: Evolution of MeOH conversion (graph a) and yield of H$_2$ (graph b), CO (graph c) and CH$_4$ (graph d) for the different catalysts studied. Operating conditions: P=1.3 bar.

4. Conclusions

The copper based CZA catalyst shows better performance than Pt based catalysts in MeOH-SR at low temperature, as it is highly active and selective to H$_2$ formation, although it promotes CO formation (by reverse-WGS reaction) above 350 °C.

The addition of CeO$_2$ to the Al$_2$O$_3$ support improves the catalytic performance of Pt supported catalysts for MeOH-SR: thus, catalyst activity and selectivity to H$_2$ increase with the content of CeO$_2$ in the Al$_2$O$_3$/CeO$_2$ support, whereas CO and CH$_4$ formation are notably suppressed. The best results in MeOH-SR with Pt based catalysts are obtained with Pt/CeO$_2$ catalyst, whose catalytic performance at high temperature (350-500 °C) is similar to that obtained with CZA catalyst. Taking into account the well known higher thermal stability of Pt based catalysts compared to Cu based catalysts, it is concluded that Pt/CeO$_2$ can be envisioned as a proper metallic function to be used in the preparation of a bifunctional catalyst for dimethyl ether steam reforming together with γ-Al$_2$O$_3$ as acid function, which requires temperatures above 350 °C for attaining high conversion in DME hydrolysis (the first step in SRD). At this high temperatures, CZA metallic function is likely to sinterize, whereas Pt/CeO$_2$ metallic function shows higher thermal stability, with a presumably lower deactivation (both by coke deposition or sintering).
References


