Preparation of CeO$_2$-Al$_2$O$_3$ Mixed Oxides by Spray Pyrolysis

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Abstract – In this work, Al$_2$O$_3$ powders loaded with 10 and 20 mol% CeO$_2$ were prepared by spray pyrolysis and conventional wetness impregnation. The prepared powders were examined and characterized using XRD, SEM, BET and TPR techniques. The oxide powders obtained from spray pyrolysis appear to be spherical and sponge-like shape. They have smaller crystallite size, higher surface area and larger pore volume comparing to the powders obtained from wetness impregnation. The surface area of the mixed oxide was found to decrease as the CeO$_2$ content increased. Platinum loaded on spray pyrolysis sample appears to be reduced easier than platinum loaded on wetness impregnation sample.

Keyword: cerium oxide, aluminium oxide, mixed oxide, spray pyrolysis, wetness impregnation
1. Introduction

The mixed oxides of Al₂O₃ and CeO₂ are well known to be the effective catalyst supports for many hydrocarbon reactions including the cracking of heavy oil, the automotive exhaust gas converter and water-gas shift reaction. This is mainly due to cerium oxide’s unique acid–base and redox properties which can affect the thermal and structure stability of the support, the dispersion of the supported metals and the oxidation and reduction of the noble metals. Its high oxygen storage capacity can also decrease the coke formation on the catalyst surface [1-4].

Spray pyrolysis is one of the synthesis technique used for the preparation of well-defined oxide powders with nano-sized particle, spherical morphology and uniform sized distribution [5]. The technique is based on the generation of micro-sized aerosol droplets and their decomposition at the intermediate to high temperatures. Due to the fact that evaporation, precipitation, drying and decomposition occur at once in a dispersed phase and in a single step, it becomes possible to control the particle properties simply by controlling the processing parameters.

The object of this work is to investigate the CeO₂-Al₂O₃ mixed oxides prepared from spray pyrolysis method and conventional wetness impregnation followed by calcination method for the application as catalyst support in the bio-oil upgrading process.

2. Experiment

The precursor solution was prepared by dissolving aluminium nitrate, Al(NO₃)₃·9H₂O (Merck) and cerium nitrate, Ce(NO₃)₃·6H₂O (Merck) in distilled water at concentration of 0.3 M. The solutions were mixed to obtain 10 and 20 mol% of CeO₂. The spray pyrolysis system used in this study is shown in Fig. 1. The precursor droplets were generated by an ultrasonic nebulizer of 1.7 MHz and were carried into a cylinder reactor inside a tube furnace by nitrogen gas with a flow rate about 1 L/min. The cylinder reactor is made from a glass tube (Vycor, Corning) of 5 cm in diameter and 90 cm in length. The tube furnace is 60 cm long equally divided into two zones, the first zone was set at 500°C and the second zone was set at 650°C. Vacuum at the outlet of the system was controlled approximately to -15 inH₂O resulting in the consumption of the precursor solution about 2.5 mL/min. The product particles were collected in the water trap.

The CeO₂-Al₂O₃ mixed oxides of 10 and 20 mol% CeO₂ were also prepared by impregnation of γ-Al₂O₃ (Merck) with a solution of cerium nitrate. Al₂O₃ powder was added into a specific amount of cerium nitrate solution and stirred for 1 hour. The mixture was dried at 120°C and calcined at 800°C for 2 hours. The mixed oxide samples were loaded with 5 wt% Pt by wetness impregnation with Cl₆H₃Pt as a precursor solution and calcined at 500°C for 2 hours.

The oxide powders obtained from each method were examined and characterized by XRD (D8 Advance, Bruker), SEM (JSM-5800LV, JEOL) and N₂ adsorption (Autosorb-1, Quantachrome Instruments) for their structure, particle morphology, specific surface area (BET) and pore size determination. Temperature programmed reduction (TPR) of the oxide powders loaded with 5 wt% Pt were also carried out with hydrogen gas.

![Fig. 1. Schematic diagram of spray pyrolysis.](image1)

![Fig. 2. XRD patterns of the prepared CeO₂-Al₂O₃.](image2)
SEM images of Al₂O₃, CeO₂ and mixed oxide samples prepared from spray pyrolysis are shown in Fig. 3 and images of the samples prepared from wetness impregnation are in Fig. 4. The oxide powders prepared from spray pyrolysis appear to be spherical as normally obtained from this synthesis technique and the particle size is about 1 µm. However, the particles of pure Al₂O₃ sample are more sponge-like shape. The spherical particles of pure Al₂O₃ sample are reported to be hollow with thin wall structure composed of nano-sized primary CeO₂ particles [6]. The average particle size of γ-Al₂O₃ used for the wetness impregnation method, as shown in the specification, is larger than 63 µm. The SEM images of Al₂O₃ powder loaded with 10 and 20 mol% CeO₂ by the wetness impregnation method displays small CeO₂ particles attached on larger Al₂O₃ support.

Table 1. Surface area, average pore diameter and pore volume of the prepared oxide powders.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Surface area, m²/g</th>
<th>Average pore diameter, Å</th>
<th>Pore volume, cm³/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP-0</td>
<td>510.8</td>
<td>62.4</td>
<td>0.796</td>
</tr>
<tr>
<td>SP-10</td>
<td>446.9</td>
<td>43.1</td>
<td>0.481</td>
</tr>
<tr>
<td>SP-20</td>
<td>271.5</td>
<td>50.8</td>
<td>0.345</td>
</tr>
<tr>
<td>WI-0</td>
<td>118.0</td>
<td>110.0</td>
<td>0.324</td>
</tr>
<tr>
<td>WI-10</td>
<td>92.7</td>
<td>105.2</td>
<td>0.244</td>
</tr>
<tr>
<td>WI-20</td>
<td>67.5</td>
<td>113.8</td>
<td>0.192</td>
</tr>
</tbody>
</table>

The TPR tests of the mixed oxide samples loaded with 5 wt% Pt as shown in Fig. 5 reveal the consumption of hydrogen in a broad temperature range. It appears that platinum compound loaded on spray pyrolysis sample seems to be reduced easier than platinum compound loaded on wetness impregnation sample. Hydrogen consumption for the reduction to metallic platinum in spray pyrolysis sample starts at temperature about 100°C and declines at temperature about 200°C while hydrogen consumption in wetness impregnation sample start around 150°C and declines around 300°C.

Fig. 3. SEM images of the spray pyrolysis CeO₂-Al₂O₃ samples (a) SP-0 [Al₂O₃], (b) SP-10, (c) SP-20 and (d) CeO₂.

Fig. 4. SEM images of the wet impregnation CeO₂-Al₂O₃ samples (a) WI-0 [γ-Al₂O₃], (b) WI-10 and (c) WI-20.

Fig. 5. H₂-TPR profiles of Pt loaded on 20 mol% CeO₂-Al₂O₃ prepared by spray pyrolysis (SP-20) and by wetness impregnation (WI-20).
4. Conclusions

CeO$_2$-Al$_2$O$_3$ mixed oxides with 10 and 20 mol% CeO$_2$ loading were prepared by spray pyrolysis and wetness impregnation methods. The oxide powders obtained from spray pyrolysis technique have smaller crystallite size, higher surface area and larger pore volume which seem to be ideal for catalyst support. However, the surface area of the mixed oxide was found to decrease as the CeO$_2$ content increased. Platinum loaded on spray pyrolysis sample appears to be reduced easier than platinum loaded on wetness impregnation sample.

Acknowledgements

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References


