Porous Al$_2$O$_3$/Al Catalyst Supports Fabricated by an Al(OH)$_3$/Al Mixture

Zhen-Yan DENG, Yoshihisa TANAKA, Yu-Fu LIU, Zhong-Zhu LIU and Yoshiio SAKKA

National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

A powder mixture of 60 vol% Al + 40 vol% Al(OH)$_3$ was used to fabricate Al$_2$O$_3$/Al supports by pressureless sintering, in vacuum, at a temperature of 600°C. Two unidirectional pressures of 30 and 120 MPa were used to prepare green compacts. A high surface area was obtained due to the transitional Al$_2$O$_3$ phases that were produced by the decomposition of Al(OH)$_3$. At the same time, the Al$_2$O$_3$ supports retained high fracture strength due to a metal network that was formed after sintering. The surface area of the specimens sintered from the compact prepared by 30 MPa was much higher than that by 120 MPa, because the high compaction pressure resulted in the high green compact density so that the pores in the sintered specimens were closed.

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Recently porous ceramic materials have received considerable attention due to their wide applications in filters, sensors and catalyst supports. Usually, the processing of Al$_2$O$_3$ catalyst supports is restricted to the transitional phases, such as \( \gamma \), \( \delta \), and \( \theta \)-Al$_2$O$_3$. Traditional methods of fabricating Al$_2$O$_3$ catalyst supports include direct sintering of the transitional phases and sol-gel processing. The Al$_2$O$_3$ supports obtained through these methods are thin films, piece-shaped samples, and small spheres. If large specimens are needed by industry, binders must be used to bind the small pieces or spheres and combine them into a large catalyst support. However, such binders considerably reduce the practical surface area of the support and degrade the mechanical properties.

In a previous work, bulk Al$_2$O$_3$ catalyst supports were successfully fabricated by a powder mixture of Al$_2$O$_3$ + Al (OH)$_3$. Superior mechanical properties and high surface area were obtained. However, pure Al$_2$O$_3$ supports usually are insulator. In some cases, good conductivity is needed for catalyst supports; for example, the electrodes of fuel cells and the devices for NO decomposition of automobile exhaust. In this work, a powder mixture of Al$_2$O$_3$ + Al (OH)$_3$ was used to fabricate Al$_2$O$_3$/Al supports. The metal Al network formed after sintering would produce good conductivity and superior mechanical properties. At the same time, the high surface area was retained due to the transitional Al$_2$O$_3$ phases that were produced by the decomposition of Al(OH)$_3$.

Highly pure Al (99.99% purity, 3 \( \mu \)m, High Purity Chemical Co., Tokyo, Japan) and Al(OH)$_3$ (99.99% purity, 2.5 \( \mu \)m, High Purity Chemical Co., Tokyo, Japan) powders were used in the present experiment. A powder mixture of 60 vol% Al + 40 vol% Al(OH)$_3$ was prepared. The powder mixture was mixed with a highly pure ethanol solution and ball-milled for 48 h, using highly pure Al$_2$O$_3$ balls, then dried and sieved using a 100-mesh nylon sieve. Green-body billets measuring \( \sim 1.2 \) cm \( \times 5.5 \) cm \( \times 0.5 \) cm were prepared by cold pressing in a stainless-steel die. Two unidirectional pressures of 30 and 120 MPa were used. The green-body billets then were sintered in a furnace, in vacuum, at a heating rate of 1°C/min. All specimens were held at a sintering temperature of 600°C for 8 hours and then cooled to room temperature at a rate of 10°C/min.

X-ray diffractometry (XRD; Model No. RINT2000, Rigaku) was used to analyze the phases in the sintered specimen. The sintered specimens were sent directly for measurement of the surface area, using the BET method, by means of N$_2$ adsorption, at 77 K (SA3100, Japan). The sintered specimens were cut into pieces measuring 3 mm \( \times 4 \) mm \( \times 40 \) mm, then ground and beveled before strength measurement. The strength was determined by three-point bend tests with a span of 30 mm and a crosshead speed of 0.5 mm/min. The morphology and pore structures of the sintered specimens were observed, using the fresh-fractured surface of the sintered specimens, by scanning electron microscopy (SEM).

Figure 1 shows an X-ray pattern for the sintered specimen. It can be seen that only metal Al and \( \gamma \)-Al$_2$O$_3$ phases existed in the sintered specimen, implying that all of the Al(OH)$_3$ phases were decomposed into \( \gamma \)-Al$_2$O$_3$ during heating. In this work, it was found that the compaction pressure has a significant effect on the relative density of the green compacts and the sintered specimens, as shown in Table 1. The relative density (71%) of the green compact prepared by 120 MPa is much higher than that (60%) by 30 MPa so that the relative density (69%) of the specimen sintered from the compact prepared by 120 MPa is much higher than that (54%) by 30 MPa. Note that the decomposition of Al(OH)$_3$ produced 60 vol% volume contraction, and therefore the relative densities of the sintered specimens are lower than that of the corresponding green compacts.

Because the high compaction pressure led to a high relative density of the sintered specimens, the fracture strength (82.5 MPa) of the specimens sintered from the compact prepared by 120 MPa is much higher than that (17.6) by 30 MPa.

Fig. 1. X-ray pattern for the specimen sintered from the compact prepared by a pressure of 120 MPa.
Table 1. Properties of Porous Al₂O₃/Al Supports

<table>
<thead>
<tr>
<th>Property</th>
<th>30</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compaction pressure (MPa)</td>
<td>30</td>
<td>120</td>
</tr>
<tr>
<td>Green compact relative density</td>
<td>60%</td>
<td>71%</td>
</tr>
<tr>
<td>Specimen relative density</td>
<td>54%</td>
<td>69%</td>
</tr>
<tr>
<td>Fracture strength (MPa)</td>
<td>17.6±1.6</td>
<td>82.5±4.6</td>
</tr>
<tr>
<td>Surface area (m²/g)</td>
<td>33.6</td>
<td>8.5</td>
</tr>
</tbody>
</table>

pores in the specimen sintered from the compact prepared by 120 MPa are closed, while the pore structures in the specimen sintered from the compact prepared by 30 MPa are open. Moreover, the fracture strength of the present Al₂O₃/Al supports is obviously higher than that of the pure Al₂O₃ supports with a similar surface area.¹⁰,¹¹

In summary, Al₂O₃/Al supports were successfully fabricated by pressureless sintering, using a powder mixture of 60 vol % Al + 40 vol% Al(OH)₃. A high surface area was obtained due to the transitional Al₂O₃ phases produced by the decomposition of Al(OH)₃. At the same time, the Al₂O₃/Al supports retained high fracture strength. Moreover, the compaction pressure has a significant effect on the surface area of the Al₂O₃/Al supports.

Fig. 2. SEM micrographs of the fracture surfaces of the specimens sintered from the compacts prepared by (a) 30 MPa and (b) 120 MPa.

However, the surface area of the sintered specimen decreased with increasing the compaction pressure; the surface area of the Al₂O₃/Al specimen sintered from the compact prepared by 120 MPa is 8.5 m²/g, and that by 30 MPa is 33.6 m²/g. The decrease in surface area by increasing the compaction pressure can be attributed to the closed pore structures in the sintered specimen, as shown in Fig. 2. Figure 2 shows that most of the pores in the specimen sintered from the compact prepared by 120 MPa are closed, while the pore structures in the specimen sintered from the compact prepared by 30 MPa are open. Moreover, the fracture strength of the present Al₂O₃/Al supports is obviously higher than that of the pure Al₂O₃ supports with a similar surface area.¹⁰,¹¹

In summary, Al₂O₃/Al supports were successfully fabricated by pressureless sintering, using a powder mixture of 60 vol % Al + 40 vol% Al(OH)₃. A high surface area was obtained due to the transitional Al₂O₃ phases produced by the decomposition of Al(OH)₃. At the same time, the Al₂O₃/Al supports retained high fracture strength. Moreover, the compaction pressure has a significant effect on the surface area of the Al₂O₃/Al supports.

References