Various metal oxides coated with a thin silica layer were prepared by two different liquid-phase deposition methods; one is the deposition of silica on the corresponding metal hydroxides using tetraethyl orthosilicate (TEOS), and the other is the hydrothermal treatment of the metal hydroxides with silica glass in basic solution. The TEOS treatment is more effective for depositing silica on the precursor hydroxides than the hydrothermal treatment employing the process of dissolution-deposition of silica. The silica-coated metal oxides of MgO, Fe_{2}O_{3}, NiO, Y_{2}O_{3}, ZrO_{2}, SnO_{2}, and Dy_{2}O_{3} have high specific surface areas $>$ 300 m$^{2}$g$^{-1}$ after heating at 773 K.

Key-words: Metal oxides, Silica coating, Hydrothermal, Base, TEOS, High specific surface area

1. Introduction

Silica deposited on metal oxides such as alumina, titania and zirconia has been in the spotlight as a solid catalyst. Recently, these silica-coated metal oxides are prepared by depositing silica on the metal-oxide supports in the vapor phase using silicon alkoxide. In the preparation, however, low surface area of the original metal-oxide supports restricts the resulting materials. Recently, we have found that silica dissolved from a glass vessel effectively deposits on zirconyl hydroxide, ZrO(OH)$_{2}$, during aging of the hydroxide. When a fresh precipitate of ZrO(OH)$_{2}$ is heated with several pieces of silica glass chips in a basic solution under hydrothermal (HT) conditions at 373 K, silica dissolved from the glass deposits on the precipitate. The specific surface area of the resulting SiO$_{2}$-ZrO$_{2}$ exceeds 240 m$^{2}$g$^{-1}$ even after heating at 773 K. An advantage of this method is to maintain the high surface area of the original metal hydroxide after silica deposition and calcination. Increase in the specific surface area of oxides is attractive for the preparation of materials. We expect that the liquid-phase deposition of SiO$_{2}$ can be applied to other metal oxides, and that silicon alkoxides are utilizable as the silica source. In this work, we investigate various metal oxides coated with SiO$_{2}$ by using tetraethyl orthosilicate (TEOS), and compare this process with the dissolution-deposition process using silica glass under HT conditions.

2. Experimental

Metal hydroxide precipitates were typically prepared by precipitation using the corresponding metal nitrates and ammonia (5 mol dm$^{-3}$) as a precipitating reagent. The exceptions in this case were SnCl$_{4}$ and SnCl$_{6}$, used as precursors of the hydroxides of Sn(II) and Sn(IV), respectively. NaOH (1 mol dm$^{-3}$) was used as the precipitating reagent for the preparation of Ni(OH)$_{2}$. The precipitates were washed with distilled water, and stirred in ethanol containing TEOS (1.387 g) at 313 K for 96 h; the amount of charged TEOS corresponds to a SiO$_{2}$ loading of 0.4 g g$^{-1}$, respectively. The resulting solids were dried at 383 K for 24 h, followed by heating in air at 773 K for 3 h at a heating rate of 1 K min$^{-1}$ to obtain SiO$_{2}$-coated metal oxide (abbreviated as TSC). Silica loading was estimated from the weight of the silica recovered from the unreacted TEOS.

Non-coated pure metal oxide (abbreviated as NCP) samples were prepared in the above-mentioned procedure without using TEOS. HT treatment of a hydroxide precipitate was performed as a reference method to obtain another SiO$_{2}$-coated (abbreviated as HTC) sample, according to the procedure detailed in a previous report. A fresh precipitate with silica glass chips was heated in a pressure vessel with a mother solution recovered in the precipitate formation at the pH of ca. 10 at 373 K for 96 h. Silica loading was estimated from the weight of the glass chips recovered after the deposition. The samples were finally heated in air at 773 K for 3 h.

A specific surface area of the sample was determined by the BET method using N$_{2}$ adsorption isotherm at 77 K. Solid-state $^{29}$Si CP-MAS NMR spectra were recorded on a DFX-300 multinuclear spectrometer (Bruker, Germany) at 59.64 MHz. X-ray diffraction patterns were recorded on an M18XHF diffractometer (Mac Science, Japan).

3. Results and discussion

In both TSC and HTC systems, we observed decreases in the TEOS concentration and in the weight of silica glass chips, respectively. Table 1 lists silica loading values, which vary with the kind of metal hydroxide precipitate used. It is obvious that reactive-TEOS treatment achieves silica deposition at low temperature, and that silica loading in TSC samples is larger than that of HTC ones. Table 1 also lists specific surface areas of the NCP, HTC, and TSC samples. Most of the NCP samples have low specific surface areas $<$ 100 m$^{2}$g$^{-1}$. In contrast, silica-coated samples (HTC and TSC) have high specific surface areas. It is significant that the TSC samples have higher specific surface areas than the HTC samples. An as-dried precipitate of pure ZrO(OH)$_{2}$ sample has the surface area $>$ 300 m$^{2}$g$^{-1}$, which decreases to only 44 m$^{2}$g$^{-1}$ after heating at 773 K. Since an as-dried HTC SiO$_{2}$-coated ZrO(OH)$_{2}$ sample also has a high surface area $>$ 300 m$^{2}$g$^{-1}$, the silica deposited on the hydroxide surface prevents the sintering and agglomeration of the fine particles.

Figure 1 shows the X-ray diffraction patterns of both NCP and TSC samples. In all the NCP samples, crystal phases appear after heating at 773 K (Fig. 1(A)). In TSC samples (Fig. 1(B)), silica-coated Y$_{2}$O$_{3}$ and La$_{2}$O$_{3}$ maintain amorphous structures after heating at 773 K. The other TSC samples of MgO and SnO$_{2}$ show diffraction peaks broader
Silica-Coated Metal Oxide Powders with High Surface Area

Table 1. Specific Surface Area of SiO₂-Coated Metal Oxides Calcined at 773 K

<table>
<thead>
<tr>
<th>Hydroxide</th>
<th>Precursor</th>
<th>NCP</th>
<th>HTC</th>
<th>TSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(II)</td>
<td>65</td>
<td>166 (0.06)</td>
<td>268 (0.31)</td>
<td>0.40</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>24</td>
<td>64 (0.07)</td>
<td>208 (0.30)</td>
<td>0.50</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>26</td>
<td>244 (0.28)</td>
<td>333 (0.40)</td>
<td>0.39</td>
</tr>
<tr>
<td>Y(III)</td>
<td>121</td>
<td>119 (0.12)</td>
<td>310 (0.40)</td>
<td>0.42</td>
</tr>
<tr>
<td>Zr(IV)</td>
<td>44</td>
<td>221 (0.10)</td>
<td>298 (0.30)</td>
<td>0.35</td>
</tr>
<tr>
<td>Sn(II)</td>
<td>20</td>
<td>43 (0.08)</td>
<td>93 (0.14)</td>
<td>0.60</td>
</tr>
<tr>
<td>Sn(IV)</td>
<td>32</td>
<td>211 (0.09)</td>
<td>241 (0.23)</td>
<td>0.35</td>
</tr>
<tr>
<td>La(III)</td>
<td>31</td>
<td>67 (0.08)</td>
<td>122 (0.21)</td>
<td>0.65</td>
</tr>
<tr>
<td>Ce(IV)</td>
<td>78</td>
<td>95 (0.05)</td>
<td>188 (0.11)</td>
<td>0.24</td>
</tr>
<tr>
<td>Pr(III)</td>
<td>65</td>
<td>-----</td>
<td>128 (0.33)</td>
<td>0.88</td>
</tr>
<tr>
<td>Nd(III)</td>
<td>63</td>
<td>-----</td>
<td>160 (0.36)</td>
<td>0.75</td>
</tr>
<tr>
<td>Dy(III)</td>
<td>55</td>
<td>-----</td>
<td>234 (0.34)</td>
<td>0.49</td>
</tr>
</tbody>
</table>

* Numbers in parentheses are silica loading values per unit weight of the core metal oxide (g. g⁻¹ support⁻¹).

b The average thickness (d) of the silica layer of the TSC sample is calculated using the following equation, d = (silica loading [g g⁻¹ support⁻¹])(1 + silica loading [g g⁻¹ support⁻¹])/2.2[g cm⁻³]/(specific surface area [m² g⁻¹]), where 2.2 g cm⁻³ is the density of amorphous silica.

than the NCP ones. This clearly indicates that the particle sizes of TSC samples are smaller than those of NCP.

Figure 2 shows ²⁹Si NMR spectra of typical TSC samples listed in Table 1. In the TSC samples such as MgO, Y₂O₃, SnO₂, and La₂O₃, ²⁹Si resonance signals are observed at approximately −80 ppm. If the silica forms either a multiple layer or a particle aggregate, Q₄ silicon, Si(OSi)₄, resonance should be observed at ca. −110 ppm. In the trilayer silica, Si located in the middle layer shows the resonance at −110 ppm. In the bilayer silica, Si located in the top layer shows the resonance from −90, Si(OSi)₂(OH)₂, to −100 ppm, Si(OSi)₃(OH). The silica of the TSC samples can be regarded as a monolayer because of the major peak at −80 ppm, which is probably attributed to the Si(OM)₂(OH)₂ structure, where M is another metal of the oxide substrate. For MgO and SnO₂ (Figs. 2a and c), the resonance peaks at around −90 and −100 ppm suggest that the silica forms a bilayer structure. The NMR results indicate that the silica deposited on the metal oxides consists of a thin layer rather than aggregates of contaminated silica particles.
Fig. 3. Relation between specific surface area and average thickness of silica.

At this point, we can calculate the average thickness of the silica thin layer deposited on the support substrate by simple geometric calculation, assuming that the silica has uniform thickness. For example, the average thickness of SiO$_2$ of the TSC-MgO sample listed in Table 1 is calculated to be 0.4 nm (=0.31[g]/1.31[g]/2.2[cm$^{-3}$]/268[m$^2$ g$^{-1}$]). Figure 3 shows the relation between the average silica thickness and the specific surface area among the samples listed in Table 1 in addition to the TSC-ZrO$_2$ samples prepared with different TEOS concentrations.

It is known that, in an alumina deposited on silica gel, the alumina prevents the sintering of the silica support during HT treatment at 373–423 K. In silica–alumina prepared by depositing silica on alumina, it has been shown that the silica core particles exhibit a heat resistance to sintering even at 1493 K. The silica deposited on alumina acts as an obstacle for the sintering of alumina because of its different structure. The silica loading of 10–15 mass.% that showed high thermal resistance in the silica–alumina corresponds to the average silica thickness of 0.41–0.62 nm. The thickness that works effectively for the prevention of sintering of alumina is similar to those observed in this work.

The average thickness of 0.4 nm, at which the specific surface area is maximized (Fig. 3), corresponds to the surface Si density of 8.9 nm$^{-2}$, which is close to the surface Si density of amorphous silica: 7.8 Si atoms nm$^{-2}$ located at or very near the surface are estimated by simple geometric calculation. This is consistent with the NMR results shown in Fig. 2: the surface silica species comprise either a monolayer or bilayer. It is speculated that the silica species deposited on hydroxide particles suppresses the sintering and crystallization of the metal oxide core.

Although silica can also deposit on oxide supports in vapor-phase processes, the resulting surface area is absolutely limited by the support materials: the specific surface areas of ZrO$_2$ and TiO$_2$ supports are at most 70 m$^2$ g$^{-1}$. In contrast, a high specific surface area is retained under mild deposition conditions which prevent aggregation of the metal hydroxide core particles in the liquid-phase process using TEOS. This is sure to be a great advantage in preparing metal-oxide composites such as a solid catalyst.

4. Conclusions

The specific surface areas of SiO$_2$-coated metal oxides through hydrolysis of TEOS were much higher than those of the corresponding non-coated ones. The values of SiO$_2$-coated MgO, NiO, Y$_2$O$_3$, ZrO$_2$, and SnO$_2$, and so forth exceeded 260 m$^2$ g$^{-1}$. Although the primary particles of the pure metal hydroxides readily aggregate into large oxides during heating, the silica species deposited on the surface of primary particles prohibits agglomeration of the core particles. The present TEOS treatment works effectively for depositing silica on the hydroxide precursor, and is more efficient for the enlargement of specific surface area of the resulting silica-coated metal oxide than the dissolution-deposition of SiO$_2$ under hydrothermal conditions.

References