NiFe$_2$O$_4$ as an Active Component of Platinum Group Metal Free Automotive Three-way Catalyst

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Raman Spectroscopy:

Fig. S1 shows the Raman spectra of NiFe$_2$O$_4$ (reCP), NiFe$_2$O$_4$ (SSR), α-Fe$_2$O$_3$ and NiO prepared by a reverse strike co-precipitation (reCP) method and a conventional solid state reaction (SSR) method, α-Fe$_2$O$_3$ and NiO. The procedure of a solid state reaction method is as follows: α-Fe$_2$O$_3$ (Purity 98%, Kishida Chemical Co., Ltd, Japan), NiO (Purity 98%, Kishida Chemical Co., Ltd, Japan) and acetone were ball-milled for 24 h in order to get a homogeneous slurry. The slurry was filtered, washed and dried overnight at 80 °C. The powder was calcined at 1000 °C for 10 h. NiFe$_2$O$_4$ (reCP) show the bands located at 344, 493, 575 and 699 cm$^{-1}$ are attributable to characteristic of spinel structure.$^2$ A$_{1g}$ mode in the 620-720 cm$^{-1}$ region corresponds to the symmetric stretching vibration of oxygen with respect to the metal ion in tetrahedral unit (MO$_4$). The presence of shoulder-like feature of A$_{1g}$ mode results from iron and nickel ion occupied the tetrahedral site in the spinel lattice.$^3$ The Raman spectra of NiFe$_2$O$_4$ (reCP) is similar to that of NiFe$_2$O$_4$ (SSR) and the bands attributable to α-Fe$_2$O$_3$ and NiO (e.g., 299 cm$^{-1}$ and 538 cm$^{-1}$) are not observed. Therefore, it is clear that NiFe$_2$O$_4$ (reCP) has a single spinel phase, which is in accordance with XRD results.
Specific activity of Fe-Ni mixed oxides:

Fig. S2 shows the specific activity, reaction rate per unit surface area, for NO reduction, C3H6 oxidation and CO oxidation under TWC conditions over Fe-Ni mixed oxides. NO reduction and C3H6 oxidation showed a volcano-relationship against Fe/Ni ratio. In contrast, for CO oxidation, NiO exhibited the highest activity and Fe1Ni7 exhibited the second highest activity.

Specific activity of NiFe2O4 prepared by solid state reaction

Table S1 Specific NO reduction rate prepared by solid state reaction (SSR) and reverse strike co-precipitation (reCP)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Specific NO reduction rate(a) / nmols(^{-1})m(^2)</th>
<th>NO conversion(b) / %</th>
<th>Surface area (c) / m(^2)g(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiFe2O4 (SSR)</td>
<td>32.2(^b)</td>
<td>2.8(^b)</td>
<td>2.22</td>
</tr>
<tr>
<td>NiFe2O4 (reCP)</td>
<td>33.7(^c)</td>
<td>54.6(^b)</td>
<td>41.3</td>
</tr>
</tbody>
</table>

\(^{a}\) at 400 °C  \(^{b}\) 17.5 mg  \(^{c}\) 4.38 mg

Table S1 shows the effect of preparation method on the three-way catalytic activity of NiFe2O4. NiFe2O4 (SSR) was prepared by solid state reaction. The NO conversion over NiFe2O4 (SSR) was less than 1/20 of that of NiFe2O4 (reCP). This is due to the significant decrease in surface area from 54.6 to 2.8 m\(^2\)g\(^{-1}\). However, the NO reduction rate per unit surface area was almost the same on these catalysts. These results indicate that the formation of NiFe2O4 is the essential factor for high NO catalytic activity.
Tolerance to H$_2$O and CO$_2$

Fig. S3 shows NO conversion under TWC conditions in the presence of large amounts of H$_2$O and CO$_2$ over NiFe$_2$O$_4$ (reCP) and Fe-Ni/CeO$_2$ at 500 °C. The NO reduction activity of NiFe$_2$O$_4$ was unchanged in the presence of 7.7% CO$_2$, but it decreased in the presence of 10% water vapor (Fig. S3(A)). Although the stability of pure NiFe$_2$O$_4$ in the presence of 10% water vapor is not good, the authors have reported that the use of CeO$_2$ support improves the stability in the presence of water shown in the Fig. S3(B).

Durability test

Fig. S4 shows time-on-stream of NO, C$_3$H$_6$ and CO conversions at 500 °C over NiFe$_2$O$_4$ (reCP). The catalytic activity was stable for 10 h on NiFe$_2$O$_4$. 

Fig. S3 NO conversion over (A)NiFe$_2$O$_4$ (B)Fe-Ni/CeO$_2$ under TWC conditions (a) without H$_2$O and CO$_2$ (b) with 10% H$_2$O (c) with 7.7% CO$_2$ (at 500 °C).
TWC catalytic activity as a function of air/fuel ratio ($\lambda$)

Fig. S5 shows TWC activity dependence on air/fuel (A/F) ratio ($\lambda$). The $\lambda$ value, which represents the excess oxygen ratio was defined as follows:

$$\lambda = \frac{[NO] + 2[O_2]}{9[C,H_6] + [CO]}$$

$\lambda$ was controlled by adjusting $O_2$ concentration. The conversions of NO, $C_3H_6$ and CO showed a similar trend on A/F ratio with Platinum-group metal catalysts, i.e. NO conversion was nearly 100% in the rich conditions, while those of $C_3H_6$ and CO decreased in the rich conditions because of insufficient concentration of oxygen. In lean conditions, the conversions of $C_3H_6$ and CO were around 100%, while the conversion of NO decreased significantly. When the A/F ratio varied from lean to rich conditions, NiFe$_2$O$_4$ showed low activity for NO reduction than that of A/F ratio varied from rich to lean conditions.

References: