Supporting Information

$NiFe_2O_4$ as an Active Component of Platinum Group Metal Free Automotive Three-way Catalyst

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Raman Spectroscopy:

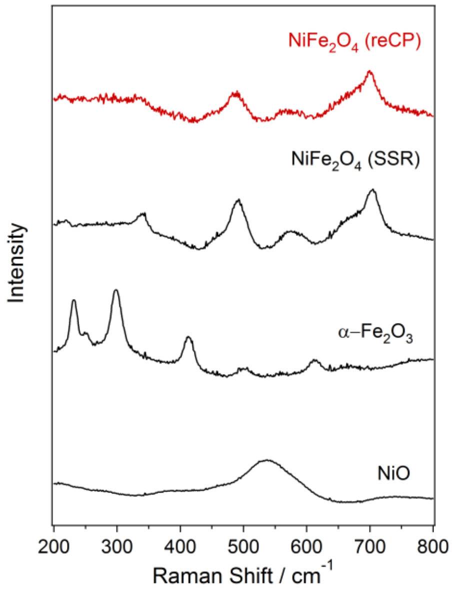

Fig. S1 Raman spectra of $NiFe_2O_4$ (reCP), $NiFe_2O_4$ (SSR), α-Fe_2O_3 and NiO

Fig. S1 shows the Raman spectra of $NiFe_2O_4$ prepared by a reverse strike co-precipitation (reCP) method and a conventional solid state reaction (SSR)[1] method, α-Fe_2O_3 and NiO. The procedure of a solid state reaction method is as follows: α-Fe_2O_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. $NiFe_2O_4$ (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 $NiFe_2O_4$ (reCP) is similar to that of $NiFe_2O_4$ (SSR) and the bands attributable to α-Fe_2O_3 and NiO (e.g., 299 cm^{-1} and 538 cm^{-1}) are not observed. Therefore, it is clear that $NiFe_2O_4$ (reCP) has a single spinel phase, which is in accordance with XRD results.

Specific activity of Fe-Ni mixed oxides:

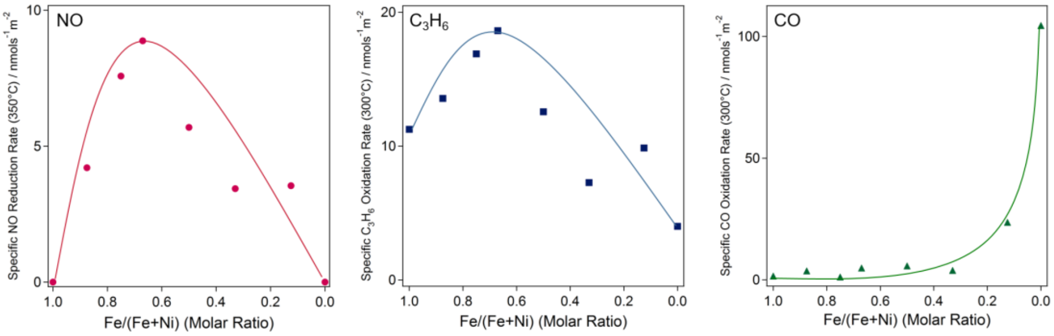

Fig. S2 Specific activity for NO reduction (350 °C), C_3H_6 oxidation and CO oxidation (300 °C) under TWC conditions over Fe-Ni mixed oxides

Fig. S2 shows the specific activity, reaction rate per unit surface area, for NO reduction, C_3H_6 oxidation and CO oxidation under TWC conditions over different Fe-Ni mixed oxides. NO reduction and C_3H_6 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 $NiFe_2O_4$ prepared by solid state reaction

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

Catalyst	Specific NO reduction rate[a] / nmols^{-1}m^{-2}	NO conversion[a] / %	Surface area / m^{2}g^{-1}
$NiFe_2O_4$ (SSR)	32.2[b]	2.8[b]	2.22
$NiFe_2O_4$ (reCP)	33.7[c]	54.6[b]	41.3

[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 $NiFe_2O_4$. $NiFe_2O_4$ (SSR) was prepared by solid state reaction. The NO conversion over $NiFe_2O_4$ (SSR) was less than 1/20 of that of $NiFe_2O_4$ (reCP). This is the 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 $NiFe_2O_4$ is the essential factor for high NO catalytic activity.

Tolerance to H_2O and CO_2

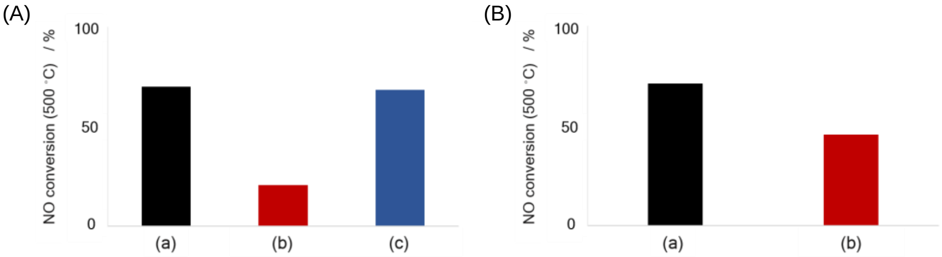

Fig. S3 NO conversion over (A)$NiFe_2O_4$ (B)Fe-Ni/CeO_2[4] under TWC conditions (a)without H_2O and CO_2 (b)with 10% H_2O (c)with 7.7% CO_2 (at 500 °C).

Fig. S3 shows NO conversion under TWC conditions in the presence of large amounts of H_2O and CO_2 over $NiFe_2O_4$ (reCP) and Fe-Ni/CeO_2[4] at 500 °C. The NO reduction activity of $NiFe_2O_4$ 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 $NiFe_2O_4$ in the presence of 10% water vapor is not good, the authors have reported[4] that the use of CeO_2 support improves the stability in the presence of water shown in the Fig. S3(B).

Durability test

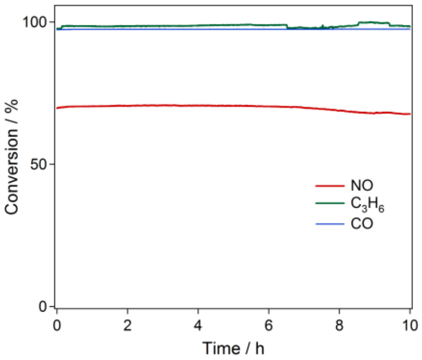

Fig. S4 Durability test over $NiFe_2O_4$ (reCP) at 500 °C.

Fig. S4 shows time-on-stream of NO, C_3H_6 and CO conversions at 500 °C over $NiFe_2O_4$ (reCP). The catalytic activity was stable for 10 h on $NiFe_2O_4$.

TWC catalytic activity as a function of air/fuel ratio (λ)

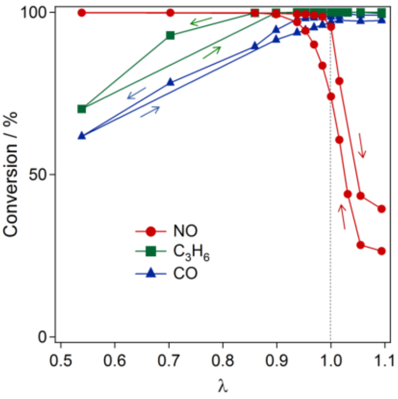

Fig. S5 Catalytic conversions of NO C_3H_6 and CO as a function of air/fuel ratio (λ) over $NiFe_2O_4$ (reCP) at 500 °C.

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

$$\lambda = \frac{[NO] + 2[O_2]}{9[C_3H_6] + [CO]}$$

λ 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, $NiFe_2O_4$ showed low activity for NO reduction than that of A/F ratio varied from rich to lean conditions.

References:

1. A. Kumar, P. Sharma, D. Varshney, *Ceram. Int.*, 2014, **40**, 12855-12860.
2. P. R. Graves, C. Johnston and J. J. Campaniello, *Mat. Res. Bull.*, 1988, **23**, 1651-1660.
3. F. Nakagomi, S. W. da Silva, V. K. Garg, A. C. Oliveira, P. C. Morais and A. Franco Jr., *J. Solid State Chem.*, 2009, **182**, 2423-2429.
4. A. Satsuma, K. Ueda, Y. Ito, C. A. Ang and J. Ohyama, *Chem. Lett.*, 2015, **44**, 703.