

Enhanced Three Way Catalytic Activity of NiFe₂O₄ by Physically Mixed Metal Oxides

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The automotive industry is the principal consumer of platinum group metals (PGM: Pt, Pd and Rh), because these elements are essential for three-way automotive catalysts (TWC) for gasoline engine vehicles. The motorization in developing countries and strict emission standards in developed countries are pushing up the demand of PGM, thus, saving PGM or PGM-free TWC are strongly required. The authors proposed NiFe₂O₄ as one of the candidate for PGM-free TWC[1], which showed higher NO reduction activity than other PGM-free catalysts ever reported[2]. However, the NO_x reduction activity is still lower than conventional PGM catalysts. The aim of this study is to clarify the promoting effect of metal oxide supports for TWC reaction on NiFe₂O₄. In order to neglect effect of dispersion and chemical state of NiFe₂O₄, physical mixtures of NiFe₂O₄ and various metal oxides are tested.

The TWC activity test was performed in a flow of NO-C₃H₆-CO-O₂ under stoichiometric conditions (NO 1,000ppm, C₃H₆ 1,000ppm, CO 4,000ppm, and O₂ 6,000ppm at a total flow rate of 60 mL min⁻¹ using 17.5 mg of catalyst, and GHSV was roughly 140,000 h⁻¹). Fig. 1 shows the temperature dependence of NO conversion over the physically mixed catalysts. Compared to NiFe₂O₄ mixed with inert quartz sand, the NO reduction activity of NiFe₂O₄ was enhanced by mixing with CeO₂ and MgO. On the other hand, the promoting effect was not observed on the mixtures with TiO₂ and Nb₂O₅.

The promoting effect was investigated in terms of reaction mechanism using in-situ FTIR. Fig. 2 shows IR spectra of the surface adsorbed species. The bands of carboxylates, i.e., mainly acetate (1425-1460 cm⁻¹) and formate (2930-2870 cm⁻¹), were detected as

adsorbed species under the reaction conditions. Comparing dynamics of these bands with kinetic analysis, surface carboxylates are found to be the reaction intermediates which act as reductants of NO into N₂. Since the rate of NO reduction and the adsorbed amount of carboxylate was correlated, it was suggested that the storage effect of carboxylate intermediates on metal oxides resulted in the enhancement of NO conversion in TWC reaction.

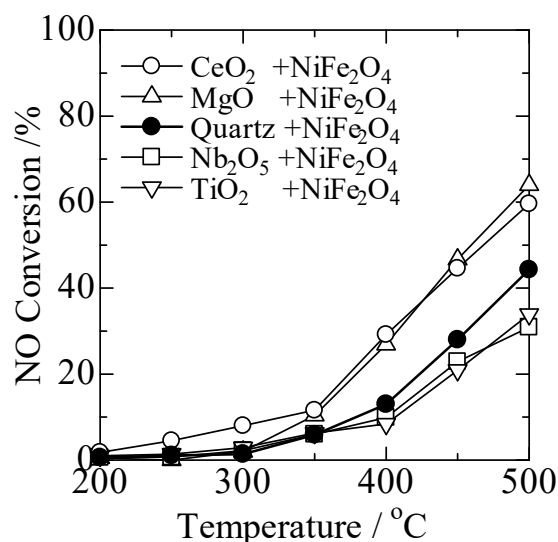


Fig. 1 NO conversion on physical mixture of NiFe₂O₄ and metal oxides.

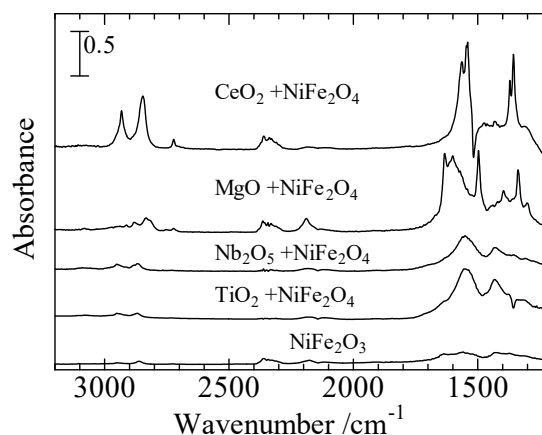


Fig. 2 In-situ FTIR spectra of adsorbed species on physical mixture of NiFe₂O₄ and metal oxides under TWC conditions at 350 °C.

REFERENCES

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