Comparative study of structure-catalytic activity relationship for Ni–Cr–Al–O and Cu–Ni–Cr–Al–O spinel oxide solid solutions

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A spinel solid solution expressed by a composition formula of CuₙNi₁₋ₓAl₁ₓCr₀.₂O₄ (0 ≤ x ≤ 0.2) was studied focusing on the role of Cu species in the catalytic activity toward NO reduction under a simulated three-way catalysis condition. X-ray Rietveld analysis revealed that Cu and Cr prefer to occupy the tetrahedral site and the octahedral site, respectively, whereas Ni and Al are distributed across both sites. Although NiAl₁.₈Cr₀.₂O₄ (x = 0) showed negligible catalytic activity for NO reduction, the partial replacement of Ni by Cu significantly enhanced the activity, achieving the highest activity at x = 0.05 not only for NO reduction but also for CO and C₃H₆ oxidation. Based on the infrared spectra and pulsed reaction experiments, it was concluded that the monovalent Cu site in the tetrahedral site plays a key role in CO chemisorption, oxygen vacancy formation, and subsequent NO reduction via the Mars–van Krevelen mechanism.

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beneficial for promoting CO–H₂O and C₂H₄–O₂ reactions, respectively. A positive synergy between these different functionalities arising from each metal element affords high NO reduction activity under a wet gas stream. However, it is still unclear how a small amount of Cu contributes to the catalytic performance of CuₓNi₀.₅₈Alₓ₁.₇₂Cr₀.₂₉O₄.

In the present study, spinel solid solutions with various amounts of Cu, CuₓNi₀.₉₅Alₓ₁.₈₇Cr₀.₂₉O₄ (0 ≤ x ≤ 0.2), were prepared to study the role of Cu in the catalytic activity for TWC reactions. Our attention was paid mainly to differences in structure and catalytic activity between solid solutions with and without Cu. The structures of the solid solutions were characterized by X-ray diffraction (XRD) Rietveld analysis, and X-ray photoelectron spectroscopy (XPS). The surface reactivity was studied using in situ infrared spectra and pulse reaction experiments. Based on these results, the possible role of Cu in the catalytic NO reductions is discussed to elucidate the structure–catalysis relationship of the multicomponent spinel solid solution as candidates for PGM-free TWC.

2. Experimental procedure

2.1 Catalyst preparation

Spinel oxides, CuₓNi₁₋ₓCr₀.₂₉Al₁.₈₂O₄ (0 ≤ x ≤ 0.2), were prepared by a polymerized complex method based on previously reported procedures. Calculated amounts of nitrates (total amounts = 30 mmol) including Cu(NO₃)₂, Ni(NO₃)₂, Al(NO₃)₃, Cr(NO₃)₃ (Wako Pure Chemical Industries, Ltd.) and citric acid (300 mmol) were dissolved in pure water. After stirring at 80 °C for 2 h, ethylene glycol (300 mmol) was added with vigorous stirring. The obtained mixture was stirred at 80 °C for a further 8 h until it turned to a polymeric gel. The gel was heated at 130 °C for 2 h and then at 400 °C for 2 h, followed by calcination at 600 °C for 5 h. The product was heated at 900 °C for 25 h in a flow of 10 % H₂O in air for thermal stabilization. Furthermore, the samples for the X-ray structure analysis were calcined at 1200 °C for 100 h to increase crystallinity.

2.2 Characterization

N₂ adsorption isotherms were obtained at −196 °C using a BelSorp Mini (Microtrac BEL) apparatus to calculate Brunauer–Emmett–Teller surface areas (Sₐ). X-ray fluorescence analysis (EDX1300, Rigaku) was used to determine the metallic compositions, which were in close agreement with the expected values. XRD was performed using monochromated Cu–Kα radiation (40 kV, 200 mA, RINT-TTR III, Rigaku) in a step-scan mode over the 2θ range of 10–120° (step size 0.02° and count time per step 4 s). To obtain the crystal structure parameters, XRD data were fitted and refined using Rietveld refinement software (RIETAN-FP). The peak shape was described by a pseudo-Voigt function, and the background level was defined by a polynomial function. The scale factor, the counter zero point, the peak asymmetry, and the unit cell dimensions were refined in addition to the atomic parameters including the site occupancies of Ni and Al. The quality of the fit to the observed data was evaluated in terms of four agreement factors, R(mean), Rwp, Rrel, and S. XPS spectra were obtained using a K-Alpha spectrometer (Thermo Scientific) under Al–Kα radiation (12 kV). The C 1s signal at 285.0 eV, which was derived from adventitious carbon, was used as a reference to correct for the effects of surface charge. The in situ fourier-transformed infrared (FTIR) spectra of the chemisorbed CO on the catalyst were acquired by a Nicolet i550 FTIR spectrometer (Thermo Fisher Scientific) with a temperature-controllable diffuse reflectance reaction cell and a HgCdTe detector. The cell was heated to 600 °C at a constant rate of 10 °C·min⁻¹, and it was maintained at this temperature for 30 min under a supply of dry He (50 cm³·min⁻¹). After being cooled to room temperature, the background spectra at different temperatures were collected under a He flow. The catalyst sample was then exposed for 10 min to a gas stream containing 1 % CO balanced with He. The cell was subsequently purged with pure He for 10 min to remove the gaseous CO before the spectrum was obtained.

2.3 Catalytic reactions

A catalytic NO–CO–C₂H₄–O₂ reaction under a wet gas stream was performed in a continuous fixed-bed reactor at atmospheric pressure. The catalyst (50 mg, 20 mesh) was fixed in a quartz tube (inside diameter 4 mm) using quartz wool, and the activity was evaluated by heating the catalyst bed from room temperature to 600 °C at a temperature ramp rate of 10 °C·min⁻¹ while supplying a simulated exhaust gas mixture (0.05 % NO, 0.50 % CO, 0.04 % C₃H₆, 0.40 % O₂, 5.00 % H₂O, and He balance, 100 cm³·min⁻¹). The gas composition corresponds to a stoichiometric air-to-fuel weight ratio of 14.6, where all gases can be completely converted into a mixture of CO₂, H₂O, and/or N₂. The effluent gas was then analyzed using nondispersive infrared NO/N₂O/CO/C₃H₆ gas analyzers (VA-3000, HORIBA). To elucidate the NO reduction mechanism, the sample was exposed to 10 % CO/He at 250 °C for 30 min and flushed with He, followed by repeated NO pulse injections under a He stream at the same temperature. The effluent gas was analyzed using a quadrupole mass spectrometer (Belmass, Microtrac BEL).

3. Results and discussion

3.1 Structure of CuₓNi₁₋ₓCr₀.₂₉Al₁.₈₂O₄

Figure 1 shows the XRD pattern of CuₓNi₁₋ₓCr₀.₂₉Al₁.₈₂O₄ (0 ≤ x ≤ 0.2) after thermal aging at 900 °C. The primary peaks of spinel oxide suggested the formation of solid solutions with cubic Fd-3mZ symmetry (No. 227). Although small peaks due to NiO were observed at x = 0.03, these impurity peaks were much less intense in the other samples. We confirmed the reproducibility of the XRD result by repeating our sample preparation two times. On the other hand, the impurity peaks of NiO disappeared when calcined at 1200 °C for 100 h. The appearance of NiO is therefore rationalized by the slower kinetics of the mixed spinel formation at lower x values. The peak width for the spinel oxide increased with decreasing x, suggesting smaller crystallite sizes. This is in accordance with the
ternary systems in the literature data.\textsuperscript{33,34} We therefore references are consistent with those in the related binary and
and Al are distributed across both sites. These site pref-
occupy the

\[ S_{\text{BET}} = 44 \text{ m}^2\cdot\text{g}^{-1} \]

\begin{table}[h]
\centering
\begin{tabular}{l|c}
\hline
\textbf{x} & \textbf{$S_{\text{BET}}$/m$^2$·g$^{-1}$} \\
\hline
0 & 44 \\
0.03 & 39 \\
0.05 & 36 \\
0.07 & 35 \\
0.1 & 30 \\
0.2 & 24 \\
\hline
\end{tabular}
\caption{BET surface area of Cu$_{x}$Ni$_{1-x}$Al$_{1.8}$Cr$_{0.2}$O$_4$}
\end{table}

largest $S_{\text{BET}}$ (44 m$^2$·g$^{-1}$) at $x = 0$, which decreased monotonically with increasing $x$ (Table 1). Among the spinel aluminates (MAl$_2$O$_4$, M = 3d transition metal) after thermal aging at 900 °C, NiAl$_2$O$_4$ showed the larger $S_{\text{BET}}$ (52 m$^2$·g$^{-1}$) compared with others (<10 m$^2$·g$^{-1}$).\textsuperscript{26} The combination of Ni and Al in the present system tends to provide the most stable and high-surface-area platform comprising a NiAl$_2$O$_4$-like solid solution. The crystal structure of NiAl$_2$O$_4$ is known as a partially inverse spinel-structure.\textsuperscript{34} The cation distribution of NiAl$_2$O$_4$ is well-known to have one of the strongest stabilization effect of the d$^8$ electronic configuration.\textsuperscript{33} Cr is well-known to have one of the strongest $O_h$ site preferences in the spinel structure.\textsuperscript{34} The cation distribution in Cu$_{0.05}$Ni$_{0.95}$Al$_{1.8}$Cr$_{0.2}$O$_4$ was studied by EXAFS in our previous study,\textsuperscript{26} which revealed that Cu and Cr prefer to occupy the $T_d$ site and the $O_h$ site, respectively, whereas Ni and Al are distributed across both sites. These site preferences are consistent with those in the related binary and ternary systems in the literature data.\textsuperscript{33,34} We therefore assume that the cation distribution remains unchanged even in the present system, which contains different ratio of Cu and Ni in Cu$_x$Ni$_{1-x}$Cr$_{0.2}$Al$_{1.8}$O$_4$ ($0 \leq x \leq 0.2$).

The crystallographic data of Cu$_x$Ni$_{1-x}$Cr$_{0.2}$Al$_{1.8}$O$_4$ were refined by comparative X-ray Rietveld analysis as shown in

\[ 2\theta / \text{degree} \]

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1}
\caption{XRD patterns of Cu$_x$Ni$_{1-x}$Al$_{1.8}$Cr$_{0.2}$O$_4$ ($0 \leq x \leq 0.2$).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2}
\caption{Rietveld X-ray powder pattern fitting for (a) NiAl$_{1.8}$Cr$_{0.2}$O$_4$ ($x = 0$), and (b) Cu$_{0.05}$Ni$_{0.95}$Al$_{1.8}$Cr$_{0.2}$O$_4$ ($x = 0.05$). The difference between the calculated and observed patterns is shown on the top.}
\end{figure}

\begin{table}[h]
\centering
\begin{tabular}{l|c}
\hline
\textbf{M} & \textbf{MAl$_2$O$_4$} \\
\hline
Ni & NiAl$_2$O$_4$ \\
Cr & CrAl$_2$O$_4$ \\
\hline
\end{tabular}
\caption{Comparison of spinel oxide solid solutions.}
\end{table}

\[ 3.2 \text{ Catalytic activity of Cu$_x$Ni$_{1-x}$Cr$_{0.2}$Al$_{1.8}$O$_4$} \]

The catalytic performance of Cu$_x$Ni$_{1-x}$Cr$_{0.2}$Al$_{1.8}$O$_4$ was evaluated using a simulated TWC reaction. Figure 3 compares the light-off characteristics of a stoichiometric NO–CO–C$_2$H$_4$–O$_2$ reaction under a wet condition (5% H$_2$O) during temperature ramping. Notably, the catalyst
without Cu (x = 0) showed negligible NO conversion up to 600 °C, whereas the substitution of Cu for Ni significantly enhanced the NO conversion as plotted in Fig. 4. The highest NO conversion was achieved at x = 0.05, which is superior to x = 0 in terms of activities not only for NO but also for CO and C3H6. The CO/C3H6 oxidation activities are superior to those of Pt/Al2O3 and Rh/Al2O3, whereas further improvement is needed for NO reduction. When the temperature ramping experiment was repeated, the light-off temperatures at 50% conversion agreed within an error of ±15 °C, indicating a sufficiently degree of reproducibility. This is in accordance with a high phase stability of the quaternary spinel oxide solid solution under the reaction atmosphere. Our previous XPS study suggested the presence of Cu⁺ in the Td site on the surface of Cu0.05Ni0.95Al1.8Cr0.2O4 (x = 0) as discussed below. When the temperature ramping experiment was repeated, the light-off temperatures at 50% conversion agreed within an error of ±15 °C, indicating a sufficiently degree of reproducibility. This is in accordance with a high phase stability of the quaternary spinel oxide solid solution under the reaction atmosphere.

Table 2. Refined structural parameters for (a) NiAl1.8Cr0.2O4 and (b) Cu0.05Ni0.95Al1.8Cr0.2O4

| (a) Position | g | x | y | z | B/10⁻²nm² |
|--------------|---|---|---|---|-----------|
| Ni²⁺ 8b | 0.150(1) | 0.375 | 0.375 | 0.375 | 0.67(2) |
| Al³⁺ 8b | 0.850(1) | 0.375 | 0.375 | 0.375 | 0.64(3) |
| Ni²⁺ 16c | 0.425(1) | 0.000 | 0.000 | 0.000 | 0.56(2) |
| Al³⁺ 16c | 0.475(1) | 0.000 | 0.000 | 0.000 | 0.56(2) |
| C³⁺ 16c | 0.100 | 0.000 | 0.000 | 0.000 | 0.56(2) |
| O²⁻ 32e | 1.000 | 0.2453(1) | 0.2453(1) | 0.2453(1) | 0.85(3) |

Space group: Fd-3m Z (No. 227), a = 8.0735(2) Å.

Rwp = 11.462 %, Rp = 8.117 %, Re = 8.228 %, S = 1.3929.

| (b) Position | g | x | y | z | B/10⁻²nm² |
|--------------|---|---|---|---|-----------|
| Cu²⁺ 8b | 0.050 | 0.375 | 0.375 | 0.375 | 0.64(2) |
| Ni²⁺ 8b | 0.110(2) | 0.375 | 0.375 | 0.375 | 0.64(2) |
| Al³⁺ 8b | 0.840(2) | 0.375 | 0.375 | 0.375 | 0.64(2) |
| Ni²⁺ 16c | 0.420(2) | 0.000 | 0.000 | 0.000 | 0.56(1) |
| Al³⁺ 16c | 0.480(2) | 0.000 | 0.000 | 0.000 | 0.56(1) |
| C³⁺ 16c | 0.100 | 0.000 | 0.000 | 0.000 | 0.56(1) |
| O²⁻ 32e | 1.000 | 0.2447(1) | 0.2447(1) | 0.2447(1) | 0.85(2) |

Space group: Fd-3m Z (No. 227), a = 8.0722(1) Å.

Rwp = 9.005 %, Rp = 6.058 %, Re = 6.923 %, S = 1.3009.

Fig. 3. Catalytic light-off curves for NO, CO and C3H6 in a stoichiometric NO–CO–C3H6–O2 reaction under wet condition (5 % H2O) over Cu0.05Ni0.95Al1.8Cr0.2O4 (0 ≤ x ≤ 0.2).

Fig. 4. NO conversion at 600 °C in stoichiometric NO–CO–C3H6–O2 reactions under wet condition (5 % H2O) over Cu0.05Ni0.95Al1.8Cr0.2O4 (0 ≤ x ≤ 0.2).
To elucidate why such a small amount of Cu in the solid solution significantly enhanced the catalytic activity, chemisorption of CO molecules was studied at different temperatures by in situ FTIR spectra as shown in Fig. 6. When NiAl1.8Cr0.2O4 (x = 0) was used, CO chemisorption was negligible in a whole range of temperature. Contrastingly, a band appeared at 2110 cm⁻¹ for x = 0.05 at ~350 °C, indicating the stretching vibration of linearly adsorbed CO on the Cu⁺ site on the surface. There is no band at the higher wavenumbers (~2190 cm⁻¹), which are reported for CO adsorbed on the Cu2⁺ sites. Therefore, the presence of Cu⁺ on the surface is supported by FTIR spectra of chemisorbed CO molecules. It should be noted that the spinel oxide phase was preserved upon exposure to CO, and no metallic or decomposed phases were formed.

The CO adsorption onto the oxide surface is followed by the reaction with the lattice oxygen exposed on the surface. The samples (x = 0 and 0.05) were exposed to 10 % CO/He at 250 °C for 30 min and flushed with He, followed by repeated NO pulse injections under a He stream at the same temperature. Figure 7 shows the effluent gases (N₂, NO and N₂O) analyzed by a quadrupole mass spectrometer. The injected NO caused negligible reactions over the sample with x = 0. For the sample with x = 0.05, however, partial consumption of NO occurred accompanied by N₂ evolution in the first several pulse cycles, decreasing with increasing numbers of pulses. These results suggest that the spinel surface provides active Cu⁺ in theTd site, which is suitable for CO adsorption, and subsequent reactions with lattice oxygen (O₂) in the framework of the spinel produce CO₂ and a surface oxygen vacancy (VO). The vacancy thus formed is then filled with oxygen from gaseous O₂ or NO to regenerate the catalyst surface as shown below.

$$\text{O}_2 + 2\text{VO} \rightarrow 2\text{OO}$$
$$2\text{NO} + 2\text{VO} \rightarrow \text{N}_2 + 2\text{O}_2$$

Based on these results, it is considered that the NO reduction over Cu0.05Ni0.95Al1.8Cr0.2O4 (x = 0.05) under the TWC condition proceeds via the so-called Mars–van Krevelen mechanism. In the first step, adsorption of CO and/or C₃H₆ molecules and their subsequent reaction with surface oxygen yields CO₂ and oxygen vacancy in the vicinity of Cu⁺. Meanwhile, the O₂ concentration in the gas phase decreases due to rapid equilibration with the oxygen vacancy. In the second step, NO adsorbs on the surface, providing an interaction between the NO and the oxygen vacancy responsible for NO reduction. The mechanism is in accordance with the delayed onset temperature of NO reduction compared with that of CO/C₃H₆ oxidation in Fig. 3. Unlike the quaternary system, the ternary compound without Cu (NiAl1.8Cr0.2O4, x = 0) showed lower activities for NO, CO, and C₃H₆. We thus conclude that Cu⁺ in theTd site plays an essential role in NO reduction during the TWC reaction, irrespective of the small concentration (~5 atom %).
4. Conclusions

The spinel solid solutions with nominal composition Cu$_x$Ni$_{1-x}$Al$_2$Cr$_{2}$O$_4$ ($0 \leq x \leq 0.2$) were prepared by a polymerized complex method to study as a possible candidate for PGM-free TWC. As-prepared compounds exhibited contrasting TWC performance according to with or without Cu; NO conversion at 600 °C was more than 70% at $x = 0.05$ in contrast to a negligible activity at $x = 0$. The ternary solid solution with $x = 0.05$, Cu replaces mainly the $T_d$ site occupied originally by Ni. The Cu in the $T_d$ site on the surface is a monovalent cation and provides an indispensable active site for CO adsorption, the formation of oxygen vacancy and subsequent NO reduction, which proceeds via the Mars–van Krevelen mechanism.

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