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Synthesis and Properties of Ni–Cu Alloy Supported on Mg–Al Mixed Oxide Catalyst for Automotive Exhaust

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A new Cu-based catalyst for automotive three way catalysts has been investigated. We succeeded in the synthesis of the Ni–Cu alloy supported on Mg–Al mixed oxide catalyst, $Ni_{0.3}Cu_{0.2}/2MgO \cdot 1/2MgAl_2O_4$. On the NO–CO reaction evaluation after pretreatment in oxidation atmosphere, the $Ni_{0.3}Cu_{0.2}/2MgO \cdot 1/2MgAl_2O_4$ showed higher activity than a Cu/Al_2O_3 catalyst. In the evaluation by using model gas simulated automotive exhaust, the $Ni_{0.3}Cu_{0.2}/2MgO \cdot 1/2MgAl_2O_4$ catalyst showed high catalytic activity, especially for hydrocarbon oxidation in reducing atmosphere.

Since the three way catalyst (TWC) was introduced to the market for the first time in 1970s, TWC has become one of the automotive parts that has the highest reliability and stability as a result of constant improvement. However, only precious metals have been used as the active species for a practical catalyst, this situation has been maintained for nearly half a century. As a result, the consumption of precious metals is likely to increase over former times by tightening emission regulation. Therefore, the reduction of the amount of precious metals[1,2] or the development of replaceable materials[3–6] have been investigated extensively. Our research team has also investigated catalysts using Fe, Co, Mn, Cu, Ni, and others as a replaceable material of precious metals.

In this study, we have investigated the possibility of Ni–Cu alloy catalysts as nonprecious metal catalysts for TWC. These catalysts were characterized using X-ray diffraction, BET surface area, and FE-SEM, and the catalytic performance was evaluated using simulated automotive exhaust gases.

The Ni–Cu alloy catalysts were synthesized by calcinations of hydrotalcite type precursors in reducing atmosphere. The catalysts, which were synthesized by the calcinations of the hydrotalcite precursors, have excellent catalytic activity owing to their large surface area, basic properties, high metal dispersion, and high thermal stability.[7,8] $Ni_{0.5-x}Cu_x/2MgO \cdot 1/2MgAl_2O_4$ ($0 \leqq x \leqq 0.4$) catalysts were prepared by the calcination of $[Ni_{0.5-x}Cu_xMg_{2.5}Al(OH)_8]1/2CO_3 \cdot 2H_2O$ ($0 \leqq x \leqq 0.4$) hydrotalcite precursors at 850 °C for 5 h in 5% H_2/95% N_2, and BET surface areas were identified as 137.9–159.5 $m^2\,g^{-1}$. Hydrotalcite-type precursors were prepared by coprecipitation using metal nitrates of $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, and $Al(NO_3)_3 \cdot 9H_2O$ with designed molar ratio.

6.9 and 14 wt % Cu/Al_2O_3, as comparison samples, were also prepared by incipient wetness impregnation and calcination at 650 °C for 1 h in air.

XRD patterns of the $[Ni_{0.3}Cu_{0.2}Mg_{2.5}Al(OH)_8]1/2CO_3 \cdot 2H_2O$ precursor and those calcined in 5% H_2/95% N_2 and in air are arranged in Figure 1. The catalyst, which was calcined in air, was confirmed to have the crystal structures of spinel-type oxide (Mg or Ni or Cu)Al_2O_4 and MgO (Figure 1a). The other one, which was calcined in 5% H_2/95% N_2, was confirmed to have the crystal structures of a Ni–Cu alloy, spinel-type oxide, and MgO, clearly (Figure 1b). 14 wt % Cu/Al_2O_3 was confirmed to have the crystal structures of CuO and Al_2O_3 (Figure 1c).

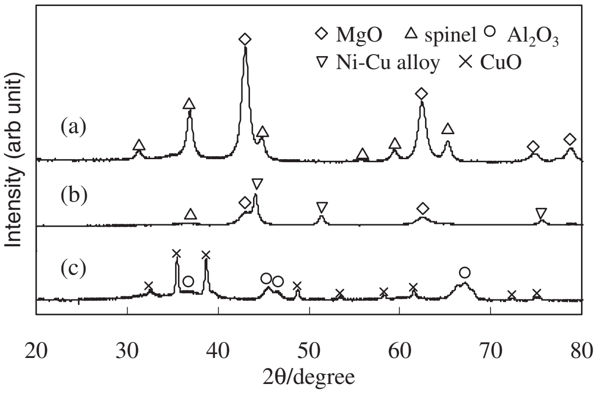

Figure 1. XRD patterns of the calcined $[Ni_{0.3}Cu_{0.2}Mg_{2.5}Al(OH)_8]1/2CO_3 \cdot 2H_2O$ hydrotalcite type precursors in air (a), 5% H_2/95% N_2 (b) and 14 wt % Cu/Al_2O_3 prepared in air (c).

Figure 2 shows XRD patterns of the Ni–Cu alloys (a) and lattice parameters (b) of $Ni_{0.5-x}Cu_x/2MgO \cdot 1/2MgAl_2O_4$ ($0 \leqq x \leqq 0.4$) catalysts. From the calculation by the Scherrer equation, crystallite sizes of Ni–Cu alloys were identified as 12.7–17.2 nm scale. The peak and lattice parameter of the Ni–Cu alloy shift toward Cu with an increase of pure Cu content in Ni-to-Cu molar ratio, and there is a linear relationship between the lattice parameter and Cu molar ratio in alloy. These results indicate that the Ni–Cu alloys, which were synthesized by a typical coprecipitation method and calcinations in reducing atmosphere, have a solid-solution phase all over the chemical compositions.

Figure 3 shows FE-SEM images of the $Ni_{0.5}/2MgO \cdot 1/2MgAl_2O_4$ and the $Ni_{0.3}Cu_{0.2}/2MgO \cdot 1/2MgAl_2O_4$. White points indicate Ni metals or Ni–Cu alloys in images. FE-SEM images clearly showed that Ni–Cu alloys are supported on oxides and smaller than Ni metals.

We evaluated the catalytic performance of the $Ni_{0.3}Cu_{0.2}/2MgO \cdot 1/2MgAl_2O_4$ and the 6.9 wt % Cu/Al_2O_3 by using the NO–CO reaction. The 6.9 wt % Cu/Al_2O_3 and the $Ni_{0.3}Cu_{0.2}/2MgO \cdot 1/2MgAl_2O_4$ contain the same amount of Cu. NO–CO reaction was carried out on the flow of NO 2000 ppm, CO 2000 ppm, and N_2 balance with GHSV = ca. 190000 h^{-1}. Each sample was pretreated in oxidation (Air/Fuel (A/F) = 15.2 in Table 1) or reducing atmosphere (A/F = 14.0 in Table 1) at 600 °C for 20 min before the evaluation. The NO conversion curve of the 6.9 wt % Cu/Al_2O_3 shifted to higher temperature

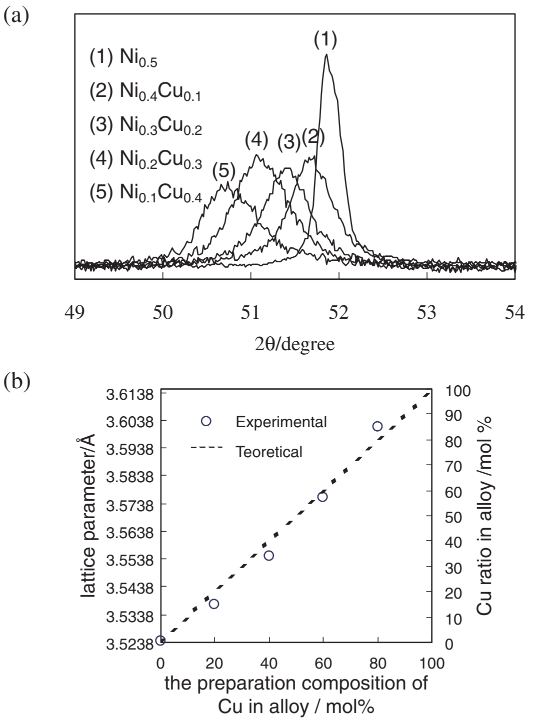

Figure 2. XRD patterns (a) and lattice parameters (b) of Ni–Cu alloys in $Ni_{0.5-x}Cu_x/2MgO\cdot1/2MgAl_2O_4$ ($0 \leqq x \leqq 0.4$) catalysts. The theoretical line was drawn by the lattice parameters of pure Cu and Ni quoted those of JCPDS card No. 04-0836 and 04-0850.

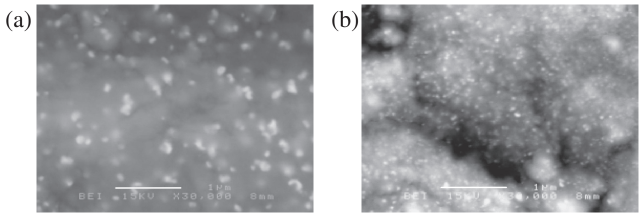

Figure 3. FE-SEM images of $Ni_{0.5}/2MgO\cdot1/2MgAl_2O_4$ (a) and $Ni_{0.3}Cu_{0.2}/2MgO\cdot1/2MgAl_2O_4$ (b). The bar in each image represents the scale of 1 µm.

Table 1. Composition of simulated model gas

A/F	Gas concentration/ppm[a]					
	CO	C_3H_6	C_3H_8	O_2	NO	CO_2
14.0	9333	500	133	1900	1700	80000
14.4	9333	500	133	4500	1700	80000
14.5	9333	500	133	5600	1700	80000
14.6	9333	500	133	6700	1700	80000
14.7	8000	500	133	7500	1700	80000
15.2	4000	500	133	9900	1700	80000

[a] 4% water vapor was added in each gas for evaluation.

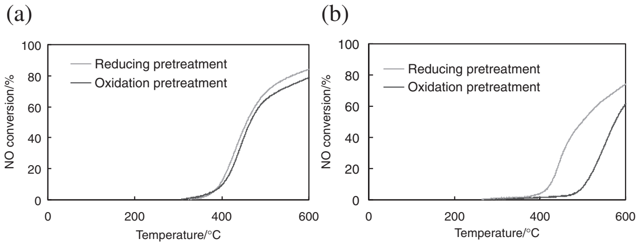

Figure 4. NO conversions of $Ni_{0.5}/2MgO\cdot1/2MgAl_2O_4$ (a) and 6.9 wt% Cu/Al_2O_3 (b) for NO–CO reaction after pretreatment.

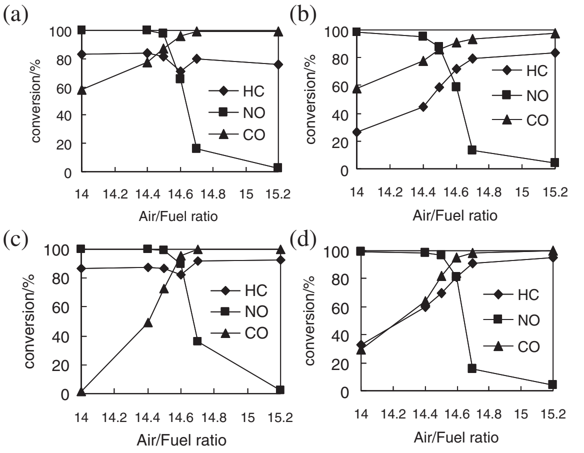

Figure 5. The catalytic performance of $Ni_{0.3}Cu_{0.2}/2MgO\cdot1/2MgAl_2O_4$ (a, c) and 14 wt% Cu/Al_2O_3 (b, d) at 600 °C. But (c, d) were evaluated on the flow of model gas without H_2O.

after pretreatment in oxidation atmosphere (Figure 4b). On the other hand, the NO conversion curve of the $Ni_{0.3}Cu_{0.2}/2MgO\cdot1/2MgAl_2O_4$ catalyst showed a little change after pretreatment in oxidation atmosphere and higher than the one of a pure Cu catalyst (Figure 4a). When Fe, Mn, Ni, and Cu are exposed in oxidation atmosphere, they are easily deactivated. But these results suggest that it is possible to suppress the surface oxidation of active metals by alloying. This oxidation resistance of active metals is a very important characteristic for automotive catalysts, because the composition of automotive exhaust gas is frequently changed in oxidation and reduction according to operating condition. We also evaluated the catalytic performance of the $Ni_{0.3}Cu_{0.2}/2MgO\cdot1/2MgAl_2O_4$ and the 14 wt% Cu/Al_2O_3 by using model gases with GHSV = ca. 190000 h^{-1} simulated automotive exhaust at 600 °C. Model gases were composed of O_2, CO, NO, CO_2, C_3H_6, C_3H_8, and H_2O with N_2 as carrier gas. Compositions of gases for each A/F are summarized in Table 1. Each sample was pretreated in reducing atmosphere (A/F = 14.0 in Table 1) at 600 °C for 10 min before the evaluation. Figures 5a and 5b show the results of mentioned two catalysts on the flow of model gas of Table 1, and Figures 5c and 5d are the results that were evaluated in the flow of model gas without H_2O. As shown in Figure 5a, in reducing atmosphere from A/F = 14.0 to 14.5, the $Ni_{0.3}Cu_{0.2}/2MgO\cdot1/2MgAl_2O_4$ showed high HC and NO conversion of over 80% and over 98%. On the other hand, the 14 wt% Cu/Al_2O_3 showed the HC conversion from 26% to 72% and the NO conversion from 98% to 88% at from A/F = 14.0 to 14.5 (Figure 5b). This suggests that the $Ni_{0.3}Cu_{0.2}/2MgO\cdot1/2MgAl_2O_4$ has higher catalytic activity for HC and NO conversion than Cu catalyst in reducing atmosphere below A/F = 14.5. Although there is no description on activity of pure Ni in this paper, the $Ni_{0.5}/2MgO\cdot1/2MgAl_2O_4$ catalyst has almost no activity for simulated model gases. The catalytic activity was dramatically improved by alloying with Ni and Cu, we guessed that high HC conversion of the $Ni_{0.3}Cu_{0.2}/2MgO\cdot1/2MgAl_2O_4$ was due to Ni in the alloy. Ni-Based catalysts are well known as reforming catalysts and have been used commercially.[9–11] Therefore, we evaluated the catalytic performance without H_2O by using the same catalysts in order to verify the reaction of HC conversion. Figures 5c and 5d show the evaluation results of the $Ni_{0.3}Cu_{0.2}/2MgO\cdot1/2MgAl_2O_4$ and the 14 wt% Cu/Al_2O_3 on the flow of model gas without H_2O. As a result, except for CO conversion, catalytic activities of both catalysts increased more than those of evaluation with H_2O. From these results, we obtained important knowledge. First, it seems that the high HC conversion of the $Ni_{0.3}Cu_{0.2}/2MgO\cdot1/2MgAl_2O_4$ is not caused by the steam-reforming reaction but oxidation or partial oxidation[12,13] of HC. As shown by Figures 5a and 5c, HC conversion maintained almost the same value regardless of H_2O in HC conversion below $A/F = 14.5$. Second, water–gas shift reaction occurred on the the $Ni_{0.3}Cu_{0.2}/2MgO\cdot1/2MgAl_2O_4$ similar to Cu-based catalyst.[14,15] In comparison of CO conversion in between $A/F = 14.0$ and 14.5 of Figures 5a and 5c, there was a large difference on CO conversion depending on addition of H_2O. At the case of the 14% Cu/Al_2O_3, a similar result was obtained from the comparison of Figures 5b and 5d.

In summary, we succeeded in the synthesis of highly dispersed Ni–Cu alloys with crystallite sizes of 12.7–17.2 nm supported on Mg–Al mixed oxide catalysts by coprecipitation and calcination in reducing atmosphere. The synthesized $Ni_{0.3}Cu_{0.2}/2MgO\cdot1/2MgAl_2O_4$ showed higher activity regardless of pretreatment in oxidation atmosphere on the NO–CO reaction and high catalytic performance for hydrocarbon in reducing atmosphere evaluation on the evaluation by using model gases simulated automotive exhaust.

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