Promoting effect of $NiAl_2O_4$ for supported Ni particles on sprayed Ni/Al_2O_3 catalysts

Nobuyuki Ichikuni*, Daiya Murata, Shogo Shimazu and Takayoshi Uematsu

Department of Materials Technology, Faculty of Engineering, Chiba University, Inage-ku, Chiba 263-8522, Japan
E-mail: ichikuni@tc.chiba-u.ac.jp

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Ni/Al_2O_3 catalysts were prepared by the spray reaction method. The NiO particles supported on $NiAl_2O_4$ were stabilized against the aggregation and converted into smaller Ni particles by H_2 reduction. The Ni particles stabilized on $NiAl_2O_4$ marked anomalous high activity for CO hydrogenation, due to the stronger interaction between Ni and $NiAl_2O_4$.

Keywords: promoting effect, Ni/Al_2O_3, spray catalyst, CO hydrogenation, EXAFS, TEM

1. Introduction

Various techniques have been applied to the preparation of supported metal catalysts, since the catalytic performance largely depends on the preparation procedure and the pretreatment. The spray reaction (spr) method is an excellent method for the syntheses of multicomponent ceramic powders and catalysts [1–6]. The sprayed particles may have the following characteristics: (1) the facile formation of not only single oxide but also various components consisting of multicomponent oxides and (2) a high miscibility of those components.

In the case of the Ni and Al binary component system, $NiAl_2O_4$ was inevitably produced. $NiAl_2O_4$ was hardly reduced by H_2 and hence thought to be an inert component. However, Bolt et al. recently reported that a discontinuous interfacial layer of $NiAl_2O_4$ slowed down the sintering of nickel metals on α-Al_2O_3 [7]. Nevertheless, it is still unclear whether the surface morphology of supported Ni is affected by the formation of aluminate and whether the aluminate does enhance the catalysis.

In this work, Ni/Al_2O_3 catalysts were prepared by the spr method and characterized. The structural effect on catalysis in CO hydrogenation was also investigated.

2. Experimental

2.1. Catalyst preparation

Ni/Al_2O_3 catalysts were prepared by the spray reaction method [5,6] using an aqueous solution of $Ni(NO_3)_2\cdot 6H_2O$ and $Al(NO_3)_3\cdot 9H_2O$. The catalyst was denoted with Ni molar concentration in percent, such as spr15. The pretreatment reduction temperature was presented in parentheses as spr15 (623 K), if needed.

2.2. Characterization

Cu Kα X-ray diffraction (XRD) measurements were performed with a MXP-3 (MAC Science Co., Ltd.). The mean crystallite sizes of NiO and Ni were determined from the fwhm of the XRD peaks using the Sherrer's equation. Temperature-programmed reduction (TPR) was carried out by monitoring the hydrogen consumption at a heating rate of 10 $K\,min^{-1}$. The surface structure of the catalyst was observed by transmission electron microscopy (TEM) operated at an accelerating voltage of 400 kV (JEOL, JEM-4000 FXII). Ni K-edge EXAFS spectra were collected at BL-10B of the PF (KEK) with a Si(311) channel cut monochromator (Proposal No. 97G001).

2.3. CO hydrogenation

CO hydrogenation was carried out in a closed circulating system equipped with a GC. The catalyst was treated with 16 kPa of oxygen at 573 K for 30 min, and 16 kPa of hydrogen at 623 or 773 K for 1 h, followed by the evacuation at the reduction temperatures for 30 min before use. The initial pressures of CO and H_2 were regulated to 6.7 and 20 kPa, respectively. Reaction products were separated by 2 m Unibeads C at 353 K and detected by TCD. The activity of the catalyst was determined from the initial rate of CH_4 formation.

3. Results and discussion

The XRD patterns for the as-sprayed catalysts showed the presence of NiO and $NiAl_2O_4$. The NiO crystallite sizes determined from the fwhm of the NiO(200) peak (table 1) were considerably small ($<$8 nm) indicating that the NiO in the as-sprayed catalyst was finely dispersed. The XRD peaks corresponding to the nickel aluminate appeared between those for the stoichiometric $NiAl_2O_4$ and

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[*] To whom correspondence should be addressed.

Table 1
Activities for CO hydrogenation and crystallite sizes of sprayed catalysts.

Catalyst	Crystallite size (nm)		H_{ad}[a]	r_0[b]	TOF[c]
	NiO[d]	Ni[e]	(10^{-5} mol g_{cat}^{-1})	(10^{-5} mol min^{-1} g_{cat}^{-1})	(min^{-1})
spr15	5.3				
spr15 (623 K)		8.2	0.65	0.66	1.0
spr30	6.9				
spr30 (623 K)		5.5	9.5	8.1	0.83
spr30 (773 K)		7.7	2.9	4.7	1.6
spr50	7.3				
spr50 (623 K)		7.3	7.6	6.2	0.81
spr50 (773 K)		16	4.1	5.8	1.4

[a] Amount of irreversibly adsorbed H_2 at 273 K.
[b] Initial rate of CH_4 formation at 513 K, $P(CO) = 6.7$ kPa, $P(H_2) = 20$ kPa.
[c] Normalized by the amount of H_2 adsorption.
[d] Determined from the NiO(200) peak.
[e] Determined from the Ni(101) peak.

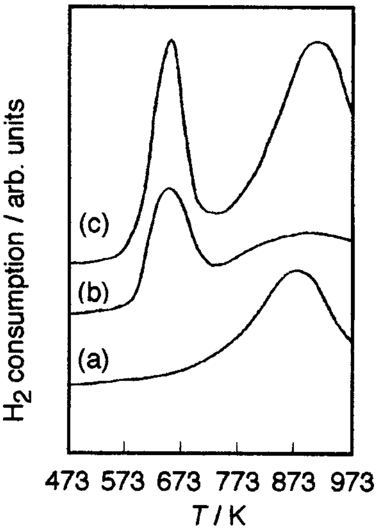

Figure 1. TPR profiles of sprayed Ni/Al_2O_3 catalysts: (a) spr15, (b) spr30 and (c) spr50.

γ-Al_2O_3. The nickel aluminate peak shifted lower to become closer to that of the stoichiometric $NiAl_2O_4$ with increasing the Ni concentration. In other words, the nickel aluminate in the sprayed catalysts is the non-stoichiometric form.

TPR profiles for spr15, spr30 and spr50 are shown in figure 1. In the cases of spr30 and spr50, two peaks at about 650 and 923 K were observed. Since the reduction temperature of a commercial NiO was reported at about 573 K [8], the first peak can be assigned to the reduction of nickel oxide weakly-interacted with the support. The second peak may indicate the reduction of non-stoichiometric nickel aluminate or nickel oxide strongly-interacted with the support. In the previous TPR study on the reducibility of nickel aluminate, a high temperature above 1073 K was required to reduce the stoichiometric $NiAl_2O_4$ [8] and the peak at about 1025 K was interpreted as the reduction of non-stoichiometric nickel aluminate in Ni/γ-Al_2O_3 [9]. The second peak appearing at 873 K did not agree with these species. A TPR peak assigned to the reduction of the amorphous overlayer of NiO has been observed at 850 K [9], while the peak corresponding to the nickel oxide interacted with the support has been observed at 778 K for $Ni/NiAl_2O_4$ [7]. XRD measurement of spr50 (773 K) could detect a broad peak corresponding to nickel oxide, suggesting the presence of the strongly-interacted NiO up to 773 K. Moreover, we observed no Al_2O_3 peaks but Ni and NiO peaks from XRD patterns for spr50 (773 K), which means that $NiAl_2O_4$ was not reduced and some NiO was reduced to Ni and the other still remained in the NiO phase. The second peak can be assigned to the reduction of the nickel oxide strongly-interacted with the aluminate support. For spr15, only one TPR peak was observed. This peak essentially corresponds to the second peak on the TPR curves of spr30 and spr50. It reveals that there is a critical content between 15 and 30 mol% for the formation of less-interacted NiO.

Though a remarkable growth of Ni metal was observed for spr50 by the reduction at 773 K, the size of Ni species was almost unchanged by the reduction at 623 K, as shown in table 1. TEM observation confirmed that large Ni particles (>16 nm) are present on spr50 (773 K), whereas the most particles remained small (<10 nm) on spr50 (623 K). This particle growth was caused by the aggregation of nickel under the high-temperature reduction.

It is interesting that both the large and the small Ni particles were observed on spr50 (773 K). In other words, the catalysts seemed to involve the two types of NiO from the TPR analysis. One was the NiO weakly-interacted and the other was the NiO strongly-interacted with the support.The former species easily aggregate to produce larger Ni particles while the latter did not glow by the high-temperature reduction at 773 K. The small particles observed in spr50 (773 K) were generated from the NiO strongly-interacted with the support.

Hence the as-sprayed Ni/Al_2O_3 catalyst had a high miscibility among NiO, non-stoichiometric $NiAl_2O_4$ and Al_2O_3, there seemed to exist the discontinuous interfacial

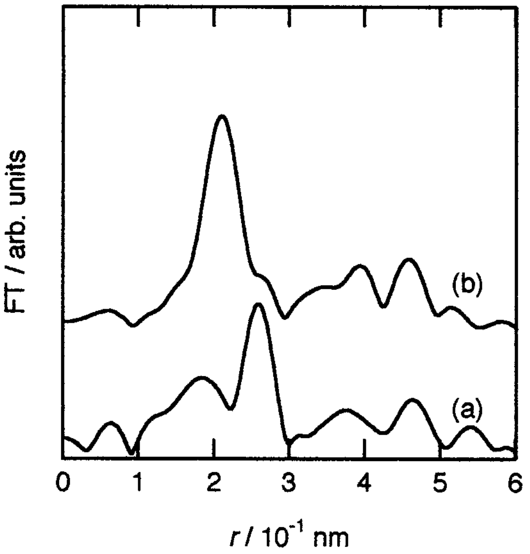

Figure 2. Fourier transforms of k^3-weighted Ni K-edge EXAFS oscillation of spr Ni/Al_2O_3 catalysts: (a) spr50 (623 K) and (b) spr50 (773 K).

layer of $NiAl_2O_4$. Thus, the small Ni particles, Ni(S), may be produced from the strongly-interacted NiO on non-stoichiometric $NiAl_2O_4$ that can provide a stabilizing effect of Ni metal, while large Ni particles, Ni(L), may be produced from the weakly-interacted NiO on Al_2O_3.

Figure 2 shows the Fourier transforms of the k^3-weighted EXAFS oscillations. The catalysts reduced at 623 K showed weak Ni metal peak besides to NiO peaks on XRD patterns. It was suggested that the catalysts reduced at 623 and at 773 K were composed of mainly NiO + $NiAl_2O_4$ and Ni + $NiAl_2O_4$, respectively. Thus, a curve fitting (CF) analysis was carried out for the spr50 (623 K) main peak using bulk NiO. The main peak of the spr50 (773 K) catalyst was reproduced using Ni foil as a reference compound. CF analysis of the spr50 (773 K) catalyst revealed that the coordination number, CN (and Debye–Waller factor), of Ni–Ni was 7.7 (0.079). Bond length of Ni–Ni was almost the same as for Ni metal.

The CN and the bond length for Ni–(O)–Ni coordination in spr50 (623 K) were determined as 6.4 and 0.294 nm, respectively. A higher reduction temperature (773 K) might not induce any serious aggregation of Ni clusters, since the CN of Ni–Ni for spr50 (773 K) was determined as 7.7. This result also suggests that the NiO supported by $NiAl_2O_4$ was stabilized against aggregation and maintained its higher dispersion.

The results for the CO hydrogenation reaction are shown in table 1. The activity of CO hydrogenation was usually normalized by the amount of hydrogen adsorption. So the number of active sites was estimated by the hydrogen chemisorption at 273 K. The TOF of spr50 (773 K) was nearly twice as high as that of spr50 (623 K). The Ni particles on spr30 (623 K) and spr50 (623 K) were produced from the weakly-interacted NiO. Thus, the increase in TOF was caused by the presence of Ni(S) due to the strongly-interacted NiO. It can be said that the stabilized Ni particles on non-stoichiometric $NiAl_2O_4$ showed higher activity to CO hydrogenation than the weakly-stabilized Ni particles on Al_2O_3 did. The mechanism of promoter effects is left still unknown, but it can be indicated that the aluminate did enhance the catalysis in the spr Ni/Al_2O_3 catalysts.

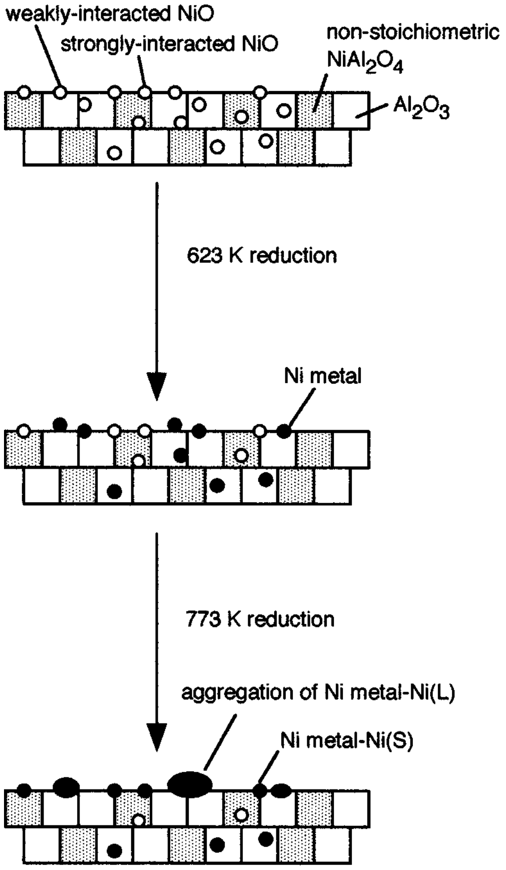

Figure 3. Schematic model of spr50 Ni/Al_2O_3 catalyst.

As is schematically summarized for spr50 in figure 3, as-sprayed catalyst consists of nickel oxide, nickel aluminate and alumina. The nickel oxide appears in two forms: one is the weakly-interacted with the support, the other was the strongly-interacted which locates on the nickel aluminate support. Only the weakly-interacted NiO was reduced by the H_2 reduction at 623 K. While by the reduction at 773 K, the aggregation of Ni species took place to produce Ni(L) and small Ni particles appeared which were produced from the strongly-interacted NiO. The latter Ni particles enhanced the activity for CO hydrogenation.

4. Conclusion

Ni/Al_2O_3 catalysts were prepared by the spray reaction method. TPR showed the two main peaks due to the NiO weakly-interacted and the NiO strongly-interacted with the support, which were located on Al_2O_3 and non-stoichiometric $NiAl_2O_4$, respectively. The latter Ni particles still retained their smaller size after high-temperature reduction (773 K). $NiAl_2O_4$ provided stabilizing effects to prevent the aggregation of Ni particles. The stabilized Ni particles on $NiAl_2O_4$ showed higher activity to CO hydrogenation than the weakly-stabilized Ni particles on Al_2O_3 did.

References

[1] J.G.M. de Lau, Am. Ceram. Soc. Bull. 46 (1970) 572.

[2] D.M. Roy, R.R. Neurgaonkar, T.P. O'holleran and R. Roy, Am. Ceram. Soc. Bull. 56 (1977) 1023.

[3] T.J. Gardner and G.L. Messing, Am. Ceram. Soc. Bull. 63 (1984) 1498.

[4] E.I. Tiffée and K. Seitz, Am. Ceram. Soc. Bull. 66 (1987) 1384.

[5] D. Li, N. Ichikuni, S. Shimazu and T. Uematsu, Appl. Catal. A 172 (1998) 351.

[6] D. Li, N. Ichikuni, S. Shimazu and T. Uematsu, Appl. Catal. A 180 (1999) 227.

[7] P.H. Bolt, F.H.P.M. Habraken and J.W. Geus, J. Catal. 151 (1995) 300.

[8] J.M. Rynkowski, T. Paryjczak and M. Lenik, Appl. Catal. A 126 (1995) 257.

[9] J.A. Peña, J. Herguido, C. Guimon, A. Monzón and J. Santamaría, J. Catal. 159 (1996) 313.