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Application of NiO–Al_2O_3 aerogels to the CO_2-reforming of CH_4[†]

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$Ni(NO_3)_2$ and $Ni(CH_3COO)_2$ were dispersed on AlOOH aerogels by supercritical drying and the activity of the resultant NiO–Al_2O_3 aerogels was investigated for the CO_2-reforming of CH_4. The aerogels showed higher and more stable activity for the reforming than an impregnation catalyst. X-ray diffraction analysis and temperature-programmed reduction suggested that fine nickel particles were formed on the aerogels with high dispersion and that they interacted strongly with alumina aerogel supports. The high performance of the aerogels was attributed to the fine nickel particles. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: nickel; aerogels; carbon dioxide; reforming of methane; X-ray

INTRODUCTION

An efficient use of greenhouse-effect gases CH_4 and CO_2 as a source of carbon is a central issue in heterogeneous catalysis. Supported nickel catalysts are used industrially for the reforming because of high activity, long-term stability and low cost. However, nickel is prone to deactivation caused by carbon formation via CH_4 decomposition and CO disproportionation, leading to the plugging of the reactor tube.[1] Considerable efforts have been concentrated on exploring catalysts that are resistant to carbon formation even at or near stoichiometric reactant ratios. A sulfur-passivated nickel[2] and noble metals[3] have been found to show resistance to carbon formation; however, the low activities of the sulfur-passivated nickel and high costs and limited availability of the noble metals have prevented the application. In previous papers, we developed carbon-free reforming nickel catalysts, the novel NiO–Al_2O_3 aerogels, prepared from cyclic nickel glycoxide, $(CH_2O)Ni$, and boehmite sol, AlOOH, by the sol-gel technique and subsequent supercritical drying.[4,5] In the aerogels, nickel ions were considered to be incorporated in γ-Al_2O_3 by replacing some parts of aluminium ions with nickel ones, i.e. nickel aluminate was considered to be formed throughout the aerogels. As a result, fine nickel particles appeared after reduction throughout the aerogel with high dispersion, which brought about not only higher activity but also much less activity for coking than impregnation catalysts.

Here, in order to explore simple methods for synthesizing NiO–Al_2O_3 aerogels, $Ni(NO_3)_2$ and $Ni(CH_3COO)_2$ are dispersed on AlOOH aerogels by supercritical drying. The catalyst performance of the resultant NiO–Al_2O_3 aerogels was examined in comparison with an impregnation NiO–Al_2O_3 catalyst. For the impregnation catalyst, Al_2O_3 aerogel was used as a catalyst support.

EXPERIMENTAL

The method for preparing AlOOH gel from aluminium triisopropoxide was described in previous papers.[4,5] After water, nitric acid, urea and isopropyl alcohol present in the gel were replaced with ethanol by dipping the gel in ethanol for 3 days, 0.1 and 0.02 mol of the gel was respectively impregnated in $Ni(NO_3)_2\cdot 6H_2O$–C_2H_5OH (2.81 g–200 ml) and in $Ni(CH_3COO)_2\cdot 4H_2O$–C_2H_5OH (0.50 g–200 ml) for 1 day. Then, ethanol only was removed by supercritical drying according to the schedule reported previously.[4,5] After supercritical

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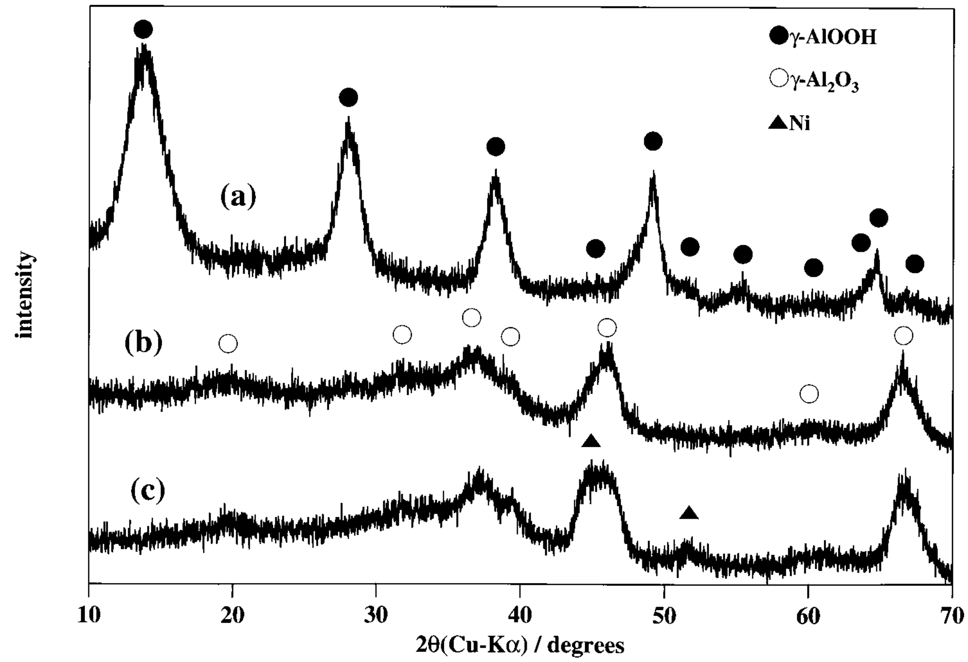

Figure 1 XRD spectra of (a) $Ni(NO_3)_2$–AlOOH aerogel after supercritical drying, (b) NiO–Al_2O_3 aerogel after calcination of $Ni(NO_3)_2$–AlOOH aerogel at 773 K for 4 h, and (c) Ni–Al_2O_3 aerogel after reduction of NiO–Al_2O_3 aerogel with hydrogen at 1073 K for 3 h.

drying, the aerogels were calcined in air at 773 K for 4 h. Before the reforming reactions, the aerogels were reduced with hydrogen (30 ml min^{-1}) at 1073 K for 3 h. For comparison, 10 wt% Ni–Al_2O_3 catalyst was prepared by impregnating Al_2O_3 aerogel (3 g) in an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (1.65 g) followed by drying and subsequently calcining at 773 K for 3 h.

Thermogravimetry (TG; Shimadzu, TGA-50) and differential thermal analysis (DTA; Shimadzu, DTA-50) were performed in air at a constant ramping rate of 5 K min^{-1}. Crystalline phases of aerogels were identified using a powder X-ray diffractometer (XRD; Rigaku, RAD-1VC) with a copper tube operated at 30 kV and 20 mA. Reduction of NiO to nickel in NiO–Al_2O_3 aerogels was investigated by temperature-programmed reduction (TPR): *ca* 25 mg of sample was put in a quartz tube (i.d. 4 mm) and the temperature was ramped at 5 K min^{-1} to 1273 K in hydrogen–argon carrier gas (5:95, 30 ml min^{-1}). The hydrogen consumption was continuously monitored by gas chromatography with a thermal conductivity detector (Shimadzu, GC-8A). BET surface area was measured by a nitrogen adsorption apparatus (Japan Bel, Belsorp 28 SP) at liquid-nitrogen temperature. Hydrogen gas adsorption was measured by a conventional pulse adsorption technique in argon carrier gas using gas chromatography with a thermal conductivity detector. Nickel loading in the catalysts was measured by atomic absorption (Shimadzu, AA-610).

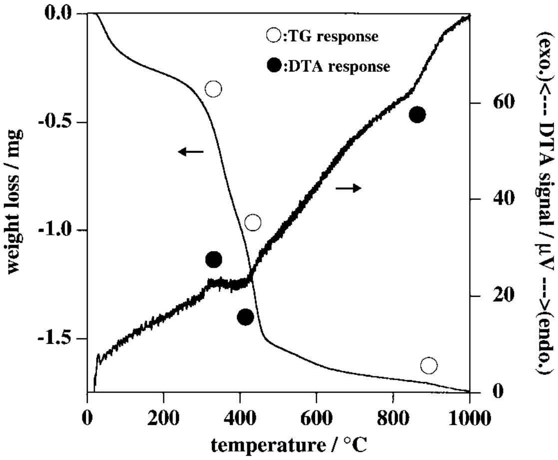

Figure 2 TG and DTA of $Ni(NO_3)_2$–AlOOH aerogel in air.

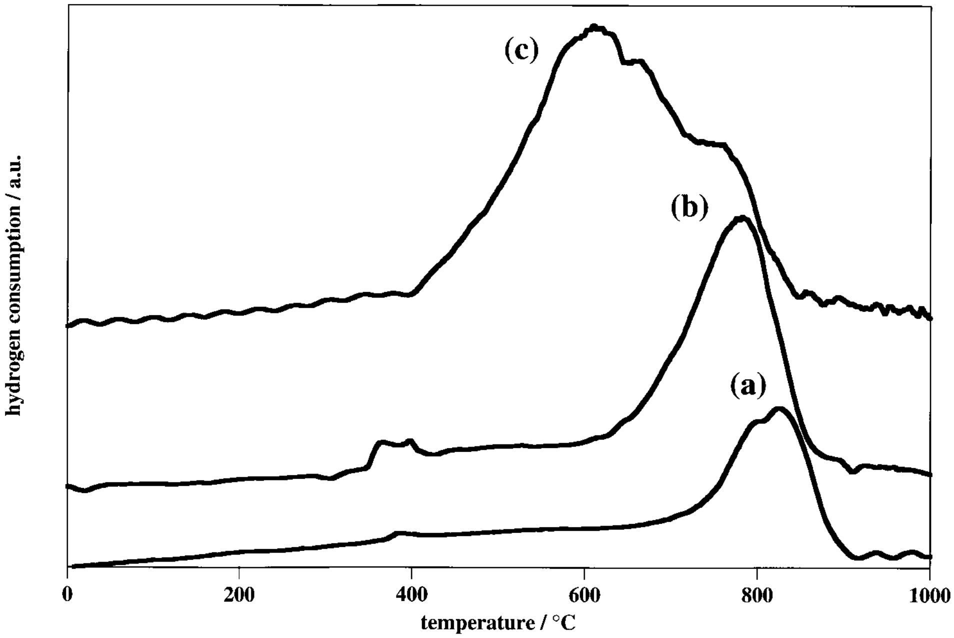

Figure 3 TPR of (a) NiO–Al_2O_3 aerogel from $Ni(NO_3)_2$ (25.4 mg), (b) NiO–Al_2O_3 aerogel from $Ni(CH_3COO)_2$ (24.9 mg), and (c) NiO–Al_2O_3 impregnation catalyst (25.3 mg).

Continuous flow reaction of CH_4–CO_2 (1:1, 60 ml min^{-1}) was carried out using a conventional fixed-bed flow reactor (i.d. 4 mm) under atmospheric pressure at 1073 K for 24 h. The effluent gases were analysed by gas chromatography with a thermal conductivity detector. The CH_4–CO_2 reforming was also investigated under the differential reactor conditions and the specific activity r/s^{-1} was calculated by dividing the rate of total CH_4 conversion with the amount of H_2 adsorbed:

$$r = \frac{\mathrm{CH_4\ conversion\ rate}\ (\mu\mathrm{mol\ s^{-1}\ g^{-1}})}{\mathrm{H_2\ adsorption}\ (\mu\mathrm{mol\ g^{-1}}) \times 2}$$

Carbon formation during CH_4–CO_2 (1:1, 40 ml min^{-1}) was investigated by TG.

RESULTS AND DISCUSSIONS

Figure 1(a) shows XRD spectrum of $Ni(NO_3)_2$–AlOOH aerogel after supercritical drying. The crystalline phase was assigned to γ-AlOOH only and no nickel-containing phases were detected. This suggests that nickel nitrate was highly dispersed on AlOOH aerogel.

Figure 2 shows the TG–DTA spectrum of $Ni(NO_3)_2$–AlOOH aerogel in air. A significant weight decrease and the corresponding exothermal peak were observed at *ca* 320 °C, indicating that organic compounds like ethanol remaining in the aerogel were burned at that temperature. After the combustion, a further weight decrease corresponding to an endothermal peak was observed at *ca* 410 °C. This must be due to a structure change from γ-AlOOH to γ-Al_2O_3 by releasing 0.5 moles of H_2O per mole of AlOOH.[4] At this temperature, Ni-$(NO_3)_2 \cdot 6H_2O$ may also be decomposed to give NiO (or nickel aluminate) by releasing NO_x and H_2O. Phase transformation from γ- to δ-Al_2O_3 was observed at *ca* 850 °C, at which temperature a slight weight decrease and a corresponding endothermal peak were observed.

Figure 1(b) shows the XRD profile of the aerogel after calcination of $Ni(NO_3)_2$–AlOOH aerogel. The calcined aerogel exhibited the γ-Al_2O_3 phase only and no nickel-containing phases were observed. Since the XRD profile for $NiAl_2O_4$ is almost the same as that for γ-Al_2O_3, nickel atoms in the aerogels are considered to be incorporated in the γ-Al_2O_3 structure by forming nickel aluminate.

TPR profiles are shown in Fig. 3. The reduction of NiO to nickel was observed at *ca* 800 °C for

Table 1 Characterization of Ni–Al_2O_3 aerogels and Ni–Al_2O_3 impregnation catalyst

Precursor	Ni content (wt %)	H_2 ads. (μmol g^{-1})	BET[1] (m^2 g^{-1})	Ni crystallite size (nm)
$Ni(NO_3)_2$	3.8	14.1	289	2.9
$Ni(CH_3COO)_2$	6.2	33.9	268	4.1
Impregnation	11.7	43.3	182	5.7

[1] Surface areas of NiO–Al_2O_3 aerogels and NiO–Al_2O_3 impregnation catalyst.

NiO–Al_2O_3 aerogels, whereas the reduction was observed at *ca* 600 °C for NiO–Al_2O_3 impregnation catalyst. This also strongly suggests that nickel is incorporated in the alumina structure, i.e. aluminium ions in tetrahedral or octahedral sites are partially replaced with nickel ions. On the impregnation catalyst, on the other hand, nickel oxide may be located on the surface of the alumina support, thereby the reduction should proceed at a lower temperature. Fig. 1(c) shows the XRD pattern after the reduction of NiO–Al_2O_3 aerogel with hydrogen, which confirmed the appearance of the nickel phase. From the peak-broadening of Ni (200), the nickel crystallite size was estimated using Scherer's equation. The results are shown in Table 1. The nickel crystallite size was *ca* 2.9–4.1 nm, suggesting that fine nickel particles are formed on the aerogels after hydrogen reduction.

In Table 1, the concentrations of nickel in the catalysts are also shown. The nickel loading was 3.8 wt% and 6.2 wt% for the aerogels prepared from $Ni(NO_3)_2$ and $N(CH_3COO)_2$ respectively, indicating that not all of the nickel was incorporated in the aerogels. This is because 10 wt% Ni–Al_2O_3 should be obtained if all of nickel were incorporated. Therefore, some of the nickel salts were considered to remain in the autoclave after the supercritical drying. As for the impregnation catalyst, on the contrary, a slightly high value (11.7 wt%) was obtained. The BET surface area of NiO–Al_2O_3 aerogels was 268–289 m^2 g^{-1}, whereas the surface area was 182 m^2 g^{-1} for the impregnation catalyst (Al_2O_3 aerogel support, 259 m^2 g^{-1}).

Figure 4 shows the effect of time on stream on CH_4–CO_2 reforming at 1073 K. The aerogels exhibited higher activities than the impregnation catalyst and the deactivation was less significant on the aerogels than on the impregnation catalyst: the initial CH_4 conversion was 83.9% and 83.8% for the aerogels prepared from $Ni(NO_3)_2$ and $Ni(CH_3COO)_2$ respectively and the final conversions were 66.5% and 69.2%, whereas CH_4 conversion was changed from 66.7 to 47.5% on the impregnation catalyst.

The coking profiles during the reforming are shown in Fig. 5. The aerogels showed much less activities for coking than the impregnation catalyst, which must be a main cause for the retardation of catalyst deactivation. The suppression of coking is ascribed to the fine nickel particles formed on the

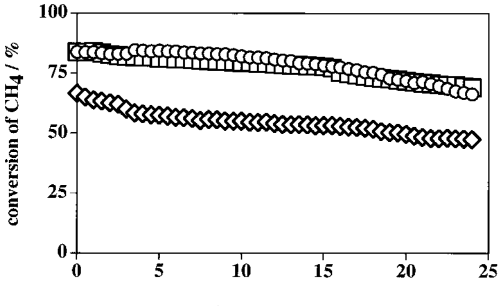

Figure 4 Effect of time on stream on CH_4–CO_2 (1:1, 60 ml min^{-1}) reaction at 1073 K for 24 h; ○: Ni–Al_2O_3 aerogel from $Ni(NO_3)_2$ (29.2 mg); □: Ni–Al_2O_3 aerogel from $Ni(CH_3COO)_2$ (29.8 mg); ◊: Ni–Al_2O_3 impregnation catalyst (31.1 mg).

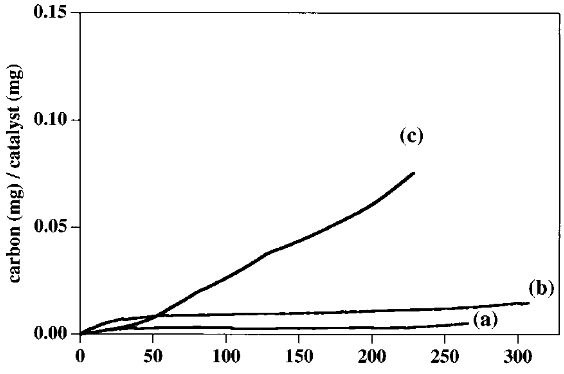

Figure 5 Carbon formation during CH_4–CO_2 (1:1, 40 ml min^{-1}) reaction at 1073 K on (a) Ni–Al_2O_3 aerogel from $Ni(NO_3)_2$ (20.4 mg), (b) Ni–Al_2O_3 aerogel from $Ni(CH_3COO)_2$ (12.1 mg), and (c) Ni–Al_2O_3 impregnation catalyst (21.0 mg).

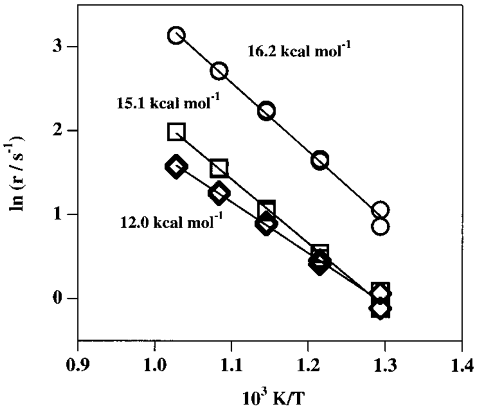

Figure 6 Arrhenius plots of specific activities and activation energies for CH_4–CO_2 (1:1, 60 ml min^{-1}) reaction under the differential reactor conditions; ○: Ni–Al_2O_3 aerogel from $Ni(NO_3)_2$ (10.3 mg); □: Ni–Al_2O_3 aerogel from $Ni(CH_3COO)_2$ (10.1 mg); ◇: Ni–Al_2O_3 impregnation catalyst (10.3 mg).

aerogels, which may inhibit carbon dissolution in the crystal and subsequent carbon nucleation.

The results of steady-state CH_4–CO_2 reforming under the differential reactor conditions are shown in Fig. 6. The specific activity was higher on the aerogels than on the impregnation catalyst, although the difference was small between the aerogel from $Ni(CH_3COO)_2$ and the impregnation catalyst. Between the aerogels, the activity was higher on the aerogel prepared from $Ni(NO_3)_2$ having finer nickel particles. This suggests that the reforming reaction is more enhanced on finer nickel particles. The enhancement of the reforming on fine nickel particles is also one of the causes for suppression of carbon formation during the reforming.

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