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Development of ultra-stable Ni catalysts for CO₂ reforming of methane

Keiichi Tomishige^{*}, Osamu Yamazaki, Yangguang Chen,
Kota Yokoyama, Xiaohong Li, Kaoru Fujimoto

Department of Applied Chemistry, School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

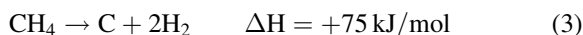
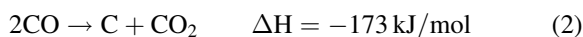
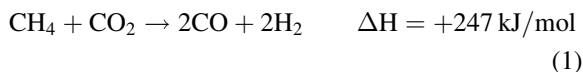
Abstract

Carbon deposition behavior in CO₂ reforming of methane, methane decomposition, and CO disproportionation on nickel-magnesia solid solution was investigated by means of thermogravimetric analysis and temperature programmed reaction of deposited carbon with carbon dioxide. It was found that rapid oxidation of CH_x on Ni surface by oxygen species from CO₂ through dissociation at metal-support interface is a key step for the inhibition of carbon formation. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Nickel-magnesia solid solution; CO₂ reforming of methane; Carbon deposition; Metal-support interface

1. Introduction

Carbon dioxide reforming of methane to synthesis gas has attracted much attention in recent years [1,2], because it is an important reaction via which the two most abundant carbon containing materials, methane as a main component of natural gas and carbon dioxide, are utilized effectively. This reforming reaction to synthesis gas has been proposed as one of the most promising techniques for utilization of these two gases.



It has been reported that the most serious problem in CO₂ reforming of methane is deactivation and destruction of catalysts caused by carbon deposition via CO disproportionation Eq. (2) and methane decomposition Eq. (3) [1,2]. Noble metal catalysts are found to be less sensitive to coking than nickel-based catalyst [3]. However, considering their high cost and limited availability, it is more desirable to develop nickel-based catalysts which are resistant to carbon deposition and have stable activity [4–11]. Recently we have reported that nickel-magnesia solid solution Ni_{0.03}Mg_{0.97}O has high and stable activity without carbon deposition for a long time (100 days) as shown in Fig. 1 [8–11]. In this report, we investigated the behavior of carbon deposition on this solid solution catalyst, MgO-supported Ni catalyst, and NiO-Al₂O₃ catalyst which was prepared by the similar method to nickel magnesite solid solution catalyst for the elucidation of formation and inhibition mechanism of carbon deposition.

^{*}Corresponding author. Tel.: +81-3-5689-0469; fax: +81-3-5689-0469; e-mail: tomi@hongo.ecc.u-tokyo.ac.jp

2. Experimental

Nickel-magnesia solid solution and $\text{NiO-Al}_2\text{O}_3$ catalysts were prepared by a coprecipitation method, in which the starting materials were $\text{Ni}(\text{CH}_3\text{COO})_2\cdot\text{Mg}(\text{NO}_3)_2$ and $\text{Ni}(\text{CH}_3\text{COO})_2\cdot\text{Al}(\text{NO}_3)_3$ mixed aqueous solution and K_2CO_3 as a coprecipitant, respectively. Nickel-magnesia solid solution and $\text{NiO-Al}_2\text{O}_3$ were prepared by being calcined at 1223 K for 10 h. Magnesia supported nickel catalysts (Ni/MgO) were prepared by impregnating MgO with $\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_2$ acetone solution. MgO was prepared by the same method as solid solution catalysts. The content of nickel is represented as a molar ratio ($\text{Ni}/(\text{Ni}+\text{Mg})$ or $\text{Ni}/(\text{Ni}+\text{Al})$). $\text{CH}_4\text{-CO}_2$ reaction was performed in a fixed bed flow reaction system, the product was analyzed by gas chromatograph. Catalysts were reduced with H_2 at 1123 K before introducing reactant gases ($\text{CH}_4/\text{CO}_2=1/1$). Thermogravimetric analysis (TGA) was performed by using TGD-7000 (ULVAC). The sample was held in a quartz basket. The reactant gas was CH_4/N_2 (25/75), CO/N_2 (25/75) and $\text{CH}_4/\text{CO}_2/\text{N}_2$ (25/25/50). Reaction conditions were as follows: a total flow rate of 80 ml min^{-1} , total pressure of 0.1 MPa, reaction temperature 773–1123 K, and catalyst weight is 0.1 g. The pretreatment of the sample is H_2 reduction at 1123 K for 0.5 h in a fixed bed flow reaction system. After this treatment, the sample was transferred from a microreactor to a quartz basket under atmosphere. Finally, the sample was re-reduced in situ with 5% H_2/He flow at 1123 K for 30 min in thermogravimetric system. The deposited carbon was also characterized by temperature programmed surface reaction (TPSR) with CO_2 . After a small amount of carbon was deposited on the catalyst via methane decomposition by TG monitoring, the samples were transferred to a fixed bed flow reactor under atmosphere and reacted with CO_2 at a heating rate of 10 K/min (temperature range: 300–1123 K), at 1123 K the temperature was maintained for 30 min after that. CO_2 flow rate was 50 ml/min. The product was only CO , which is analyzed by FID detector equipped with methanator. As a reference, we also investigated CO_2 TPSR profiles on reduced samples without exposition to air. The sample was reduced in fixed bed flow reactor. The amount of H_2 and CO adsorption was measured by volumetric method.

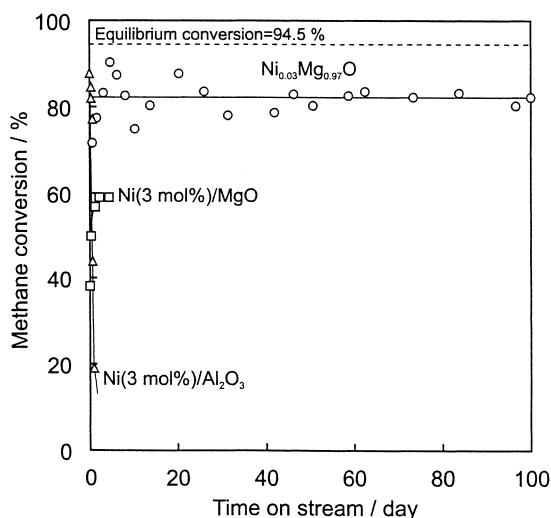


Fig. 1. Reaction time dependence of methane reforming with CO_2 on Ni-based catalysts. Reaction condition: reaction temperature 1123 K, $W/F=1.2\text{ g h/mol}$, $\text{CH}_4/\text{CO}_2=1/1$, catalyst weight: 0.1 g.

3. Results and discussion

Figs. 2–4 show TGA results on the samples under CH_4+CO_2 , CH_4 and CO at 773 K. Under CH_4+CO_2 reaction, no carbon deposition occurred on $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$ solid solution catalyst, but on $\text{NiO-Al}_2\text{O}_3$ (3 mol %) and 3 mol % Ni/MgO , amount of

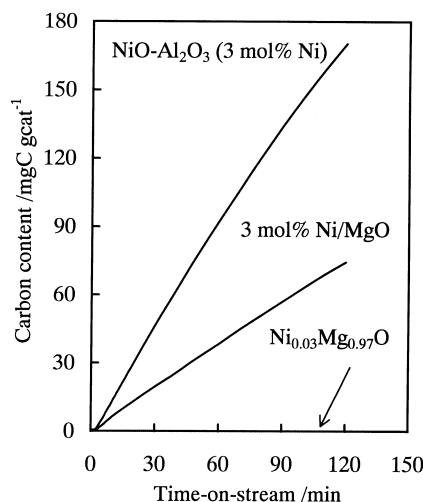


Fig. 2. TGA result of $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$, 3 mol % Ni/MgO and $\text{NiO-Al}_2\text{O}_3$ (3.0 mol %) under CH_4+CO_2 . Reaction temperature: 773 K, $\text{CH}_4/\text{CO}_2/\text{N}_2=25/25/50$, flow rate: 80 ml/min .

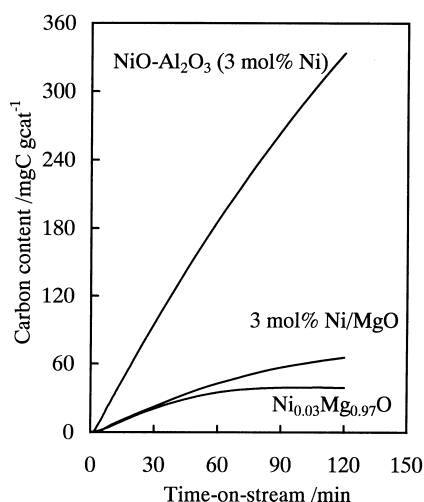


Fig. 3. TGA result of $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$, 3 mol % Ni/MgO and $\text{NiO-Al}_2\text{O}_3$ (3.0 mol %) under CH_4 . Reaction temperature: 773 K, $\text{CH}_4/\text{N}_2=25/75$, flow rate: 80 ml/min.

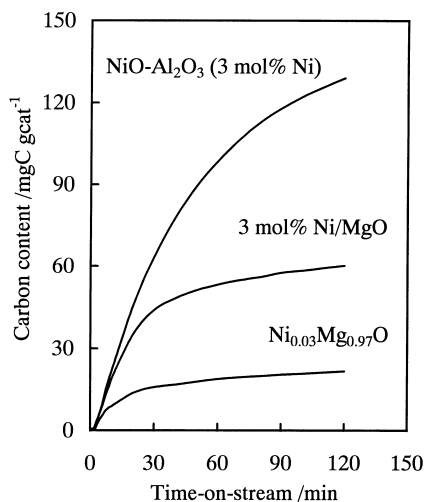


Fig. 4. TGA result of $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$, 3 mol % Ni/MgO and $\text{NiO-Al}_2\text{O}_3$ (3.0 mol %) under CO . Reaction temperature: 773 K, $\text{CO}/\text{N}_2=25/75$, flow rate: 80 ml/min.

deposited carbon was increased almost linearly with time on stream, and this indicated that deposited carbon is whisker-like carbon. It has been reported that the whisker carbon does not cause the catalyst deactivation [12]. Under CH_4 and CO flow condition, carbon deposition was observed even on $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$, the rate of carbon formation tends to be decreased with time on stream and finally reach the

saturation. This seems to be due to the reverse reaction of Eqs. (2) and (3). The amount of carbon formation from methane decomposition was larger than that from CO disproportionation. And under these conditions, the order of carbon formation rate is $\text{NiO-Al}_2\text{O}_3$ (3 mol %) $>$ 3 mol % Ni/MgO $>$ $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$. In addition, there seems to be some induction period for a few minutes at the initial stage.

The results of catalyst characterization and the comparison of initial reaction rate of carbon deposition is listed in Tables 1 and 2, respectively. $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$ catalyst was found to have nickel particles with high dispersion as reported previously [13]. $\text{NiO-Al}_2\text{O}_3$ (3 mol %) was found to have lower dispersion than $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$ and 3 mol % Ni/MgO had very low dispersion. TOF of CO formation was higher on the catalyst with lower dispersion. This corresponds to the ensemble size for methane dissociation. The rate difference between methane decomposition and CO_2 reforming of methane indicates an ability of CO_2 to inhibition of carbon formation. This order was $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$ $>$ 3 mol % Ni/MgO $>$ $\text{NiO-Al}_2\text{O}_3$ (3 mol %) as listed in Table 2. This tendency can be related to be surface basicity of support oxide and nickel particle size. Surface basicity is expected to be $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$ 3 mol % Ni/MgO $>>$ $\text{NiO-Al}_2\text{O}_3$ (3 mol %). This is probably because the surface basicity is much related to the activation of CO_2 . In addition, the order of CO_2 effect also corresponds to nickel dispersion, $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$ $>$ 3 mol % Ni/MgO . This corresponds to the distance between nickel surface and the metal-support interface.

Fig. 5(a)–(c) show the CO_2 TPSR profiles on the samples before and after carbon deposition. In the TPSR profile of $\text{NiO-Al}_2\text{O}_3$ (3 mol %), only a large peak was observed at about 800 K. This peak can be attributed to the deposited carbon. In the TPSR profiles of $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$ and 3 mol % Ni/MgO after the carbon deposition, the peak at about 800 K was also observed. On all these catalysts, the peak temperature of the reaction between carbon and CO_2 was almost the same, and this indicated that the reactivity of deposited carbon with CO_2 is the same regardless of catalysts. This can be explained by no interaction between catalyst surface and deposited carbon because of the morphology of whisker-like carbon. CO formation was observed at lower temperature 473–673 K only on the reduced sample. This may

Table 1
Catalyst properties

Catalyst	Amount of adsorption		D_{red}^c (%)	$D_{\text{isp.}}^d$ (%)	BET (m^2/g)	R_{CO}^e ($\mu\text{mol g}^{-1}$)	TOF ^f (s^{-1})
	H_2^a ($\mu\text{mol g}^{-1}$)	O_2^b					
$\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$	3.1	10.5	2.9	29.5	19	40	6.5
3.0 mol % Ni/MgO	3.9	226.5	62.4	1.7	16	160	20.5
$\text{NiO-Al}_2\text{O}_3$ (3.0 mol %)	7.6	78	27.0	9.7	85	166	10.9

^a Adsorption temperature: 298 K.

^b Adsorption temperature: 873 K.

^c Reduction degree of Ni estimated by $2 \times (\text{amount of } \text{H}_2 \text{ adsorption}) / (\text{total amount of Ni})$.

^d Dispersion of Ni estimated by $(\text{amount of } \text{H}_2 \text{ adsorption}) / (\text{amount of } \text{O}_2 \text{ adsorption})$.

^e Reaction condition: 0.1 MPa, $\text{CH}_4/\text{CO}_2=1/1$, 773 K, $W/F=0.1 \text{ g hmol}$.

^f TOF was calculated by amount of H_2 adsorption.

Table 2
Carbon formation rate at initial stage under CO_2 reforming of methane, and CH_4 decomposition, and CO disproportionation

Catalyst	Temperature ^a	TOF (s^{-1})			Δr (s^{-1}) ^e
		$\text{CH}_4\text{-CO}_2^b$	CH_4^c	CO^d	
$\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$	773	0.00	0.11	0.26	0.11
	973	0.00	0.19	0.03	0.19
	1123	0.00	0.46	0.00	0.46
3.0 mol % Ni/MgO	773	0.07	0.13	0.17	0.06
	973	0.04	0.19	0.19	0.15
	1123	0.08	0.27	0.04	0.19
$\text{NiO-Al}_2\text{O}_3$ (3.0 mol %)	773	0.08	0.16	0.13	0.08
	973	0.08	0.10	0.06	0.02
	1123	0.04	0.06	0.00	0.02

^a Reaction temperature.

^b $\text{CH}_4/\text{CO}_2/\text{N}_2=25/25/50$, total flow rate: 80 ml min^{-1} , 0.1 g catalyst.

^c $\text{CH}_4/\text{N}_2=25/75$, total flow rate: 80 ml min^{-1} , 0.1 g catalyst.

^d $\text{CO}/\text{N}_2=25/75$, total flow rate: 80 ml min^{-1} , 0.1 g catalyst.

^e Rate difference between CH_4 decomposition and CH_4+CO_2 reforming reaction.

be due to the reaction between reduced Ni and CO_2 , and the starting temperature on $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$ was 40 K lower than that on 3 mol % Ni/MgO. This indicated high ability of $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$ for the reduction of CO_2 . This is consistent with the catalyst deactivation by oxidation by CO_2 and H_2O at low reaction temperature as reported previously [14]. Total amount of CO formation at this temperature range is larger than that of reduced nickel estimated by O_2 adsorption measurement. This peak can also be attributed to CO formation by the reaction between support surface and CO_2 . In addition, CO formation was observed at higher temperature ($>773 \text{ K}$). At the present stage, we can not give a clear interpretation for these peaks. One

explanation could be related to the slow reaction of CO_2 with oxygen vacancy in the bulk of oxide support which is formed during the reduction pretreatment.

From TGA results, it was found that the ability of CO_2 for the inhibition of carbon deposition is higher over the catalyst on the support with higher basicity and higher nickel dispersion. From CO_2 TPSR profiles, it was found that the reactivity of deposited carbon is almost the same on the catalysts tested. These two findings suggest that the rapid removal of the precursor of carbon before converting it to whisker carbon is very important for the development of catalyst without carbon deposition. The reaction intermediates of whisker carbon formation are CH_x

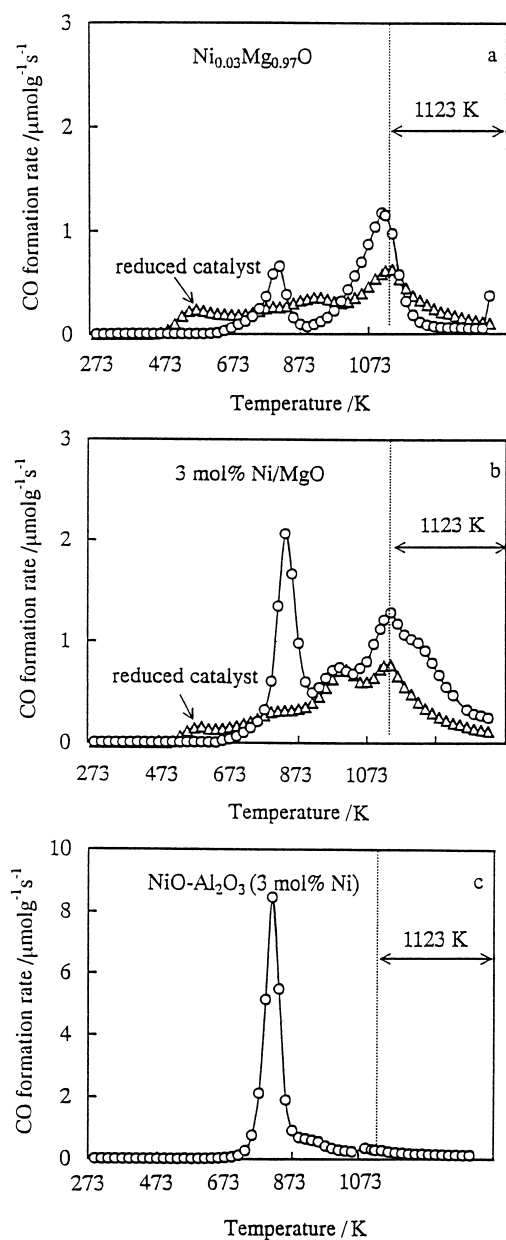


Fig. 5. CO_2 TPSR profiles on (a) $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$, (b) 3 mol % Ni/MgO and (c) $\text{NiO-Al}_2\text{O}_3$ (3.0 mol %) before (Δ) and after carbon deposition (\circ). H_2 reduction at 1123 K for 30 min. Reaction conditions of carbon deposition: $\text{CH}_4/\text{N}_2=25/75$, 773 K, 80 ml/min. Conditions of CO_2 TPSR: 298–1123 K, heating rate 10 K/min. Catalyst weight: 0.1 g.

species adsorbed on Ni, surface Ni carbide and bulk Ni carbide. In the present study, the carbon formation is considered to be inhibited by the reaction between

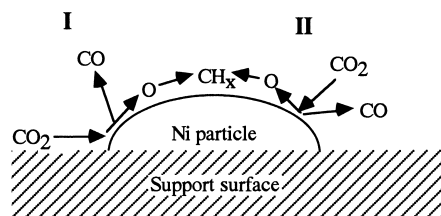


Fig. 6. Scheme of the reaction of CH_x species with CO_2 .

these reaction intermediates and CO_2 . The reaction scheme is shown in Fig. 6. There are two paths for the activation of CO_2 . One is the activation of CO_2 adsorbed on support surface at interface between metal and support (path I). The other path is the activation of CO_2 on nickel metal surface (path II). The present study indicated that path I should be more effective for the inhibition of carbon formation than path II. Rapid oxidation of CH_x on Ni surface by oxygen species from CO_2 through dissociation at metal-support interface is a key step for the inhibition of carbon formation.

References

- [1] J.R. Rostrup-Nielsen, *Stud. Surf. Sci. Catal.* 81 (1994) 25.
- [2] S. Wang, G.Q. Lu, *Energy and Fuel* 10 (1996) 896.
- [3] J.R. Rostrup-Nielsen, J.H.B. Hansen, *J. Catal.* 144 (1993) 38.
- [4] Z. Zhang, X.E. Verykios, *Appl. Catal., A: General* 138 (1995) 109.
- [5] Z. Zhang, X.E. Verykios, S.M. MacDonald, S. Affrossman, *J. Phys. Chem.* 100 (1996) 744.
- [6] Y.H. Hu, E. Ruckenstein, *J. Catal.* 163 (1996) 306.
- [7] E. Ruckenstein, Y.H. Hu, *Appl. Catal., A: General* 133 (1995) 149.
- [8] O. Yamazaki, T. Nozaki, K. Omata, K. Fujimoto, *Chem. Lett.* (1992) 1953.
- [9] O. Yamazaki, K. Tomishige, K. Fujimoto, *Appl. Catal., A: General* 136 (1996) 49.
- [10] K. Tomishige, Y. Chen, K. Yokoyama, Y. Sone, K. Fujimoto, *Shokubai* 39 (1997) 70.
- [11] K. Tomishige, K. Fujimoto, *Catalysis Surveys from Japan* 2 (1998) 3.
- [12] J.R. Rostrup-Nielsen, *Catalysis Science and Technology*, In: J.R. Anderson, M. Boudart (Eds.), Springer, Berlin, Germany, vol. 5, 1984, p.3.
- [13] Y. Chen, K. Tomishige, K. Fujimoto, *Appl. Catal., A: General* 165 (1997) 335.
- [14] Y. Chen, O. Yamazaki, K. Tomishige, K. Fujimoto, *Catal. Lett.* 39 (1996) 91.