Doped Ni catalysts for methane reforming with CO_2

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Pb, Sb, Bi and Te doped Ni catalysts were prepared and used for methane reforming with CO_2 in order to diminish coke deposition. It was found that small amounts of Pb doped Ni catalysts exhibited excellent coke resistance ability with minor loss of the reforming activity. As the added amount of Pb increased from 0 to 0.015 (mole ratio between Pb/Ni), coke formation rate decreased from 166.7 mg-coke/g-cat h (on Ni/SiO_2) to 0, while the reforming activity decreased slightly from 73.2% to 63.3% (conversion of CO_2) at 800 °C, 60,000 ml(STP)/g-cat·h (CH_4 $CO_2 = 1:1$, no dilution gas in feed). Higher amounts of Pb and Sb, Bi, Te made Ni catalyst deactivated for methane reforming with CO_2.

KEY WORDS: methane, CO_2 reforming, doped Ni catalysts.

1. Introduction

Methane reforming with CO_2 is of great industrial interest because of the lower H_2/CO ratio in product gas which is suitable for the synthesis of oxygenated derivatives [1]. During the past 20 years, this reaction has attracted much attention as both methane and CO_2 are greenhouse gases and their utilizations are environmental friendly.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad (\Delta G = -44.7\,\mathrm{kJ}, 800\,^\circ\mathrm{C}) \qquad (1)$$

But thermodynamic calculations indicate that the formation of carbon is also favorable in the reforming process [2].

$$CH_4 \rightarrow C + 2H_2 \qquad (\Delta G = -27.2\,\mathrm{kJ}, 800\,^\circ\mathrm{C}) \qquad (2)$$

Supported Ni catalyst is popularly reported for its higher activity and low price [3–14], while coke deposition, which will block the reactor and make the catalyst deactivated is the main problem. A lot of methods and promoters have been reported in order to decrease coke deposition on nickel. Alkaline and alkaline earth metals were used as promoters to nickel catalyst in order to increase the gasification of surface carbon via increasing the adsorption and decomposition of CO_2 by several groups [13–17]. Rare earth metals such as lanthanum and cerium were employed as support and/or promoters of Ni in order to depress the coke deposition [11,13,18,19]. Co, Cu, Zr, Mn, Mo, Ti, Ag and Sn were also used as promoters of supported Ni catalyst to increase its coke resistance ability [20]. Coke deposition was depressed in some extent by these methods, but they decreased the reforming activity of Ni catalyst.

According to the coke formation mechanism summarized by Trimm [21], Kroll *et al.* [22] and Bradford *et al.* [23], nickel carbide (such as Ni_3C [22]), which would accumulate on the surface of Ni and cause the formation of whisker coke, is formed through the interaction between 2p electrons of carbon atoms with the 3d electrons of nickel. Some metals (such as Ge, Sn, Pb, As, Sb or Bi) possess similar electronic structure as carbon, as all of them contain “spare” p electrons in their outer shell close to a stable s-orbital, that is, it is possible for these metals to react with Ni 3d electrons, and then reduce the formation of nickel carbide [21]. Among these recommended elements, the excellent promotion effect of Sn were confirmed by Trimm [21], Nicho *et al.*[24,25] and our previous work [26]. It was found that small amounts of Sn doped Ni catalysts exhibited excellent coke resistance ability in the dry reforming process of CH_4. In this paper, Pb, Sb, Bi and Te that possess similar electronic structure as carbon and Sn were introduced into Ni catalysts and used for methane reforming with CO_2.

2. Experimental

Catalysts used in this research were prepared by co-impregnation method. $Ni(NO_3)_2{\cdot}6H_2O$ and each of $Pb(NO_3)_2$, $SbCl_3$, $Bi(NO_3)_3{\cdot}5H_2O$, $TeCl_4$ (Wako Pure Chemicals, Japan) were dissolved in ethanol, then SiO_2 (or α-Al_2O_3) was added, dried in vacuum and finally calcined at 800 °C for 3 h.. The loading amount of Ni is 10 wt% of the support and the added amounts of

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dopant were defined as the atomic ratios between dopant and nickel.

Experiments were carried out in a continuous flow system specially designed for this reaction (Ohkura, Japan). Feed gases were controlled by mass flow meter (MASFLO-OVAL, Japan) and the system operated automatically under the control of computer. Catalyst was first reduced in a mixture of $Ar + H_2$ (Ar 40 ml/min, H_2 10 ml/min) in a quartz reactor (6 mm inner diameter) at 650 °C for 1 h. Reforming reaction was carried out in a stoichiometric CH_4 (>99.99%) and CO_2 (>99.99%) (1:1) without dilution. The outlet gas was cooled by ice water and analyzed by an online gas chromatography (Yanaco G2800, Japan) automatically every 30 min. Conversions of CH_4 and CO_2 were calculated from reforming reactions (equation (1)) and trans water-gas-shift-reaction (equation (3)):

$$H_2 + CO_2 = CO + H_2O \qquad (\Delta G = 0.55\,\mathrm{kJ}, 800^\circ\mathrm{C}) \tag{3}$$

Each used catalyst was characterized by TG–DTA (Rigaku TAS-200, Japan) in order to detect the amount of coke formed during the reaction.

H_2 temperature-programmed reduction of Pb-doped Ni/α-Al_2O_3 was carried out in an auto-sorption system equipped with an online mass spectrometer (TPD51, Belsorp, Japan) in 5% H_2 (He in balance) from 100 to 950 °C at 15 °C/min. The 4-h used $Pb_{0.01}Ni/\alpha$-Al_2O_3 catalyst was characterized with field emission scanning electron microscopy (FE-SEM) (Hitachi S-4000, Japan) and field emission transmission electron microscopy (FE-TEM) (Hitachi HF-2000, Japan). And the operation procedures of these characterizations were described in detail in previous papers [9–11,17,26].

3. Results and discussions

Figure 1 presents the influence of Pb on the activity of Ni/SiO_2 for methane reforming with CO_2. As the amount of Pb increased form 0 to 0.015 (Pb/Ni mol ratio), the coke formation rate decreased sharply from 166.7 mg-coke/g-cat h (on Ni/SiO_2) to 0, while the reforming activity decreased slightly from 73.2% to about 63.3% (conversion of CO_2). Higher amounts of Pb (Pb/Ni = 0.02, 0.04) made the catalyst deactivated quickly.

Similar results were also detected on Pb-doped Ni/α-Al_2O_3 catalysts, in which the coke formation rate decreased quickly from 45.0 mg-coke/g-cat h (on Ni/α-Al_2O_3) to 0 (on $Pb_{0.01}Ni/\alpha$-Al_2O_3), and the reforming activity decreased slowly under the same reaction conditions (800 °C, space velocity 60,000 ml/g-cat h). Higher amounts of Pb made the catalytic activity of pure Ni lost. (figure 2).

From the electronic structure of Pb, it was clear that Pb atom contains same amount of "spare" p electrons in its outer shell as carbon, when Pb was added to the supported Ni catalyst, its "spare" p electrons might react with the 3d electrons of nickel to form some kind of surface compounds as it was predicted [21] and confirmed in Ni–Sn system [24–26]. This kind of surface compounds can resist the formation of nickel carbide in some extent and then retarded the deposition of carbon. According to the above results, we think that trace amount of surface Pb–Ni compounds is helpful for the coke resistance ability of Ni, while higher amount of Pb and/or formed surface Pb–Ni compounds make the catalytic ability of pure Ni lost. Another possible effect of Pb in the doped Ni catalysts is its ensemble size control on the surface nickel species. H_2-TPR analysis results of different amounts of Pb-doped Ni/α-Al_2O_3

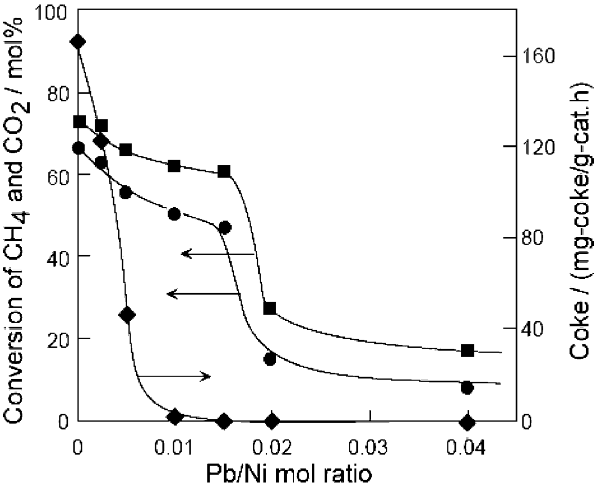

Figure 1. Activity of different amounts of Pb-doped Ni/SiO_2 catalysts (■) conversion of CO_2 (mol%), (●) conversion of CH_4 (mol%) and (♦) coke formation rate (mg-coke/g-cat h). Reaction conditions:800 °C, catalyst 50 mg, CH_4 25 ml/min (STP), CO_2 25 ml/min (STP), space velocity 60,000 ml/(g-cat h).

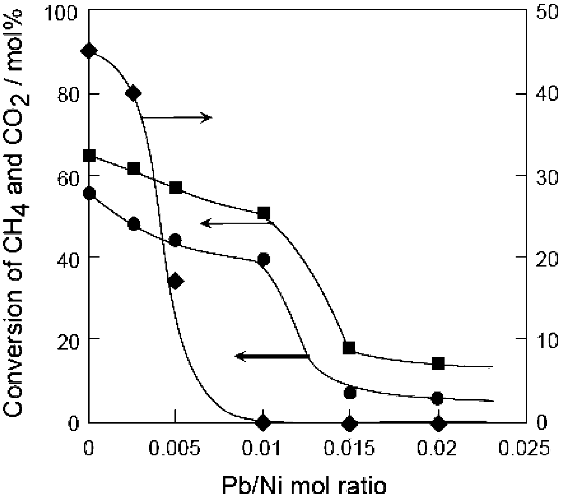

Figure 2. Activity of different amounts of Pb-doped Ni/α-Al_2O_3 catalysts (■) conversion of CO_2 (mol%), (●) conversion of CH_4 (mol%) and (♦) coke formation rate (mg-coke/g-cat h). Reaction conditions: 800 °C, catalyst 50 mg, CH_4 25 ml/min (STP), CO_2 25 ml/min (STP), space velocity 60,000 ml/(g-cat h).

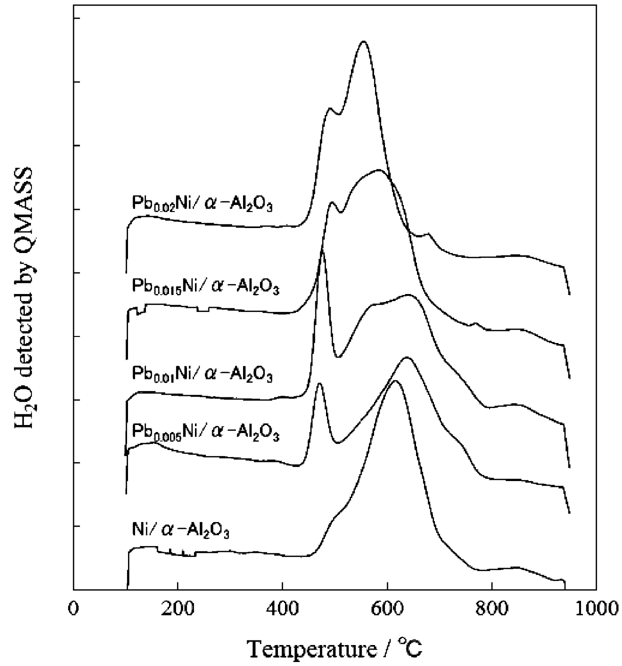

Figure 3. H_2-TPR profile of different amounts of Pb-doped Ni/ α-Al_2O_3 catalysts Analysis conditions:5% H_2, (50 ml/min, He in balance), 15 °C/min.

catalysts showed that the main reduction peak of surface Ni oxides (at 620 °C) shifted to the low temperature side continuously with the added amount of Pb and also the small shoulder peak at 480 °C, which could be assigned as the reduction of higher dispersed Ni species [9–11,17,26] became obviously in Pb-doped catalysts (figure 3). The clear FE-SEM images of used $Pb_{0.01}Ni/\alpha$-Al_2O_3 (4 h on stream) disclosed that coke deposition was suppressed by added Pb and Ni existed mainly in small Ni particles (ca. less than 60 nm) (figure 4). FE-TEM images of the same sample further confirmed the Ni dispersed highly on the surface of support (figure 5). Serious sintering of Ni particles in used Ni/α-Al_2O_3 was detected both in this research (figure 6) and our previous

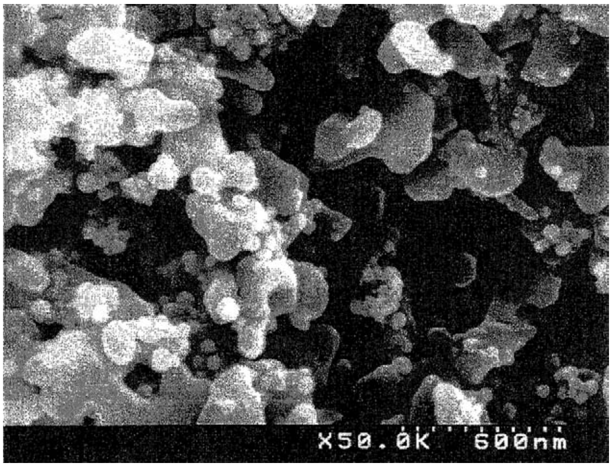

Figure 4. FE-SEM images of used $Pb_{0.01}Ni/\alpha$-Al_2O_3 catalyst.

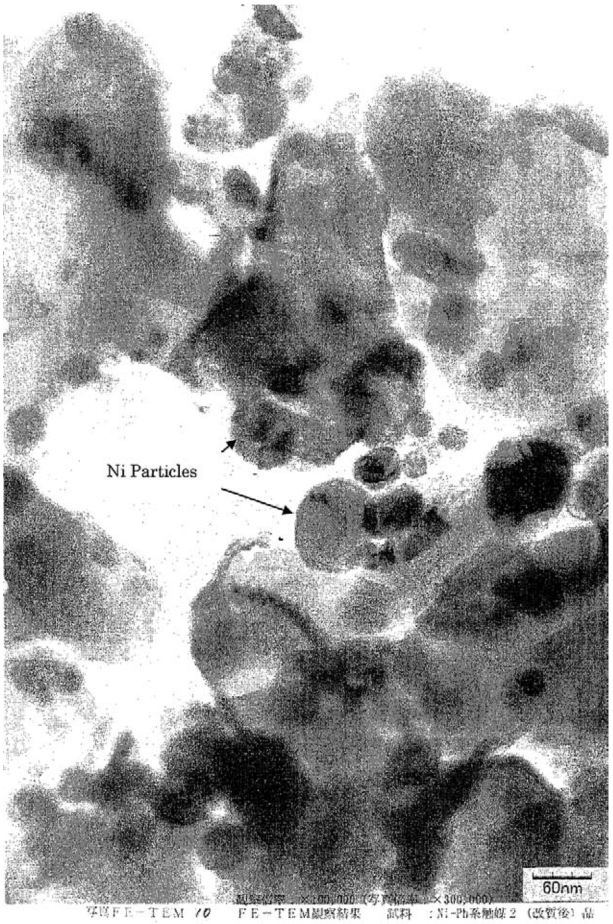

Figure 5. FE-TEM images of used $Pb_{0.01}Ni/\alpha$-Al_2O_3 catalyst.

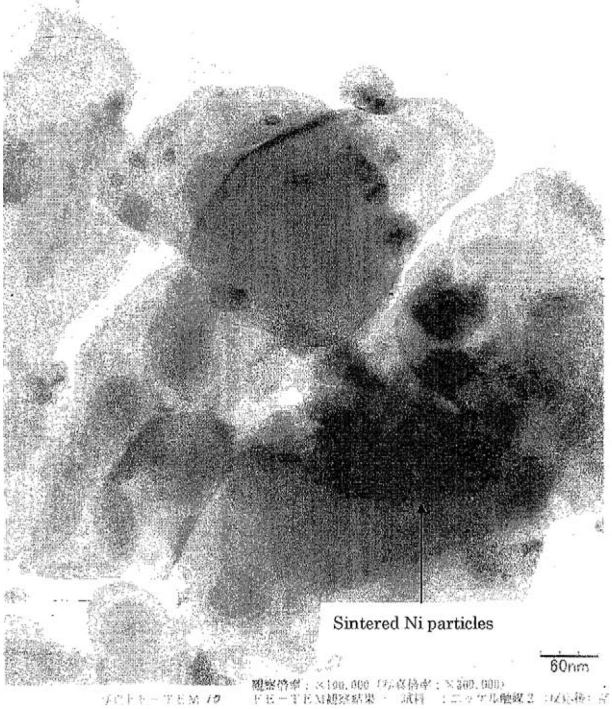

Figure 6. FE-TEM images of used Ni/α-Al_2O_3 catalyst.

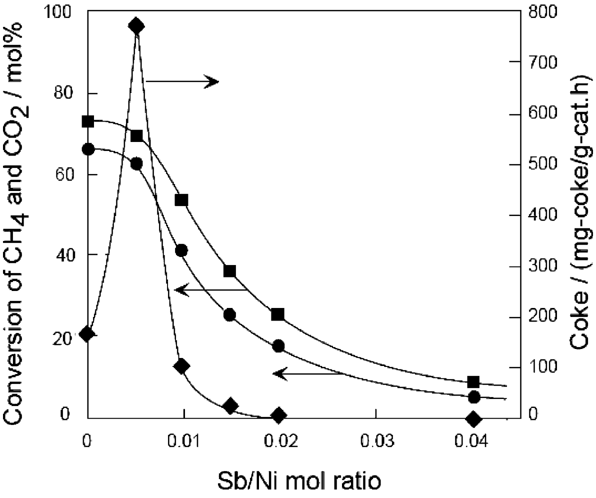

Figure 7. Activity of different amounts of Sb-doped Ni/SiO_2 catalysts (*square*) conversion of CO_2 (mol%), (*let*) conversion of CH_4 (mol%) and (*mond*) coke formation rate (mg-coke/g-cat h). Reaction conditions:800 °C, catalyst 50 mg, CH_4 25 ml/min (STP), CO_2 25 ml/min (STP), space velocity 60,000 ml/(g-cat h).

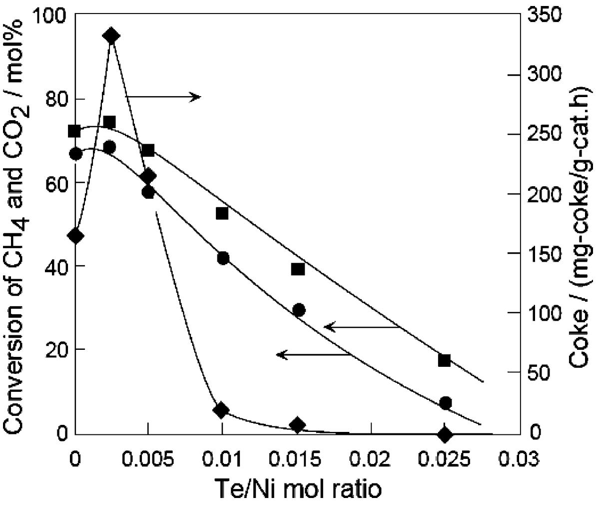

Figure 9. Activity of different amounts of Te-doped Ni/SiO_2 catalysts (*square*) conversion of CO_2 (mol%), (*let*) conversion of CH_4 (mol%) and (*mond*) coke formation rate (mg-coke/g-cat h). Reaction conditions:800 °C, catalyst 50 mg, CH_4 25 ml/min (STP), CO_2 25 ml/min (STP), space velocity 60,000 ml/(g-cat h).

work [26]. These results inferred that Pb might retard the sintering of Ni during the reforming process.

Figures 7, 8 and 9 showed the influence of Sb, Bi and Te on the reforming activity of Ni/SiO_2. Though trace amount of Sb and Te increased the coke formation rate of Ni/SiO_2, higher amount of these metals made the catalyst deactivated as both the coke formation rate and reforming activity decreased with the increasing added amounts of Bi, Sb and Te. These results might be caused by the unselective reaction between Bi, Sb, Te with the surface Ni clusters (both coke formation active sites and the reforming active sites). Thermodynamic calculations confirmed that the formation of surface Ni alloys such as NiSb, NiBi and NiTe are favorable both in the reduction step (at 650 °C in H_2 atmosphere, table 1) and in the reforming process (at 800 °C in CH_4 atmosphere, table 2). Especially in the reforming process, these surface alloys might be formed more favorable than the activation of CH_4 on the surface of Ni. That is, these formed alloy (and/or surface compounds) would make the catalytic activity of Ni lost [21]. As the added amounts of these promoters are limited, the possible formed alloys were not detected

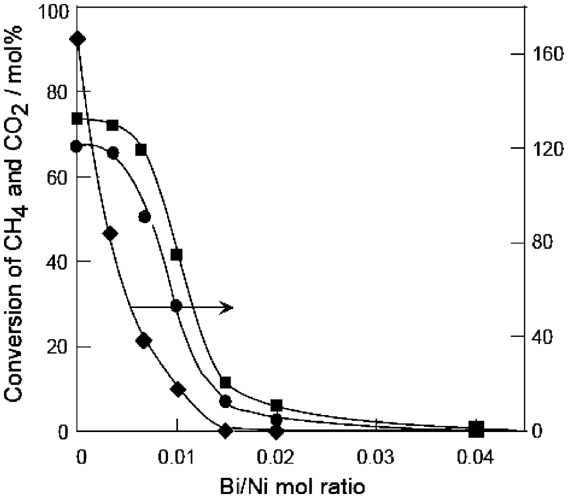

Figure 8. Activity of different amounts of Bi-doped Ni/SiO_2 catalysts (*square*) conversion of CO_2 (mol%), (*let*) conversion of CH_4 (mol%) and (*mond*) coke formation rate (mg-coke/g-cat h). Reaction conditions:800 °C, catalyst 50 mg, CH_4 25 ml/min (STP), CO_2 25 ml/min (STP), space velocity 60,000 ml/(g-cat h).

Table 1
Thermodynamic of Ni alloys formation during the reduction step (650 °C, in 20% H_2).

Reactions	Δ*G*/kJ	Δ*H*/kJ
$NiO + 1/2\ Sb_2O_3 + 5/2\ H_2 \rightarrow NiSb + 5/2\ H_2O$	−188.8	−121.3
$NiO + 1/2\ Bi_2O_3 + 5/2\ H_2 \rightarrow NiBi + 5/2\ H_2O$	−178.7	−110.5
$NiO + TeO_2 + 3\ H_2 \rightarrow NiTe + 3\ H_2O$	−317.0	−228.4

(These data were calculated by the HSC CHEMISTRY 4.0 software, Outokumpu Research Oy, Pori, Finland, A. Roine.)

Table 2
Thermodynamic of Ni alloys formation during the reforming reaction (800 °C).

Reactions	Δ*G*/kJ	Δ*H*/kJ
$Ni + Sb \rightarrow NiSb$	−80.4	−107.7
$Ni + Bi \rightarrow NiBi$	2.4	−18.9
$Ni + Te \rightarrow NiTe$	−34.3	−59.1
$Ni + 1/3\ CH_4 \rightarrow 1/3\ Ni_3C + 2/3\ H_2$	8.0	53.5

(These data were calculated by the HSC CHEMISTRY 4.0 software, Outokumpu Research Oy, Pori, Finland, A. Roine.)

via XRD, XPS or TEM–EDX in our laboratory, further experiments and fine characterizations are in proceeding.

4. Conclusions

Small amounts of Pb-doped Ni catalysts exhibited excellent coke resistance ability with minor lose of reforming activity, while Sb, Bi and Te made the catalytic activity of Ni deactivated for methane reforming with CO_2. According to the recommended coke formation mechanism, we concluded that small amount of Pb on the surface of Ni might hinder the formation of nickel carbide. And the ensemble size control of surface Ni by added Pb was also confirmed by H_2-TPR, FE-SEM and FE-TEM characterizations.

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