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Improved resistance against coke deposition of titania supported cobalt and nickel bimetallic catalysts for carbon dioxide reforming of methane

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The catalytic behavior of bi-metallic Co–Ni/TiO_2 catalysts for CO_2 reforming of CH_4 to synthesis gas was investigated under atmospheric pressure with a particular attention to carbon deposition. The catalysts with optimized Co/Ni ratios showed high catalytic stability towards the reaction with very little amount of deposited carbon at a wide range of reaction temperature (773–1123 K). The results suggest that adjusting of composition of the active metals (Co and Ni) can kinetically control the elementary steps (formation of carbon species and its removal by oxygen species) of CH_4/CO_2 reaction.

KEY WORDS: cobalt; nickel; bimetal; titania; methane; CO_2 reforming; strong resistance to coking.

1. Introduction

The reforming of methane to synthesis gas has been recognized as a starting process applied in industry to generate hydrogen, hydrocarbons and so on [1–4]. Carbon dioxide (dry) reforming of methane to synthesis gas ($CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$) has been of considerable industrial and academic attention for more than a decade [5–9]. Undesirable carbon formation on the catalyst is the crucial issue to develop efficient catalysts for the reaction.

Supported noble metals, such as Rh, Ru, Pd, Pt and Ir, can provide operations with lower carbon deposition in CH_4/CO_2 reaction [6]. However, from a practical point of view, noble metals are expensive and less available. Supported Ni catalysts are well studied due to its low cost; however, nickel easily induces formation of graphitic carbon on the catalyst, causing the catalyst deactivation and plugging of the reactor tube [4,6].

Cobalt has also attracted researchers' interest as an active metal for dry reforming of methane [10–14]. It has been shown that the optimized Co/TiO_2 catalysts are highly tolerant of coking during dry reforming of methane, even at the total pressure of 2.0 MPa where carbon formation is highly possible [10–12]. Instead, the Co/TiO_2 catalysts lose its activity due to oxidation of the metallic cobalt, which has been confirmed by formation of $CoTiO_3$ phase under the reaction conditions [13].

A key step of CO_2 reforming of CH_4 is an elementary reaction between carbon species derived from CH_4 and oxygen species derived from CO_2 [13,14]. If the formation of remaining species derived from CH_4 on the metal (CH_x species) is much faster than its removal by oxygen species derived from CO_2, carbon formation would be prevailing. Now, it is possible to control the rates of those steps by adjusting the metal composition of cobalt (oxygen species formation favored) and nickel (carbon species formation favored) supported on titania. In fact, 0.5 wt% CoNi/TiO_2 with optimum metal compositions (Co/Ni = 90/10 in molar ratio) exhibits remarkable stability of catalysis with only insignificant amount of coke deposition after the run at 2 MPa [12]. However, the behavior of these system has not been well studied. In this contribution, the catalytic activity and stability of the Co–Ni/TiO_2 catalysts have been investigated under various conditions (different reaction temperature and space velocity) at 0.1 MPa with particular attention to carbon formation. The bimetallic cobalt–nickel catalysts have been compared with mono-metallic cobalt and nickel catalysts. The role of Co–Ni combination shall be disclosed in more detail.

2. Methods

2.1. Catalyst preparation

Co–Ni/TiO_2 catalysts were prepared by impregnating TiO_2 (Ishihara Sangyo, A-100), which had been calcined at 773 K for 15 h with an aqueous solution of $Co(NO_3)_2{\cdot}6H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$ (Wako Pure Chemical Industries Ltd.). Metal loading was set to 10 wt% in total. The catalysts were dried at room temperature and 373 K, followed by calcination at 673 K in flowing air in order to remove ligands from the precursor. The

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resultant catalyst powder was pressed into pellets, crushed and sieved to obtain grains with diameters between 600 and 900 μm. The Co/Ni molar ratio (m/n) is denoted in a parenthesis as CoNi(m:n)/TiO_2.

2.2. CH_4/CO_2 reaction

Details of reaction procedure have been described elsewhere [13]. Typically, 0.5–1.0 g of the catalyst was loaded into a fixed-bed tubular inconel reactor (ID 6 mm). The catalysts were reduced *in situ* in a H_2 flow at 1123 K for 1 h. CH_4/CO_2 gases were introduced into the catalyst bed at a total flow rate of 20 or 50 mL min^{-1} (space velocity (SV) 1200 or 6000 mL h^{-1} g-cat^{-1}). The reaction temperature was carried out at 773–1123 K under atmospheric pressure. The reactants and products were analyzed with an on-line gas chromatgraph (Aera, M-200) equipped with Porapak Q column, Molecular Sieve 5A column, and two thermal conductivity detectors (TCDs).

2.3. Catalyst characterization

Deposited carbon was analyzed by temperature-programmed oxidation (TPO) method. The catalyst after reaction was heated up to 1273 K at a heating rate of 10 K min^{-1} in O_2/He mixture (5/95 v/v with a total flow of 50 mL min^{-1}). CO_x gases derived from carbon deposited were passed through a methanator and monitored by using a flame ionization detector (FID).

XRD analysis was performed with a Rigaku MULTIFLUX X-ray diffractometer instrument with monochoromatized CuK_α. Metal crystallite sizes were calculated from line broadening using the Scherrer's equation [15].

The amounts of chemisorbed CO were determined by a pulse method. The amount of 0.1 g of catalysts was reduced *in situ* at required temperatures for 1 h in H_2 flow, and flushed with He ($>$99.999% purity) at each temperature for 15 min. Pulses (pulse volume: 1.08 mL) of 1% CO in He gas were injected through the catalysts at room temperature until no further adsorption of CO was detected with a TCD.

3. Results and discussion

3.1. Influence of Co/Ni ratio

Co/Ni ratio in the catalyst affects the catalytic property significantly. Figure 1 shows CH_4 conversions over Co–Ni/TiO_2 at 1023 K and the amounts of deposited carbon after 24 h-test, plotted against Ni content. Co/TiO_2 (0% of Ni) lost its activity at the very beginning of the reaction due to the oxidation of metallic cobalt [13]. In comparison, CoNi(90:10)/TiO_2 showed relatively high and stable activity. The catalytic activities increased with increasing Ni content gradually. Remarkably, the deactivation was not observed after 24 h-test for all the Co–Ni/TiO_2 catalysts. On the other hand, when Ni content was high (≥90% Ni), the amount of deposited carbon increased drastically.

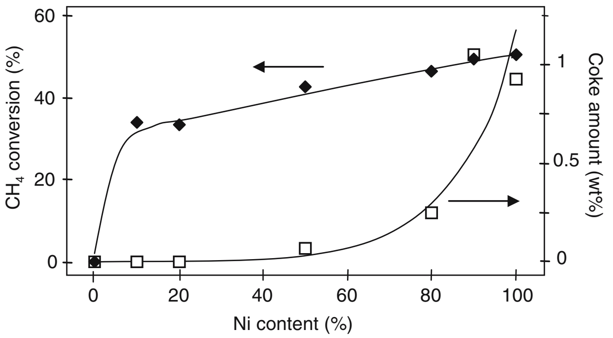

Figure 1. CH_4 conversion and the amount of deposited carbon after 24 h-test vs Co/Ni ratio for Co–Ni/TiO_2 ($CH_4/CO_2 = 1$; 1023 K; 0.1 MPa; SV = 6000 mL g-cat^{-1} h^{-1}).

Table 1 compiles the amount of chemisorbed CO, metal crystallite size and turn over frequency (TOF) at 1 h time on stream for CH_4 conversion for Co–Ni/TiO_2 with different Co/Ni ratio. Metal crystallite size was comparable among all the Co–Ni/TiO_2 catalysts. The amount of chemisorbed CO increased as Ni content in the catalyst increased. However, except for Co/TiO_2, TOFs showed similar values among all the Co–Ni/TiO_2. It can mean that cobalt begins catalyzing the reaction as effectively as nickel only when nickel was present in the same catalyst. If cobalt atom is close to nickel atom, the cobalt can be kept reduced during the reaction. It seems that the difference in catalytic behavior can not be attributed to the difference in physico-chemical properties (metal particle size and surface area), but more to the reactivity of the metals towards CH_4/CO_2. Further investigation on the state and reactivity of bimetallic catalysts is in progress [16].

3.2. Influence of reaction temperature

The Co–Ni/TiO_2 showed high stability and high coke tolerance during the reaction at 1023 K. Hence, the

Table 1

Influence of Co/Ni ratio on CO chemisorption capacity, metal crystallite size and turn over frequency (TOF) for Co–Ni/TiO_2

Co:Ni	Metal crystallite size[a] (nm)	The amount of CO chemisorbed (μ mol g-cat^{-1})	TOF for CH_4 at 1 h (s^{-1})
0:100	34	2.20	4.7
10:90	37	1.91	4.9
20:80	37	1.79	4.1
50:50	33	1.83	4.0
80:20	37	1.44	4.2
90:10	34	1.48	4.2
100:0	33	1.08	1.0

[a] Calculated from line broadening using the Scherrer's equation [15].

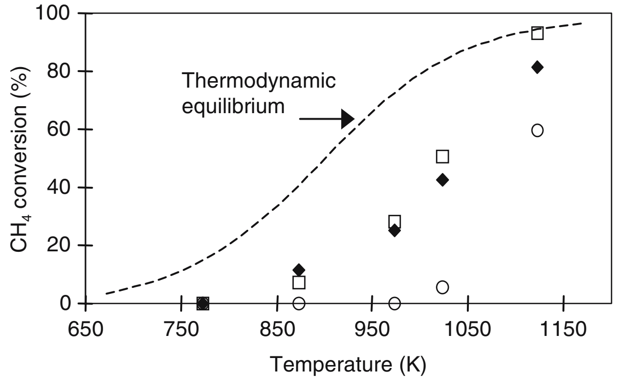

Figure 2. Comparison of CH_4 conversions at 1 h time on stream for (□) Ni/TiO_2, (◆) Co–Ni(50:50)/TiO_2 and (○) Co/TiO_2 at different reaction temperatures. ($CH_4/CO_2 = 1$; 0.1 MPa; SV = 6000 mL g-cat^{-1} h^{-1}).

CoNi(50:50)/TiO_2 was tested at various reaction temperatures and compared with mono-metallic catalysts. Figure 2 shows CH_4 conversions against reaction temperature and table 2 compiles the amounts of deposited carbon after 24 h at each reaction temperature.

At 773 K, both mono-metallic and bi-metallic catalysts showed no catalytic activities. Particularly, no carbon deposition occurred on the bi-metallic catalyst. The first reaction step of CH_4/CO_2 reforming is considered to be CH_4 decomposition on the active metal to produce coke species (typically, CH_x species ($x < 4$) [6]), followed by removal of the coke species by active oxygen species derived from CO_2 on the surface [6,13,14]. On the metallic sites (Co or Ni), CH_4 decomposition should occur at this temperature [17,18]. Although XRD patterns of the catalysts after the reaction did not show any oxidized metal phase at this temperature, it is most likely that oxidation of metallic surface took place, inhibiting the decomposition of CH_4. The reason is based on the fact that there is no carbon formation on the catalysts after reaction. This is in agreement with the study of a Ni–Mg–O solid solution catalyst at this range of reaction temperature, proposing that when the reaction is operated at lower temperatures, the oxidation of nickel could occur [19,20].

Table 2
The amount of deposited carbon for Ni/TiO_2, Co–Ni(50:50)/TiO_2 and Co/TiO_2 at different reaction temperatures ($CH_4/CO_2 = 1$; 0.1 MPa; SV = 6000 mL g-cat^{-1} h^{-1})

Reaction temperature (K)	Coke amount (wt%)		
	Ni	Co–Ni	Co
773	0.85	n.d[a]	n.d[a]
873	9.59	0.17	n.d[a]
973	2.80	0.12	n.d[a]
1023	0.93	0.07	n.d[a]
1123	1.93	0.04	n.d[a]

[a] n.d (not detected) indicates below 0.01 wt%.

The Co/TiO_2 catalyst showed very low catalytic activity with a wide range of reaction temperature. The catalyst did not show any catalytic activity below 1023 K, most probably due to oxidation of the metallic cobalt [13]. The catalyst showed the activity clearly above 1123 K; however, the activity was still lower than those of bi-metallic and mono-metallic nickel catalysts. No carbon deposition was observed over the Co/TiO_2 catalysts.

Now, both the Co–Ni(50:50)/TiO_2 and Ni/TiO_2 catalysts showed catalytic activities without any deactivation at and above 873 K. At lower temperatures (873–1023 K) the catalytic activities were comparable for Co–Ni(50:50)/TiO_2 and Ni/TiO_2. At higher reaction temperatures (≥1023 K), the activity of Co–Ni(50:50)/TiO_2 catalyst was lower than that of the Ni/TiO_2. The amounts of deposited carbon were very small regardless of reaction temperatures for Co–Ni(50:50)/TiO_2 (< 0.2 wt%). In contrast, the Ni/TiO_2 experienced extensive carbon formation during the reaction. Especially at 873 and 973 K, the amounts of deposited carbon were significantly high (2.8 and 9.6 wt%). This is probably why the Ni catalyst showed lower catalytic activity than the bi-metallic catalyst in the lower temperature range. Generally, it is considered that deposited carbon originates from CH_4 decomposition ($CH_4 \rightarrow C + 2H_2$; $\Delta H° = 75$kJ mol^{-1}) and CO disproportionation ($2CO \rightarrow C + CO_2$; $\Delta H° = -171$ kJ mol^{-1}). It is reasonable to attribute main source of the carbon to CO produced, at least at these temperatures (873–973 K) because the CO disproportionation is exothermic reaction and favored at lower temperatures, in contrast to endothermic CH_4 decomposition. According to this discussion, at 773 K, where the catalysts showed no activity to the reforming, it can be considered that CO formation and the subsequent carbon deposition hardly took place.

3.3. CH_4/CO_2 reaction at 873 K

It was found that the reaction at lower temperatures, e.g. 873 K, can cause severe carbon formation over Ni/TiO_2 (table 2). It is also suggested that carbon mainly originates from CO produced by the reforming. Therefore, further investigation was carried out at the reaction temperature of 873 K. Figure 3 shows time on stream versus CH_4 conversions, and table 3 shows comparison of catalytic activities and the amount of deposited carbon for the Co/TiO_2, CoNi(50:50)/TiO_2 and Ni/TiO_2 catalysts at 873 K. The Co/TiO_2 catalyst showed no activity toward the reaction. Among the catalysts operated at SV of 6000 mL g-cat^{-1} h^{-1}, the catalytic activities were in the order, Co–Ni(50:50)/TiO_2 > Ni/TiO_2 > Co/TiO_2. When the Co–Ni(50:50)/TiO_2 catalyst was operated at lower SV of 1200 mL g-cat^{-1} h^{-1}, the higher conversion was achieved and remarkably it still showed high stability. Nature of coke resistance was

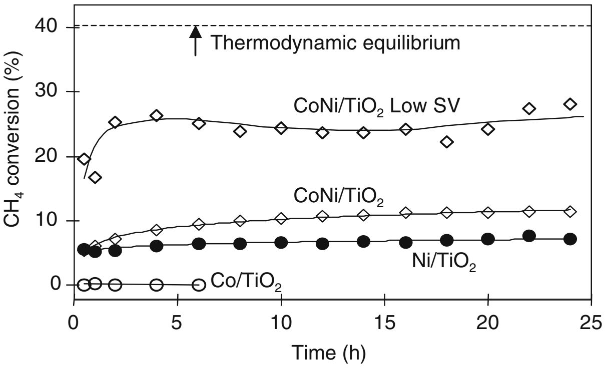

Figure 3. Time on stream vs CH_4 conversion for Co/TiO_2, Co–Ni(50:50)/TiO_2, and Ni/TiO_2 during CH_4/CO_2 reaction. ($CH_4/CO_2 = 1$; 0.1 MPa; 873 K. SV: 6000 mL g-cat^{-1} h^{-1}. Low SV: 1200 mL g-cat^{-1} h^{-1}).

retained even at higher conversions and yields (table 3). The amount of carbon formed for Co–Ni(50:50)/TiO_2 (0.62 wt%) was much smaller than that for the Ni/TiO_2 (9.59 wt%) which give lower CO yield. Bimetallic catalyst was found to be highly effective to suppress the carbon formation.

3.4. Long-term test over Co–Ni/TiO_2

Long-term catalytic tests (100 h) were carried out over the Co–Ni(50:50)/TiO_2 and Co–Ni(80:20)/TiO_2 catalysts at 1023 K and at low SV of 1200 mL g-cat^{-1} h^{-1} (figure 4). Figure 2 shows time on stream versus CH_4 conversions for those catalysts. Conversions of CH_4 reached 73.6 and 68.1% for the Co–Ni(50:50)/TiO_2 and Co–Ni(80:20)/TiO_2 catalysts, respectively. The catalysts showed highly stable activities during the period of study for 100 h. The amounts of carbon deposited on the Co–Ni(50:50)/TiO_2 and Co–Ni(80:20)/TiO_2 were very small even after 100 h test; 0.19 and 0.01 wt%, respectively. It should be noted that the amounts observed were lower than that observed on Ni/TiO_2 catalyst after 24 h-test (0.93 wt%), showing lower conversions and yields (see figure 1).

It was revealed that the Co–Ni/TiO_2 catalysts with the appropriate Co/Ni ratio showed high stability and strong tolerance to carbon deposition during CO_2 reforming of CH_4 under the condition where undesirable carbon formation is highly favorable. Adjustment of composition of cobalt and nickel for the Co–Ni/TiO_2 catalyst system can change its catalytic reactivity for CH_4/CO_2 reforming.

Table 3
Comparison of coke amounts among the catalysts after the reaction at 873 K

Catalyst	Space velocity (mL h^{-1} g-cat^{-1})	CH_4 conv. (max.) (%)	CO yield (max.)(%)	Coke amount (wt%)
Co–Ni(50:50)	1200	28.1	28.1	0.62
Co–Ni(50:50)	6000	11.4	14.0	0.17
Ni	6000	7.6	9.2	9.59
Co	6000	0.1	0	n.d[a]

[a] n.d (not detected) indicates below 0.01 wt%.

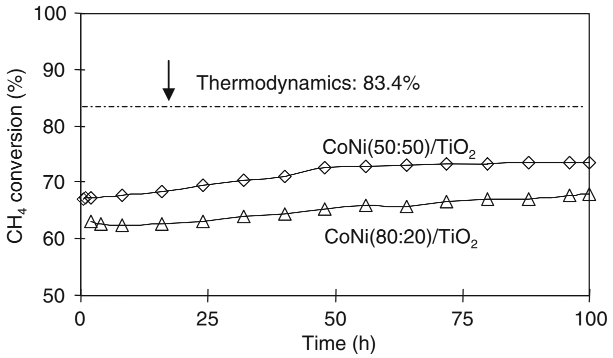

Figure 4. Time on stream versus CH_4 conversions for Co–Ni/TiO_2 ($CH_4/CO_2 = 1$; 1023 K; 0.1 MPa; SV = 1200 mL g-cat^{-1} h^{-1}).

4. Conclusions

The bimetallic Co–Ni/TiO_2 showed highly stable activities and high resistance to coking during CO_2 reforming of CH_4 at a wide range of reaction temperature (773–1123 K). The mono-metallic Co/TiO_2 catalyst showed tendency to oxidation of the active metal during the reaction. On the other hand, Ni/TiO_2 catalyst experienced a marked coking, especially at relatively lower temperature of 873 K, which implies that the carbon mainly originate from produced CO. In fact, the Co–Ni/TiO_2 catalyst showed much higher residence to coking than the Ni/TiO_2 catalyst even at higher CO yields. The mixture of cobalt and nickel inhibit both the oxidation of metal (tendency of cobalt catalyst) and the carbon deposition (tendency of nickel catalyst).

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