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Methanation of carbon dioxide over $LaNi_4X$-type intermetallic compounds as catalyst precursor

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Abstract

The hydrogenation of carbon dioxide is catalyzed over intermetallic compounds $LaNi_4X$ (X ≡ Ni, Cr, Al, Cu) at a reaction temperature as low as 250 °C under 5 MPa, where $LaNi_5$ and $LaNi_4Cr$ are significantly active. On the basis of X-ray diffraction analyses of the catalysts after the reaction, the catalytic activity seemingly depends on the amounts of metallic nickel formed by decomposition of the intermetallic compounds during the reaction, and the compounds preserving the alloy structure are less active.

Keywords: Intermetallic compounds; Rare earth metals; Carbon dioxide; Hydrogenation; Catalysis

1. Introduction

Since hydrogen storage alloys are expected to activate hydrogen, they have often been employed as catalysts for the hydrogenation of unsaturated compounds, such as ethylene, propene, 1-undecene, and 2-methyl-1,3-butadiene [1–4]. The alloys also catalyze the hydrogenation of carbon monoxide to methane [5–7]. However, the alloys previously reported as hydrogenation catalysts for carbon monoxide were perfectly decomposed under the reaction conditions and lost their hydrogen storage ability. Thus, the catalytic activity should be due to metallic aggregations generated from the alloys, while the activity of the hydrogen storage alloy itself has not been clarified [8,9].

We have studied the catalytic activity of a series of hydrogen storage alloys, mainly containing lanthanum and nickel, to find the effective catalyst species for the reduction of carbon dioxide known as a global warming gas, and also to examine the contribution of hydrogen storage ability to catalysis.

2. Experimental details

The intermetallic compounds $LaNi_4X$ (X ≡ Ni, Cr, Al, Cu) were prepared by arc-melting metal constituents in a copper crucible under 66.7 kPa argon atmosphere. The ingots were pulverized by hydrogen absorption into powder, then sieved into 0.07–0.11 mm particles. In a typical experiment, 1.0 g intermetallic compound was packed in the stainless tube reactor. Pretreatment was carried out with a stream of diluted hydrogen (1% H_2 in N_2) at the rate of 100 ml min^{-1} under atmospheric pressure at 250 °C for 12 h, then the reaction gas ($[H_2]/[CO_2] = 4$) was introduced under 5 MPa at the rate of 50 ml min^{-1}. The effluent gas was analyzed with an on-line gas chromatograph using a packed column of MS-13X (4 m). Hydrogen chemisorption was carried out with a Quantasorb Jr.

3. Results and discussion

The hydrogenation of carbon dioxide took place under 5 MPa at a reaction temperature as low as 250 °C over $LaNi_4X$. The exclusive product was methane, and a small amount of ethane was obtained (Table 1). No carbon monoxide was detected. The conversion of carbon dioxide was 93% over $LaNi_5$, and the selectivities to methane and ethane in the product were 98% and 2% respectively. The methanation activities of $LaNi_4Al$ and $LaNi_4Cu$ were poor at 250 °C. A commercially available nickel powder and Ni/La_2O_3 catalyst prepared by coprecipitation of $Ni(NO_3)_2$ and $La(NO_3)_3$ ($[Ni]/[La] = 5$ in atomic ratio) showed a slight methanation activity at this temperature.

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Table 1
Catalytic activity of $LaNi_4X$

X	CO_2 conversion (%)	Selectivity (%)		H_2 chemisorption (μmol g-cat^{-1})	Turnover number (10^3 s^{-1})
		CH_4	C_2H_6		
Ni	93	98	2	44	79
Cr	93	98	2	48	73
Al	4	100	0	~0	≈0
Cu	4	100	0	~0	≈0
Ni powder [a]	1	100	0	3	14
Ni/La_2O_3 [b]	8 [c]	90	0	16	19

Reaction temperature, 250 °C; reaction pressure, 5 MPa.
[a] Type 210 nickel powder (INCO Co., Ltd.) was used.
[b] Prepared by coprecipitation of $Ni(NO_3)_2$ and $La(NO_3)_3$ ([Ni]/[La] = 5 in atomic ratio).
[c] Carbon monoxide was detected with a selectivity of 10%.

The hydrogen chemisorption was measured to estimate the number of nickel atoms on the surface of the sample (Table 1). The methanation activity corresponded to the amount of hydrogen adsorbed on the nickel. The turnover number, defined as the number of CO_2 molecules converted to methane per active site per unit time, for each catalyst was determined from the hydrogen chemisorption (Table 1).

The dependence on pressure of the hydrogenation of carbon dioxide was measured over $LaNi_5$ (Table 2). The conversion of carbon dioxide over $LaNi_5$ increased with an increase in pressure of the reactants. However, even under atmospheric pressure, 56% of carbon dioxide converted to methane and carbon monoxide with selectivities of 98% and 2% respectively. A small amount of ethane was obtained as a minor product under high pressures. The BET surface area determined by krypton adsorption was less than 1.5 m^2 g^{-1} for all catalysts taken out from the reactor.

To confirm the structure of $LaNi_4X$ after the reaction, we recorded X-ray diffraction (XRD) patterns for each catalyst taken out from the reactor after 6 h on the reaction stream. As shown in Fig. 1, the peaks attributed to metallic nickel ($2\theta = 44.7°$, 52.2°) appeared in the patterns for $LaNi_5$ and $LaNi_4Cr$ which were active

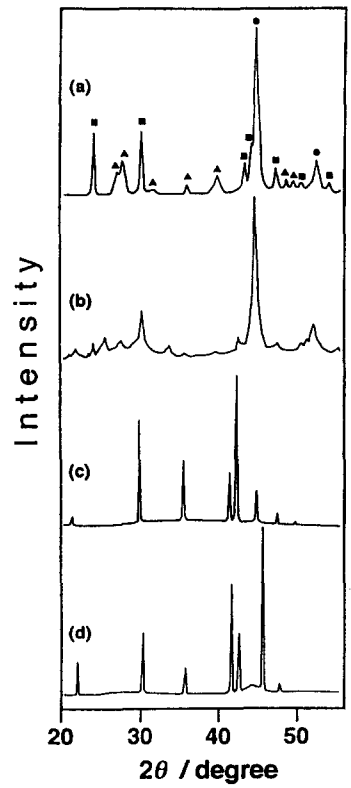

Fig. 1. XRD patterns of $LaNi_4X$ after CO_2 methanation; target, Cu Kα: (a) $LaNi_5$, (b) $LaNi_4Cr$, (c) $LaNi_4Al$, (d) $LaNi_4Cu$; ● peaks attributed to Ni, ■ peaks attributed to $La(CO_3)(OH)$, ▲ peaks attributed to $La(OH)_3$.

Table 2
Influence of reaction pressure

Total pressure (MPa)	CO_2 conversion (%)	Selectivity (%)	
		CH_4	C_2H_6
0.1	56 [a]	98	0
1	82	99	1
2	89	99	1
3	92	99	1
4	94	99	1
5	95	99	1

Catalyst, $LaNi_5$; reaction temperature, 300 °C.
[a] Carbon monoxide was detected with a selectivity of 2%.

catalysts, while these two samples were completely decomposed and no longer had hydrogen storage ability. The peaks for $La(CO_3)(OH)$ and for $La(OH)_3$ were also observed. However, no peaks due to metallic nickel were found in the XRD patterns of $LaNi_4Al$ and $LaNi_4Cu$. Although these two catalysts are supposed to retain their hydrogen storage ability, the catalytic activities were poor. There is no correlation between the hydrogen storage ability and the catalytic ability. The source of the activity can be attributed mainly to

the new sites generated by decomposition of the intermetallic compounds, and metallic nickel on the surface could be the active site for the reaction. However, nickel powder and Ni/La_2O_3 obviously containing metallic nickel were less active, suggesting that the activity is not simply due to the metallic nickel. Lanthanum carbonate appeared in the catalyst by the interaction between lanthanum and carbon dioxide during the reaction. Hence, carbon dioxide could be activated on the surface of a lanthanum compound such as lanthanum hydroxide which is basic. Inui and Takeguchi reported that the existence of lanthanum oxide was effective for methanation [10]. Yamashita et al. also pointed out the importance of the interaction between nickel and lanthanum in amorphous alloys for the generation of active sites for carbon monoxide hydrogenation [11]. The contribution of lanthanum to the catalysis is now under investigation.

4. Summary

The intermetallic compounds $LaNi_5$ and $LaNi_4Cr$, catalyzed effectively the methanation of carbon dioxide; the XRD patterns of these catalysts showed the formation of metallic nickel in the structure during the reaction. Aggregation of metallic nickel hardly took place in $LaNi_4Al$ and $LaNi_4Cu$ which were inactive at 250 °C. Hence, it can be concluded that the presence of metallic nickel in the structure is essential for high catalytic activity to the conversion of carbon dioxide, but at the same time, the presence of lanthanum in the solids could also be indispensable to high activity.

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