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Hydrogenation of Solid State Carbonates[†]

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$NiCO_3$ and $CoCO_3$ react with hydrogen to produce methane at 200—250 °C without any additional catalysts, and some alkali or alkaline-earth metal carbonates are also hydrogenated at 300—400 °C to form methane using transition metal powders as a catalyst.

The reduction of carbon dioxide has become a subject of active interest[1—3] concerned with the pollution problem. Carbon dioxide contained in exhaust gas can be readily collected in a form of carbonate by passing the exhaust gas through an alkaline solution. On the other hand, most part of carbon on the earth (>99.9%) exists as carbonates such as $CaCO_3$ (limestone etc.). These facts suggest it is important to develop a high efficient process of carbonate reduction to form organic compounds using the carbonates as a carbon source. However, there are only a few reports about the reduction of carbonates, and they were studied in aqueous solutions.[4—7] In this letter, we report catalytic hydrogenation of several solid state carbonates to form methane as a new reduction process of carbonates.

Commercial transition metal powders, Fe (ULVAC, average diameter = 20 nm), Co (ULVAC, 20 nm), Ni (ULVAC, 20 nm), Pd black (Wako Pure Chemical), Pt black (Engelhard), and Cu (ULVAC, 50 nm), were used as catalysts without any treatment. Catalyst powders (40 mg) were mechanically mixed with carbonate (2.00 g) in an agate mortal for 5 minutes just before use. The catalytic reaction was carried out in a fixed bed flow reactor at atmospheric pressure. Products were analyzed by gas chromatography (Ohkura Model 202 and Model 802) using MS13X (thermal conductivity detector), PPQ (thermal conductivity detector), VZ10 (flame ionization

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[†] Dedicated to celebrate 80th birthday of professor emeritus Osamu Simamura of The University of Tokyo.

detector), and PEG1000 (flame ionization detector) columns (detection limit; 0.7 μmol h^{-1} for CO_2 and CO, 0.003 μmol h^{-1} for hydrocarbons and alcohols).

The results of the hydrogenation of carbonates are shown in Table 1. Methane was found to be produced from various carbonates. The formation of carbon monoxide, methanol, and higher hydrocarbons was negligible (CO < 0.7 μmol h^{-1}, other < 0.3 μmol h^{-1}) in all reactions.

Table 1. Hydrogenation of several carbonates catalyzed by transition metals[a)]

			Reaction	Products (μmol h^{-1})[b)]	
Run	Carbonate	Catalyst	temp / °C	CO_2	CH_4
1	$NiCO_3 \cdot Ni(OH)_2 \cdot 4H_2O$	-	200	770	72
2	$CoCO_3$	-	200	13	97
3	Li_2CO_3	Ni	400	nd	1.3
4	Na_2CO_3	Ni	400	nd	2.5
5	K_2CO_3	Ni	400	trace (< 2)	1.8
6	$4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$	Ni	300	290	1600
7	$BaCO_3$	Ni	400	nd	1.8
8	$CaCO_3$	Fe	400	nd	6.4
9	$CaCO_3$	Co	400	nd	45
10	$CaCO_3$	Ni	400	nd	95
11	$CaCO_3$	Ni	300	nd	8.5
12	$CaCO_3$	Ni	200	nd	3.7
13	$CaCO_3$	Pd black	400	nd	0.7
14	$CaCO_3$	Pt black	400	nd	26
15	$CaCO_3$	Cu	400	nd	2.4
16	$CaCO_3$	-	400	nd	nd
17[c)]	$CaCO_3$	Ni	400	2	nd

a) A mixture of carbonate (2.00 g) and catalyst (0.04 g) was used in all reactions. Gas flow rate; H_2 4.8 mL min^{-1} + He 4.8 mL min^{-1}. b) Product gas analysis was performed at 0.5—1 h after the reaction started, except run 1 (55 h) and run 2 (7 h). c) Gas flow rate; He 10.0 mL min^{-1} (without H_2).

Nickel carbonate and cobalt carbonate were hydrogenated to form methane at 200 °C without any catalysts (runs 1 and 2). In these cases, carbon dioxide was also evolved by the thermal decomposition of the carbonates during the reaction. Induction period for the methane formation was observed in these reactions. The methane formation rate reached the maximum at 7 h after the reaction started in the case of $NiCO_3$ (72 μmol h^{-1}), and at 55 h in the case of $CoCO_3$ (97 μmol h^{-1}). At higher reaction temperature (250 °C), methane and carbon dioxide were formed explosively. In the hydrogenation of $NiCO_3$, methane was formed to the extent of the complete consumption of H_2 (12 mmol h^{-1}), and in that of $CoCO_3$, methane formation rate reached 2 mmol h^{-1}. The induction period observed for the methane formation and the formation of metallic Ni and Co particles, which were confirmed by X-ray diffraction analysis, suggest that the metallic Ni or Co formed at the beginning of the reaction would work as a catalyst of the hydrogenation.

Non-transition metal carbonates, such as Li_2CO_3, Na_2CO_3, K_2CO_3, $MgCO_3$, $CaCO_3$, and $BaCO_3$, were hydrogenated to form methane in the presence of a Ni ultra fine powder catalyst (runs 3—7, 10). Especially $MgCO_3$ was readily hydrogenated at 300 °C to produce a considerable amount of methane. It is noteworthy that carbon dioxide was not evolved at all in the hydrogenation of Li_2CO_3, Na_2CO_3, $CaCO_3$, and $BaCO_3$.

Other transition metals (Fe, Co, Pd, Pt, and Cu) were also employed as a catalyst in the hydrogenation of $CaCO_3$ (runs 8, 9, and 13—15). Methane was the only product for all metal catalysts. As shown in Table 1, the order of the catalytic activity was Ni > Co > Pt > Fe > Cu > Pd. As a matter of course, no methane was produced in the control experiment without any catalysts (run 16) nor without hydrogen gas flow (run 17).

Methane was formed even at relatively low temperature such as 300 °C or 200 °C in the Ni-catalyzed hydrogenation of $CaCO_3$ (runs 11 and 12). Although the rate of methane production was decreased with decreasing reaction temperature, it is remarkable that the hydrogenation of $CaCO_3$ proceeded at 400—500 °C lower than the decomposition temperature of $CaCO_3$ (899 °C).

In the Ni-catalyzed hydrogenation reaction of $CaCO_3$ at 400 °C, the methane formation rate was constant for a long period. For example, in run 10, methane was produced with a constant rate ($\approx$ 70 μmol h^{-1}) for 7 days. After 15 days, the total amount of methane reached 19 mmol, corresponding to 95% conversion for the amount of $CaCO_3$ used. The reaction residue was shown to be a mixture of CaO and $Ca(OH)_2$ from X-ray diffraction analysis. From this result, the hydrogenation reaction can be represented as follows:

$$CaCO_3 + 4H_2 \rightarrow CH_4 + Ca(OH)_2 + H_2O, \quad (1)$$

$$CaCO_3 + 4H_2 \rightarrow CH_4 + CaO + 2H_2O. \quad (2)$$

At the present stage of this work, it is difficult to conclude whether methane was formed directly from $CaCO_3$ or formed *via* two steps, thermal decomposition of $CaCO_3$ to release CO_2 followed by the hydrogenation of the CO_2. In the Ni-catalyzed hydrogenation of $CaCO_3$, the rate of methane formation at 400 °C is much larger than that of CO_2 evolution at the same temperature without hydrogen (run 17). Taking account of this fact, the former path, i.e. the direct hydrogenation of $CaCO_3$ (not *via* CO_2), seems more plausible. Probably, $CaCO_3$ was hydrogenated directly on the surface of $CaCO_3$ (not on the Ni catalyst surface) by the hydrogen spiltover from a Ni surface.

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