Methane formation by metal-catalyzed hydrogenation of solid calcium carbonate

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A study of the hydrogenation of solid $CaCO_3$ has shown that the addition of Pd and Ir catalysts causes a change in the gaseous product and, consequently, in the kinetics of the reaction. In the absence of catalyst, CO is formed at higher than 700 K with the activation energy of 236 kJ/mol and a nearly half order with respect to H_2 pressure, which is explained by the mechanism consisting of predecomposition and reduction. In the presence of the catalysts, CH_4 is exclusively formed even at 573 K at which the equilibrium decomposition pressure of $CaCO_3$ is extremely low, 1.1×10^{-5} Torr. Activation energies found in the range 105–118 kJ/mol and the H_2-pressure dependence of the initial rate suggest the direct interaction of $CaCO_3$ with spilt-over hydrogen atoms.

Keywords: calcium carbonate, metal-catalyzed hydrogenation, methane formation

1. Introduction

On heating most solid carbonates readily evolve CO_2 which can be converted by catalytic hydrogenation into carbon-containing compounds, such as CH_4 and CH_3OH. One might, therefore, expect that these compounds can be produced in a one-step process when the carbonates are heated with metal catalysts in the presence of H_2. Such a possibility was first examined by Tsuneto et al. [1] with mechanical mixtures of alkaline or alkaline-earth metal carbonates and transition metal powders, and proved by the selective formation of CH_4 in the stream of H_2 at 673 K. Since this reaction system is very interesting as one of the simplest methods for utilizing the abundant mineral $CaCO_3$, though not so favorable not only thermodynamically but also economically, further systematic investigations are needed for a better understanding of the mechanism. Thus, in the present work, we report a kinetic study of the hydrogenation of solid $CaCO_3$ with and without metal catalysts, such as Pd and Ir, which are supported on the surface of the solid reactant in order to obtain reproducible rate data.

2. Experimental

Solid samples used here were $CaCO_3$ of guaranteed grade (Wako Pure Chem.), $CaCO_3$ with 5 wt% Pd and $CaCO_3$ with 5 wt% Ir (Johnson Matthey, Japan). The metal-loaded samples were treated with H_2 at 373 K for 15 h before use. BET areas and percent metal exposed (D) were determined by the volumetric adsorption of Kr at liquid-nitrogen temperature and H_2–O_2 titration [2,3] at 300 K, respectively, by which the samples were characterized as follows:

$CaCO_3$: 5.5 m^2/g,
5 wt% $Pd/CaCO_3$: 7.0 m^2/g ($D = 3\%$),
5 wt% $Ir/CaCO_3$: 6.9 m^2/g ($D = 32\%$).

The temperature-programmed hydrogenation (TPH) and decomposition (TPDec) techniques were employed for examining the catalytic effect of Pd and Ir. In these experiments, solid samples containing 15 mg $CaCO_3$ were heated at a rate of 3 K/min in a stream of atmospheric H_2 or He (60 ml/min) and the effluent was monitored with a TCD detector after being passed through a cold trap cooled at dry-ice temperature. Two apparatuses were used for isothermal kinetic runs carried out at less than 200 Torr of H_2 usually with solid samples containing 100 mg of $CaCO_3$: One is a Cahn electrobalance (reaction volume: 3,620 ml), which was also used to follow the decomposition of $CaCO_3$ in vacuum (2×10^{-2} Torr). The other is a closed circulation apparatus (reaction volume: 275 ml) equipped with a Baratron capacitance manometer, a sampling tube for GC analyses and a cold trap for removing the gaseous product H_2O. When this apparatus was used, H_2 pressure was kept constant during the reaction by making up for the loss estimated from an observed pressure-drop, assuming the following overall reaction:

$$CaCO_3 + 4H_2 \rightarrow CaO + CH_4 + 2H_2O \qquad (1)$$

The occurrence of this reaction was confirmed by XRD and GC examinations of products, in addition to the weight loss measurements described later. All the gases of more than 99.99% purity (Takachiho Chem.) were used as supplied.

3. Results and discussion

3.1. Temperature-programmed hydrogenation (TPH)

Figure 1 shows the TPH data obtained from 5 wt% Ir/$CaCO_3$ (curve (A)), 5 wt% Pd/$CaCO_3$ (curve (B)) and pure $CaCO_3$ (curve (C)), together with the TPDec data from pure $CaCO_3$ (curve (D)) for comparison.

All the TPH curves occur at lower temperatures than the TPDec curve, though their shapes and peak maxima are different from one another, depending on both the presence and kind of metal catalysts. GC analyses of the effluent showed that CH_4 existed exclusively in curves (A) and (B), while CO and CO_2 in curve (C). Curve (C) is characterized to have no high-temperature tail, similarly to the TPDec curve, indicating that the gas transport properties through the bulk solid do not influence the TPH data of pure $CaCO_3$. It has been recognized that the vacuum decomposition of $CaCO_3$ is controlled by the transfer of produced CO_2 away from the outer sample surfaces [4], and hence adsorbed CO_2 is considered to play an important role also in the hydrogenation of $CaCO_3$ without catalyst. Curves (A) and (B) for the metal-loaded samples, on the other hand, have high-temperature tails and begin to occur at significantly lower temperatures (about 573 K for curve (A)) than curve (C). This finding can be explained by an increase in available reactive hydrogen, probably adsorbed H atoms, at low temperatures owing to the presence of Ir and Pd, since the starting temperature of the reduction of metal oxides by H_2 is known to be lowered by the addition of transition metals which are able to dissociate H_2 molecules [5]. In addition, the equilibrium decomposition pressure of $CaCO_3$ at 573 K is extremely low, or 1.1×10^{-5} Torr according to the empirical equation proposed by Hill and Winter [6]. It seems, therefore, quite likely that with the metal catalysts present hydrogenation reaction is initiated by a direct interaction of $CaCO_3$ and spilt-over H species. The difference in peak maximum between curves (A) and (B) may be related to the catalytic activities of Pd and Ir, but their activities cannot be compared precisely from the TPH data alone because of a large difference in metal dispersion.

3.2. Isothermal hydrogenation without catalyst

In the absence of catalyst, 700 K was the lowest temperature at which the hydrogenation of $CaCO_3$ takes place at a measurable rate. CO was produced solely (700–773 K) or together with the decomposition product, CO_2 (above 773 K). A considerable difference was observed between the time-courses of the two products. At 833 K, for example, CO pressure increased steadily with time, while CO_2 pressure reached abruptly in the very beginning of the reaction to 0.17 Torr which is slightly lower than the equilibrium decomposition pressure of $CaCO_3$ (0.86 Torr) and then changed very little. Therefore, the fact that no detectable CO_2 was observed in the reactions below 773 K is conceivable, considering the detection limit of the GC used, since the Hill and Winter equation [6] shows the decomposition pressure to be less than 0.1 Torr below 773 K.

Figure 2 shows the results of rate studies carried out at 748 K in a closed circulation apparatus varying the amount of $CaCO_3$ at a fixed H_2 pressure of 100 Torr.

It is to be noted that initial rates are all the same, in spite of differences in the amount of $CaCO_3$. On the other hand, a nearly half order with respect to H_2 pressure was observed. These findings can be explained by the following mechanism consisting of predecomposition and reduction, and probably involving dissociation of H_2 as a rate-determining step:

$$\begin{aligned} &CaCO_3 \rightarrow CaO + CO_2 \\ &CO_2 + H_2 \rightarrow CO + H_2O \end{aligned} \tag{2}$$

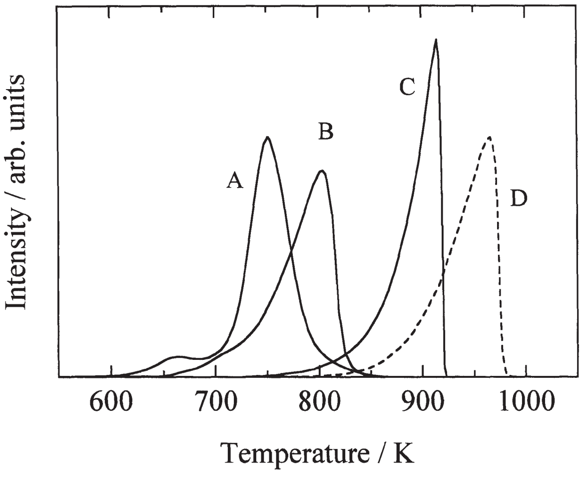

Figure 1. Temperature-programmed hydrogenation of 5 wt% Ir/$CaCO_3$ (curve (A)), 5 wt% Pd/$CaCO_3$ (curve (B)) and pure $CaCO_3$ (curve (C)), and comparison to temperature-programmed decomposition of pure $CaCO_3$ (curve (D)) in He. Heating rate: 3 K/min, flow rate: 60 ml/min, the effluent detected: CH_4 (curves (A) and (B)), CO + CO_2 (curve (C)).

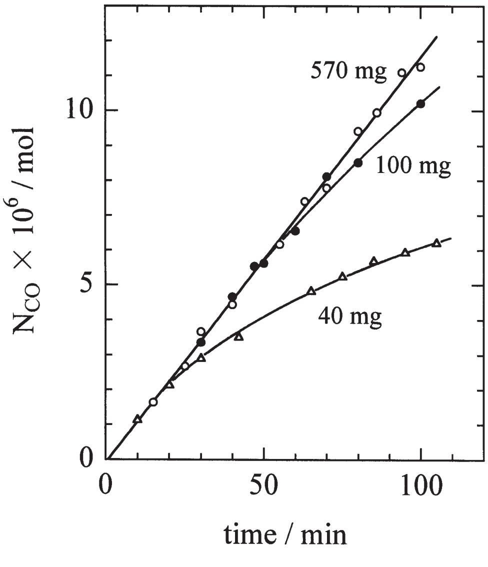

Figure 2. CO production as a function of reaction time in the hydrogenation of different amounts of pure $CaCO_3$ at 100 Torr H_2 and 748 K.

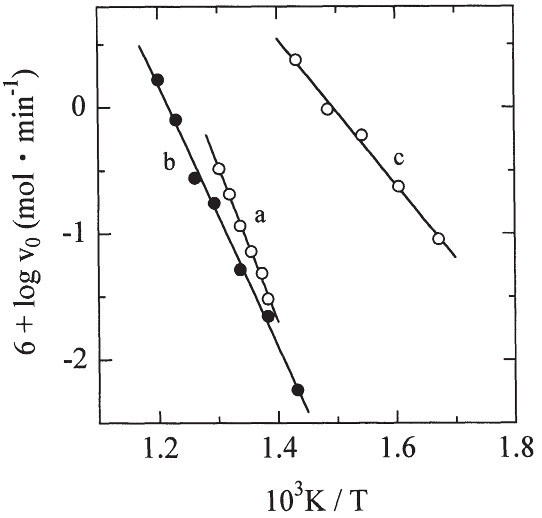

Figure 3. Effect of temperature on initial reaction rate, v_0. (a) CO formation in the hydrogenation of 570 mg pure $CaCO_3$ ($P_{H_2} = 100$ Torr, closed circulation apparatus), (b) decomposition of 100 mg pure $CaCO_3$ (vacuum, electrobalance), (c) CH_4 formation in the hydrogenation of 106 mg 5 wt% Ir/$CaCO_3$ ($P_{H_2} = 100$ Torr, closed circulation apparatus).

This mechanism is consistent with the TPH results described above and also with the characteristic time-course of CO_2 formation. Temperature dependence of the rate of CO formation was investigated with 570 mg of $CaCO_3$ at 100 Torr of H_2. The results obtained are shown in figure 3(a) in the form of an Arrhenius plot, together with plot (b) for the vacuum decomposition of $CaCO_3$. Plot (c) for the Ir-catalyzed hydrogenation of $CaCO_3$ will be discussed later.

From the slope of the linear plots, (a) and (b), apparent activation energies were calculated to be 236 and 199 kJ/mol, respectively. This difference, though small, might not be due to experimental uncertainties, since all of the values so far found for the vacuum decomposition are less than 210 kJ/mol [7]. Another feature of the figure is that the reaction with H_2 proceeds faster than the vacuum decomposition at a given temperature, suggesting that adsorbed CO_2 interacts faster with hydrogen than would be desorbed solely, especially below 773 K.

3.3. Isothermal metal-catalyzed hydrogenation

Both of the Pd- and Ir-catalyzed reactions were investigated at temperatures in the range 573–698 K. In this temperature range, the formation of CH_4 according to reaction (1) is thermodynamically not so favorable; for example, $K_P = 3.28 \times 10^{-3}$ atm^{-1} at 673 K, which shows the equilibrium pressure of CH_4 to be about 7.6 Torr in the presence of 100 Torr H_2. This equilibrium is established when 146 mg of $CaCO_3$ is hydrogenated in the electrobalance, while 11.2 mg in the closed circulation apparatus. In the former apparatus, therefore, the amount of $CaCO_3$ usually used (100 mg) will undergo complete hydrogenation at 673 K without removing the gaseous product H_2O if H_2 pressure is kept at 100 Torr. This was confirmed by the observation of a weight loss of 43.8 mg, quite close to the expected value of 44 mg. In the experiments with the latter apparatus, however, the removal of H_2O vapor was neccesary to shift the equilibrium. Irrespective of the apparatus used, reaction curves showed a deceleratory process. When compared in the initial constant-rate region (within about 6% conversion of $CaCO_3$), however, the reaction proceeded about 2.7 times as slowly in the electrobalance as in the closed circulation apparatus. The retardation in the former apparatus may be caused by the adsorption of H_2O vapor on the metal catalysts and/or solid reactant.

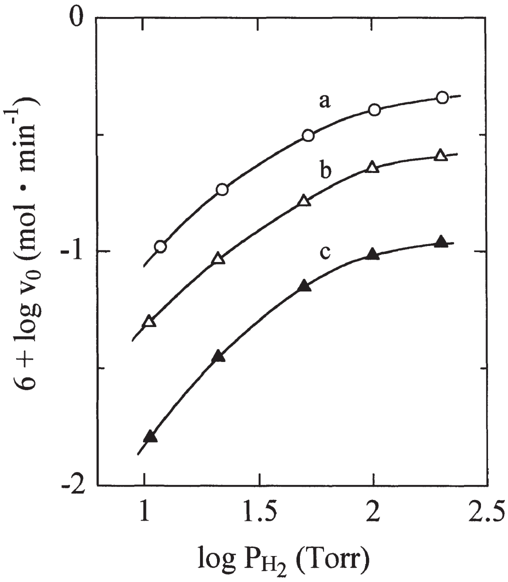

Figure 4. Effect of P_{H_2} on initial CH_4 formation rate, v_0, for the metal-catalyzed hydrogenation of $CaCO_3$ in an electrobalance. (a) 5 wt% Ir/$CaCO_3$ at 673 K, (b) 5 wt% Pd/$CaCO_3$ at 673 K, (c) 5 wt% Pd/$CaCO_3$ at 648 K. Sample weight: 106 mg.

Rate data obtained in the initial region of the Ir-catalyzed reaction carried out in the closed circulation apparatus are shown by plot (c) in figure 3, from which the apparent activation energy was determined to be 111 kJ/mol. Essentially the same activation energies were obtained when the electrobalance was used: 105 and 118 kJ/mol for the Ir- and Pd-catalyzed reactions, respectively. All these values are much lower than the standard enthalpy of decomposition of $CaCO_3$ (174 kJ/mol at 673 K), indicating that decomposition processes to form CO_2 are not involved in the metal-catalyzed hydrogenation. Therefore, it can be concluded that $CaCO_3$ directly interacts with H atoms spilt-over from metal surfaces in the first step of the reaction to form CH_4, at least under the conditions studied here (below 698 K). Figure 4 shows the dependence of initial rate of CH_4 formation on H_2 pressure.

In every case, the rate increases steadily with increasing H_2 pressure and appears to attain a constant value at sufficiently high pressures. Such a tendency can be interpreted as a kinetic transition from slightly higher than first-order at low pressures to zero-order at high pressures. Then, the rate data shown in the figure were analyzed with the following equation, in a similar form to the Langmuir adsorption isotherm:

$$v_0 = \frac{P^n}{a + cP^n}, \qquad (3)$$

where v_0 is an initial rate, P is H_2 pressure and a, c and n are constants. The equation with $n = 1.5$ was found to provide a satisfactory kinetic description of the reaction, though limited to the initial region. There still exists uncertainty, however, as to why the kinetic order is 1.5, but the relationship represented by equation (3) suggests that the rate of the dissociative adsorption of H_2 on metal surfaces may be fast enough compared with overall reaction rate. This is consistent with the conclusion of a direct interaction of $CaCO_3$ and spilt-over H atoms, from which reaction intermediates are suggested to be formed in the surface layer of $CaCO_3$. Experiments for investigating the intermediates are now in progress to establish the mechanism of metal-catalyzed hydrogenation of $CaCO_3$.

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