Kinetic study of metal-catalyzed reaction of solid calcium oxide with gas mixtures of methane and water vapor to form hydrogen

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With noble metal catalysts (Pd, Pt, Rh, Ir) present, hydrogen is formed by the interaction of solid calcium oxide with gas mixtures of methane and water vapor, according to $CaO + CH_4 + 2H_2O \rightarrow CaCO_3 + 4H_2$. Among the metals, Ir and Rh are so active that the reaction takes place at temperatures as low as 600 K. Rate data obtained with these metals show a nearly first order with respect to CH_4 pressure, while a negative order with respect to H_2O vapor pressure. The apparent activation energies are 171 and 217 kJ/mol for the Ir- and Rh-catalyzed reactions, respectively. On the other hand, Ni does not catalyze the reaction below 733 K, probably due to its strong interaction with H_2O vapor.

KEY WORDS: hydrogen formation; calcium oxide; methane; water vapor; metal catalysts

1. Introduction

It has been shown in our previous study of the hydrogenation of solid $CaCO_3$ [1] that the presence of metal catalysts such as Ir and Pd provides a specific pathway by which methane can be formed with the transformation of $CaCO_3$ to CaO even at 573 K, significantly lower than the temperature required for the non-catalyzed hydrogenation. The conversion of $CaCO_3$, however, is limited by chemical equilibrium ($K_P = 3.6 \times 10^{-3}$ at 600 K), suggesting a latent possibility of its reverse process,

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

This reaction is of much interest as being a simple process for producing pure hydrogen. Such a characteristic feature should be presented only in the temperature range where the decomposition pressure of $CaCO_3$ is very low, or alternatively the solid reactant CaO can serve to absorb CO_2 effectively. At high temperatures in the range 1000–1100 K which are usually applied for the conventional reforming processes [2,3], CO and CO_2 may be produced together with H_2, since the solid product becomes unstable and exhibits high decomposition pressure in the range 41–257 Torr which can be evaluated from the empirical equation proposed by Hill and Winter [4]. Thus, it is important to see if reaction (1) really takes place in the above limited range of temperature. The actual occurrence of this reaction was confirmed at 673 K in a preliminary experiment with Ir catalyst. In this article, we report the catalytic properties of five transition metals (Ni, Pd, Pt, Ir and Rh), together with some kinetic data obtained with the latter two metals which exhibit higher activity than the others.

2. Experimental

Metal catalysts were supported on the reactant CaO, in order to obtain reproducible rate data. Solid samples in this form (metal/CaO) were prepared from corresponding 5 wt% metal/$CaCO_3$ (or metal oxide/$CaCO_3$), before use. Commercial reagents Pd/$CaCO_3$ (Johnson Matthey), Ir/$CaCO_3$ (Johnson Matthey) and Pt/$CaCO_3$ (Wako Pure Chem.) were used as purchased, while Rh/$CaCO_3$ and NiO/$CaCO_3$ were prepared by deposition–precipitation from aqueous solutions of $RhCl_3{\cdot}3H_2O$ and $Ni(NO_3)_2$, respectively. These were subjected to the temperature-programmed hydrogenation carried out in a flow apparatus at a rate of 3 K/min up to 863 K. Weight-loss measurements with a Cahn electrobalance and XRD analyses confirmed the almost complete conversion of the carbonate into CaO. BET area and metal dispersion of solid samples thus obtained were determined by Kr adsorption at 77 K and O_2 chemisorption at room temperature, respectively. Isothermal kinetic runs were usually carried out with a solid sample containing about 8 mg of CaO in a closed circulation apparatus (reaction volume 275 ml) equipped with a Baratron capacitance manometer, a sampling tube for GC analyses and a U-shaped trap for condensing H_2O vapor. Each run was initiated by admitting usually a 1 : 1 mixture of CH_4 and H_2O vapor into the apparatus containing the sample preliminarily treated with 20 Torr of H_2 at reaction temperature (593–733 K), and followed manometrically. All the gases of more than 99.99% purity (Takachiho Chem.) were used as supplied.

3. Results and discussion

X-ray diffraction examinations showed that the solid samples prepared by the temperature-programmed hydrogenation of metal/$CaCO_3$ (or NiO/$CaCO_3$) contained no

Table 1
Physical properties of solid samples.

Sample	Preparation source[a]	Specific area (m^2/g)	Dispersion (%)
Ni/CaO	$NiO/CaCO_3$	15	1
Pd/CaO	$Pd/CaCO_3$	17	5
Ir/CaO	$Ir/CaCO_3$	22	17
Rh/CaO	$Rh/CaCO_3$	30	13

[a] Metal loading 5 wt%.

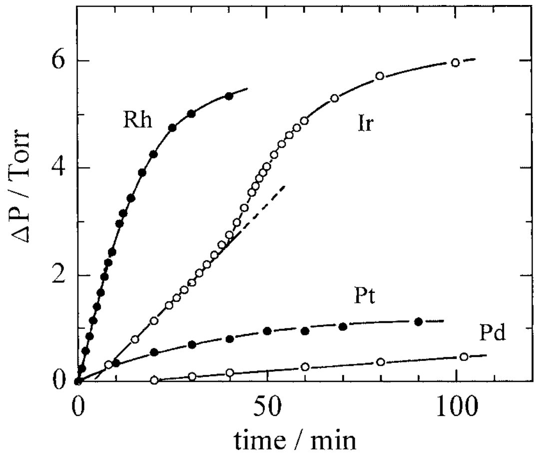

Figure 1. Pressure change against time curves for Ir-, Pd- and Pt-catalyzed reactions at 683 K and Rh-catalyzed reaction at 653 K: CaO 7.9 mg, $P^0 =$ 22.6 Torr ($CH_4/H_2O = 1$).

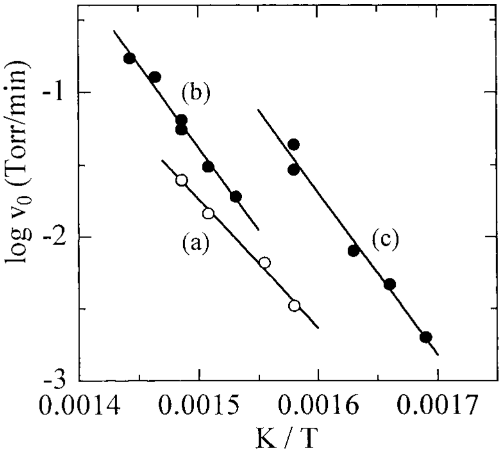

Figure 2. Effect of temperature on the initial rate, v_0, in stage I (a) and stage II (b) of Ir-catalyzed reaction and Rh-catalyzed reaction (c). CaO 7.9 mg, $P^0 = 22.6$ Torr ($CH_4/H_2O = 1$).

other materials than metal and CaO, and moreover that the CaO was transformed to calcite without any detectable change of the metal catalysts by the reaction with a gas mixture of CH_4 and H_2O. Diffraction peaks of Ir and Rh were much broader than those of Pd, Pt and Ni, suggesting a large difference in the size of metal particles. This was confirmed by the dispersion measurements with O_2, as shown in table 1.

The dispersion of Pt on CaO (not measured) is estimated to be as small as that of Ni, since the value of $D = 2\%$ was obtained for $Pt/CaCO_3$.

3.1. Kinetic results

Among the five metals used, Pd, Pt, Ir and Rh were found to catalyze reaction (1) at temperatures below 733 K, but Ni did not at all. Figure 1 shows typical reaction curves at 683 K, except 653 K for a Rh-catalyzed reaction.

In all cases shown, hydrogen was selectively formed. Trace amounts of CO and CO_2 were sometimes detected, especially when the reaction was carried out at temperatures higher than 673 K. In the Ir-catalyzed reaction shown in figure 1, for example, the products detected after 300 min were as follows:

$$H_2\ 19.0_0\ \text{Torr}, \quad CO\ 0.0_6\ \text{Torr}, \quad CO_2\ 0.0_6\ \text{Torr}.$$

As can be seen from the figure, Rh- and Ir-catalyzed reactions proceed faster than Pt- and Pd-catalyzed ones. This difference may arise essentially from the difference in metal dispersion, and hence it is difficult to make direct comparison of their catalytic activities. It seems reasonable, however, to conclude that Rh is more catalytically active than Ir, because of similar metal dispersion. Another interesting feature of the figure is that the Ir-catalyzed reaction is accelerated abruptly after an initial linear progress to a certain extent and thereby reveals two distinct stages (I and II). The reason for such an anomalous behavior is not clear at present, but we feel that it is attributable to the contribution of a certain surface step peculiar to solid-state reactions, *e.g.*, a nucleation step (formation and growth of reaction nuclei) which is known to be sensitive to surface properties and to affect the overall kinetic obedience. The acceleration point defined by the conversion at which the reaction is abruptly accelerated varied with the initial ratios of the reactants, such as CH_4/H_2O and $(CH_4/H_2O)/CaO$, but not significantly with temperature. This enabled us to determine the activation energy for stage II, using the slope of a reaction curve obtained immediately after the acceleration point.

Temperature dependence of the rate of reaction (1) was investigated with 7.9 mg of CaO and an 1 : 1 gas mixture (CH_4/H_2O). The results obtained are shown in figure 2 in the form of Arrhenius plots. From the slopes of linear plots (a) and (b) apparent activation energies E_a were calculated to be 171 and 220 kJ/mol for stages I and II of the Ir-catalyzed reaction, respectively. The latter is essentially the same as the value of 217 kJ/mol determined from plot (c) for the Rh-catalyzed reaction, suggesting that the rate-determining step of this reaction might be the same as that of stage II of Ir-catalyzed reaction. It is also interesting to note that all of the energies obtained here are much larger than the energies E'_a for the reverse reaction (metal-catalyzed hydrogenation of solid $CaCO_3$) which have been previously determined to be in the range 105–118 kJ/mol [1]. Since reaction (1) is slightly endothermic, *e.g.*, $\Delta H^0 = 8.6$ kJ at 700 K, it is evident that the well-known relationship $\Delta H^0 = E_a - E'_a$ does not hold in the present case. This might be due to the fact that E'_a is derived from the reverse reaction carried out

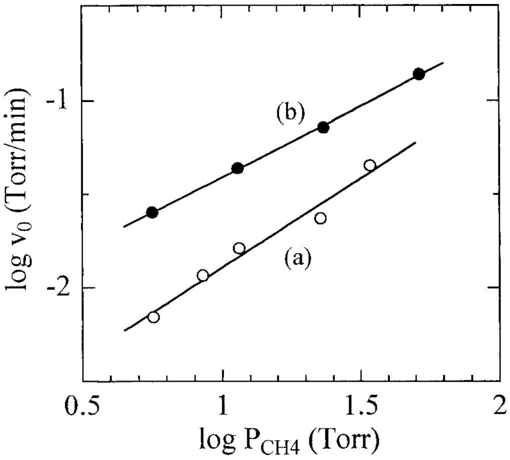

Figure 3. Effect of CH_4 pressure on the initial rate, v_0, in stage I of Ir-catalyzed reaction at 673 K (a) and Rh-catalyzed reaction at 633 K (b). CaO 7.9 mg, $P^0_{H_2O} = 11.3$ Torr.

in a dry atmosphere [1], contrary to E_a for reaction (1) in which H_2O vapor is essential.

Rate studies were also carried out by varying CH_4 pressure at a fixed H_2O pressure of 11.3 Torr at 673 K (Ir/CaO) or 633 K (Rh/CaO). The results obtained are shown in figure 3.

From the slopes of linear plots, the order with respect to CH_4 pressure was determined to be 1.0 for stage I of the Ir-catalyzed reaction and 0.8 for the Rh-catalyzed one, indicating that CH_4 is adsorbed weakly on the catalysts. Dependence of the initial rate on H_2O vapor pressure was investigated in a similar manner. Typical results obtained for Rh-catalyzed reaction at 633 K are as follows:

$$v_0 = 0.078 \text{ Torr/min } (1.1_7\ \mu\text{mol-H}_2\text{/min}),$$

$$\text{at } P^0_{H_2O} = 8.07 \text{ Torr};$$

$$v_0 = 0.042 \text{ Torr/min } (0.63\ \mu\text{mol-H}_2\text{/min}),$$

$$\text{at } P^0_{H_2O} = 15.93 \text{ Torr}.$$

The same trend was observed for Ir-catalyzed reaction. These indicate the reaction order with respect to H_2O vapor pressure to be negative, but an exact value could not be determined, because of an experimental limitation of its maximum pressure (about 20 Torr at room temperature).

3.2. Catalytic activity of Ni

Possible explanations for the observation that Ni exhibits no activity in catalyzing reaction (1) below 733 K include the inhibition by either the accumulation of carbon species on the surface, strong interaction between Ni and the support CaO, or a poisoning effect of H_2O vapor. Recently, Choudhary and Goodman have studied a new process named “Stepwise steam reforming of methane” [5] in which a step to produce H_2 and surface carbon from CH_4 is followed by a separate step for removing the carbon *via* reaction with water, and reported that the process is successfully operated in cycles on zirconia-supported Ni catalyst in the temperature range 648–673 K, which is closely similar to the present condition. This suggests the first explanation to be ruled out. As for the second explanation, Zhang *et al.* have already confirmed that there exists no detectable solid reactions between Ni (or NiO) and CaO [6]. Choudhary and Rajput reached the same conclusion [7]. These considerations and the fact that Ni has a stronger affinity for H_2O vapor than Ir and Rh suggest the third explanation to be the best conceivable.

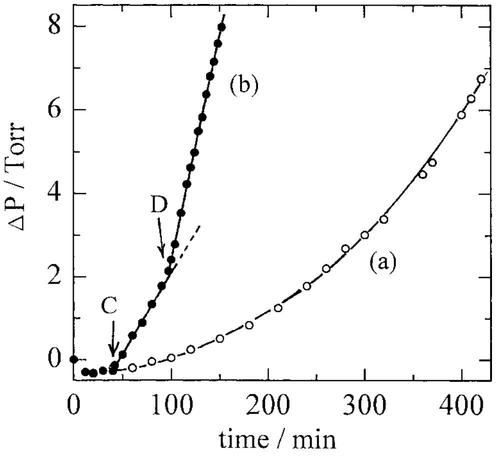

Figure 4. Pressure change against time curve for Ni-catalyzed reaction at 853 K (a) and the influence of abrupt changes in gas-phase composition (b): H_2 (20 Torr) was added at C, and H_2O vapor pressure was reduced from about 10 to 4 Torr at D. CaO 7.9 mg, $P^0 = 22.6$ Torr ($CH_4/H_2O = 1$).

In order to see if this is really adequate, reaction temperature was raised to 853 K, at which no reaction occurs in the absence of Ni. Figure 4(a) shows the pressure change in a Ni-catalyzed reaction initiated by admitting 22.7 Torr of a 1 : 1 gas mixture onto 7.9 mg of Ni/CaO.

GC analyses showed the simultaneous formation of H_2 with CO and CO_2. The amount of CO increased steadily with time, while CO_2 was kept at less than the decomposition pressure of $CaCO_3$ (1.2 Torr) throughout the reaction. The products detected after 24 h were as follows:

$$H_2\ 28.5_2 \text{ Torr}, \quad CO\ 8.4_7 \text{ Torr}, \quad CO_2\ 0.7_2 \text{ Torr}.$$

It is interesting to note that the reaction was accelerated continuously up to near the end point. In order to elucidate the reason for this accelerative progress, gas-phase composition was abruptly changed during the reaction. Curve (b) shows the result of an experiment in which about 20 Torr of H_2 was suddenly added at point C and then H_2O vapor pressure was reduced from about 10 to 4 Torr at point D by cooling a cold-trap at 0 °C. Rate enhancement at points C and D demonstrates the promoting effect of H_2 and retarding effect of H_2O vapor, respectively. Since Ir- and Rh-catalyzed reactions were found to be little affected by H_2 addition, the rate enhancement at point C can be ascribed to an increase in the number of catalytically active sites. Thus, it seems likely that H_2 acts to keep the Ni surface clean by reacting with a thin oxide layer possibly formed by the interaction of H_2O vapor. Practically, the crystalline phase of NiO was not detected by XRD, even after exposing Ni/CaO to 12 Torr of H_2O vapor

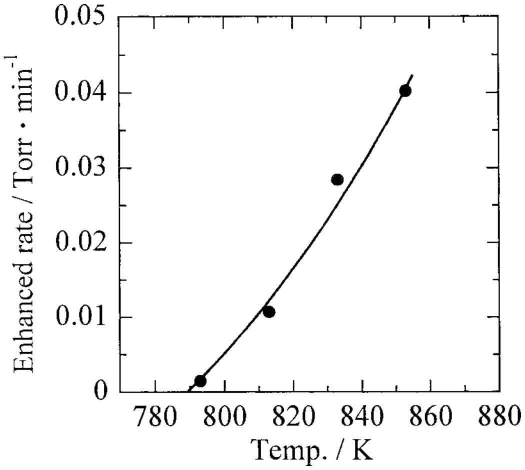

Figure 5. Rate enhancement caused by H_2 addition at different temperatures, in the initial region of Ni-catalyzed reaction: CaO 7.9 mg, $P^0 = 22.6$ Torr ($CH_4/H_2O = 1$).

for 1 h at 673 K. This result, however, is not sufficient justification for excluding the formation of the oxide layer.

Another experiment to investigate the lowest temperature at which H_2 exerts its promoting effect has been carried out at temperatures below 853 K. The results obtained are shown in figure 5, in which enhanced rates are plotted against temperature.

It is clear that reaction (1) does not take place below about 790 K even if 20 Torr of H_2 is present. This temperature is significantly high, compared to those (648–673 K) applied for the stepwise steam reforming of methane on Ni/ZrO_2 [5]. This difference might reflect the metal–support interaction.

Some suggestions will be made concerning the mechanism of reaction (1). It has been recognized that CH_4 easily cracks on metals. This and the fact that no reaction occurs on pure CaO below 853 K suggest that CH_4 activation, or C–H bond breaking which leads to the possible formation of hydrogenated carbon species, usually denoted by CH_x, favorably occurs on the metal crystallites under the present conditions. The accelerative progress of Ni-catalyzed reaction, which is due to a steady increase of H_2 produced and also to a decrease of H_2O vapor with time, is another support of the activation process. On the other hand, H_2O vapor interacts with both the support CaO and metal particles. When interacting with H_2O, the surface of CaO may be fully covered by OH species, while metals may lose a part of their activity for C–H bond breaking. Thus, it may be expected that the CH_x species migrate to the edge of metal crystallites, and then interact with OH species on CaO to form carbon-containing species, such as formates or bicarbonates, which are finally converted into carbonates. It is well known that CaO acts as an excellent catalyst for coal- and tar-gasification with steam [8,9], in which CaO is assumed to interact directly with the surface of coal and decompose them to adsorbed carbon and gaseous materials including H_2 and CH_4 at the first step of its catalysis. Under the present low-temperature conditions, however, a similar step (catalysis by CaO) would not be involved. Further detailed studies by means of XPS and FT-IR are necessary, for better understanding of reaction (1).

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