

Selective formation of methane in reduction of CO₂ with water by Raney alloy catalyst

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Abstract

The reduction of carbon dioxide with water has been investigated for the direct synthesis of methane in the presence of Raney alloy. The reduction of CO₂ using Raney Fe in an aqueous alkali solution gave selectively an alkali formate 32.9% based on the alkali employed. The similar reaction using Raney Ni gave methane (25.7%) in high selectivity together with a small amount of an alkali formate (4.2%). The mixed catalyst of Raney Fe and a supported ruthenium catalyst on activated carbon (Raney Fe–Ru/C) exhibited a high catalytic activity for the reduction of CO₂ and gave exclusively methane in moderate yield (45.3%). The reaction products were also controlled by the reaction temperatures, i.e., the yield and selectivity of methane increased with an increase in the reaction temperatures by suppressing the formation of an alkali formate. The apparent activation energy for the formation of methane was estimated to be 17 kcal/mol for the Raney Fe–Ru/C mixed catalyst in aqueous NaOH solution. The mechanism for the unique methanation of CO₂ involving formate intermediate is discussed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Methane formation; CO₂ reduction; Raney alloy catalyst

1. Introduction

The utilization of CO₂ has recently received much attention since the global warming mainly due to CO₂ was recognized as one of the most serious problems in the world. Although, catalytic hydrogenation of CO₂ into valuable chemicals and fuels, such as methane and methanol [1–6], has been recently recognized as one of demanding recycling technologies, most of these previous studies have been limited to the use of hydrogen gas (H₂) which is mainly prepared by water gas shift reaction that pro-

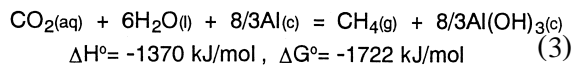
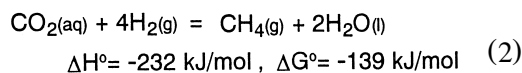
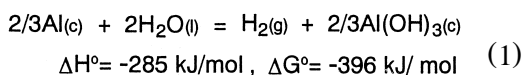
duced CO₂ as a fatal by-product. Therefore, these studies are inconsistent with the purpose of the promising approaches to CO₂ fixation. The direct utilization of water for the reduction of CO₂ is one ultimate goal of chemists, since water is the vast natural resource of hydrogen sufficient to reduce the large quantity of CO₂ at a time. Furthermore, the reduction of CO₂ in aqueous solution is a particularly attractive approach to the utilization of CO₂, as water is the common solvent for the recovery of CO₂ from process flue gases.

We previously reported that the reduction of CO₂ to potassium formate is effectively proceeded by palladium chloride catalysis in aque-

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ous potassium hydroxide [7]. We have now widened the scope of the previous study with particular attention to search for the possibility of the reduction of CO₂ with water as hydrogen source and convert them into useful chemical materials.

We now report the unique methanation of CO₂ using water–Raney alloy system as molecular hydrogen provider in place of H₂ (Eqs. (1)–(3)), where Al-cited equations is an aluminum metal originating from Raney alloy). This methanation cannot be carried out catalytically with respect to the Raney alloy, but methane was obtained selectively in acceptable yield. No such thermochemical reduction of CO₂ with water instead of H₂ have been reported so far.



2. Experimental

2.1. Materials

Raney alloy, 5% carbon-supported ruthenium (Ru/C), and other metal catalysts were purchased from Nacalai Tesque and used without further purification. Carbon dioxide was commercially supplied by Kyoto Teisan, and used without further purification.

2.2. Measurements

The GC analysis was performed on a Hitachi GC-O23 using a column packed with active carbon for gaseous products. The peak areas

were determined by using a Shimadzu chromatopac C-R6A integrator. The HPLC analysis for alkaline metal formate was carried out on a Shimadzu LC-10A using a column packed with SCR-101H (25 cm × 6 mm) eluted with aqueous perchloric acid (pH 2.1) solution. The contents of alkali and alkaline-earth metal carbonate and hydrogencarbonates in the aqueous solution were determined by the classical titration method with 0.1 M HCl using phenolphthalein and methyl orange as an indicator.

2.3. General procedure

The reaction was carried out using batch reactor in a large excess of water. A typical procedure is as follows. Sodium hydroxide (10 mmol), Raney Fe (0.2 g), 5% carbon-supported ruthenium (Ru/C) (0.05 g), and water (8 ml) were charged into a shaking-type autoclave (made of stainless-steel; ca. 30 ml) containing several stainless-steel stir balls. After the contained air was carefully replaced by argon, the autoclave was pressurized with CO₂ (50 atm) at room temperature, and then the autoclave was heated and shaken constantly at 380°C for 2 h, the total pressure then reached to 320 atm. After the autoclave had been rapidly cooled by air-blowing, the reaction gas was collected in a gas-burette, and then determined by GC. The remaining reaction mixture was taken into water, and then the solid materials were filtered off. The filtrate was subjected to the titration of alkali compounds and the HPLC analysis of alkaline metal formate.

2.4. Determined of initial rate

Kinetic measurement was carried out at the reaction temperature ranging from 240 to 340°C. First, a mixture of Raney Fe (0.2 g), Ru/C (0.2 g), and CO₂ (50 atm) was charged into the autoclave as described above. After the autoclave had been heated at a required temperature (ca. 30 min), aqueous 1.25 mol/l NaOH solution (8 ml) was introduced into the autoclave by

pump, and immediately the shaking was started. After a required reaction time, the autoclave was allowed to cool to room temperature rapidly. The work-up and analysis were carried out as above. The initial rate v_o was determined from the experimental equation: $y = t/(at + b)$, where y = yield of methane (mmol), t = reaction time (min), and a and b = constants. Further, the initial rate, $v_o = (dy/dt)_o = 1/b$ (mmol/min).

3. Results and discussion

3.1. Activity and selectivity of catalysts in the reduction of CO₂

Table 1 presents the typical results of the activities of Raney alloy catalysts and the catalytic activities of an additive catalysts to promote CO₂ reduction with water at 380°C using the batch system operating. For example, when a mixture of CsOH (10 mmol) and 1:1 Raney

Fe (0.2 g), and 5% carbon-supported ruthenium (Ru/C) (0.05 g) in water (8 ml) was heated under the pressure of CO₂ (50 atm at room temperature) at 380°C for 2 h, then the total pressure increased to 320 atm, and methane was obtained as a main product (45.3% yield or 90.8 mol/Ru atom) along with a very small amount of cesium formate (1.2%), and a liberation of H₂ (30%) as show in run 4 in Table 1. Where the yield is defined as a product molar percent relative to employed alkali metal hydroxide (CsOH). First, we examined the catalytic activities of typical Raney alloy catalysts, such as Raney Fe, Raney Ni, Raney Co, and Raney Cu, for the CO₂ reduction under the conditions described above. As shown in Table 1, these Raney alloy catalysts exhibited the different activities for the reaction, i.e., Raney Fe, Raney Co, and Cu alloy gave cesium formate as a main product, while Raney Ni alloy gave methane in high selective. Interestingly, the addition of Ru/C catalyst to the Raney Fe system exhibited more activity to promote the formation of methane than that of Raney Ni and Raney Ni–Ru/C mixed catalyst (runs 4 and 8 vs. 6 in Table 1). Other mixed catalysts (runs 9–11 in Table 1) were inferior to that of the Raney Fe–Ru/C mixed catalyst in yield and in selectivity of the methanation. It should be noted that the formation of CO [8–10] and C₂–C₄ hydrocarbons [11,12] obtained by others in CO₂–H₂ systems was not observed at all in the present reactions. This efficient methanation for Ru catalyst had been reported in previous studies on the reduction of CO₂ with H₂ [8,13–15], which were conducted at higher partial pressure of H₂ than that of CO₂ (H₂/CO₂ = 3–4). It is noteworthy that the present methanation gave similar results to that of the high ratio H₂/CO₂ system in H₂–CO₂ methanation, because a relative ratio of a liberated H₂ to CO₂ during the present methanation is usually very small (H₂/CO₂ = 0.1–0.12). The higher selectivity observed for methane formation may be due in part to catalytic cracking of higher molecular weight hydrocarbon products. This was tested

Table 1
Catalytic activity for the reduction of CO₂ with water^a

Run	Catalyst	Products (%) ^b			
		CH ₄	Formate	CO	H ₂
1	none	0	8.3	2.1	43.9
2	Raney Fe ^c	0	32.9	4.0	123.8
3	Raney Co ^c	5.0	20.9	2.4	75.2
4	Raney Ni ^c	25.7	4.2	trace	15.2
5	Raney Cu ^c	0	23.8	2.7	90.8
6	Raney Fe–Ru/C ^d	45.3	1.2	0	30.0
7 ^e	Raney Fe–Ru/C ^d	25.7	1.4	0.3	7.5
8	Raney Ni–Ru/C ^d	32.0	1.6	0	6.1
9	Raney Fe–Rh/C ^f	5.6	3.5	3.5	115.2
10	Raney Fe–Pd/C ^g	0	30.8	4.3	143.4
11	Raney Fe–Ru/Al ₂ O ₃ ^h	23.7	13.1	2.6	67.8

^aThe reaction were carried out in a stainless-steel autoclave (30 ml). Conditions: Raney alloy (0.2 g), additive catalyst (0.05 g), CsOH (10 mmol), H₂O (8 ml), CO₂ (50 atm at room temperature), 380°C, and 2 h.

^bDetermined by HPLC and GLC, and based on base employed.

^c1:1 Raney alloy powder.

^d5% Carbon-supported Ru powder.

^eNaOH (10 mmol) used in place of CsOH.

^f5% Carbon-supported Rh powder.

^g5% Carbon-supported Pd powder.

^h5% Alumina-supported Ru.

by injecting ethane (2.5 mmol) into the reaction medium (Raney Fe–Ru/C) under similar conditions to run 6 in Table 1 without CO₂. Methane was obtained in a yield of 1.95 mmol and a slight ethane (0.15 mmol) were detected by GC. Hence, the cracking of higher hydrocarbons afforded during CO₂ methanation cannot be overlooked.

The difference in the catalytic feature between Raney Ni and Raney Fe for the methanation is due to the differing oxidation-reduction potential of both metals. It is well known that at high temperature, iron metal has a higher tendency toward the oxidation by water than nickel metal ($\text{H}_2\text{O} + \text{Fe} = \text{FeO} + \text{H}_2$) [16]. Therefore, Raney Fe–Ru/C mixed catalyst is more effective promoter for H₂ liberation than Raney Ni system and a more selective catalyst for the methanation.

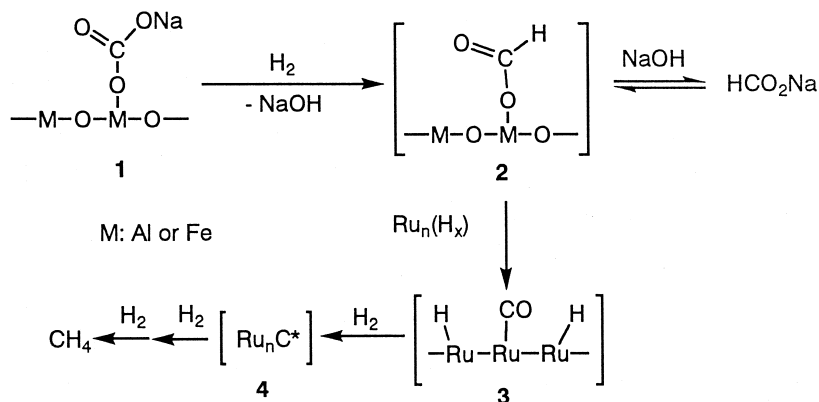
Also, we have found a significant effect of alkali metal ion added, especially cesium ion, i.e., the yield of methane in an aqueous CsOH solution was about double of that in an aqueous NaOH solution (compare runs 6 and 7 in Table 1). The high effectiveness of cesium ion has been observed in our previous study [17] and in other reported for water–gas shift reaction [18]. The difference in reactivity among the alkali metal ions is ascribed to those differing size. The cesium ion, which has the largest ionic radius, is considered to be only weakly paired with the CO₂ as a carbonate. This would pre-

sumably facilitate the activation of the CO₂ by interaction with the surface of the catalyst as will be described later (Scheme 1).

In the absence of a catalyst (run 1 in Table 1), the reaction afforded a small amount of cesium formate (8.1%) and CO (2.1%) with the liberation of H₂ (43.9%). This may explain that the metals dissolved from the reactor can become incorporated in the reaction mixture due to corrosion and act catalyst.

3.2. Effects of the reaction variable

To obtain a deeper insight into the feature of the methanation, we investigated the reduction of CO₂ using Raney Fe–Ru/C mixed catalyst and an aqueous NaOH solution in place of CsOH one as follows, because the NaOH solution is more convenient medium than other alkali solution for CO₂ recovery. In search for the optimum reaction conditions, the effect of the reaction temperature on the yields and products distribution was examined in an aqueous NaOH solution to give the results shown in Fig. 1. The reaction temperature has a marked effect on product distribution. At low temperatures (< 240°C), the total yield of sodium formate and methane was less than 14 mol%, and the formate formed in high selectivity. The formation of methane increased at the expense of the formation of sodium formate as the temperature is increased; the highest yield (26%) and selec-



Scheme 1.

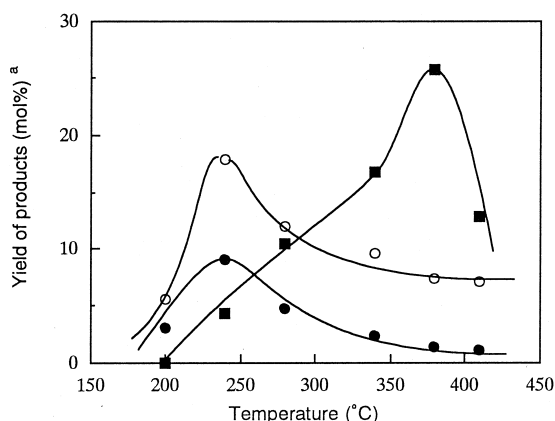


Fig. 1. Effect of reaction temperature on the reduction of CO_2 with water in the presence of Raney Fe–Ru on carbon mixed catalyst. Conditions: Raney Fe (0.2 g), 0.5% Ru on carbon (0.05 g), NaOH (10 mmol), H_2O (8 ml), CO_2 (50 atm at room temperature), 2 h. ●, HCO_2Na ; ■, CH_4 ; ○, H_2 . ^aBased on NaOH employed.

tivity (95% based on the sum of methane and formate formed) of methane were achieved at about 380°C . Since the critical point of water is 374.2°C , the change in the physical property of the reaction medium could be the cause for such variation of the reactivity. At the temperature below the critical point of water, the reaction proceeds mostly in liquid phase, while at supercritical region, the water is expected to be sufficiently gas-like phase.

Table 2 shows the effects of the concentration of NaOH and the partial pressure of CO_2 on the yields of products for the CO_2 reduction at 280°C . The dependence of the formate formation on the concentration of NaOH was more significant than that of the formation of methane. The formation of methane proceeded even without base (run 1 in Table 2). The yield of sodium formate increased continuously with increasing concentration of NaOH, whereas both yields of methane and H_2 increased with an increase in the concentration of NaOH up to 1.25 mol/l and then levels off in the same tendency as H_2 liberation.

The effect of the partial pressure of CO_2 on the yields of methane and sodium formate was sharp at low pressure (< 2 atm), and ap-

proached to zero-order dependence at a high pressure (> 5 atm). A control experiment conducted in the absence of CO_2 gave neither methane nor sodium formate but only resulted in H_2 liberation. This result implies that the carbon of methane and metal formate originates from the CO_2 carbon employed.

The time-yield profile of the products in the reduction of CO_2 under various amount of Ru/C catalyst is shown in Fig. 2a and b, respectively. When only Raney Fe was used as catalyst, sodium formate (marked ○ in Fig. 2b) is a main product over the reaction times. As shown in Fig. 2, an addition of Ru/C catalyst to the Raney Fe system caused the formation of methane, and the rate of methane formation increased with increasing amount of Ru/C added (Fig. 2a). One characteristic behavior in the reaction is a rapid formation of sodium formate in an early stage (Fig. 2b), i.e., the yield of sodium formate reached to its maximum value in the early stages (ca. 0.5 h), and the maximum value decreased with increasing amount of Ru/C accompanying an enhancement of the rate of methanation. The most important feature of this reaction is that the yield of methane increased at the expense of the formate formation as the reaction proceeds.

Table 2
Effect of the amount of NaOH and pressure of CO_2 on the yield of products at 280°C ^a

NaOH (mol^{-1})	CO_2 (atm) ^b	Products yield (mmol) ^c		
		CH_4	HCO_2Na	H_2
0	50	0.623	0	0.146
0.25	50	0.765	0.021	0.213
0.625	50	0.812	0.089	0.363
1.25	50	1.045	0.466	1.100
2.50	50	1.095	0.902	1.010
1.25	0	0	0	6.376
1.25	2	0.810	0.355	3.102
1.25	5	0.920	0.477	1.607
1.25	20	0.954	0.454	1.269

^aThe reactions were carried out in a stainless-steel autoclave (30 ml). Conditions: Raney Fe (0.2 g, unpretreatment), 5% Ru–carbon (0.05 g), H_2O (8 ml), 280°C , 2 h.

^bAt room temperature.

^cDetermined by HPLC and GLC.

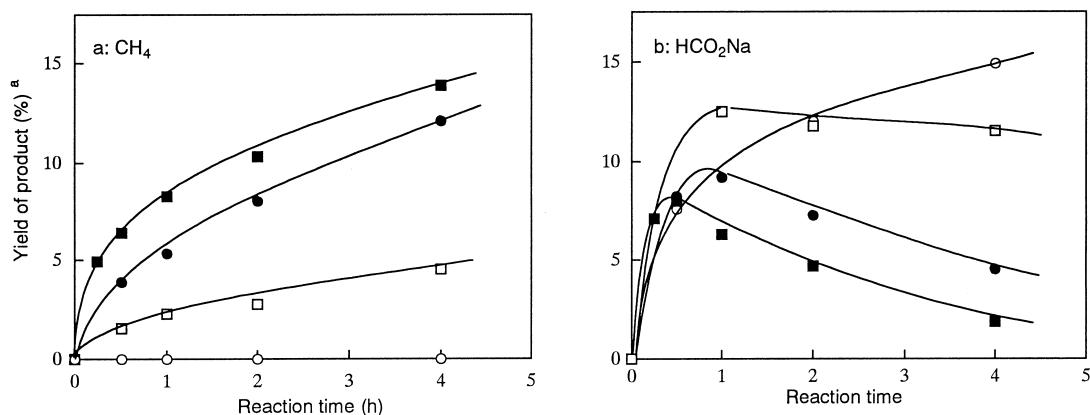
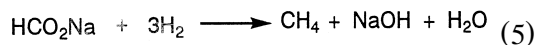
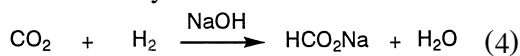


Fig. 2. Effect of the amount of Ru/C on the product yields. Condition: CO₂ (50 atm at room temperature), NaOH (10 mmol), Raney Fe (0.2 g), H₂O (8 ml); 280°C. ^aBased on NaOH employed. ○, Ru/C = 0; □, Ru/C = 0.01 g; ●, Ru/C = 0.03 g; ■, Ru/C = 0.05 g.

These findings indicate that the Ru catalyst plays an essential role in conversion of the formate into methane, and the formate is an intermediate in the methanation. The overall reaction is supposed to proceed in two steps, i.e., first reduction of CO₂ to sodium formate (Eq. (4)) followed by the slower Ru-catalyzed hydrogenation to give methane (Eq. (5)). This is also supported by the observation that the reaction of sodium formate (10 mmol) in place of CO₂ under the similar condition to run 6 in Table 1, at 320°C instead of 380°C, gave methane in 18% yield.



3.3. Kinetic study

Direct comparison of the activation energy obtained in the present work with previous works is difficult, since previous studies were carried out in different reactor systems under different conditions, but some features may be discussed for reference. We examined the variation of the reaction rate with temperature in the range from 240 to 340°C and estimated an

apparent activation energy (E'_a). The results are shown in Fig. 3 and Table 3. The initial rates (v_0) were determined from the data at early period (< 2 h) to avoid possible complications due to the factors such as change in catalytic activity. The initial rates interpolated to 253°C and apparent activation energy for the methanation of CO₂ are summarized in Table 3 and compared with data in those references where a continuous flow system has been used. The initial rate of the present methanation is some smaller than that of CO₂-H₂ methanation, but is about seven times that of CO-H₂ methanation [8]. The apparent activation energy for the present methanation was estimated to be approximately 71 kJ/mol from the Arrhenius plot in the range of 240–280°C. This value (71 kJ/mol) is close to the values of CO₂-H₂ methanation using Ru/C (82 kJ/mol) [8], Ru/Al₂O₃ (67 kJ/mol) [13], and Ru/SiO₂ (72 kJ/mol) [10]. Also, the methanation of CO-H₂ reported proceeds with much higher activation energy of 109 kJ/mol [8], in which the hydrogenation step of a surface carbon to methane has been proposed as the determining step [19].

The Arrhenius plot for the methanation is not linear as shown in Fig. 3b. A tendency of decrease in activation energy for the methanation at higher temperature is usually observed in a catalytic reaction. Although no direct evidence

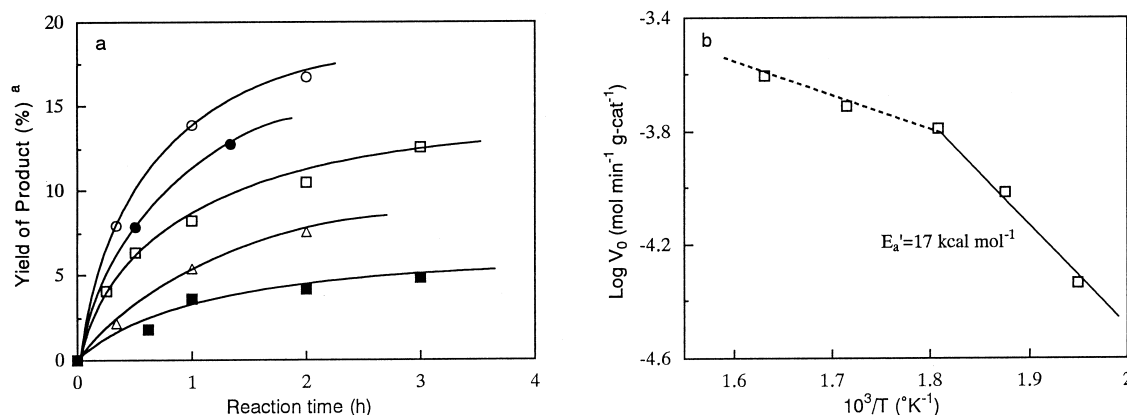


Fig. 3. Effect of reaction temperature on the formation of methane and Arrhenius plot. Reaction conditions: CO₂ (50 atm at room temperature), Raney Fe (0.2 g), 5% Ru/C (0.05 g), NaOH (10 mmol), H₂O (8 ml). ^aBased on NaOH employed. ■, 240°C; △, 260°C; □, 280°C; ●, 310°C; ○, 340°C.

was obtained to prove this behavior, this behavior is mainly ascribed to the following two reasons. One is the difference of reaction phase of water, i.e., noncritical and supercritical conditions. Under the supercritical conditions, the reaction most likely follows a gas–solid heterogeneous reaction, wherein the density of water is significantly low [20] and a solution and dissociation of the formate intermediate becomes unfavorable. Another reason is that the deposition of carbonaceous materials on the surface of ruthenium catalyst is occurring to deactivate the catalyst, especially at high temperatures. Such a tendency was also reported by other systems [9,10,19].

As concerns the mechanisms of methane synthesis in the CO₂–H₂ reaction, two main routes can be considered: (1) the removal of O from CO₂ occurs in a stepwise manner, and the surface carbon formed is hydrogenated into methane, and (2) through the formation of a surface complex which is subsequently into methane. Some studies provide evidence that the first of these proposed mechanisms may be correct and that CO₂ methanation on a wide variety of catalysts involves, firstly, the CO₂ dissociation to CO followed by further dissociation of CO to a carbon intermediate which is hydrogenated to methane [8–10,13–15,21,22]. It has been also shown [8] that the concentration

Table 3
Comparison of kinetic data with those from previous studies

Catalyst system (precursor)	Reaction	Initial rate (253°C) × 10 ⁶ (mol/min/g cat)	E _a ^a (kJ/mol)
5% Ru/C–Raney Fe ^b	CO ₂ /H ₂ O	71.1 ^c	71 (240–280°C)
4.3% Ru/C ^d	CO ₂ /H ₂ (1/4)	116.4	82 (205–300°C)
Ru/Al ₂ O ₃ ^e	CO ₂ /H ₂ (1/3)		67 (203–283°C)
Ru/SiO ₂ ^f	CO ₂ /H ₂ (1/4)		72 (230–290°C)
1.4% Ru/C ^d	CO/H ₂ (1/3)	10.2	109 (~ 250°C)

^aApparent activation energy.

^bThis study.

^cThis value as estimated by interpolation.

^dData from Ref. [8].

^eData from Ref. [13].

^fData from Ref. [10].

of the surface species CO and carbon on the Ru particles is much lower during the CO₂–H₂ reaction than during the CO–H₂ one. Therefore, the surface active carbon formed would be exclusively hydrogenated to methane. The near agreement of the activation energy of the present methanation with that of the previous CO₂–H₂ methanation supports to this mechanism. However, as described above, the facts that the formate formed rapidly at an early stage, the production of CO was not observed even if without base, and the methanation did not proceed in the absence of Ru catalyst, are suggesting that a mechanism involving a formate intermediate and its methanation on Ru catalyst. It is possible to presume that the present methanation proceeds via the formate intermediate (abbr. surface formate) **2** as shows in Scheme 1, i.e., the CO₂ is first adsorbed as a metal carbonate **1**, and is then reduced to the surface formate **2**, which is in equilibrium with the formation of alkali formate. The surface formate **2** decomposes on the Ru catalyst, yielding adsorbed CO **3** which may rapidly decompose to a surface active carbon **4** rather than desorb into the gas phase as CO molecules, and is then in turn hydrogenated to methane in the same manner as CO methanation [8,23]. Here the primary role of the Ru is to activate the nascent hydrogen molecule, which interacts with formate **2** to cause the methanation. The presence of such intermediate formate species has been proposed for the conversion of CO₂ to CO [13–15,18,24].

4. Conclusion

Methane or alkali formate was easily produced from CO₂–H₂O system by Raney Fe–Ru/C mixed catalysis, with a selectivity which depends on the reaction temperature. The fact that the mixed catalyst not only represent potential catalyst for the liberation of H₂ from water, but also as effective CO₂ methanation in an aqueous alkali system, renders the system inter-

esting with respect to the use of CO₂ for the production of substitute natural gas.

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