

Reduction of alkali metal carbonate to methane with water in the presence of Raney alloy

Kiyoshi Kudo^{*}, Koichi Komatsu

Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611, Japan

Received 15 October 1998; accepted 19 November 1998

Abstract

In the presence of Raney alloy, the direct reaction of alkali or alkali–earth metal carbonates with water resulted in reduction of the carbonates to give methane in high selectivity at a temperature near the critical point of water ($\sim 380^{\circ}\text{C}$). Raney Ni showed an efficient activity to promote the methanation. On the contrary, Raney Fe did not cause the methanation, but the addition of catalytic amount of a carbon-supported ruthenium (Ru/C) to the Raney Fe brought about a highly selective reduction of the carbonates to methane. The reaction was also controlled by the reaction temperatures, i.e., the selectivity and yield of methane increased with increasing temperature suppressing the formation of metal formate. One characteristic in the present reaction is a rapid formation of a considerable amount of metal formate at an initial stage. It is proposed that the formation of methane from metal carbonate occurs via the formation of metal formate and its subsequent hydrogenation by nascent hydrogen which is produced from water by action of Raney alloy. The apparent activation energy for the methanation of Na_2CO_3 on Raney Fe–Ru/C mixed catalyst was estimated to be 14 kcal mol^{-1} . © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Methanation; Alkali carbonate; Water; Raney alloy; Alkali formates; Ruthenium on carbon

1. Introduction

Natural metal carbonates, in particular, the abundant alkali metal and alkaline–earth metal carbonates are formed by various carbonization processes with atmospheric CO_2 . They not only represent an important buffer system within the ecological carbon cycle, but also play an important part for the natural fixation of CO_2 , which is one of the so-called ‘greenhouse gases’ and make a significant contribution to the global warming at present.

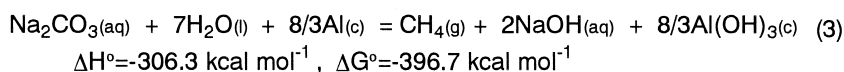
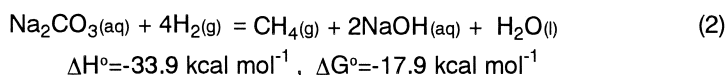
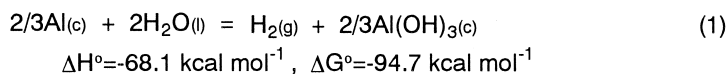
Catalytic hydrogenation of CO_2 to give valuable chemicals and fuels such as methanol and methane has recently been recognized as one of important recycling technologies for emitted CO_2 . Although methanation [1,2] or methanol synthesis [3–6] have been actively studied recently, most of these previous studies have been limited to the use of hydrogen gas (H_2) which is mainly prepared by

^{*} Corresponding author. Tel.: +81-774-38-3172; Fax: +81-774-38-3178; E-mail: komatsu@scl.kyoto-u.ac.jp

water gas shift reaction that produces CO₂ is as a fatal by-product. The direct utilization of water for the reduction of CO₂ or metal carbonate 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.

Recently, some interesting attempts have been made to convert some metal carbonates into hydrocarbons, but in spite of high temperatures such as 800°C [7] or 400°C [8], the realized yields were unfortunately too low. We previously reported that palladium chloride is a very efficient catalyst for the reduction of potassium carbonate to afford potassium formate in aqueous solution under the pressure of H₂ [9].

In the course of our studies on the reduction of CO₂ with water (H₂O) in the presence of Raney alloy [10], we observed that the combination system of Raney alloy and a catalytic amount of carbon-supported ruthenium (Ru/C) causes an unique thermal reduction of the carbonate to methane with H₂O in place of H₂ (Eqs. 1–3), where Raney alloy acts as a generator of H₂ from water and serves as a thermodynamic sink for the reaction. Although methane can be synthesized by the hydrogenation of CO₂ with H₂, the direct synthesis of methane via the thermochemical reaction of alkali carbonate and H₂O is very attractive.



In this paper, we report the unique methanation of an alkali or alkaline–earth metal carbonates with H₂O via alkali formate, which occurs in the presence of a heterogeneous carbon-supported ruthenium (Ru/C) catalyst and Raney alloy. Although this reaction cannot be carried out catalytically with respect to Raney alloy, methane was obtained selectively in acceptable yields.

2. Experimental

2.1. Materials

Alkali and alkaline–earth metal carbonates were obtained commercially, and were further dried by heating (at 180°C) under reduced pressure before use. Raney alloy, carbon-supported ruthenium, and other metal catalysts were purchased from Nacalai Tesque 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 hydrogen carbonates 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 carbonate (5 mmol), Raney Fe (0.2 g), 5% carbon-supported ruthenium (Ru/C) (0.05 g), and H₂O (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 mixture was heated and shaken constantly at 380°C for 2 h, the pressure then reached to 220 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. The yield of products cited in this paper is defined as a molar percent relative to employed carbonate.

2.4. Determined of initial rate

Kinetic measurement was carried out at the reaction temperature ranging from 280 to 380°C. First, a mixture of Na₂CO₃ (5 mmol), Raney Fe (0.2 g), and Ru/C (0.05 g) was charged into the autoclave as described above. After the autoclave had been heated at a required temperature (ca. 30 min), H₂O (8 ml) was introduced into the autoclave by pump, and immediately the shaking was started and the time was recorded as the zero of the reaction time. 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_0 was determined from the experimental equation, $y = t/(at + b)$, where y is the yield of methane (mmol), t is the reaction time (min), and a and b are constants. Further, the initial rate, $v_0 = (dy/dt)_0 = 1/b$ (mmol min⁻¹).

3. Results and discussion

3.1. Activity and selectivity of the methanations

When Na₂CO₃ (5 mmol) was treated with 50% Raney Fe (0.2 g) in the presence of 5% carbon-supported ruthenium (Ru/C) (0.05 g) in H₂O (8 ml) at 380°C for 2 h, the total pressure reached to 220 atm under this conditions, methane was selectively produced in a yield of 18.2% along with a small amount of sodium formate (0.5%) and a significant amount of H₂ (98.5%) as shown in run 1 in Table 1. The yield of the products cited in Table 1 is defined as a products molar percent relative to employed carbonate. First, we examined the activities of two Raney alloys, Raney Fe and Raney Ni, for the methanation under the conditions described above. Both the Raney alloys exhibited the different behavior for the reaction, i.e., Raney Fe alone did not exhibit any activity for the formation of methane and sodium formate from Na₂CO₃, while Raney Ni exhibited an activity as shown in runs 2 and 4 in Table 1. It is noteworthy that when a catalytic amount of Ru/C was added to the Raney Fe system, methanation occurred more effectively than that of Raney Ni (runs 1 vs. 4 in

Table 1
Reduction of metal carbonates with water in the presence of Raney alloy^a

Run	Carbonate	Catalyst	Product yields (%) ^b			
			CH ₄	Formate	H ₂	
1	Na ₂ CO ₃	Raney Fe–Ru/C	18.2	0.5	98.5	
2		Raney Fe	0	0	139.1	
3 ^c		Ru/C	1.9	0.9	–	
4	NaHCO ₃ ^d	Raney Ni	15.5	2.5	27.5	
5		Raney Ni–Ru/C	20.1	2.0	42.8	
6		Raney Fe–Ru/C	16.3	0.4	19.4	
7		Cs ₂ CO ₃	Raney Ni–Ru/C	26.9	2.9	6.6
8			Raney Fe–Ru/C	24.3	0.5	12.6
9	MgCO ₃	Raney Ni	5.2	1.0	119.5	
10		Raney Ni–Ru/C	15.9	2.2	4.3	
11		Raney Fe–Ru/C	12.0	0.5	12.6	
12		CaCO ₃	Raney Ni	4.1	1.0	118.3
13	Raney Ni–Ru/C		15.7	2.0	49.7	
14	Raney Fe–Ru/C		12.7	0	72.0	
15	(NH ₄) ₂ CO ₃	Raney Fe–Ru/C	14.2	0.2	41.5	

^aAll the reactions were carried out with 50% Raney metal (0.2 g), 5% Ru/C (0.05 g), carbonate (5 mmol), and H₂O (8 ml) under Ar atmosphere at 380°C for 2 h.

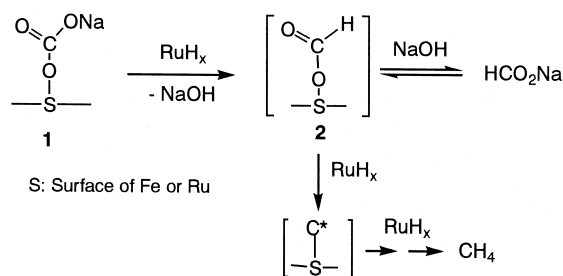
^bYields were calculated on the basis of carbonate loaded.

^cThis reaction was carried out under hydrogen pressure (7 atm) without Raney alloy.

^d10 mmol.

Table 1). Although the additive effect of Ru/C catalyst on Raney Ni for the methanation of alkali metal carbonate was much smaller than that on Raney Fe (run 5 in Table 1), the greater effects were observed especially for the reactions of alkaline-earth metal carbonates (runs 9 vs. 10, 12 vs. 13 in Table 1). Other additive catalysts such as PdCl₂, Pd/C, Rh/C and Ru/alumina were inferior to that of Ru/C in yield and selectivity of the methanation. This efficient methanation for Ru catalyst had been reported in previous studies on the reduction of CO₂ with H₂ [11–15]. Interestingly, the formation of CO [11,16] and C₂–C₄ hydrocarbons [17,18] reported by others in the CO₂–H₂ systems was not observed at all in the present reactions. It should be noted that when Ru/C catalyst only was used for the reaction of Na₂CO₃ with H₂ (7 atm), yields of both methane and sodium formate were almost negligible (run 3 in Table 1). This result suggests that the additional effect of Ru/C on the methanation is responsible for a synergistic effect with Raney alloy metals. A control experiment conducted in the absence of alkali metal carbonates, gave neither methane nor metal formate but only resulted in H₂ liberation. This result implies that the carbon of methane and metal formate originates from the carbonate carbon employed.

We also compared the reactivities of several alkali and alkaline–earth metal carbonates. As is apparent from Table 1, alkali metal carbonates, especially Cs₂CO₃ (runs 7 and 8 in Table 1), gave higher yields in the methanation. Other alkaline–earth metal carbonates, such as magnesium and calcium carbonate, showed somewhat lower yields than that of alkali metal carbonates (runs 9–14 in Table 1). Barium carbonate did not show appreciable yield of the products, presumably because of its high stability under given condition, since the starting material was recovered unchanged at all. It is noteworthy that ammonium carbonate, (NH₄)₂CO₃, also gave methane in almost comparable yield with that of alkaline–earth metal carbonates under the similar conditions (run 15 in Table 1). The higher reactivity of Cs₂CO₃ has been observed in our previous study: a reductive capture of CO₂ with CO to give oxalate [19,20]. The difference in reactivity among the carbonate salts is ascribed to the



Scheme 1.

differing sizes of the alkali metal ions. The cesium ion, which has the largest ionic radius, is considered to be only weakly paired with the counter-anion of the carbonate. This would presumably facilitate the activation of the carbonate by interaction with the surface of the catalyst as will be described later (Scheme 1).

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 ($\text{H}_2\text{O} + \text{Fe} = \text{FeO} + \text{H}_2$) [21]. Therefore, Raney Fe–Ru/C mixed system is not only more selective catalyst for the methanation, but more effective promoter for H_2 liberation than Raney Ni system.

3.2. Effects of the reaction variable

To obtain a deeper insight into the feature of the methanation, we thus investigated the reaction of Na_2CO_3 using Raney Fe–Ru/C mixed catalyst as follows. In search for the optimum reaction conditions, the effect of the reaction temperature on the yield and products distribution was examined for Na_2CO_3 to give the results shown in Fig. 1. The formation of methane increased at the expense of the formation of sodium formate as the temperature is increased; the highest yield and selectivity of methane were achieved at about 380°C . Decreasing the temperature to 250°C greatly retarded the methanation, and the yield of sodium formate increased. Since the critical temperature of H_2O is 374.2°C , the change in the physical property of the medium could be the cause for such variation of

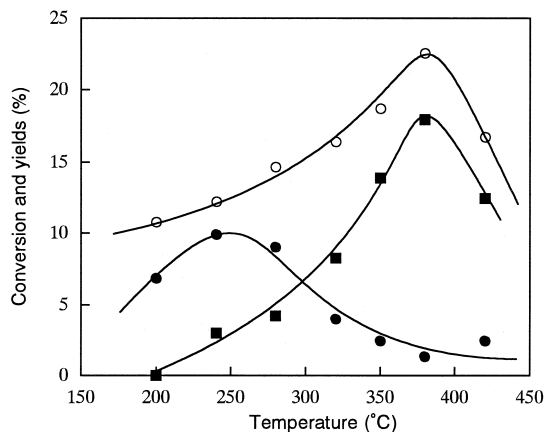


Fig. 1. Effect of reaction temperature on the reduction of Na_2CO_3 with water in the presence of Ru/C–Raney Fe catalyst. Conditions: Na_2CO_3 (5 mmol), Raney Fe (0.2 g), 0.5% Ru/C (0.05 g), H_2O (8 ml), Ar (5 atm), 2 h. ● HCO_2Na , ■ CH_4 , ○ conversion.

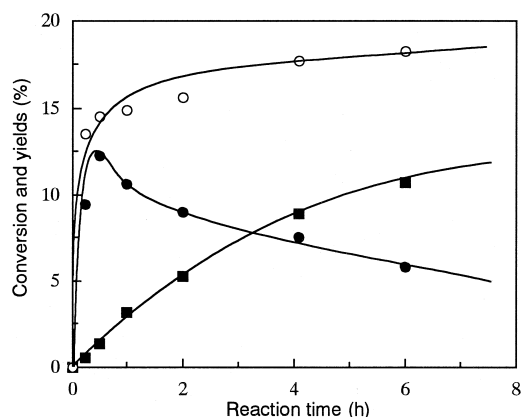


Fig. 2. Time-course of the reduction of Na_2CO_3 with water at 280°C . Conditions: Na_2CO_3 (5 mmol), Raney Fe (0.2 g), 0.5% Ru/C (0.05 g), H_2O (8 ml), Ar (5 atm). ● HCO_2Na , ■ CH_4 , ○ conversion.

the reactivity. At the temperatures below the critical point of H_2O , the reaction proceeds mostly in liquid phase, while at supercritical region, the H_2O is expected to be sufficiently gas-like phase.

A typical time-yield profile of the products in the reaction of Na_2CO_3 at 280°C and 70 atm is shown in Fig. 2. In this reaction, both the liberation of H_2 (Eq. 1) and the reduction of carbonate (Eq. 2) proceeded at the same time, and the rate of the liberation of H_2 was more than faster that of carbonate reduction. At an early stage (a reaction time of ca. 0.5 h), the yield of sodium formate reached to its maximum value, and then the yield of methane gradually increased at the expense of the formate formation as the reaction proceeded. Such a behavior as shown in Fig. 2 had been observed previously in the methanation of CO_2 with H_2O by Ru/C–Raney Fe combined system [10]. The reaction rate gradually decreased at a later stage. Even after a prolonged reaction, the change in product yields was little. As will be discussed below, the presence of a maximum in yield of the formate is of interest in connection with an activation step of carbonate. The maximum yield of the formate decreased with increasing amount of Ru/C or with increasing temperature accompanying an enhancement of the rate of methanation.¹ These findings indicate that the Ru catalyst plays an essential role not only in the formation of the formate, but also in the conversion of the formate into methane. The overall reaction is supposed to proceed in two steps, i.e., first reduction of Na_2CO_3 to sodium formate (Eq. (4)) and its subsequent hydrogenation to give methane (Eq. (5)). This is also supported by the observation that the reaction of sodium formate (10 mmol) in place of a metal carbonate under the similar condition to run 1 in Table 1, at 320°C instead of 380°C , gave methane in 18% yield.



3.3. Kinetic study

Finally, we examined the variations of the reaction rate with temperature in the range from 280 to 380°C and estimated an apparent activation energy (E'_a). The results are shown in Fig. 3. The initial

¹ For example, in the reaction of NaHCO_3 , when the amount of Ru/C was varied from 0.01 to 0.05 g, the maximum yield decreased from 12.4% to 8.0%, and the initial rate of the methanation increased from 6.9 to 60 $\mu\text{mol min}^{-1}$ at 280°C .

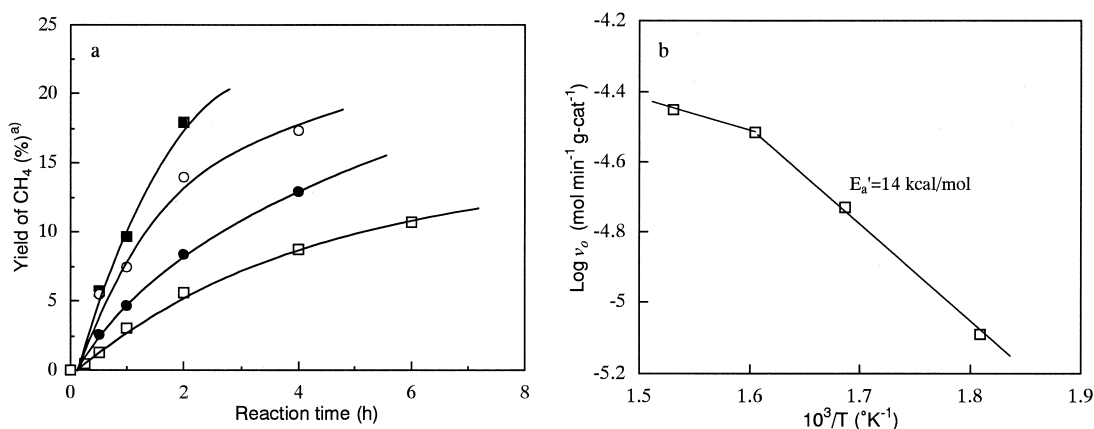


Fig. 3. Effect of reaction temperature on the reaction rate of the methanation (a) and its Arrhenius plots (b). Conditions: Na₂CO₃ (5 mmol), Raney Fe (0.2 g), 0.5% Ru/C (0.05 g), H₂O (8 ml), Ar (5 atm). (a) Mole per mole carbonate. □ 280°C, ● 320°C, ○ 350°C, ■ 380°C.

rates (v_0) were determined from the data at early period (< 2 h) to avoid possible complications due to the factors such as a change in the catalytic activity. The initial rate interpolated to 253°C and the apparent activation energies E'_a for the methanation of Na₂CO₃ are summarized in Table 2 and compared with data for the methanations of CO₂-H₂O [10] and CO₂-H₂ [11]. Direct comparison of the kinetic data 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. The initial rate (v_0) of the present methanation of Na₂CO₃ is much smaller than that of the methanations of CO₂-H₂O [10] and CO₂-H₂ [11] on Ru/C catalyst. Also, this value is only about half of the methanation rate of CO-H₂ on Ru/C [11]. The apparent activation energy (E'_a) for the present methanation was estimated to be approximately 14 kcal mol⁻¹ in the range of 280–350°C. This value is lower than the value of 17 kcal mol⁻¹ found for the methanation of CO₂-H₂O [10]. Also, this value is lower than that of the methanations with H₂-CO₂ on Ru/C catalyst (19.7 kcal mol⁻¹) [11], Ru/Al₂O₃ (16.1 kcal mol⁻¹) [12], and Ru/SiO₂ (17.2 kcal mol⁻¹) [15]. While the methanation of CO-H₂ reported [11] proceeds with a much higher activation energy of 26.2 kcal mol⁻¹, in which the hydrogenation step of a surface carbon to methane has been proposed as the rate determining step [22].

The Arrhenius plot is not linear as shown in Fig. 3b. A tendency of decrease in activation energy for the methanation at higher temperatures is usually observed in a catalytic reaction. This behavior is

Table 2
Comparison of kinetic data with previous studies for methanation

Catalyst system (precursor)	Reaction	Initial rate v_0 (253°C) × 10 ⁶ (mol min ⁻¹ g-cat ⁻¹)	E'_a (kcal mol ⁻¹)
5% Ru/C-Raney Fe ^b	Na ₂ CO ₃ /H ₂ O	4.6 ^c	14 (280–350°C)
5% Ru/C-Raney Fe ^d	CO ₂ /H ₂ O	71.1 ^c	17 (240–280°C)
4.3% Ru/C ^c	CO ₂ /H ₂ (1/4)	116.4	19.7 (205–300°C)
1.4% Ru/C ^c	CO/H ₂ (1/3)	10.2	26.2 (~ 250°C)

^aApparent activation energy.

^bThis study.

^cThis value was estimated by interpolation from higher temperature.

^dData from Ref. [10].

^eData from Ref. [11].

mainly ascribed to the following two reasons. One is the difference of reaction phase of water, i.e., non-critical 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 [23] and a solution and dissociation of the carbonate becomes unfavorable. This assumption was also inferred from the complete heterogeneous gas–solid reaction, i.e., the reaction of run 1 in Table 1, however, the use of H₂ (10 atm) in place of H₂O showed quite low reactivity to give methane (2.1%). 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 tendencies were also reported by other systems [15,16,24].

Although it is difficult to rationalize the exact mechanism for the present methanation, it is possible to presume that the present methanation would proceed via the formation of formate-like intermediate (the ‘surface formate’) **2** as assumed previously for the methanation of CO₂ with H₂O [10] (Scheme 1); thus, the carbonate is first activated as adsorbed carbonate **1**, and is then subjected to reduction by ruthenium hydride to form **2**, which would be in equilibrium with alkali metal formate, followed by reductive dissociation of the formate ion to activate the active surface carbon, which could be then hydrogenated to methane. The presence of such intermediate formate species has been proposed for CO₂ methanation with H₂ on rhodium and ruthenium catalyst [12–14,22,25,26]. In our results, differences in the reaction rates and activation energies were obtained for the methanations of Na₂CO₃ and CO₂ as shown in Table 2, suggesting at first sight that both the reactions proceed via different mechanisms. In the light of the identical features in temperature-yields and time-course behavior (Figs. 1 and 2) for both the methanations, however, both methanations follow the same reaction path as shown in Scheme 1: upon absorption in alkali solution, CO₂ is converted to carbonate ion before reacting with a metal surface to yield **1**.

In conclusion, the readily available alkaline carbonate was selectively converted to methane by the action of water in acceptable yields. This system might be worthy of attention from the viewpoint of the increasing atmospheric CO₂ concentration.

Acknowledgements

The authors are grateful to Mr. M. Yasumoto for his valuable contribution in manufacturing and assembling the high-pressure experimental equipments.

References

- [1] T. Inui, M. Funabiki, Y. Takegami, *Ind. Eng. Chem. Prod. Res. Dev.* 19 (1980) 385.
- [2] G.D. Weatherbee, C.H. Bartholomew, *J. Catal.* 68 (1981) 67.
- [3] E. Ramarosan, R. Kieffer, A. Kiennemann, *J. Chem. Soc., Chem. Commun.* (1982) 645.
- [4] B. Denise, R.P.A. Sneed, *Appl. Catal.* 28 (1980) 235.
- [5] Y. Aminomiya, *Appl. Catal.* 30 (1987) 57.
- [6] T. Inui, T. Takeguchi, *Catal. Today* 10 (1991) 95.
- [7] A. Reller, C. Padest, P. Hug, *Nature* 329 (1987) 527.
- [8] F. Akiyama, *Bull. Chem. Soc. Jpn.* 69 (1996) 1129.
- [9] K. Kudo, N. Sugita, Y. Takezaki, *Nippon Kagaku Kaishi* (1977) 302.
- [10] K. Kudo, K. Komatsu, *J. Mol. Catal. A: Chemical*, in press.
- [11] C. Moreno-Castilla, M.A. Salas-Peregrin, F.J. Lopez-Garzon, *J. Mol. Catal. A: Chemical* 95 (1995) 223.
- [12] F. Solymosi, A. Erdohelyi, M. Kocsis, *J. Chem. Soc., Faraday Trans. 1* 77 (1981) 1003.
- [13] F. Solymosi, A. Erdohelyi, T. Bansagi, *J. Chem. Soc., Faraday Trans. 1* 77 (1981) 2645.

- [14] F. Solymosi, A. Erdohelyi, T. Bansagi, *J. Catal.* 68 (1981) 371.
- [15] G.D. Weatherbee, C.H. Bartholomew, *J. Catal.* 87 (1984) 352.
- [16] G.D. Weatherbee, C.H. Bartholomew, *J. Catal.* 77 (1982) 460.
- [17] W. Ross Hastings, C.J. Cameron, M.J. Thomas, M.C. Baird, *Inorg. Chem.* 27 (1988) 3024–3028.
- [18] T. Inui, M. Funabiki, Y. Takegami, *J. Chem. Soc., Faraday Trans. 1* 76 (1980) 2237.
- [19] K. Kudo, F. Ikoma, S. Mori, K. Komatsu, N. Sugita, *J. Chem. Soc., Chem. Commun.* (1995) 633.
- [20] K. Kudo, F. Ikoma, S. Mori, K. Komatsu, N. Sugita, *J. Chem. Soc., Perkin Trans. 2* (1997) 679.
- [21] D.C. Grenoble, M.M. Estadt, *J. Catal.* 67 (1981) 90.
- [22] S.D. Jackson, R.B. Moyes, R. Whyman, *J. Chem. Soc., Faraday Trans. 1* 83 (1987) 905.
- [23] M.J. Antal, W.S.L. Mok, T.A. Raissi, *J. Anal. Appl. Pyrol.* 8 (1985) 291.
- [24] R.Z.C. van Meerten, J.G. Vollenbroek, M.H.J.M. de Croon, P.F.M.T. van Nisselrooy, J.W.E. Coenen, *Appl. Catal.* 3 (1982) 29.
- [25] Y. Amenomiya, G. Pleizier, *J. Catal.* 76 (1982) 345.
- [26] A. Deluzarche, J.P. Hindermann, R. Kieffer, *J. Chem. Res.* (1981) (S) 72, (M) 934.