

Mechanochemical activation of catalysts for CO₂ methanation

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Abstract

The hydrogenation of CO₂ to CH₄ was carried out using MgO-mixed catalysts of Ru, Ni, Fe or their combinations at temperatures ranging from 80 to 150°C under initial pressures of 100 Torr CO₂ and 500 Torr H₂. The effect of the mechanical milling of catalysts on the reaction was investigated. It was found that (1) the yield of CH₄ strongly depended on the kind of catalysts; the highest yield was achieved with Ru–MgO catalyst and the lowest yield with Ni–Fe catalyst. (2) Mechanochemically activated catalysts largely increased the production rate of CH₄ and considerably decreased the activation energy of the reaction from 74 kJ/mol to 41 kJ/mol for Ru–MgO catalyst.

Keywords: Mechanochemical activation; Milling; Carbon dioxide; Methane; Catalytic hydrogenation; Activation energy

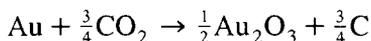
1. Introduction

Physical and chemical properties of solids like various metals and ceramics can be affected by many factors, one of which may be the mechanical treatment. Changes in physico-chemical properties of the solids occur during mechanical treatment such as milling: formation of nascent surface, change in specific surface area of solid particles, decrease in crystallite size, emission of exoelec-

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trons, and so on. Temperature and pressure also increase, especially at the points of collision between the solids. As a result, the chemical reactivity of the solids will increase considerably by mechanical treatment (mechanochemistry) [1].

Extensive studies on mechanochemistry have been carried out, and the work has been summarized by Heinicke [2]. It has been found that many reactions, including oxidation and reduction, synthetics and decomposition, inorganic and organic reactions, are activated through mechanochemical ways. We have also reported mechanochemically activated reactions such as polymerization of vinyl monomers [3] and synthesis of organo-aluminum compounds [4]. Mechanical energy affects the reactions mainly in the following ways. First, it enables reactions which do not occur thermally because of the positive free energy change. A good example may be the formation of Au_2O_3 in the following reaction in which the change of free energy ΔG is +377 kJ/mol and which in general cannot occur in a thermal reaction process [5].



Another effect is increasing the reaction rate and decreasing the activation energy of the reaction. For instance, the reaction rate of $\text{Ni} + 4\text{CO} \rightarrow \text{Ni}(\text{CO})_4$ was found to increase with increasing amount of mechanical energy added [6,7]. In the case of hydrogenation of benzene to cyclohexane using Ni as a catalyst [8], the activation energy of 42 kJ/mol was obtained in general chemical reaction, whereas it decreased to 33 kJ/mol by pre-milling Ni catalyst and further decreased to 26 kJ/mol for the reaction during milling. These studies showed that the mechanical energy could be kept on the catalyst for a certain period even after the mechanical activation was terminated.

It was also demonstrated that mechanochemical reactions give products different from the corresponding thermal reactions. Further, mechanochemical reactions showed a smaller dependence on temperature and pressure, compared to thermal reactions [2].

In this paper, the authors investigated the effect of mechanical activation of catalysts on the methanation of CO_2 by milling the metal catalysts. On this reaction there are a lot of studies in which the effects of various supports and metals have been extensively investigated. For example, Weatherbee and Bartholomew [9] studied the activity of various metallic catalysts supported on SiO_2 at 450–650 K and 140–1030 kPa and found that the activity decreased in the order of $\text{Co} > \text{Ru} > \text{Ni} > \text{Fe}$, but the selectivity of CH_4 was $\text{Ru} > \text{Co} > \text{Ni} > \text{Fe}$. Murakami and co-workers [10,11] investigated the effect of various supports of Ni catalysts and found the reactivity of the catalysts depended strongly on the kind of supports in the order of $\gamma\text{-Al}_2\text{O}_3 \approx \text{MgO} \approx \text{SiO}_2 > \alpha\text{-Al}_2\text{O}_3 > \text{TiO}_2 \approx \text{SiO}_2 \cdot \text{Al}_2\text{O}_3$. The reason for higher activity of Ni/MgO catalyst was attributed to the basic properties of the MgO support on which CO_2 could be strongly adsorbed and kept on the catalyst even at higher temperatures.

In the present study, the mechanochemical activation of catalysts for CO₂ methanation will be reported using Ru, Ni, Fe or combinations as catalysts, together with MgO which is usually used as basic support. The reactions were carried out at temperatures ranging from 80 to 150°C under the initial pressures of 100 Torr CO₂ and 500 Torr H₂ (1 Torr = 133.32 Pa), together with mechanically milling the catalysts with a vibration-type ball mill. The experiments without milling were also carried out for the purpose of comparison. It was found that the rate of CH₄ formation increased and the activation energy of the reaction decreased by mechanical milling.

2. Experimental

2.1. Catalysts

The powdery metals used as catalysts in the present study, Ni (> 99.0%), Fe (> 98.0%), Ru (> 98.0%), and MgO (> 99.0%, as promoter), were obtained from Kanto Chem. Co., Inc., Japan. Gaseous reactants CO₂ (> 99.9%), H₂ (> 99.999%) and O₂ (> 99.5%) were supplied by Nippon Sanso Co. Ltd., Japan. Table 1 summarizes the amounts of the catalysts used for each experiment.

2.2. Apparatus

In the present study, a vibrating mill was used to carry out the mechanochemical CO₂ methanation. The schematic diagram of the mill (model MB-1, Chuo Kakoki Co. Ltd., Japan) is shown in Fig. 1. The stainless steel milling pot (54.9 mm I.D., 115 mm in length) used as reactor (Fig. 2), which could be heated up to 500°C by an inner electric heater, was fixed on springs. The milling pot was connected with the motor using a flexible coupling. The shaft connecting the pot is forced out of the central position by the unbalance pulley. Thus, the pot was made to swing circularly on a plane perpendicular to its axle when the motor was started. As a result, the milling balls inside the pot also vibrate, and the

Table 1
Amount of the catalysts (grams) tested in the present study

Catalyst	Ru	Ru–MgO	Ru–Fe–MgO	Ni–MgO	Ni–Fe	Ni–Fe–MgO
Fe	–	–	14.0	–	14.0	14.0
Ni	–	–	–	14.7	14.7	14.7
Ru	3.03	3.03	3.03	–	–	–
MgO	–	2.02	2.02	2.02	–	2.02

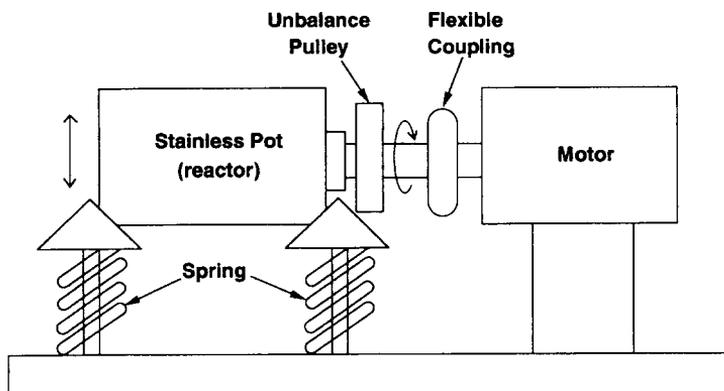


Fig. 1. Schematic diagram of the ball mill apparatus used for the mechanochemical reactions in the present study.

metal catalysts will be milled due to stressing, shocking, pressing and shearing effects. The amplitude and the milling force could be adjusted by changing the position of the unbalance pulley. The motor speed was controlled by an inverter (model HFC-VWS, Hitachi Co. Ltd., Japan) and determined with a stroboscope.

Since the temperature used to control the heater and the temperature of the catalyst in the pot were not the same, the difference was measured previously and the latter was used as the reaction temperature in this study.

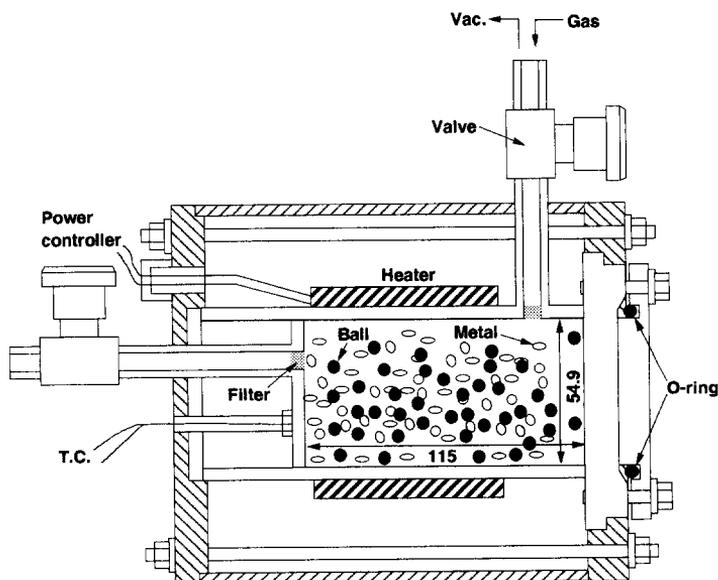


Fig. 2. Configuration of the stainless steel made pot used as reactor.

2.3. Experimental procedures

Stainless steel balls (diameter 10 mm, total number 150) and the desired amounts of powdery metals and/or MgO were put into the pot, and the pot was then degassed with a rotary vacuum pump. After the pressure decreased to about 10^{-3} Torr, the pot was heated to 120°C and kept at that temperature for one hour to remove any adsorbed water on the surface of the balls and catalysts. After this pretreatment, the pot was adjusted to the reaction temperature, and the reactants CO₂ and H₂ under a certain pressure were introduced into the pot, and the hydrogenation of CO₂ began, together with milling the catalysts (referred to below as the milling system). The partial pressures of CO₂ and H₂ in the pot were 100 and 500 Torr, respectively. The motor speed and the amplitude of vibration for milling were maintained at 1100 rpm and 6 mm, respectively, in the present study. The reaction time was generally one hour except where stated otherwise. The experiments without milling balls were carried out under the same conditions (referred to below as the mixing system).

After each experiment, the gaseous products were sampled to an IR gas cell (50 Torr). A FT-IR spectrometer (model JASCO FT/IR 7300, Japan Spectroscopic Co., Ltd.) was used to determine the peak intensity at 3017 cm⁻¹, which was assigned to the C–H stretching vibration of CH₄. A linear relationship between the peak intensity and the partial pressure of CH₄ was established prior to the experiments using a series of standard gas mixtures of CH₄ in CO₂–H₂ (1:5) with a total pressure of 50 Torr in the IR cell. Using this calibration curve and the peak intensity experimentally obtained, the partial pressure and then the yield of CH₄ were calculated.

Changes of catalyst particles were observed with a scanning electron microscope (SEM) and the distributions of each element were measured by electron probe microanalysis (EPMA) after the experiments.

3. Results and discussion

3.1. Catalytic activity of various catalysts

Fig. 3 shows the effect of reaction temperature on CH₄ yield using Ru–MgO and Ni–MgO catalysts under mixing and milling conditions. At first, it can be seen that in the case of the Ru–MgO catalyst no CH₄ formation was observed at the temperatures below 80°C under mixing conditions. The formation began at higher temperatures and the yield increased with the temperature. It reached 31% at 130°C, but leveled off at 180°C. On the other hand, CH₄ formation (1.8% yield) was observed even at room temperature when the Ru–MgO catalyst was activated mechanically by milling. The yield increased considerably with increasing temperature. It increased from 11% at 80°C to 96% at 180°C.

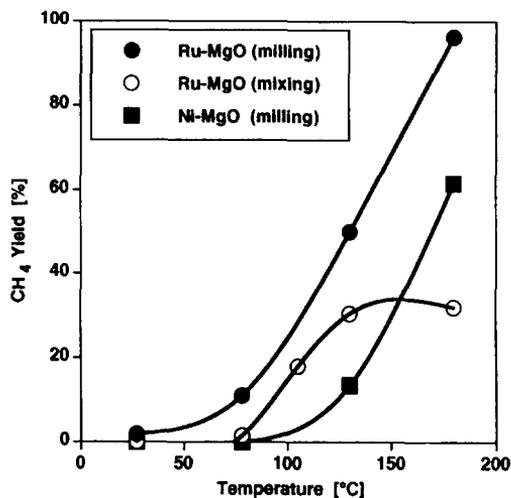


Fig. 3. Effect of temperature on CH₄ yield over Ru-MgO and Ni-MgO catalysts under milling or mixing conditions (reaction time, 1 h).

Similar results have been obtained over Ni-MgO catalyst, although its activity was less than that of the Ru-MgO catalyst. With the Ni-MgO catalyst, CH₄ formation needed temperatures higher than 100°C. The yield was only 13% at 130°C, and it increased considerably to 62% at 180°C. Because MgO itself showed little activity on CO₂ methanation in the preliminary experiments, the difference between Ru-MgO and Ni-MgO catalysts was attributed to the activity of Ru and Ni themselves.

The above results showed that the catalysts under milling exhibited a higher

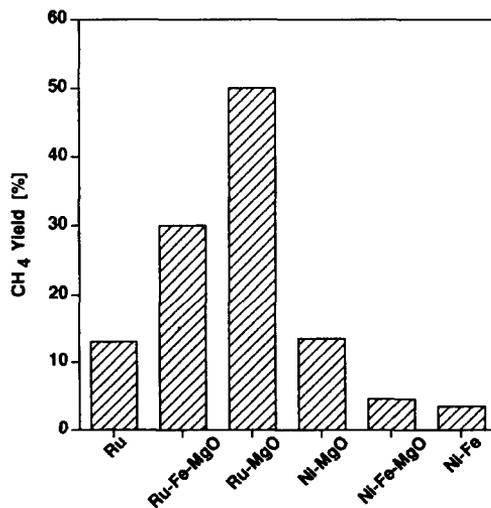


Fig. 4. CH₄ yield over various catalysts tested under milling conditions (130°C, 1 h).

activity than those in the case without milling. This means that the catalysts have been activated mechanochemically.

Shown in Fig. 4 are the results with various catalysts at 130°C for one hour. Obviously, the lowest yield was achieved with the Ni–Fe catalyst and the highest yield with the Ru–MgO catalyst, respectively, although the amount of Ru used was small (see Table 1). Fe powders were added to promote the milling, but the addition of Fe to Ru–MgO or Ni–MgO catalysts decreased the CH₄ yield considerably. The reason for the low activity of Fe-containing catalysts was that the active surface of Ru and Ni particles was partially covered by Fe particles during milling, which are less active than Ru or Ni, and show little activity on CO₂ methanation [9].

Also, it is noteworthy that the addition of MgO, a basic oxide, to Ru increased the yield of CH₄ considerably. It has been pointed out that MgO promotes the reaction by strongly adsorbing CO₂, an acidic gas [10,11]. The effect of MgO will be discussed below.

Conclusively, the activity of the catalysts tested for CO₂ methanation was in the order Ru–MgO > Ru–Fe–MgO > Ru ≈ Ni–MgO > Ni–Fe–MgO > Ni–Fe in the present study. These results agree with the literature [9] in which the activity of various metallic catalysts supported on SiO₂ was found to be in the order Ru > Ni > Fe for CO₂ methanation.

3.2. Mechanochemical activity

As shown above, the catalysts could be activated by mechanical milling. The effect of mechanical milling on the kinetics of CO₂ methanation were further investigated.

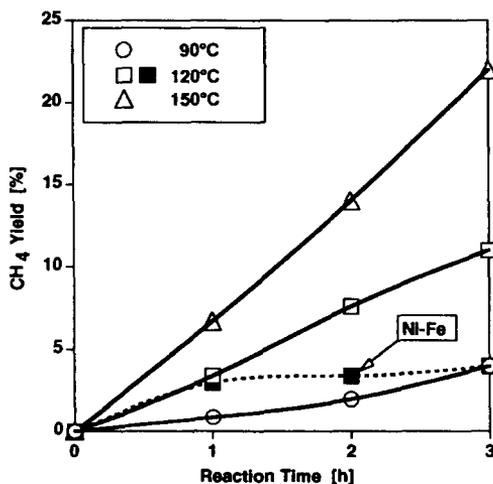


Fig. 5. Dependence of CH₄ yield on the reaction time over Ni–Fe–MgO and Ni–Fe catalysts under milling conditions.

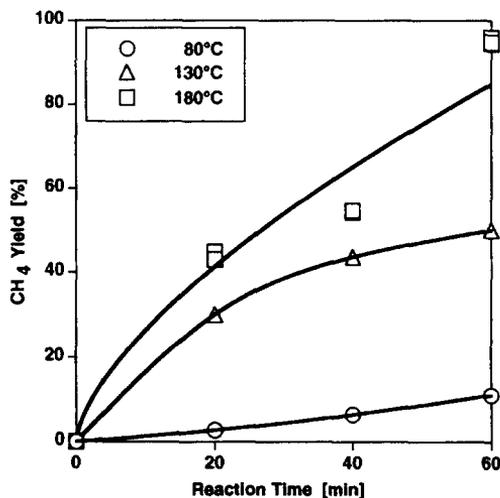


Fig. 6. Dependence of CH₄ yield on the reaction time over Ru–MgO catalyst under milling conditions.

Fig. 5 shows the dependence of the accumulated yield of CH₄ on reaction time using the Ni–Fe–MgO catalyst under milling conditions. The yield increased with increasing reaction time at the temperatures tested. At 120°C, for example, the yield at one hour is ca. 3%, and it reached 10% after 3 h. When the temperature was raised to 150°C, 22% yield is achieved after 3 h. If MgO was not present, in contrast, just a small increase in yield was observed with the reaction time, as shown in the figure by a dashed line.

The results with Ru–MgO catalyst are shown in Fig. 6 under milling conditions. CH₄ yield increased considerably with the reaction time and the

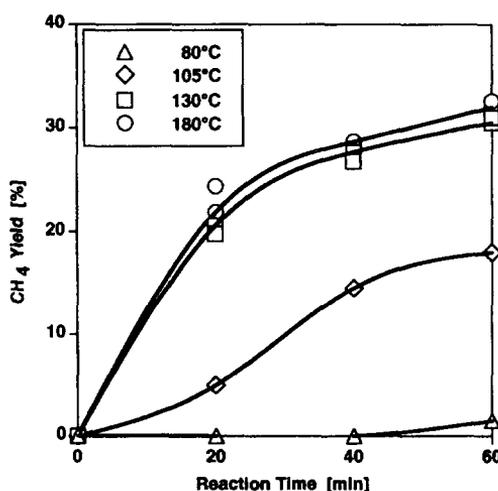


Fig. 7. Dependence of CH₄ yield on the reaction time over Ru–MgO catalyst under mixing conditions.

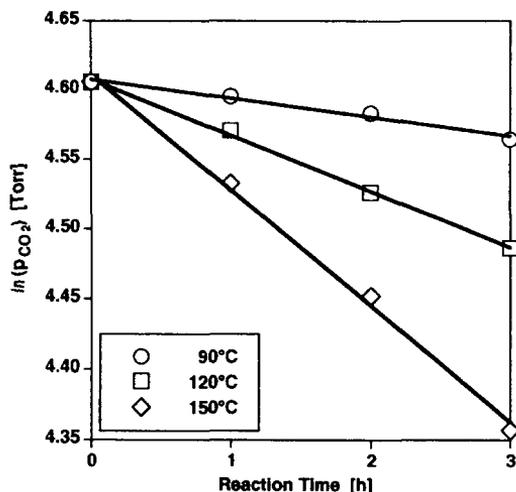


Fig. 8. Relationship between the partial pressure of CO₂ and the reaction time over Ni-Fe-MgO catalyst under milling conditions.

temperature. A yield as high as 96% was achieved at 180°C for one hour. However, the results under mixing conditions were very different (Fig. 7). At temperatures below 130°C, the yield was low and it increased with the time and temperature. When the temperature was raised from 130°C to 180°C, however, just a little increase in yield was observed. This suggests that the diffusion processes of the reactants to the surface of the catalyst particles became at least partially rate-determining at this temperature range in the mixing system.

In order to estimate the kinetics of CO₂ methanation in the present study, the reaction was simply assumed to be first order with respect to CO₂ and zero order with respect to H₂ because excess H₂ was introduced compared to CO₂. Thus the reaction rate could be described as Eq. 1, and Eq. 2 is then obtained by integrating Eq. 1.

$$-d p_{\text{CO}_2} / dt = k \cdot p_{\text{CO}_2} \quad (1)$$

$$\ln p_{\text{CO}_2} = k \cdot t + \ln p_{\text{CO}_2}^0 \quad (2)$$

where k [h⁻¹] is the rate constant, t [h] is reaction time, $p_{\text{CO}_2}^0$ and p_{CO_2} [Torr] are the partial pressure of CO₂ at reaction time 0 and t , respectively.

The relationship between $\ln p_{\text{CO}_2}$ and t over Ni-Fe-MgO catalyst is shown in Fig. 8 as an example. Good straight lines were obtained, suggesting that the assumption of a first order reaction was quite reasonable. The rate constants k were then obtained from the slopes of the straight lines at different temperatures.

The Arrhenius plots for Ru-MgO and Ni-Fe-MgO catalysts are shown in Fig. 9. It is clear that the rate constant k for Ru-MgO catalysts in the milling system is always higher than that in the mixing system. These results mean that the mechanical activation of catalysts increased the reaction rate considerably.

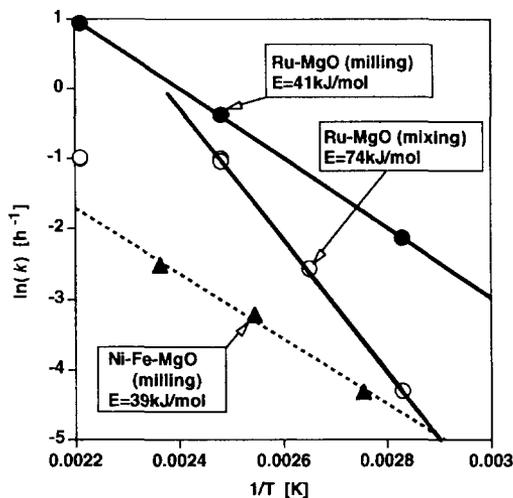


Fig. 9. Arrhenius plots for CO₂ methanation over Ru–MgO and Ni–Fe–MgO catalysts.

Further, the apparent activation energy of the CO₂ methanation was calculated from the Arrhenius plots (note that the rate constant k at 180°C in the mixing system on Ru–MgO catalyst was not used in the calculation). The results, together with the literature values, are summarized in Table 2.

An apparent activation energy of 41 kJ/mol was obtained for Ru–MgO catalyst in the milling system. In the mixing system, on the other hand, it was 74 kJ/mol, which agreed well with the value of about 67–82 kJ/mol for Ru/Al₂O₃ or Ru/SiO₂ catalysts (see Table 2). This means that the activation energy has decreased by about 30 kJ/mol by mechanical activation.

Table 2

Comparison of the apparent activation energy E for CO₂ methanation over various catalysts

Catalyst	Temp. (K)	Total pressure	Feed	E (kJ/mol)	Reference
Ru–MgO	353–453	80 kPa	H ₂ /CO ₂ = 5	41	this work (milling)
Ru–MgO	353–453	80 kPa	H ₂ /CO ₂ = 5	74	this work (mixing)
0.5%Ru/Al ₂ O ₃	473–623	atm. ^a	H ₂ /CO ₂ = 2–4	71	[12]
5%Ru/Al ₂ O ₃	475–550	atm.	H ₂ 30–80% CO ₂ 10–40%	67	[13]
0.5%Ru/SiO ₂	500–550	atm.	H ₂ 4%, CO ₂ 1%	68	[9]
	502–563	atm.	H ₂ /CO ₂ = 4	72	
0.7–3.3%Ru/SiO ₂	500–523	atm.	H ₂ 18%, CO ₂ 6%	82	[14]
Ni–Fe–MgO	363–393	80 kPa	H ₂ /CO ₂ = 5	39	this work (milling)
3%Ni/Al ₂ O ₃	525	?	?	71	[15]
26.5% γ -Ni/Al ₂ O ₃	473–503	atm.	0.22–2.38%CO ₂ in H ₂	106	[16]
3%Ni/SiO ₂	500–575	140 kPa	H ₂ 4%, CO ₂ 1%	80	[17]
5%Ni/SiO ₂	500–523	atm.	H ₂ 18%, CO ₂ 6%	82	[14]
20%Ni/SiO ₂	450–500	atm.	CO ₂ pulse in H ₂	79	[10,11]
15%Fe/SiO ₂	526–572	atm.	H ₂ /CO ₂ = 4	134	[9]

^a atm.: atmospheric pressure.

The same effect was observed for the Ni–Fe–MgO catalyst. An activation energy of 39 kJ/mol was obtained under milling conditions, compared to about 80 kJ/mol over Ni/SiO₂ or Ni/Al₂O₃ catalysts or 134 kJ/mol for 15%Fe/SiO₂ catalyst for CO₂ methanation (see Table 2).

A decrease in activation energy has been reported for the hydrogenation of ethylene by mechanical milling [18]. The process of mechanical milling and the ensuing changes in the structure of the catalyst caused by milling are very complicated. One of the important sources for mechanochemical activity is the nascent surfaces formed by mechanical treatment. We have reported that nascent nickel surfaces show such a high activity that aromatic compounds decomposed on the surface even at room temperature [19]. Similarly, the mechanical activation of catalysts in the present study could be simply explained as follows. In the mixing system, the reactants were adsorbed and reacted on the surfaces of catalysts. In this case, no nascent surfaces of catalyst particles could be formed, and the activity of the catalyst decreased due to the deposition of carbonaceous matter and/or other reasons (deactivation). The rate of product formation would decrease with increasing reaction time. On the other hand, in the milling system, the nascent surfaces of the catalyst particles on which the reactions occur were continuously formed. As a result, the activity of the catalysts did not decrease and CH₄ yield increased with the reaction time and temperature.

3.3. Effect of mechanical pretreatment

To investigate the effect of pre-activation of catalysts by milling, the catalysts were pretreated as follows. First, the catalysts were milled in H₂ or O₂ atmosphere or in vacuum for one hour, followed by degassing for one hour. After this pre-activation, reactant gases were introduced into the pot and the reactions were carried out under milling conditions. The yield was almost the same, suggesting that the pre-milling (or pre-addition of mechanical energy) played only a minor role in mechanochemical activity compared with the milling during reaction. In other words, the mechanical activation of catalysts could only be found by *in situ* milling in the present study.

3.4. Change of catalyst particles by milling

Changes in the shape and size of catalyst particles during milling were observed using a scanning electron microscope (SEM). Fig. 10 shows the SEM photographs of the Ni–Fe–MgO catalyst as an example. Clearly the relative number of larger particles and then the average diameter of the catalyst particles increased with increasing milling time. Further, it could be observed that the larger particles were formed by aggregation of many small particles during milling. A significant increase in specific surface area, as determined by the BET method, was not observed with increasing milling time. In addition, the

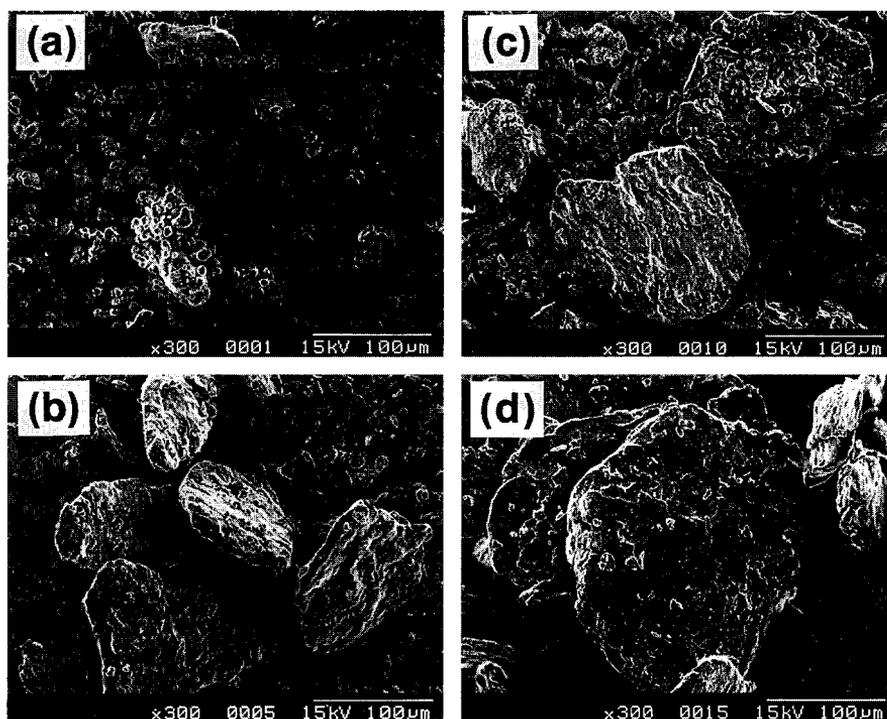


Fig. 10. SEM photographs for Ni–Fe–MgO catalyst. Milling time: (a) 1 h; (b) 2 h; (c) 3 h; (d) 6 h.

EPMA measurements showed that Ni, Fe and MgO particles were uniformly distributed and aggregated during milling. Therefore, the main reason for the mechanochemical activity might not be the increased surface area, but changes in surface structure, for example, nascent surfaces formed by milling.

3.5. Role of MgO

As mentioned earlier, the existence of MgO promoted CH_4 production (Fig. 4), and the yield increased with the reaction time over the Ni–Fe–MgO catalyst compared to the small increase without MgO (Fig. 5). To make the effect of MgO clear, the next auxiliary experiments were carried out under milling conditions. First, the experiments were carried out repeatedly using the same Ni–Fe–MgO catalyst at 120°C and the reaction time for each experiment was one hour. Between the experiments the system was degassed for one hour and a mixture of reactant gases was introduced. The results are shown in Fig. 11. Obviously, the amount of CH_4 increased almost linearly with the repeated use of the catalyst. At long degassing times of 24 hours or longer the yield decreased, as indicated by arrows in the figure. A considerable amount of CH_4 (28 Torr) was obtained from the 22nd experiment which was, in fact, 7.5 times

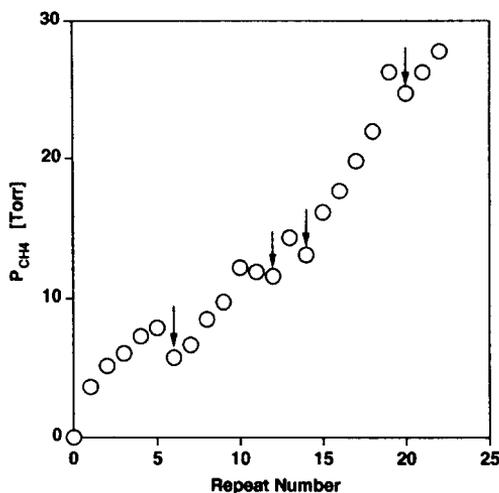


Fig. 11. Partial pressure of CH_4 formed in the repeat experiments over Ni-Fe-MgO catalyst at $120^\circ C$ (reaction time, 1 h for each experiment). Arrows mean that the degassing time before introducing the reactants is 24 h or longer.

that of the first experiment. Such results were not observed in the absence of MgO.

The catalyst used for a total of 22 cycles of repeat experiments was further milled in 600 Torr of pure H_2 atmosphere (Fig. 12). Even when CO_2 was not introduced, a comparable amount of CH_4 was formed and it decreased with repeated use. Obviously, some carbonaceous materials have formed and accumulated on the catalyst surface during the reaction. Such carbonaceous materials

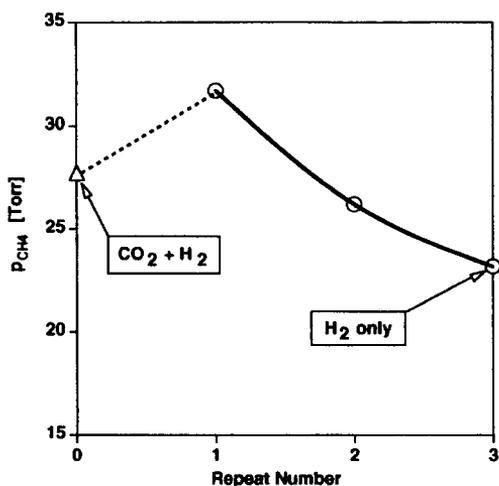


Fig. 12. Partial pressure of CH_4 formed from carbonaceous materials adsorbed on Ni-Fe-MgO catalyst ($120^\circ C$, 1 h each experiment).

were very active and could not be removed by degassing. Instead of MgO, same moles of MgCO₃ were milled under H₂ (600 Torr) atmosphere and only a small amount of CH₄ (1.2–1.8 Torr) was obtained.

It has been suggested by Mori et al. [10,11] that the high activity of MgO supported catalysts comes from the basic property of MgO on which CO₂ molecules are strongly adsorbed and kept on the catalyst even at higher temperatures at which CH₄ was formed. However, the intermediate of the reaction is not clear yet. The above experiments showed that MgCO₃ as the intermediate might not be possible, because no peaks assigned to MgCO₃ were found in the IR spectra of used catalysts. Further study is necessary to make the mechanism of CO₂ hydrogenation clear.

4. Conclusions

In the present study, the results of CO₂ methanation were reported using MgO-mixed catalysts of Ru, Ni, Fe or their combinations. The effect of mechanical milling on the reaction was investigated. It was found that milling the catalysts increased the production rate of CH₄ and considerably decreased the activation energy of the reaction. An apparent activation energy of 39 kJ/mol and 41 kJ/mol was obtained for Ni–Fe–MgO and Ru–MgO catalysts, respectively, under the milling system, which was almost half that under the mixing system without mechanical activation.

References

- [1] P.A. Thiessen, K. Meyer and G. Heinicke, *Grundlagen der Tribochemie*, Akademie-Verlag, Berlin, 1967.
- [2] G. Heinicke, *Tribochemistry*, Akademie-Verlag, Berlin, 1984.
- [3] Y. Tamai and S. Mori, *Z. anorg. allg. Chem.*, 476 (1971) 221.
- [4] S. Mori, O. Kuriyama, Y. Maki and Y. Tamai, *Z. anorg. allg. Chem.*, 492 (1982) 200.
- [5] P.A. Thiessen, G. Heinicke and E. Schober, *Z. anorg. allg. Chem.*, 377 (1970) 20.
- [6] G. Heinicke and K. Sigrist, *Z. anorg. allg. Chem.*, 350 (1967) 148.
- [7] G. Heinicke, *Z. anorg. allg. Chem.*, 324 (1963) 173.
- [8] G. Heinicke and I. Lischke, *Z. Chem.*, 11 (1971) 332.
- [9] G.D. Weatherbee and C.H. Bartholomew, *J. Catal.*, 87 (1984) 352.
- [10] T. Mori, H. Masuda, H. Imai and Y. Murakami, *J. Chem. Soc. Japan*, 11 (1979) 1443.
- [11] T. Mori, H. Masuda, H. Imai and Y. Murakami, *J. Chem. Soc. Jpn.*, 11 (1979) 1449.
- [12] P.J. Lunde and F.L. Kester, *Ind. Eng. Chem. Proc. Des. Dev.*, 13(1) (1974) 27.
- [13] F. Solymosi, A. Erdohelyi and M. Kocsis, *J. Chem. Soc., Faraday Trans. 1*, 77 (1981) 1003.
- [14] T. Inui and M. Funabiki, *Chem. Lett.*, (1978) 251.
- [15] D.J. Darensbourg, C.G. Bauch and C. Ovalles, *Rev. Inorg. Chem.*, 7 (4) (1985) 315.
- [16] T. Van Herwijnen, H. Van Doesburg and W.A. De Jong, *J. Catal.*, 28 (1973) 391.
- [17] G.D. Weatherbee and C.H. Bartholomew, *J. Catal.*, 68 (1981) 67.
- [18] G. Heinicke, *Schmiertechnik*, 13 (1966) 81.
- [19] S. Mori and M. Yoshida, *Tribol. Trans.*, 31 (1988) 128.