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Conversion of CO_2 to useful substances with composite iron, nickel, and copper catalysts*

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Abstract: Composite materials of Fe/Al_2O_3, which consist of small particles of iron supported by thermally stable alumina even at 500–700 °C, have been widely used in the water-gas shift reaction for natural gas reforming. Therefore, Fe/Al_2O_3 is one of the promising candidates for re-transformation of exhausted CO_2 into fuels such as alcohols and hydrocarbons. The development of a CO_2 reforming system using the composite materials of Fe/Al_2O_3 through CO_2 reduction to CO, dissociation of water into hydrogen, and methanol synthesis has been investigated. It was found that dry and steam (i.e. wet) reforming of CO_2 produced almost the same amount of CO. At a temperature above 500 °C, maximal and saturated yields of CO and H_2 from CO_2 and water were obtained. However, this CO_2 reforming system requires higher-pressure conditions from several tens to hundreds standard atmospheric pressure in order to achieve high yield and selectivity for methanol production. In this study we developed the modified CO_2 reforming system by the utilization of Ni and/or Cu instead of Fe in order to obtain other types of useful products such as CO, CH_4, and carbon, more efficiently and selectively under atmospheric pressure. When Ni or Cu was used, conversion of CO_2 was reduced to 76%, while 9% of methane was detected in the case of Ni. On the other hand, though the CO_2 conversion reduced half of the Fe, the selectivity of CO from CO_2 increased to 95% in the case of Cu.

Key words: Iron catalyst; CO_2 reduction; Water-gas shift reaction; Methanol synthesis
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1 Introduction

Since iron-based catalysts have been widely used in the water-gas shift reaction for natural gas reforming (Kodama et al., 2001) as well as the Fischer-Tropsch reaction (Bian et al., 2002; Dry, 2002), iron is one of the promising catalysts for reduction of exhausted CO_2 into useful substances such as CO, CH_4, CH_3OH, and carbon.

However, it requires unusual reaction conditions such as coexistence of Au and Ti under high pressure (Chen and Bahnemann, 2000), a composite catalyst with expensive Rh (Luo et al., 2001), or a continuous supply of H_2 (Ando et al., 2000). The product selectivity is also usually low because of the lability of the surface of the iron during the reaction and simultaneous side reactions readily occur.

In this study, for enhancement of the catalytic activities and stabilization of the fine structure of the iron catalyst, various kinds of support materials such as silica, alumina, titania, and zirconia were examined and it was found that aluminum oxide was the most stable even at high temperatures of 500–700 °C and was effective for the catalytic reactions because of its sustention of the large surface area. A novel catalytic system for reduction of CO_2 using the composite iron catalysts with Al, Ca, Co, Cr, Cu, Mg, Mn, Ni, Ti, and/or Zn as the promoting components has also been examined.

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The primal reactions consist of (1) CO_2 reduction to CO, (2) dissociation of water with reduced iron into hydrogen and iron oxide, (3) methanol synthesis, and (4) water-gas shift reaction to hydrogen and CO_2. On the other hand, hydrogenations of CO_2 were also performed with Fe/Al_2O_3 at 500 °C in advance of the reexamination of H_2 generation from water without any prospect for recycling the oxidized iron. It was found that CO forms from CO_2 constantly for 4 h at least by using the reactor in this hydrogenation. Changing the ratios of H_2/CO_2 from 1 to 4 or 8 resulted in the improvement of CO_2 conversion. The selectivity of CO from CO_2 was the same value in every case. When Ni or Cu instead of Fe was loaded onto Al_2O_3, conversion of CO_2 was reduced, while methane was detected in the case of Ni. While the CO_2 conversion reduced half of the Fe, the selectivity of CO from CO_2 increased in the case of Cu.

2 Methods

Composite materials of Fe/Al_2O_3 were prepared by the core-precipitation method (O'Brien et al., 2000). For the addition of promoters, their nitrates or chlorides were used. The resulting solids of iron hydroxide were calcined in air at 700 °C for 2 h. The catalyst was pretreated with a hydrogen stream (100 ml/min) under atmospheric pressure at 500 °C for 4 h. The products were completely reduced as confirmed by measurements of the powder X-ray (CuKα 35 kV, 15 mA, 1/8° min^{-1}) diffraction patterns. The peaks are relatively sharp, corresponding to crystallite sizes of 191–314 nm by Debye-Scherrer analysis (Niederberger et al., 2002).

The CO_2 reforming was carried out with a fixed-bed reactor made of a stainless steel tube with 8-mm inside diameter as shown in Fig. 1.

After mixing CO_2 and steam in the gasifier, the mixed gas was made to flow through the stainless tube, in which Fe/Al_2O_3 was packed, in the furnace. Liquefied products passing through the cooling condenser and gasified products were separated and analyzed by gas chromatography (Shimadzu GC-12A, detector: thermocouple detector, column: molecular sieve 5A for H_2 and CO, Polarpack Q for CH_4 and CO_2, or Hitachi G-3900, detector: flame ionization detector, column: CP-polar PLOT U for methanol). In the case of batch reaction, a quartz test tube with 8-mm inside diameter was used.

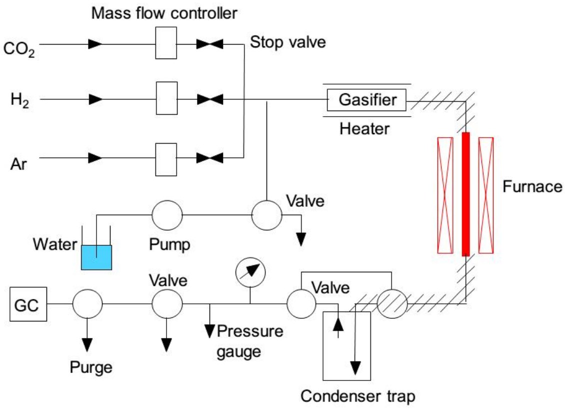


Fig. 1 Schematic illustration of a fixed-bed flow reactor

3 Characterization of the surface of the iron catalyst

Through the reactions of CO_2 or water with reduced iron (20–30 μm, granular) at 300–500 °C, it was confirmed that the primal reactions are as follows: CO_2+reduced iron→CO+iron oxide; H_2O+reduced iron→H_2+iron oxide.

In any case, since the phase transitions of the iron compounds and the redox processes were promoted through the reactions, acceleration of the reactions with increasing surface area of the iron was observed. Serious retardation by the carbon deposition on the iron-surface and the sintering of the iron through the migrations of iron atoms at higher temperatures were also observed. Such sintering sometimes resulted in the blockage of the flow reactor. Fig. 2 indicates scanning electron microscope (SEM) images of small Fe particles before and after the

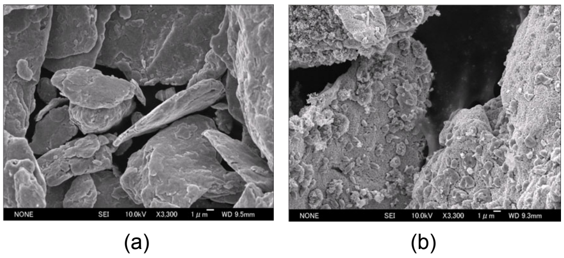

(a) (b)

Fig. 2 SEM images of small Fe particles before (a) and after (b) the reaction with CO_2 and water at 500 °C for 4 h

reaction with CO_2 and water at 500 °C for 4 h. It was found that the surface morphology of iron was altered and the formation of granular magnetite (Fe_3O_4) after the reaction was confirmed.

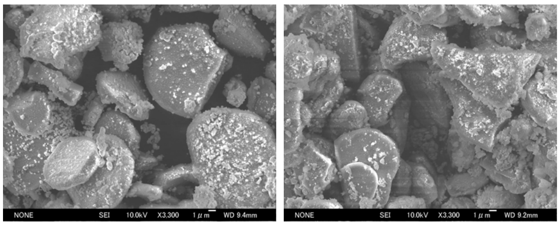
In order to prepare the composite iron catalysts with a larger surface area, a loading method and core-precipitation (ppt) method were examined. Silica or alumina was used as the substrate for the loading method with $Fe(OH)_3$, which was attached to the surface of the substrate as 35% (in weight) Fe through calcination at 700 °C for 2 h, followed by reduction at 500 °C for 4 h. In the case of the core-ppt method, alumina, silica, titania, and zirconia were used as heat-resistant and hard-reductive cores. Sol states of the core-compounds in aqueous Na_2CO_3 were stirred at 50 °C, and aqueous $Fe(NO_3)_3 \cdot 9H_2O$ was gradually dropped into the above sol mixtures followed by further ripening for 1 h. After filtration, ppt was washed with water and dried at 60 °C, followed by calcination at 700 °C for 2 h, and reduction at 500 °C for 4 h. Table 1 summarizes the surface areas of the synthetized catalysts determined by Brunauer-Emmett-Teller (BET) analyses and the crystalline sizes estimated by the analyses of the X-ray diffraction (XRD) patterns.

Table 1 BET surface area and crystalline size of composite iron catalysts (35% Fe/substrate)

Method	Supporter	BET surface area (m^2/g) After calcination[a]	BET surface area (m^2/g) After reduction with H_2[b]	Crystalline size[c] (nm)
Loading	SiO_2	132.2	128.3	32.1
	Al_2O_3	93.0	88.9	25.6
Core-ppt	SiO_2	109.8	105.6	29.2
	Al_2O_3	81.5	88.2	23.2
	TiO_2	31.5	30.3	36.1
	ZrO_2	20.8	24.8	30.7

[a] At 700 °C, for 2 h; [b] At 500 °C, for 4 h; [c] After reduction with H_2

The order of the large BET surface area is silica>alumina>titania>zirconia as shown in Table 1. Through the reduction with H_2 at 500 °C, most of the surface areas have been reduced except the cases of alumina and zirconia treated by the core-ppt method. From the strong XRD pattern observed at 2θ=44.55°, which is assigned to be iron, the crystalline size was estimated from Scherre's equation and is summarized in the right column of Table 1. The smallest crystalline size of Fe was attained in the case of 35% Fe/Al_2O_3. The order of the smaller crystalline sizes in the series of core-ppt method is alumina<silica<zirconia<titania. Using the core-ppt method resulted in the relatively small crystalline sizes of Fe as compared with those of the loading method. Fig. 3 shows the SEM images of Fe/Al_2O_3 before and after the reaction with CO_2 and water at 500 °C for 4 h. It was confirmed that no remarkable changes in their morphology and size of the small Fe particles have been observed before or after the reaction.



(a) (b)

Fig. 3 SEM images of Fe/Al_2O_3 before (a) and after (b) the reaction with CO_2 and water at 500 °C for 4 h

4 Dry reforming of CO_2

After the reaction of CO_2 with reduced iron (20–30 μm, granular) at 500 °C, cementite of carbonized iron (Fe_3C) was accumulated on the surface of the catalyst, and this was confirmed by XRD measurement (Fig. 4). Since Fe_3C reacts easily with water, contacting the Fe_3C with steam at 300 °C resulted in the disappearance of Fe_3C (Fig. 4) and the formation of methanol (Fig. 5). Through the electron probe micro analyzer (EPMA) surface elemental analyses and XRD measurements of the iron catalyst before and after the reaction, it was found that almost all of the carbon components had been fixed onto the surface of Fe as amorphous carbon and crystalline graphite, in part. The primal reactions consist of (1) CO_2 reduction to CO, (2) dissociation of water with reduced iron into hydrogen and iron oxide, (3) methanol synthesis, and (4) water-gas shift reaction to hydrogen and CO_2.

5 Steam reforming of CO_2

There is no remarkable difference of the yield of CO (and produced amount of H_2 from water) between the dry and the steam reforming of CO_2 to CO, and this is indicated in Figs. 5 and 6. It was also confirmed that the produced amount of synthetic gas was saturated when the reaction temperature was raised over 500 °C. Under atmospheric pressure, the yield and the selectivity of alcohol and other liquefied hydrocarbons are quite low. It inevitably requires the conditions under high pressure of several to hundreds MPa to get high yield and high selectivity for methanol (or ethanol) production.

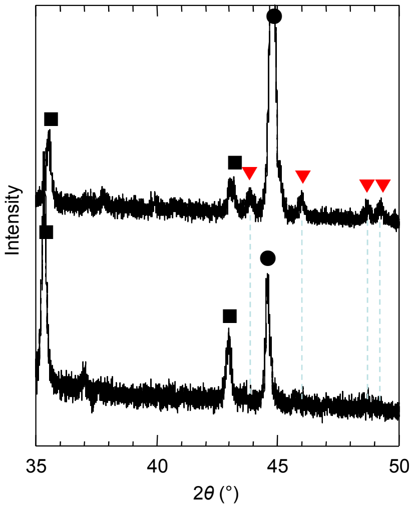


Fig. 4 XRD patterns of small Fe (1 mmol) particles: after the reaction of CO_2 (550 μmol) at 500 °C for 3 h (above); after substitution of the inner gas to argon and the addition of water (50 μl) to the above sample at 300 °C for 3 h (below); ●: Fe; ■: Fe_3O_4 (magnetite); ▼: Fe_3C (cementite)

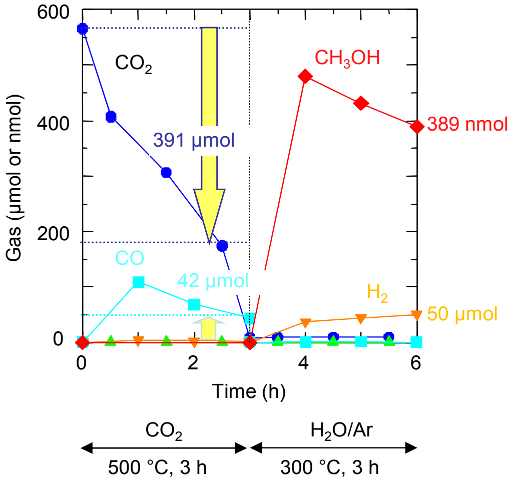


Fig. 5 Time-course changes of the components of the gas in the batch type reactor for dry reforming of CO_2 (550 μmol) with Fe (1 mmol) at 500 °C for 3 h, and water (50 μl) after substitution of the inner gas to argon at 300 °C for 3 h

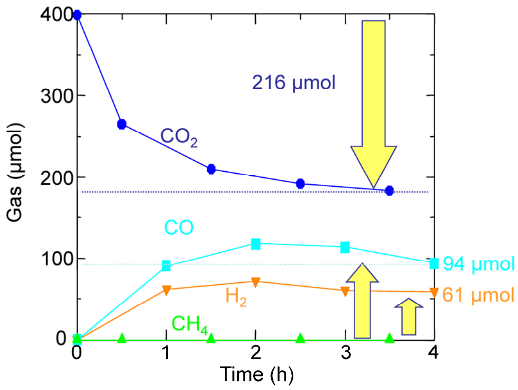


Fig. 6 Time-course changes of the components of the gas in the batch type reactor for CO_2 (400 μmol) steam reforming with Fe (1 mmol) and water (10 μl) at 500 °C

6 Water-gas shift reaction

Small amount of methanol (i.e. yield of 4% based on the initial amount of CO) was obtained from the synthetic gas as shown in Fig. 7. Though the yield of methanol (4%) is about 50 times higher than that of steam reforming of CO_2 (yield 0.08% based on the initial amount of CO_2), it is still low. The most preferential molar ratio of H_2/CO for methanol production is found to be 3 or 4. It was also found that much amount of hydrogen is required through water-gas shift reaction.

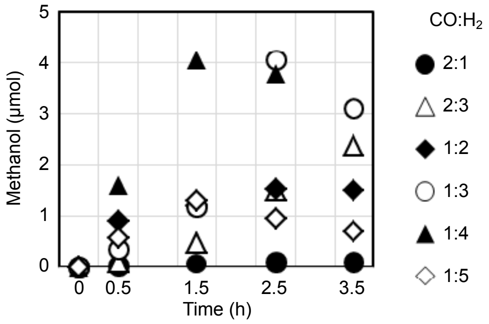


Fig. 7 Methanol synthesis with CO (100 μmol) and Fe (1 mmol) under atmospheric pressure at 270 °C

Ca, Mn, Ni, Cu or Mg as the promoter was added into the iron catalyst and used for the water-gas shift reaction as indicated in Fig. 8. Among the promoters tested, Cu showed high heat-resistivity and high activity in terms of H_2 production, since Cu is supposed to retard the carbon deposition onto the surface of the catalyst.

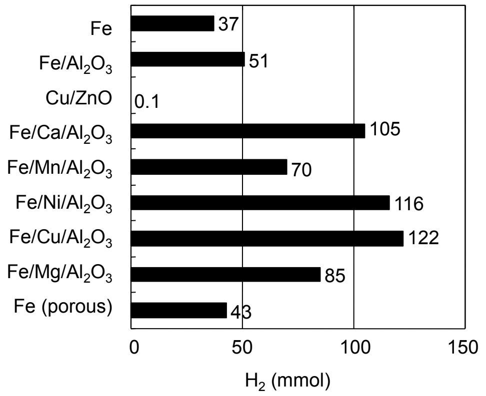


Fig. 8 Water-gas shift reaction with CO (300 μmol), H_2O (10 μl), Fe or Cu (1 mmol) under atmospheric pressure at 350 °C for 1 h. Chemical composition of the catalysts was as follows: 35% Fe-loaded Al_2O_3 with 1/10 molar ratio (i.e. [promotor]/[Fe]) of promotor of Ca, Mn, Ni, Cu or Mg. Molar ratio of [Cu]/[Zn] was 7/3 for Cu/ZnO

7 Hydrogenations of CO_2

Hydrogenations of CO_2 were performed with Fe/Al_2O_3 at 500 °C in advance of the reexamination of H_2 generation from water without any prospect for recycling the oxidized iron. It was found that CO forms from CO_2 constantly for at least 4 h using the reactor in this hydrogenation. Changing the ratios of H_2/CO_2 from 1 to 4 or 8 resulted in the up-conversion of CO_2 from 25% to 40% or 62%, respectively. The selectivity of CO from CO_2 was the same value of 85% in every case. When Ni or Cu instead of Fe was loaded onto Al_2O_3, conversion of CO_2 was reduced to 76%, while, 9% of methane was detected in the case of Ni. On the other hand, though the CO_2 conversion reduced half of the Fe, the selectivity of CO from CO_2 increased to 95% in the case of Cu (Fig. 9).

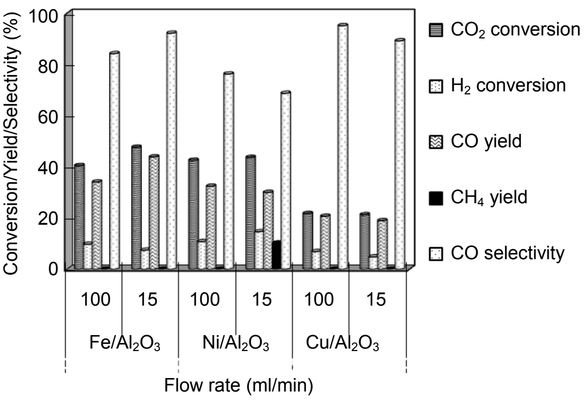


Fig. 9 Hydrogenation of CO_2 with 1 mmol of Fe-, Ni- or Cu of 35% metal–loaded Al_2O_3 under the flow of H_2/CO_2=4, at 500 °C for 1.5 h

8 Conclusions

Reforming of CO_2 with various composite materials of Fe/Al_2O_3 through CO_2 reduction to CO, dissociation of H_2O into H_2, and methanol synthesis has been investigated. It was found that dry and steam (i.e. wet) reforming of CO_2 produced almost the same amount of CO. At a temperature above 500 °C, the yields of CO and H_2 from CO_2 and H_2O were saturated. In order to achieve higher-yield and selectivity for useful substances, we developed the modified CO_2 reforming system by using Ni or Cu instead of Fe under atmospheric pressure. When Ni or Cu was used, though the selectivity of CO from CO_2 was reduced from 85% to 76%, 9% of methane was detected in the case of Ni. While the CO_2 conversion reduced half of the Fe, the selectivity of CO from CO_2 increased to 95% in the case of Cu. Changing the ratios of Fe, Ni and/or Cu on the composite materials to examine and regulate the yield and the selectivity of the products such as CO, CH_4, and C is promising for further enhancement. Improvements to the fixed bed reactor for establishment of an efficient recycle process of reduced iron from iron oxide are also crucial for prolongation of the sustainability of the reaction system.

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中文概要

题　目： **复合铁、镍、铜催化剂用于二氧化碳的资源化**

目　的： 1. 对现有的 CO_2 重整系统中铁系催化剂进行改进以期获得更高的产率和产物选择性；2. 实现反应体系中催化剂的高效回收以延长反应体系的可持续性。

创新点： 1. 开发复合铁、镍、铜催化剂用于水煤气变换反应，获得了更高的产物选择性；2. 提高了 CO_2 重整体系在常压条件下液态烃类的产率。

方　法： 1. 由核心沉淀法制得复合铁/氧化铝催化剂；2. 在固定床反应器中进行 CO_2 重整反应。

结　论： 1. 干、湿条件下的 CO_2 重整过程产生相同数量的CO；当温度高于 500 °C 时，CO 的产率达到饱和。2. 采用镍作为铁催化剂助剂时，CO 的选择性从85%降低到 76%，但是产物中可检出 9%的甲烷。3. 采用铜作为铁催化剂助剂时，尽管 CO_2 的转化率降低了一半，然而 CO 的选择性提高到了 95%。

关键词： 铁催化剂；二氧化碳减排；水煤气变换；甲醇合成