Reduction of Carbon Dioxide in γ Ray Irradiated Carbon Dioxide : Water System Containing Cu^{2+} and SO_3^{2-}

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Enhancing effect of various metal powders, metal oxides, metal ions, and inorganic anions on reduction of CO_2 in γ ray irradiated CO_2-water systems were investigated. Experimental results showed that Cu^{2+} and SO_3^{2-} have large enhancing effect. Furthermore, their synergical enhancing effect was found. The enhancing factor was about 100-fold.

Many researchers are endeavoring to develop effective methods for removing or fixing CO_2 in the atmosphere. For example, several chemical approaches such as catalytic,[1-3] electrochemical,[4-6] and photochemical[7,8] methods are being widely investigated to fix CO_2. In general, it is very difficult to convert CO_2 to a reduced substance such as hydrocarbon because it has the lowest reactivity among the carbon containing compounds. On the other hand, ionizing radiation is known to often stimulate chemical reactions. It has been reported that CO_2 can be decomposed by ionizing radiation at room temperature,[9] although the decomposition efficiency is very low due to the regeneration of CO_2 by the recombination reactions of the radicals and atom produced during the irradiation.[10,11]

Recently, γ ray induced CO_2 reduction to CO and hydrocarbon such as CH_4 and C_2H_6 are reported in a water containing Fe powder.[12,13] If CO_2 could be reduced efficiently by the aid of radiation exposure, it would be eminently meaningful to the mankind. Firstly, radiation from spent nuclear fuels as well as radioactive wastes, which is being or will be a severe environmental problem, could be utilized effectively. Secondly, it could be used for decreasing CO_2 in the atmosphere. Thirdly, if hydrocarbon compounds could be further produced, CO_2 could be used as a source of clean fuels and important chemical materials. Based on this consideration, we are carrying out the γ ray irradiation experiments to find an effective CO_2 reduction system. Our first endeavor is to investigate enhancing effect of various inorganic chemicals on the γ ray induced CO_2 reduction. A small amount (0.02 g) of each chemical such as Fe, $FeSO_4$, $FeCl_3$, Fe_2O_3, Cu powder, CuO, $CuSO_4$, $CuCl_2$, $NiSO_4$, $ZnSO_4$, ZnS, CdS, TiO_2, $CoCl_2$, Ag_2SO_4, Al powder, Na_2SO_3, or $NaNO_2$ was introduced into a glass pipette tube with 10 cm long tip part (internal diameter: 2 mm) and 5 cm long bottom part (internal diameter: 7 mm), which was sequentially washed with water, 0.1 mol dm^{-3} HCl, and water in an ultrasonic water bath and heated in a 300 °C oven for 10 min, beforehand. The bottom part was then heat-sealed with a high temperature gas burner. About 2 mL water was introduced into the pipette tube, and the chemical in the pipette tube was dissolved or dispersed in the water. After the solution or suspension in the pipette tube was bubbled with CO_2 gas for about 30 min, middle of the tip part was also heat-sealed. The volume of gas phase in the pipette tube was about 0.5 mL. The pipette tubes were fixed on a block of wood, and then placed around a ^{60}Co γ ray source (the Institute of Scientific and Industrial Research, Osaka University) for a certain period at room temperature. Dose rate of the γ ray irradiation was about 1 kGy h^{-1}. After the irradiation, the pipette tube was immersed into water. The tip end was scrupulously opened in the water, and a gas sample of 100 μL of the gas phase in the tube was taken by a syringe needle. It was immediately injected into a gas chromatograph (Hitachi G-3500) with a separation column (3 mm ID × 2 m, GL Science) of active carbon, a methanizer for converting CO and CO_2 into methane, and an FID detector. The detection limits of the GC for CO, CH_4, and C_2H_6 were about 5 ppm.

Table 1 shows concentrations of CO, CH_4, and C_2H_6 detected from various CO_2-water systems after 18 hours irradiation of γ ray. The concentration ranges in Table 1 are obtained from 4–6 radiation experiments carried out in different days.

Table 1. Concentrations of CO, CH_4, and C_2H_6 in various sample systems after 18 h γ ray irradiation

Sample systems[a]	CO/ppm	CH_4/ppm	C_2H_6/ppm
Air	N.D.[b]	N.D.	N.D.
Water	N.D.	N.D.	N.D.
c.b.w.[c]	40-55	5-10	N.D.
Fe powder-c.b.w.[d]	60-80	423-545	40-55
$FeCl_3$-c.b.w.	280-355	10-20	N.D.
$FeSO_4$-c.b.w.	450-520	10-20	N.D.
Fe_2O_3-c.b.w	80-100	5-10	N.D.
Fe_3O_4-c.b.w	80-100	5-10	N.D.
Cu powder-c.b.w.	40-70	5-10	N.D.
$CuSO_4$-c.b.w.	470-565	20-50	N.D.
CuO-c.b.w.	105-130	5-10	N.D.
$CoCl_2$-c.b.w.	250-360	5-10	N.D.
$NiSO_4$-c.b.w.	100-120	5-10	N.D.
$MnCl_2$-c.b.w.	180-200	5-10	N.D.
$ZnSO_4$-c.b.w.	120-140	5-10	N.D.
$AgSO_4$-c.b.w.	220-280	5-10	N.D.
KCl-c.b.w.	40-55	5-10	N.D.
$CaCl_2$-c.b.w.	40-55	5-10	N.D.
ZnS-c.b.w.	50-65	5-10	N.D.
CdS-c.b.w.	70-80	5-10	N.D.
Al powder-c.b.w.	80-120	5-10	N.D.
$NaNO_3$-c.b.w.	80-120	5-10	N.D.
$NaNO_2$-c.b.w.	180-350	5-10	N.D.
Na_2SO_3-c.b.w.	600-770	5-10	N.D.
Na_2SO_3-$CuSO_4$-c.b.w	4000-6000	5-10	N.D.

[a]Sample concentrations were 0.01g mL^{-1}. [b]Not detected. [c]CO_2 bubbled water. [d]in the system with Fe powder, no CO was detected, but both CH_4 (510-620 ppm) and C_2H_6 (60-80 ppm) were detected before the irradiation. On the other hand, none of CO, CH_4, and C_2H_6 were detected in others before the irradiation.

Glass pipette tubes filled with air, water, and CO_2-bubbled water were firstly irradiated to investigate the backgrounds of the production of CO and CH_4. No detectable CO, CH_4, and C_2H_6 were found in the irradiated air and water. However, about 40–55 ppm CO and 5–10 ppm CH_4 were detected after 18 h-irradiation in the CO_2-bubbled water. This means that a part of CO_2 was reduced to CO and even CH_4 in the CO_2 bubbled water by the irradiation. Secondly, the reported CO_2-water system containing Fe powder was investigated. As shown in footnotes of Table 1, no CO but a large amount of CH_4 and C_2H_6 were detected before the irradiation. This means that a part of CO_2 was reduced to CH_4 and C_2H_6 in the system even without the irradiation. After the irradiation CO was increased to about 60–80 ppm, but both CH_4 and C_2H_6 were decreased in comparison with those before the irradiation. The increase of CO in the system with Fe powder comparing with that without Fe powder suggests that Fe powder has a little enhancing effect in the CO_2 reduction to CO. The decrease of CH_4 and C_2H_6 after the irradiation might be due to the decomposition effect of the γ ray, by which many organic compounds are known to be decomposed.[14] Therefore, in the system with Fe powder, CH_4 and C_2H_6 were not produced by the irradiation of γ ray. Its detail will be reported elsewhere.

In addition to Fe powder, other chemicals of Fe (Fe^{2+}, Fe^{3+}, Fe_2O_3, Fe_3O_4), Cu (powders of Cu, CuCl and CuO, Cu^{2+}) and Al (Al powder, Al^{3+}) were also added into the CO_2 bubbled water to investigate their enhancing effects. The chemicals of Cu and Al were tried since a Cu electrode and Al particles have been reported to be efficient in the electrochemical reduction of CO_2[4] and H_2 gas evolution in γ ray irradiated water,[15] respectively. Furthermore, semiconductor particles (TiO_2, ZnS, and CdS) were also investigated since photocatalytic reduction of CO_2 has been reported.[16,17] Experimental results show that the largest amount of CO and CH_4 were produced in the system containing Cu^{2+} in these chemicals. The Cu^{2+} might act as a catalysis or directly take part in the CO_2 reduction reaction. On the other hand, most of these chemicals have little enhancing effect in CH_4 production.

Other metal ions such as Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}, Ag^{+}, Ca^{2+}, and K^{+} were also investigated to compare with Cu^{2+}. The results show that some of them have enhancing effect in CO_2 reduction to CO, but their enhancing effect were smaller than that of Cu^{2+}. In addition to metal ions, reductive inorganic anions SO_3^{2-} and NO_2^{-} were also investigated. Carbon dioxide is known to be decomposed by γ ray as follows,[10]

$$CO_2 + \gamma\ \text{ray} = CO + O \qquad (1)$$

The reductive anion such as SO_3^{2-} is expected to combine with the oxygen O as follows,

$$SO_3^{2-} + O = SO_4^{2-} \qquad (2)$$

The experimental results show that both SO_3^{2-} and NO_2^{-} enhanced the CO_2 reduction to CO, and the CO concentration in the system with SO_3^{2-} is larger than that containing Cu^{2+}. Therefore, a chemical which would react with O and produce a stable compound such as SO_4^{2-} would enhance the CO_2 reduction efficiency.

Furthermore, both Cu^{2+} and SO_3^{2-} were added into the CO_2 bubbled water. The last line in Table 1 shows that the largest concentration of CO was detected when Cu^{2+} and SO_3^{2-} were coexist (its G value was about 0.1). The enhancing factor is about 100-fold comparing to the system without them. This result suggests that Cu^{2+} and SO_3^{2-} have synergical enhancing effect in the CO_2 reduction. Although the exact reaction mechanisms remain to be investigated, above results suggest that it might be a meaningful method to find out an effective CO_2 reduction system by considering the synergical enhancing effect of various chemicals.

Although CO production was greatly enhanced by the existence of Cu^{2+} and SO_3^{2-}, neither increase of CH_4 nor C_2H_6 was observed. In all of the systems, the maximum CH_4 concentration was observed in the system containing Cu^{2+}, its G value was about 10^{-4}. It is well known that various active species containing H such as H·, H, ·OH, and H_2 are easily generated in γ ray irradiated water.[14] The production of CH_4 is expected from the reaction of these active species with CO_2 or reduction product CO. However, as stated above CH_4 will be decomposed meanwhile in the irradiation of γ ray. The experimental results suggest that the decomposition might be more easier than the production. Accordingly, some inhibitors to the decomposition reaction might be required to the production of CH_4.

The CO concentration was increased with both the irradiation time and the dose rate of γ ray. However, the CH_4 concentration seems to be independent of irradiation time, but increased with the decrease of the dose rate. The details and the reaction mechanisms will be reported later.

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