Decomposition of CO_2 into CO and O in a Microwave-Excited Discharge Flow of CO_2/He or CO_2/Ar Mixtures

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Decomposition of CO_2 in a fast electric discharge flow of CO_2/He or CO_2/Ar mixtures was studied by observing UV and visible emission spectra. The decomposition efficiency of CO_2 in CO_2/Ar mixtures was higher than that in CO_2/He mixtures. More than 90% of CO_2 in CO_2/Ar mixtures was selectively decomposed into CO and O at a microwave power of 100–200 W, and CO_2 and Ar flow rates of 25 and 1000 sccm, respectively, at a total pressure of 0.5 Torr.

Since CO_2 is a major source of the greenhouse effect, novel removal techniques are being developed to remove CO_2 from combustion gases. Various catalytic reduction processes, direct decomposition into C_n, CO, and O_2 in an electric discharge, and plasma-assisted catalytic systems have been proposed.[1–3] If CO_2 can be decomposed without using catalysts, a convenient removal process can be developed. Here, we applied a fast electric discharge-flow system to the removal of CO_2 in CO_2/He or CO_2/Ar mixtures. The decomposition efficiency and the decomposition products of CO_2 were analyzed using UV and visible emission spectroscopy.

The discharge-flow apparatus used for the present study of the CO_2 removal was similar to that reported previously.[4] It consisted of a stainless-steel main flow tube and two quartz discharge tubes. The discharge-flow apparatus was continuously evacuated using a 10 m^3/min booster pump. CO_2 and He or Ar gases were kept at a constant mass flow rate and various mixtures of them were fed into a 2.45-GHz microwave discharge operated at an output power of 50–200 W. The flow rates of He and Ar were 2000 and 1000 sccm (standard cubic centimeter per minute), respectively. The partial pressures of CO_2, He, and Ar in CO_2/Ar or CO_2/He mixtures were 0.004–0.02, 0.1, and 0.06 Torr (1 Torr = 133.33 Pa), respectively, while that of He used for the generation of the lowest excited triplet $He(1s2s{:}2^3S)$ state was 0.4 Torr.

UV and visible emission spectra resulting from the $He(2^3S)$ reactions were used as a new method to monitor CO_2 and its discharge products. The metastable $He(2^3S)$ atoms with an available energy of 19.82 eV, and He^+ and He_2^+ ions were generated by a second microwave discharge of pure He gas in a quartz tube. He^+ and He_2^+ ions were prevented from entering the reaction zone by a pair of ion-collector grids placed on an exit opening of the discharge tube. The emission spectra resulting from the reactions of $He(2^3S)$ with CO_2 and its discharge products were dispersed in the 190–600 nm region with a Spex 1250 M monochromator equipped with a cooled Hamamatsu Photonics R376 photomultiplier. Photon signals from the photomultiplier were digitized using an AD converter and stored in a microcomputer.

Possible stable final gaseous products resulting from the decomposition of CO_2 are CO and O_2. It is known that Penning ionization of $He(2^3S)$ with CO_2, CO, and O_2 provides the following emitting excited species:[5–7]

$$He(2^3S) + CO_2 \rightarrow CO_2^+(A^2\Pi_u, B^2\Sigma_g^+) + He + e^-, \quad (1)$$

$$He(2^3S) + CO \rightarrow CO^+(A^2\Pi, B^2\Sigma^+) + He + e^-, \quad (2)$$

$$He(2^3S) + O_2 \rightarrow O_2^+(A^2\Pi_u) + He + e^-. \quad (3)$$

These processes could be monitored by observing $CO_2^+(A\rightarrow X, B\rightarrow X)$, $CO^+(A\rightarrow X, B\rightarrow X)$, and $O_2^+(A\rightarrow X)$ emission systems in the 190–600 nm region. Here, X, A, and B denote the ground state and 1st and 2nd excited states of molecular ions, respectively.

Figure 1(a) shows a typical emission spectrum of a CO_2/He mixture obtained by switching off the microwave discharge. The spectrum is composed of $CO_2^+(A\rightarrow X, B\rightarrow X)$ emissions from process (1). By switching on the microwave discharge, the emission intensities of $CO_2^+(A\rightarrow X, B\rightarrow X)$ decrease, while $CO^+(A\rightarrow X, B\rightarrow X)$ emissions appear, as shown in Figure 1(b). No $O_2^+(A\rightarrow X)$ emission was observed under the present experimental conditions, though it was detected by the addition of pure O_2 into the discharge flow. When the buffer He gas was replaced by Ar, similar emission spectra were observed.

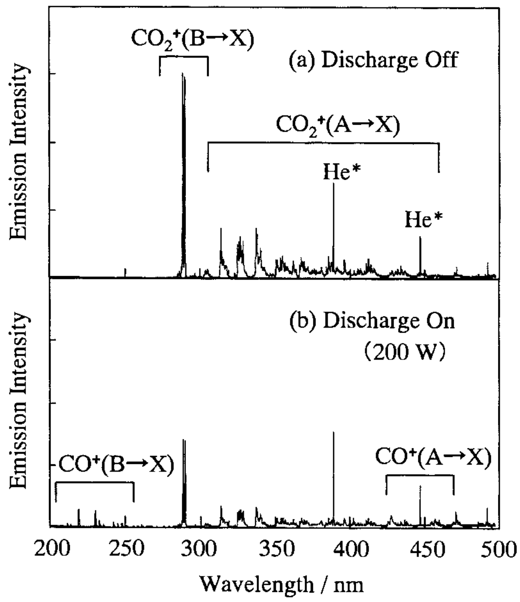

Figure 1. Emission spectra resulting from Penning ionization of $He(2^3S)$ with a CO_2/He mixture at a CO_2 flow rate of 100 sccm.

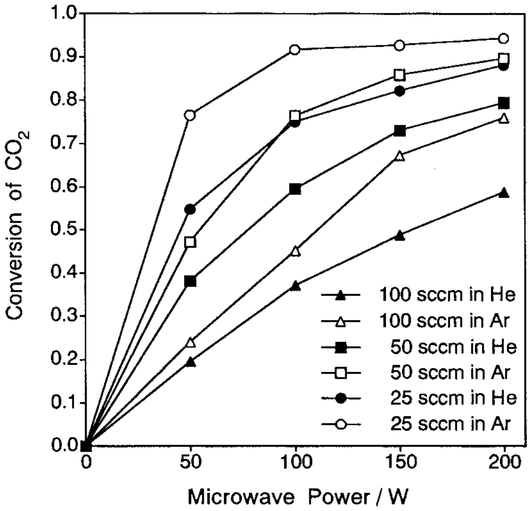

Figure 2. The dependence of conversion of CO_2 in CO_2/He and CO_2/Ar mixtures on the microwave power.

In order to examine the optimum decomposition conditions, the decomposition efficiency of CO_2 was measured as a function of the microwave power at CO_2 flow rates of 25, 50, and 100 sccm. The decomposition efficiency of CO_2 was determined from the reduction of the $CO_2^+(B \rightarrow X)$ band, as shown in Figure 1. Figure 2 shows the dependence of the conversion of CO_2 on the microwave power in CO_2/He and CO_2/Ar mixtures. With increasing microwave power from 0 to 200 W, the conversion of CO_2 increases. The conversion of CO_2 increases with decreasing the CO_2 flow rate from 100 to 25 sccm in both CO_2/He and CO_2/Ar mixtures. It should be noted that CO_2 in CO_2/Ar mixtures is decomposed more efficiently than that in CO_2/He mixtures, even though the Ar flow rate is a half of the He flow rate. It is clear from Figure 2 that more than 90% of CO_2 is decomposed at microwave power of 100–200 W in CO_2/Ar mixtures at the lowest CO_2 flow rate of 25 sccm.

In the microwave discharge of CO_2/He and CO_2/Ar mixtures, the following electron-impact dissociation and ionization (4a)–(4c), Penning ionization (5a)–(5c), and dissociation process (6), dominantly occur at first, leading to CO, O, CO_2^+, CO^+, and O^+:

$$e^- + CO_2 \rightarrow CO + O + e^-, \quad (4a)$$
$$\rightarrow CO_2^+ + 2e^-, \quad (4b)$$
$$\rightarrow CO^+ + O + 2e^-. \quad (4c)$$

$$He(2^3S) + CO_2 \rightarrow CO_2^+ + He + e^-, \quad (69\%) \quad (5a)$$
$$\rightarrow CO^+ + O + He + e^-, \quad (4.5\%) \quad (5b)$$
$$\rightarrow O^+ + CO + He + e^-, \quad (27\%) \quad (5c)$$

k_5(total) = 6.0×10^{-10} cm^3 molecule^{-1} s^{-1} [ref 8,9],

$$Ar(^3P_{0,2}) + CO_2 \rightarrow CO + O(^3P) + Ar, \quad (6)$$

$k_6 = 5.9(^3P_0)$ and $5.3(^3P_2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} [ref 10, 11].

Subsequent electron–ion recombination process (7) will take place in the discharge and downflow region:

$$CO_2^+ + e^- \rightarrow CO + O, \quad (7)$$

$k_7 = 3.8 \times 10^{-7}$ cm^3 s^{-1} [ref 12].

In addition, the following three-body recombination processes may take place:

$$CO + O + M \rightarrow CO_2 + M, \quad (8)$$

$k_8 = 6.6 \times 10^{-33}\exp(-2173/T)$ cm^6 molecule^{-2} s^{-1}[ref 13],

$$O + O + M \rightarrow O_2 + M, \quad (9)$$

$k_9 = 2.76 \times 10^{-31}/T$ cm^6 molecule^{-2} s^{-1}[ref 13],

where M stands for third-body CO_2, He, or Ar. Two-body rate constants of the above three-body recombination reactions (8) and (9) at an M pressure of 0.5 Torr and 300 K were calculated to be 7.6×10^{-20} and 1.5×10^{-17} cm^3 molecule^{-1} s^{-1}, respectively, from the relation k_x[M] for x = 8 and 9. Since these values are much smaller than k_5–k_7, three-body processes (8) and (9) will be insignificant under the present experimental conditions. A higher decomposition efficiency of CO_2 into CO + O in CO_2/Ar mixtures than that in CO_2/He mixtures is probably due to the fact that dissociation process (6) is a fast direct decomposition process of CO_2 into CO + O in CO_2/Ar mixtures, while a sufficient amount of slow electrons is required for the formation of CO + O via process (7) in CO_2/He mixtures.

The lack of the $O_2^+(A \rightarrow X)$ emission indicated that O_2 concentration in the observation of emission spectra was too low to detect the $O_2^+(A \rightarrow X)$ emission because a high buffer gas pressure was required for the formation of O_2 from three-body process (9).

In conclusion, CO_2 could be efficiently decomposed by a microwave discharge of CO_2/He or CO_2/Ar mixtures. A cheaper Ar was found to be more effective for the preferential decomposition of CO_2 into CO + O at a low CO_2 flow rate of 25 sccm. The He(2^3S) reactions could be used as a new technique for monitoring the decomposition process of CO_2 in a discharge flow of CO_2/He or CO_2/Ar mixtures. We are planning further study of the decomposition of CO_2 in the presence of N_2, O_2, and H_2O at higher pressures for the practical application of this technique to CO_2 removal from combustion gases.

References and Notes

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