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Profiles of Carbon Dioxide Decomposition in a Dielectric-Barrier Discharge-Plasma System

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Decomposition of CO_2 to CO and O_2 in Ar stream has been investigated under atmospheric pressure by the use of a dielectric-barrier discharge plasma reactor. CO_2 dissociation was found to proceed in accordance with the stoichiometry of $2\ CO_2 = 2\ CO + O_2$ at considerable rates, which increased with increasing the input voltage, the CO_2 concentration in Ar, and the heat of oxide formation of the corresponding metallic component used as the electrode. From kinetic and spectroscopic measurements, the major pathway of CO_2 decomposition was speculated to be promoted by a synergetic effect between plasma excitations in the gas phase and catalytic actions of the electrode surface.

During the last decade a rapid increase in the concentration of man-made CO_2 on our planet has become the serious problem to be urgently solved from an environmental point of view. It must be a good solution to use positively exhausted CO_2 as a resource in chemical industries. It is difficult for thermodynamically stable CO_2, however, to be activated efficiently via conventional thermal and catalytic reaction processes. Cold plasmas can be used to excite gaseous species and, in certain cases, non thermodynamic equilibrium can be obtained to selectively activate stable small molecules. A limited number of practical studies concerning plasma reactions are available due to problems associated with low yields from the use of low pressure, mass-transfer limitations, and high operational costs.

Recently, we have been investigating the performances of nonthermal discharge-plasma systems in the decompositions of stable small compounds, such as NO,[1] H_2O,[2] and CO_2,[3,4] at atmospheric pressure. Ihara et al. studied in detail the reduction of CO_2 with H_2O to produce oxalic acid, H_2O_2[5] and CH_3OH[6] in microwave-induced plasma systems also under atmospheric condition. Jogan et al., on the other hand, studied direct decomposition of CO_2, and estimated the energy efficiency of a ferroelectric packed-bed plasma reactor.[7] In the present study the direct decomposition of CO_2 was investigated by using a nonthermal dielectric-barrier discharge system in order to understand the behavior of CO_2 molecules in the Ar plasma zone.

Experimental

The dielectric-barrier discharge (silent discharge) plasma reactor used in this work is illustrated in Fig. 1. The inner electrode with an outside diameter of 8 mm and a length of 70 mm was supported at the center of a quartz tube with an inside diameter of 10 mm by tube fittings (Swagelok made of perfluoroalkoxide). Three kinds of metal rods (Cu, Ni, and Fe) were examined as the inner electrode in order to check the catalytic effects of the electrode surface. As the outer electrode, the quartz tube was tightly surrounded by a cylindrical jacket made by metallic aluminum having a length of 70 mm. When an ac current at a high voltage above 1 kV was supplied into an Ar stream, the homogeneous light of a cylindrical discharge was observed between the inner electrode and the quartz wall of the reactor tube.

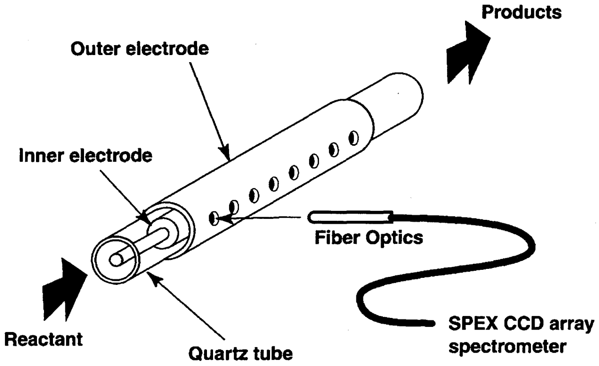

Fig. 1. Dielectric-barrier discharge reactor used in the present work.

The CO_2 decomposition was carried out under atmospheric pressure by using a conventional flow system, described elsewhere.[1,2] Reactant gas mixtures (CO_2 in Ar) were supplied into the reactor from high pressure cylinders through mass-flow controllers. The reaction products were monitored continuously by a mass spectrometer (Ulvac MM-100) with a multi-channel programmer through an orifice sampling system, and analyzed periodically by gas chromatography with three types of columns (Polapak Q, active carbon, and Unipak S) through six-port valves with a sampling loop of 1 cm^3.

Electric power was supplied to the reactor by an ac high-voltage power supply (Trek-20/20) with a function generator (Wavetec FG-2A). During operation, such electric parameters as the a.c. wave shape, input voltage, current and frequency were continuously monitored by a multi-channel digital oscilloscope (Yokogawa DL-1200). The input power was calculated by the mean square voltage, and the current was measured with an oscilloscope.[8]

The diagnostics of the plasma zone were performed by a visible-ultra violet spectrometer (SPEX 270-M) attached to a back-thinned illuminated CCD array matrix detection system (ISA).[1,3] Emission lights from the eight small windows with a diameter of 1.5 mm, located in the center of the outer electrode jacket (Fig. 1), were collected and directed into the spectrometer through eight glass-fiber optic cables with an outside diameter of 1 mm. Short periods of integration from 0.01 to 1 s and large numbers of accumulations from 20 to 200 times were applied to prevent saturation of the CCD matrix detector. The Ar emission lines in the spectra were accurate to ±0.1 nm.

Result

Effect of Input Voltage. The input voltage was recognized to play the most important role among the electric parameters. When a power with a higher voltage above 1 kV was supplied to the reactor where pure Ar was flowing, a homogeneous cylindrical light was observed and an appreciable current passed between the inner electrode and the quartz wall of the reactor. Several lines of the emission spectra were observed during the Ar discharge. Figure 2(a) shows the intensities of the emission spectra due to typical Ar excitations,[9] i. e., 696, 706, 750, and 811 nm. The intensities of these spectra increased rapidly along with an increase in the input voltage. All of these spectra, furthermore, could be extrapolated onto one point at about 1 kV on the axis of input voltage, suggesting that the break-down voltage of the Ar discharge was 1 kV in the present system. This value of the break-down voltage did not depend on the metallic component of the inner electrode among Cu, Ni, and Fe.

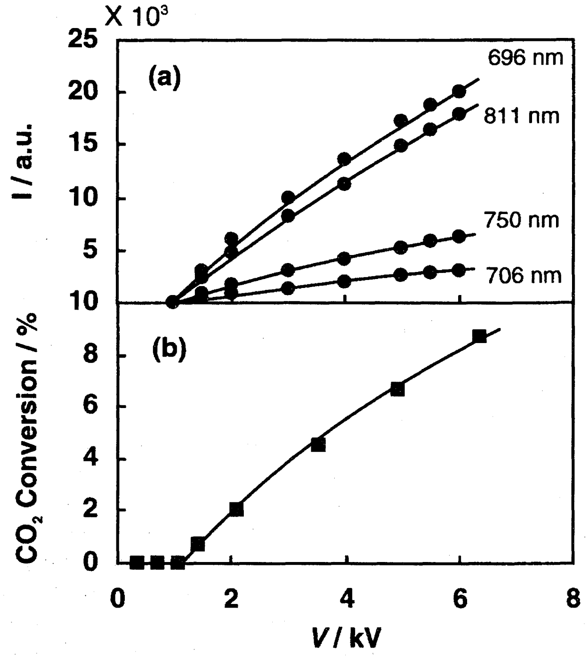

Fig. 2. Effects of the input voltage on the intensities of emission spectra from pure Ar gas (a) and on the CO_2 conversion with a reactant mixture of 10% CO_2 in Ar (b). Inner electrode, Cu; total flow rate, 50 $cm^3\ min^{-1}$.

Upon introducing CO_2 into the Ar stream, reddish-purple light turned to bright pink, although no appreciable changes in the voltage and current were observed. The sine wave the shape of voltage on the oscilloscope, at the same time, became noisy, indicating a "showering arc" due to the excitation of CO_2 molecules. A comparatively small emission of heat was recognized during the discharge, i. e., the temperature of reactor wall gradually increased with time on stream and became constant at about 330 K in 20 min after the discharge started.

The CO_2 conversion to CO and O_2 was recognized above about 1 kV and increased with increasing the input voltage, as represented in Fig. 2(b). A similar dependence in conversion on the input voltage was recognized by Shepelev et al. in the partial oxidation of methane using a silent discharge reactor.[10] From the point of view that the minimum voltage for the CO_2 decomposition well coincided with the break-down voltage for the Ar discharge, the reaction was considered to be promoted by Ar excitation, i. e., charge and energy transfers probably occurred from excited Ar species to reactant CO_2 molecules.

Table 1 shows the representative products in steady-states of CO_2 decomposition. The reaction products consisted of only three kinds of species, i. e., CO_2 unreacted, CO and O_2 in the gas phase and no substantial formation of carbonaceous product was observed on the electrode surface. The amount of the CO_2 consumption ($[CO_2]_c$) was almost equal to that of the CO formation ($[CO]_f$) which was twice as much as that of the O_2 formation ($[O_2]_f$). The ratios of each species, $[CO]_f/[CO_2]_c = 1$ and $[CO]_f/[O_2]_f = 2$, were, furthermore, independent of the input voltage. The reaction was, therefore, found to proceed in accordance with the stoichiometry of $2CO_2 = 2CO+O_2$ under these mild conditions examined. At higher voltages above 9 kV and higher frequencies above 30 kHz, however, substantial amounts of the carbon formation were observed on the surface of the inner electrode during CO_2 decomposition, even in the Ar stream.

Effect of CO_2 Concentration. Figure 3 shows the effects of the CO_2 concentration in Ar on the decomposition reaction. The intensities of the emission spectra due to the excitation of Ar atoms dramatically decreased upon the introduction of only a small concentration of CO_2 (2%) into

Table 1. The Influence of Input Voltage on Reaction Products of the CO_2 Decomposition[a)]

Voltage/kV	Amount/μmol min^{-1}			Ratio	
	$[CO_2]_c$	$[CO]_f$	$[O_2]_f$	$[CO]_f/[CO_2]_c$	$[CO]_f/[O_2]_f$
2.1	4.8	4.3	2.2	0.9	1.9
3.5	9.5	9.3	4.7	1.0	2.0
5.0	13.6	14.1	6.9	1.0	2.0
6.4	17.6	19.8	9.0	1.1	2.2

a) Frequency, 1 kHz; inner electrode, Cu; flow rate, 50 ml min^{-1}; CO_2 concentration, 10% in Ar.

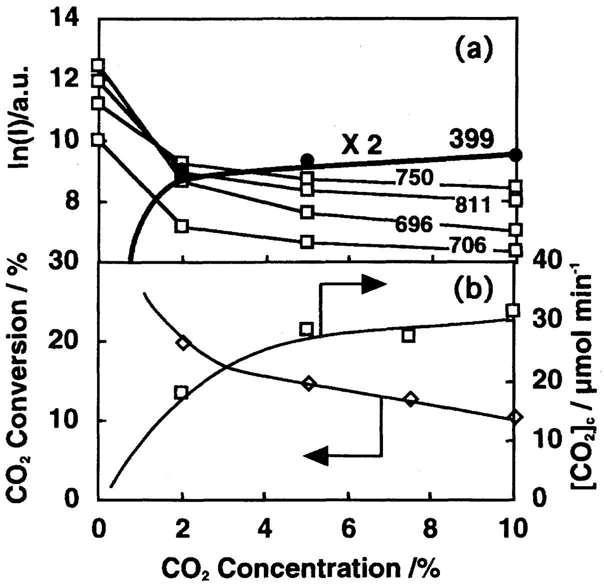

Fig. 3. Effects of the CO_2 concentration in Ar on the intensities of emission spectra from the reactant mixture (a) and on the conversion and rate of CO_2 decomposition (b). Inner electrode, Cu; input voltage, 7 kV; total flow rate, 50 cm^3 min^{-1}.

the Ar stream, as shown in Fig. 3(a). Then, they gradually decreased with increasing the CO_2 concentration in the Ar stream. This figure might indicate additional evidence of the charge and energy transfer from the excited Ar species to the reactant CO_2 molecules. The charge and energy transfer occurred quite effectively in the presence of small amounts of CO_2. In this dielectric-barrier discharge system, only one distinct peak for the excitation of CO_2 molecules could be observed at 399 nm of the wavelength, which was considered to be due to the CO^+ species. The intensity of this spectrum increased correspondingly with decreasing those due to the excited Ar species.

With increasing the CO_2 concentration in the Ar stream, on the other hand, the CO_2 conversion decreased, whereas the rate of decomposition increased, as represented in Fig. 3(b). Only a small conversion of the CO_2 decomposition was recognized to proceed in the absence of the Ar carrier gas under a similar mild condition (not shown), indicating that the reaction was promoted by charge and energy transfers from excited Ar species to CO_2 molecules.

Effect of Electrode Metal. In order to confirm catalytic effects in this reaction system, the CO_2 decomposition was performed in the reactor with Cu, Ni, Fe rods as the inner electrodes. In this series of comparative experiments, the relative intensities of the Ar emission spectra were almost the same for all metal electrodes examined, suggesting that the exciting and quenching processes of the Ar species in the plasma zone did not change due to the metal components of the electrode. The effect of the metallic component of the electrode on the CO_2 decomposition is shown in Fig. 4. The rates of decomposition carried out in various input voltages increased with increasing the heat of corresponding metal oxide formation, i. e., the rate of CO_2 decomposition increased in the order of Cu < Ni < Fe.

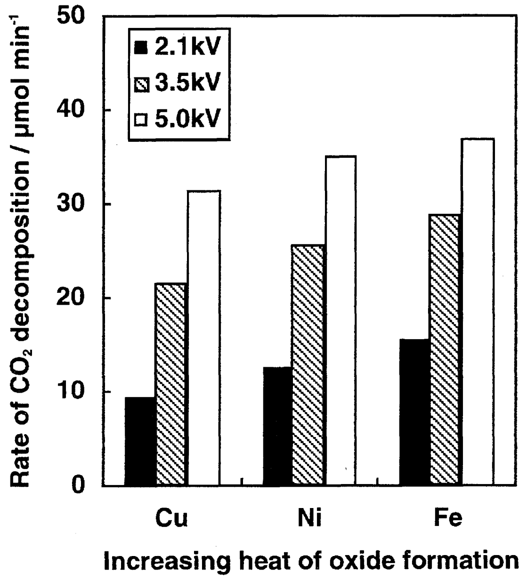

Fig. 4. Effect of metallic component of the inner electrode on the rates of CO_2 decomposition. Reactant mixture, 10% CO_2 in Ar; total flow rate, 50 cm^3 min^{-1}.

Among these metal electrodes, no virtual difference was recognized in the selectivity of the products ($[CO]_f/[O_2]_f$ = 2) and in the minimum voltage for the reaction (ca. 1 kV). This probably suggests that the CO_2 decomposition with different electrodes proceeded via a similar mechanism of the excitation and energy-transfer process in the plasma zone. This difference of the reaction rates among the different metals were, therefore, considered to suggest the difference in catalytic activity of the inner electrode surface.

Discussion

The emission control of CO_2 has become a global concern.[11] An enhanced greenhouse effect due to increased CO_2 emission from man-made sources is expected to have profound effects on the global climate.[12] Although the direct decomposition of CO_2 to CO and O_2, itself, is considered not to be very useful in practical applications from the view point of energetics, the simplicity of the reaction is suitable as a model reaction to understand the reactivity of CO_2 and to analyze the mechanism of the plasma-reaction system. It has already been known that plasmas easily break down CO_2 to CO and O_2 and coke.[13] In the present work carried out in an Ar stream under mild conditions, furthermore, the stoichiometric reaction was found to proceed from mass-balance calculations of the carbon components, i. e., the ratio $[CO]_f/[O_2]_f$ was always 2, as represented in Table 1.

Large consumptions of energy are, generally speaking, considered to be one of the important problems to be improved in the application of plasmas for chemical reactions. It is very difficult, however, to compare the energy consumption in the plasma systems with the conventional thermal and/or catalytic process. A useful quantity for evaluating the energy consumption in plasma systems is the energy yield (Ey), defined by Jogan, Mizuno, Yamamoto, and Chang[7] as the amount of decomposed CO_2 in grams by 1 kilowatt-hour of power supplied by the reactor (gCO_2/kWh). The estimated energy yields in the present system are cited in Table 2. The Ey value obtained in the present work was almost of the same magnitude as those obtained in a ferroelectric-packed reactor,[7] and increased with decreasing the input power.

Here, the energy efficiency of the present reactor has been estimated by a semi-empirical calculation, i. e., the ratio of the theoretical value of energy required for CO_2 dissociation (C–O bond energy in CO_2 molecules is 798.9 $\mathrm{kJ\,mol^{-1}}$)[14] and the experimental value of the power consumption. The energy efficiencies calculated for this reactor are also given in Table 2. It is, therefore, indicated that 6—23% of the supplied energy is used for CO_2 dissociation itself in the present system.

An appreciable amount of carbon formation has been observed on the electrode surface[2] in the absence of Ar gas. Direct plasma decomposition of pure CO_2 proceeds via the following two reaction pathways involving electron impact:[15]

$$\mathrm{CO_2 + e^- \longrightarrow CO + O + e^-} \tag{1}$$

$$\mathrm{CO_2 + e^- \longrightarrow C + O_2 + e^-} \tag{2}$$

The branching of pathways (1) and (2) depends on the vibrational excited-state CO_2 molecules.

Argon used as a diluent gas was found to play an important role,[2,3,16] since only a small conversion of the CO_2 decomposition was observed in the case where pure CO_2 was used as the reactant gas. Because small amounts of CO_2 were introduced, large changes were observed in the relative intensities of the Ar emission lines, and a broad peak due to emission from CO^+ appeared additionally, as shown in Fig. 3(a). This suggests that the excited state of Ar is consistent with the established mechanisms of charge and energy transfer from the Ar^+ (and/or ${Ar_2}^+$) species[2,15] to CO_2 molecules as a dominant pathway in the ultimate decomposition of CO_2.[15,17] The role of Ar gas and such charge and energy-transfer mechanisms in the plasma zone were also supported by evidence that the break-down voltage of the Ar plasma well coincided with the minimum voltage for the CO_2 decomposition, as shown in Figs. 2(a) and 2(b).

The break-down voltage of Ar discharge and the emission spectra due to Ar excitations were almost independent of the metallic component of the electrode. On the other hand, the rate of CO_2 decomposition depends on the metallic component of the inner electrode (Fig. 4). This evidence, therefore, indicates the catalytic role of the electrode surface. We have already observed small broad peaks with a vibrational structure due to emission from the ${CO_2}^+$ species in a region of wave number from 330 to 375 nm in the CO_2 in a He stream by a glow-discharge reactor.[4] Although such a spectrum, unfortunately, could not be recognized in the present experiments performed in an Ar stream by the dielectric-barrier discharge system, ${CO_2}^+$ was supposed to be the key excited species in the CO_2 decomposition.

According to this speculation, the reactive ${CO_2}^+$ species produced in the plasma zone would interact with the metallic component of the electrode surface to form the corresponding metal oxide and CO^+ species, latter of which was recognized in the plasma zone (Fig. 3). As represented in Fig. 4, therefore, the over-all rate of CO_2 decomposition increased with increasing the affinity between metal and oxygen. In this figure the strength of the interaction is represented by the heat of oxide formation for each metal component of the inner electrode.

From these points of view, the major reaction pathway of CO_2 decomposition in the present reactor might consist of five steps, i. e., (3) excitation, (4) charge transfer, (5) surface reaction, (6) desorption, and (7) neutralization, as follows:

$$\mathrm{Ar \longrightarrow Ar^+ + e^-} \tag{3}$$

$$\mathrm{Ar^+ + CO_2 \longrightarrow Ar + {CO_2}^+} \tag{4}$$

$$\mathrm{{CO_2}^+ + M \longrightarrow CO^+ + M\text{–}O} \tag{5}$$

$$\mathrm{2Me\text{–}O \longrightarrow 2Me + O_2} \tag{6}$$

$$\mathrm{CO^+ + e^- \longrightarrow CO} \tag{7}$$

where M and M–O represent the electrode metal and the corresponding metal oxide, respectively. In the endothermic step (6) the partially oxidized metal component (M–O) is speculated to release O atoms as O_2 molecules by hot electrons and/or Ar^+ ions impacting. Although metal effects have been observed in various plasma processes, including decompositions[1,2] and synthesis reactions,[17] further detailed investigations are, of course, required to gain insight into the role of the metallic components of the electrode surface.

Conclusions. In an Ar stream, a selective decomposition of CO_2 to produce CO and O_2 effectively proceeded in a dielectric-barrier discharge plasma reactor under atmospheric

Table 2. The Energy Yield and Efficiency on Various Discharge Voltages in the CO_2 Decomposition[c)]

V(rms)/kV	Power/W	Rate/mol h^{-1}	E_y/g $(kWh)^{-1}$ [a)]	Efficiency / % [b)]
1.9	0.5	5.7E-04	46.5	23.5
3.4	2.1	1.1E-03	23.6	11.9
4.9	4.8	1.6E-03	14.9	7.5
6.2	8.3	2.4E-03	12.5	6.3

a) Energy yield, E_y, was calculated with the equation described as below, $E_v/\mathrm{g\,(kWh)^{-1}} = \frac{\text{Amount of decomposed } CO_2/\text{g}}{\text{Supplied power/kWh}}$. b) Efficiency was calculated with the equation defined as follows, $\text{Efficiency}/\% = \frac{\text{Bonding energy/kJ mol}^{-1} \times \text{Rate/mol h}^{-1} \times \text{Time/h}}{\text{Supplied power/kJ}} \times 100$. c) Interior electrode, Cu; frequency, 1 kHz (sin wave); CO_2 concentration, 10%; flow rate, 50 $\mathrm{cm^3\,min^{-1}}$.

condition. The reaction rate increased with increasing the supplied power and the CO_2 concentration in Ar. The major reaction pathway in the plasma zone was considered to involve Ar excitation and charge/energy transfer from excited Ar atoms to CO_2 molecules. A difference in the reaction rate with various electrode metals was speculated to be due to the catalytic activity of the metallic component of the electrode surface.

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