Greenhouse Gas Control Technologies
P. Riemer, B. Eliasson and A. Wokaun, editors

MODIFICATION OF NaY ZEOLITE IN A CORONA DISCHARGE AND ITS APPLICATION FOR THE REDUCTION OF CARBON DIOXIDE

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ABSTRACT

An experimental investigation on plasma catalytic reduction of carbon dioxide has been performed by using corona discharge in the presence of NaY zeolite. It has been confirmed experimentally that the basicity of zeolites will be increased both in strength and amount of base sites when the zeolite is present in a corona discharge or in the after-glow region. To compare the behavior with other CO_2 reductions in an AC ferroelectric packed bed reactor and a DC corona torches, a gas mixture of CO_2, N_2 and O_2 has also been used for non-equilibrium plasma catalytic CO_2 reduction. The experiments confirmed that the plasma catalytic technique over NaY zeolite is more efficient for CO_2 reduction.

INTRODUCTION

Many attempts have been made recently to find ways for emissions reduction and control of CO_2 because it is believed that CO_2 emissions leads to the greenhouse effect. The CO_2 emitted from flue gases contributes most of industrial CO_2 emissions. Typical flue gas emitted from a coal-fired power station contains 10 to 15% of CO_2. It has been suggested that the CO_2 separated from flue gas be liquefied and stored in the deep sea or in abandoned mine. The costs from these proposed systems will result in a 70% increase in the cost of power plants and the overall power plant efficiency will be reduced to 34% from the current 42% [1]. Cold Plasmas have been extensively investigated for cleanup of flue gas to remove NO_x and SO_2. Higashi *et al.* [2] and Xie *et al.* [3] have studied on reduction of CO_2 from flue gas using a corona discharge. A further improvement has also been studied [4]. Such technology has potential applications, such as the commercial production of CO. Recently, a plasma catalytic processing has been found to be very promising for CO_2 reduction [5]. We report here our recent results of plasma catalytic CO_2 reduction over NaY zeolite in a corona discharge.

EXPERIMENTAL

The quartz tube reactor (with an I.D. of 7 mm) for plasma catalytic CO_2 reduction consists of two axially centered electrodes, a top wire electrode and a lower circular plate electrode, as has been discussed previously [6-8]. The gap between the two stainless steel electrodes is 10 mm. The reactor was heated by a cylindrical furnace, placed around the reactor. An Omega K-type thermocouple was attached to the outside wall of the reactor to monitor and control the gas reaction temperature. The temperature measured in this way has been calibrated and the calibration has been discussed elsewhere [6,7]. All the experiments were operated at atmospheric pressure. The flow rates of feed gases CO_2, N_2 and O_2 were regulated by three Porter Instrument Co. model 201 mass flow controllers. The feed and the exhaust gases were analyzed by an on-line gas chromatograph (HP 5890 equipped with a thermal conductivity detector (TCD)). The gas discharge is generated between these two electrodes by using a high voltage dc power supply (Model 210-50R, Bertan Associates Inc.). The lower plate electrode is always kept at a potential of zero volt (i.e., grounded). The catalyst powder, NaY zeolite, was also held on the lower plate electrode. The catalyst bed is about 8 mm deep, thus the wire electrode is situated about 2 mm above the catalyst bed. The zeolite NaY was used as received from Aldrich. With such an experimental device, the energy yield of this plasma catalytic CO_2 reduction is defined as following:

$$\text{Energy yield} = \text{The amount of } CO_2 \text{ reduced / the applied power} \quad (1)$$

RESULTS AND DISCUSSION

Temperature programmed desorption (TPD) of carbon dioxide has been used to characterize the basicity of NaY zeolite and the plasma effect on this property. The procedure of this characterization, including adsorption in the presence of plasma [9], has been discussed in detail elsewhere [9,10]. The characterization showed that the amount

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and strength of base sites of NaY zeolite in the presence of the corona discharge are significantly higher than those in the absence of the corona discharge, as shown in Figure 1. This suggests that CO_2 chemisorption on NaY zeolite is significantly enhanced by corona discharge. Such enhanced CO_2 chemisorption may lead to a more significant CO_2 reduction.

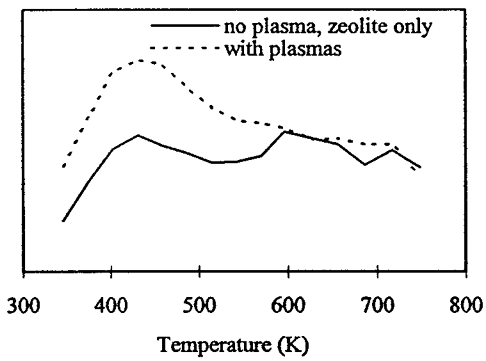

Figure 1. CO2 TPD characterization of NaY
temperature for CO2 adsorption: 323 K

The principal products formed during plasma catalytic CO_2 reduction over NaY were CO and oxygen. There was also some conversion of nitrogen found (1%-4%) but any nitrogen-containing products remain unknown with present analyses. The same phenomenon has been observed during reduction of CO_2 by DC corona torches [4]. Plasma catalytic CO_2 reduction over NaY zeolite involves both heterogeneous and homogeneous reactions. Experiments showed that gas temperature, flowrate and applied power have significant effects on the plasma catalytic CO_2 reduction over NaY zeolite. To confirm the effectiveness and efficiency of plasma catalytic CO_2 reduction over NaY at different temperatures, a pure CO_2 system has been examined. Figure 2 shows the effect of gas temperature on plasma catalytic CO_2 reduction at flowrates of 15 cm^3/min and 100 cm^3/min. The results show that a higher temperature does not induce higher CO_2 conversion. One reason for this temperature effect is that higher gas temperature favors the reverse reaction of CO_2 reduction, especially for the lower flowrate reactions as shown in Figure 2.

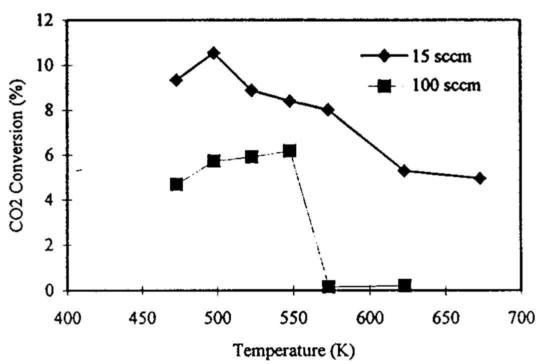

Figure 2 Temperature effect
input power: 9.76 w; pure carbon dioxide; atmospheric pressure

To compare with other CO_2 reductions, in an AC ferroelectric packed bed reactor and in DC corona torches, a gas mixture of CO_2, N_2 and O_2 has been used for plasma catalytic CO_2 reduction. The molar composition feed ratio of

$N_2/O_2/CO_2$ is 75/15/10. The principal products of the plasma catalytic CO_2 reduction in the presence of N_2 and O_2 is CO and O_2. No significant conversion of N_2 was observed for all the experiments conducted (the N_2 conversion was between 1%-4%).

The experiments showed that a higher applied voltage (more than 9.0 kV) was needed to generate a stable gas discharge in the absence of NaY, while the corona discharge in the presence of NaY was very stable even at 6.0 kV. This suggests that the use of the zeolite helps to initiate and stabilizes a sustained corona discharge and a catalyst enhanced gas discharge [6-8] is achieved. Typical current-voltage characteristics in the presence of NaY for a gas flowrate of 37.5 cm^3/min show that the current increases only slightly with increasing applied voltage once the discharge is initiated, while the input power increases linearly with the increasing voltage. The conversion of carbon dioxide also increases almost linearly with the increasing applied voltage.

To compare the energy yield of plasma CO_2 reduction, we choose two typical plasma techniques, the AC silence discharge using a ferroelectric packed bed reactor [5] and DC corona torches [4], that are considered as very efficient for CO_2 reduction. Table 1 shows the comparative results with these three plasma techniques. It is clear that non-equilibrium plasma catalytic CO_2 reduction over NaY zeolite is more efficient than the other two techniques.

Table 1. Comparative results of plasma CO_2 reduction

method	applied voltage (kV)	applied power (w)	feed ratio of $N_2/O_2/CO_2$	feed rate (cm^3/min)	energy yield for CO_2 (g/kwh)	reduced CO_2 concentration	ref.
Plasma catalytic over NaY	7.5	9.1	75/15/10	37.5	129.3	18.0%	this work
	7.5	9.8	pure CO_2	15.0	179.5	9.3%	
DC Corona Torches	45	~22.5	74.4/15.8/9.8	700.0		~5,000 ppm	4
Silent Discharge		~2.7	75/15/10	1400.0	~73	~1030 ppm	5
		~36	75/15/10	500.0	~28	~20,000 ppm	5

CONCLUSION

1) The basicity of NaY will be significantly modified when it is present in a corona discharge;
2) Increasing gas temperature has a negative effect on plasma catalytic CO_2 reduction over NaY;
3) Plasma catalytic CO_2 reduction over NaY zeolite is more efficient for CO_2 reduction, compared to some other plasma techniques for CO_2 reduction.

ACKNOWLEDGMENT

Support from the US Department of Energy (under Contract No. DE-FG21-94MC31170) is greatly appreciated. The assistance from graduate students, Chris Gordon, Phil Howard, Terence Caldwell and David Larkin, is also appreciated.

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