Plasma assisted catalytic decomposition of CO_2

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ABSTRACT

In this research, conversion of carbon dioxide in the presence of TiO_2 supported NiO catalyst has been investigated in a pulsed surface-wave sustained microwave discharge. The catalyst is prepared by combination of impregnation and plasma-treatment methods. The decomposition of TiO_2 supported nickel nitrate was done by plasma, induced in three different gases (O_2, Ar, CO_2). NiO/TiO_2 catalysts were formed. The supplied gas has a prominent effect on the chemical and physical properties of the prepared catalysts. The catalyst prepared with an Ar plasma increases almost by a factor of 2 the CO_2 conversion and energy efficiencies, while the O_2 or CO_2 plasma prepared catalysts show little effect on the CO_2 conversion in comparison with catalyst-free plasma assisted dissociation. The results from the catalyst characterization by different techniques demonstrated that Ar plasma pre-treatment resulted in formation of oxygen vacancies. Dissociative electron attachment of CO_2 at the catalyst surface enhanced by oxygen vacancies and plasma electrons could explain the improved conversion and energy efficiency. A constant catalytic activity was observed indicating continuous catalyst regeneration under reactor conditions. A mechanism of plasma-catalysis synergy is proposed.

1. Introduction

The decrease of natural reserves of fossil fuels and the greenhouse effect from CO_2 emissions generated by anthropomorphic activities drives the search for new "green" sources of fuels. A promising solution is the usage of electrical energy produced, for example, by renewable or nuclear sources for dissociation of CO_2 or other greenhouse gases and their conversion into synthetic fuels which can be easily stored. In this context, the CO_2 re-utilization to synthesize syngas, fuels or chemical compounds as well as pure CO_2 dissociation into CO and O_2, attract a lot of attention.

Different techniques for conversion of CO_2 into value-added chemical compounds or fuels have been developed and studied, namely thermolysis, photocatalysis and electrochemical methods [1–8]. The thermal CO_2 splitting is thermodynamically and energetically favorable only at very high temperatures (1400–1800 °C) and the conversion efficiency is very low [1]. A membrane reactor system, such as calcium oxide zirconia membrane, may enhance the process [2]. CO_2 conversion efficiency of 21.5% was reached at 1700 °C in thermal CO_2 dissociation which is considerably higher than the CO_2 conversion efficiency of 1.2% at the same temperature in pure thermal process [2]. Although photocatalytic conversion of CO_2 shows great potential at the present time by using solar energy, the drawbacks are the low CO_2 conversion efficiency (e.g. <1%), long periods of irradiation for the catalyst activation, and specific requirements for the bandgap energy of the catalyst [3–7]. High-temperature electrolysis seems to be promising considering the electric energy to liquid fuel energy conversion that reaches 78–87% [4,8]. However, it has disadvantages like using scarce or expensive materials, high operating temperature (800–1000 °C), heating of the whole system, large size of the system, and short durability of the electrodes. The energy efficiencies are defined in different ways for the thermal, photocatalytic and electrolytic CO_2 dissociation and cannot be compared directly. An alternative method to the techniques described above can be plasma or plasma-catalysis CO_2 dissociation since plasma can be easily sustained by a power source. In addition, as we discuss below, it is possible to use abundant, durable and not expensive materials for catalysts. In the past decade, non-thermal plasmas have been shown to be effective and efficient in activation of CO_2 [9–23]. Liu et al. [9] reviewed non-thermal plasma technologies for the utilization of carbon dioxide.

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Fridman [10] reviewed the plasma physics of CO_2 reduction to CO and its application. To synthesize fuel from CO_2, it is combined with a hydrogen-containing gas such as H_2 [24–26], CH_4 [27–33], or H_2O [34–37].

There have been several studies of plasma-assisted dissociation of pure CO_2 in the recent years [11–13]. Results are also reported for mixtures of CO_2 with an inert gas [14–23]. However, a trade-off between the energy and conversion efficiencies is observed in plasma processing. We propose plasma assisted catalytic process with plasma-activation of the catalysts to increase energy efficiency while maintaining high conversion rate. The combination of heterogeneous catalysis and plasma activation, known as plasma-catalysis, has attracted increasing interest [38,39]. On one hand, the catalyst can increase reaction rates and selectivity. On the other hand, the non-thermal plasma provides the energy to drive highly endothermic processes such as CO_2 dissociation. Plasma-catalytic processes have great potential to reduce the activation barrier of different reactions and improve the conversion rates. The non-thermal plasma itself can influence the acid-base nature of the supports, enhance the dispersion of the supported metals, and even adjust the microstructure of the metal nanoparticles and metal-support interface [9,38], and in this way change the catalyst properties. All these factors contribute in different ways to enhancing the energy efficiency of the plasma process as well as the catalyst stability, due to a synergy that occurs between the catalyst and the plasma [33]. Plasma-catalysis has been widely investigated for gaseous pollutant abatement [38,39] and dry reforming of methane [27,29,30,33]. For the latter application, significant attention has been given to supported Ni catalysts due to their low cost and wide availability. Most of these studies focused primarily on identifying plasma-catalytic chemical reactions to maximize process performance, while the dynamic plasma-catalyst interaction have received less attention.

Up to now, few studies have investigated the non-thermal plasma driven catalysis for the CO_2 decomposition [15,19]. Brock et al. [15] studied the catalytic effect of metallic coating on the decomposition of CO_2 in fan-type AC glow discharge plasma reactors, using a gas mixture of 2.5% CO_2 in He. They showed that a Rh coated reactor has the highest activity for the CO_2 decomposition compared to the reactors coated with Cu, Au, Pt, Pd and mixed rotor/stator systems (Rh/Au and Au/Rh). Spencer and Gallimore [19] experimentally investigated the conversion of CO_2 in an atmospheric pressure microwave plasma-catalytic system. The results showed that Rh/TiO$_2$ coating on a monolithic cordierite structure used as a catalyst actually caused a drop in conversion efficiency due to reverse reactions occurring on the surface. The use of plasma techniques in catalyst preparation, regeneration and catalytic reactions were already reviewed in several works [40–42]. However, the influence of the gases used for plasma pre-treatment of the catalyst has not been investigated.

To our knowledge, the decomposition of pure CO_2 in a surface-wave sustained microwave discharge combined with TiO$_2$ supported NiO catalysts has not been investigated previously. Microwave plasma has been proven to be the most efficient plasma for pure CO_2 dissociation [10,24]. In addition, the advantages of the microwave plasma for greenhouse gas dissociation compared to other types of discharges were discussed in our previous work dealing with the simultaneous plasma-assisted dissociation of CO_2 and H_2O [34]. In the present work, we use plasma pre-treatment as a replacement of the conventional calcination in the catalyst preparation process. The influence of three different discharges, i.e. O_2, Ar, or CO_2 discharge, on the CO_2 conversion and energy efficiencies is studied. The fresh catalysts treated in the plasma-catalytic reactor were characterized by X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET) methods, Transmission electron microscopy (TEM), Raman Spectroscopy, and Ultraviolet–visible

(UV–vis) spectroscopy. The interactions between plasma and catalyst as well as the possible mechanism for CO_2 decomposition on the catalyst surface and catalyst regeneration are reported.

2. Experimental

2.1. The microwave discharge reactor

The experimental setup for pulsed microwave plasma generation used in this work is shown in Fig. 1. The discharge is generated at 915 MHz in a double-walled quartz tube with a 14 mm inner diameter and 31 cm length, cooled by 5 °C oil flowing between the inner (quartz) and the outer (polycarbonate) tubes. The CO_2 or the other gases are injected from the top of the system. The flow rate is regulated by electronic mass flow controllers ranging between 0 and 3 standard liter per minute (slm). A reactor containing the catalyst is connected to the end of the plasma tube so that the catalyst is positioned at around 3 cm below the plasma tube end. The following operating parameters were used for all plasma-catalysis CO_2 dissociation experiments: pure CO_2 is supplied at flow rate of 2 slm, the mean input power is 1000W at a pulse frequency of 1.67 kHz, which corresponds to a specific energy input of 6.95 eV/molecule. The pressure in the post discharge is set to 1330 Pa (10 Torr). The whole system is surrounded by a grounded aluminium grid to prevent any leakage of microwave radiation into the outer space. Pulsed plasmas with pulse duration of 300 μs, and a period of 600 μs were used. The impedance of the waveguide can be adapted by an automatic three stubs system in order to minimize the reflected microwave power. With this system, the reflected power measured for each condition is below the detection limit of the measuring probe and hence the reflected power is considered equal to zero. A more detailed description of the microwave set-up can be found in Ref. [34].

2.2. Mechanisms for CO_2 dissociation and product analyses

The dissociation of a CO_2 molecule is represented by the following global reaction [10]:

$$CO_2 \rightarrow CO + \frac{1}{2}O_2, \quad \Delta H = 2.9 \, eV/molecule \tag{1}$$
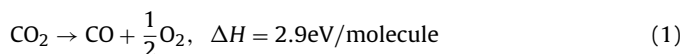
The following parameters describe the dissociation efficiency in the present study. By definition [10], the energy efficiency η of a dissociation process is given by:

$$\eta_{CO_2} = \frac{\Delta H}{E_{CO}} \tag{2}$$

where ΔH is the dissociation enthalpy of the global reaction [Eq. (1)], i.e. 2.9 eV/molecule, and E_{CO} is the specific energy input per molecule, i.e. the actual energy supplied to produce one CO molecule. The specific energy input per molecule, E_{CO}, is given by the ratio of the discharge power to the gas flow rate through the discharge volume and is measured in eV per molecule.

The composition of the post-discharge is analyzed by using a gas chromatograph (GC) (Bruker) equipped with a carbon molecular sieve column and a molecular sieve 5A column in series and connected to a thermal conductivity detector, which allowed a determination of the concentrations of O_2, CO and CO_2.

The conversion of CO_2 is calculated by comparing the GC CO_2 peak area before and after plasma processing. The conversion efficiency of CO_2 is calculated based on the following ratio:

$$CO_2 \, \text{Conversion efficiency} \, (\%) = \frac{\text{moles of } CO_2 \text{ converted}}{\text{moles of } CO_2 \text{ in feed}}$$
$$\times 100\% \tag{3}$$