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Plasma-assisted reduction of a NiO/Al_2O_3 catalyst in atmospheric pressure H_2/Ar dielectric barrier discharge

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ABSTRACT

Plasma-assisted reduction of a NiO/Al_2O_3 catalyst has been carried out in a H_2/Ar dielectric barrier discharge at atmospheric pressure and low temperature (<300 °C). The time evolution of H_2 consumption, the gaseous products, as well as the discharge power and temperature during the plasma reduction of NiO/Al_2O_3 have been investigated to get a better understanding of the reduction mechanisms involved in the plasma process. The effect of the Ni conductive metal sites on the physical characteristics of the H_2/Ar discharge has also been examined. The results show that the discharge power linearly increases during the plasma-reduction process, accompanied by an increase in transferred charge from 88 nC to 119 nC due to the formation of more conductive metallic Ni in the discharge gap. It is also found that plasma reduction does not change the size of Ni particles.

1. Introduction

In the past decade, the combination of non-thermal plasma and heterogeneous catalysis, known as plasma-catalysis for environmental pollution control and energy conversion has attracted great interest due to the combined advantages of fast chemical reactions at low temperatures due to non-thermal plasma and high selectivity from the catalysis [1–4]. The interactions between plasma and catalyst are very complex in a single-stage plasma catalysis system where the catalyst is placed directly in the plasma. Both the chemical and physical properties of the plasma and catalyst can be modified by one another changing the performance of the chemical processing [5]. Previous studies have shown that the combination of plasma with catalyst can generate a synergistic effect, which significantly reduces the activation temperature of the catalyst and improves the activity and stability of the catalyst, resulting in the enhancement of the conversion of feed gas and energy efficiency for the generation of target gas products [4,5]. The major applications of plasma-catalysis include the removal of environmental pollutants in waste gas streams and the conversion of hydrocarbons for the production of high value fuels and chemicals such as hydrogen, methanol and carbon nanomaterials [4–16]. Recently, the idea of plasma-catalysis has been further extended to the preparation and treatment (e.g. reduction) of supported metal catalysts at low temperatures as an attractive possible alternative to the conventional thermal reduction processes [17–30]. Plasma-reduction of catalysts has been reported to have several advantages including short treatment time, low temperature process with low energy consumption, the use of inexpensive and non-hazardous reducing agents and enhanced physical and chemical properties of the prepared catalyst [25]. Recently, Liu et al. have reported the use of a H_2/N_2 atmospheric pressure glow discharge plasma jet for calcination and reduction of $NiO/\gamma\text{-}Al_2O_3$ and NiO/SiO_2 catalysts [17,18]. A short plasma treatment time of 10 min resulted in improved dispersion and reduced Ni particle size, in comparison with a sample reduced thermally over 2 h. The plasma-reduced samples had a higher specific surface area due to a reduction in sintering at low temperature, which is known to be a major drawback of thermal reduction methods. Noble metal catalysts including Rh, Ir, Pd, Pt, Ag and Au supported on various materials have been successfully reduced in an argon glow discharge by Cheng et al. [19]. The authors suggested that high energetic electrons generated in the plasma act as the reducing species and that this is independent of the type of plasma-forming gas. Hofft and Endres have also shown that such electrons contribute to the formation of noble metal and even semiconductor nanoparticles in ionic liquids by a plasma electrochemistry process [21]. Wang et al. [20] have proposed that an indirect plasma-reduction mechanism may exist where adsorbed H_2O on the catalyst surface may dissociate under discharge conditions producing H^* radicals and hydrated electrons e_{aq}, which are both strong reducing species [22]. In support of this hypothesis

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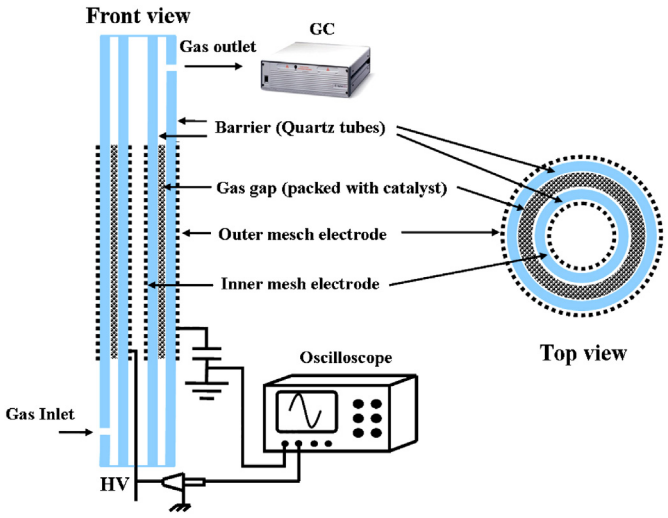

Fig. 1. Schematic diagram of the experimental setup.

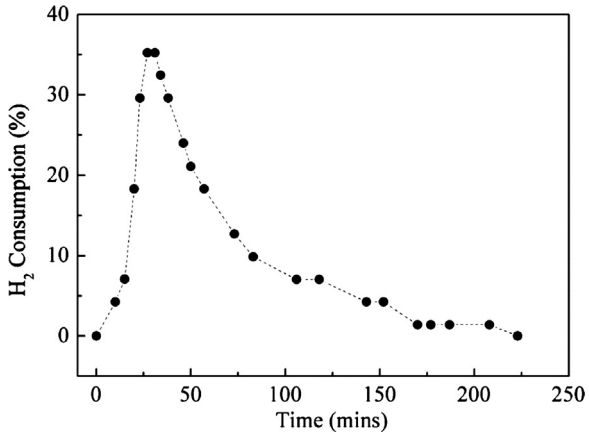

Fig. 2. H_2 consumption during reduction of NiO/Al_2O_3 in a 20 vol.% H_2/Ar DBD.

Pd/HZSM-5 catalyst was successfully reduced in an O_2 glow discharge [23]. However, they were unable to reduce $Ni(NO_3)_2$, $Fe(NO_3)_3$ and $Co(NO_3)_2$ catalysts in an argon glow discharge; in these cases, only decomposition to the oxide forms was observed [19,24]. IR imaging of the glow discharge reactor shows that the catalyst bed was close to room temperature (<30 °C) under the discharge conditions [25].

Plasma-reduction is limited to Pt and Co based catalysts in a dielectric barrier discharge (DBD) H_2/N_2 discharge [27]. However, the catalyst temperature under discharge conditions was not measured during these experiments and therefore it is difficult to deduce the reduction mechanisms involved. In addition, the detailed understanding of plasma-reduction process from both a chemical and physical perspective is still very patchy. Further investigations in this area are required in order to define the reaction mechanisms for the plasma-reduction of metal catalysts. In particular, whether plasma-reduction of metal catalysts is a consequence of plasma-activated species or whether the reduction is an effect of the elevated temperature under discharge conditions.

NiO/Al_2O_3 catalysts are used commercially for large-scale production of hydrogen via steam methane reforming (SMR), prior to which they are reduced to Ni/Al_2O_3 by hydrogen-containing gases or natural gas-steam mixtures at elevated temperatures [31]. The reduction generates active Ni sites, which are effective for hydrogen production from methane. In this work, plasma-assisted reduction of a 33 wt.% NiO/Al_2O_3 catalyst is carried out in a coaxial DBD reactor using 20 vol.% H_2/Ar as the reducing gas. Analyses of time-resolved gas compositions exiting the reactor provides information about the reactions occurring both in the plasma volume and on the catalyst surface. In addition, the effect of Ni reduction on the physical properties of the plasma has been investigated.

2. Experimental

The experiments have been carried out in a double dielectric barrier discharge reactor, as shown in Fig. 1. Detailed description of the experimental setup can be found in our previous work [9–11]. The DBD reactor consists of two coaxial quartz tubes, both of which are covered by a stainless steel mesh electrode. The inner electrode is connected to a high voltage output and the outer electrode is grounded via an external capacitor. The length of the discharge region is 55 mm with a discharge gap of 4.5 mm. The DBD reactor is supplied by an AC high voltage power supply with a peak-to-peak voltage of 24 kV and a variable frequency of 30–40 kHz. The applied voltage is measured by a high voltage probe, while the total current is recorded by a current monitor (Bergoz CT-E0.25). The voltage on the external capacitor is measured to obtain the charge generated in the discharge. All the electrical signals are sampled by a four-channel digital oscilloscope (Tektronics TDS2014). A LABVIEW control system is used for the online measurement of the discharge power by the area calculation of the Q-U Lissajous figure. An equivalent electrical circuit of the DBD reactor for the calculation of physical parameters (e.g. gas gap voltage, breakdown voltage and effective capacitance) of the discharge can be found in our previous work [9].

Reduction of a commercial catalyst, 33 wt.% NiO/Al_2O_3 (Johnson Matthey) prepared by incipient wetness impregnation has been carried out using a mixture of 20 vol.% hydrogen in argon as the plasma working gases. The total gas flow rate is 100 ml min^{-1}. The fresh catalyst in the form of NiO/Al_2O_3 is crushed to give non-uniformly sized pellets (18.6 g, 0.85–5 mm) and fully packed into the discharge region of the reactor, where it is held in place with quartz wool. X-ray diffraction (XRD) patterns of the catalyst samples are recorded by a Philips X'Pert diffractometer using a Cu-K_α radiation at 40 kV and 30 mA in the 2θ range from 20° to 90°. Prior to each experiment, the system is purged to remove air and stabilise the gas mixtures. The plasma is turned on at $t = 0$ and the gases exiting the reactor were analysed by micro-GC at regular intervals. A trap cooled by solid CO_2 is placed at the exit of the plasma reactor in order to condense any liquid products. Experiments are carried out under conditions of approximately constant applied voltage and optimised frequency (~35 kHz).

3. Results and discussion

3.1. Reduction of NiO/Al_2O_3 in H_2/Ar discharge

Reduction of NiO/Al_2O_3 by 20 vol.% H_2 in an argon carrier gas has been carried out in a coaxial DBD reactor. The consumption of H_2 during the plasma reduction process is shown in Fig. 2. Although H_2O is the only product of NiO reduction by the H_2/Ar discharge (Eq. (1)), the presence of small amounts of carbon-containing gases CO_2, CO and CH_4 have been detected and are shown in Figs. 3 and 4.

$$NiO + H_2 \rightarrow Ni + H_2O \quad (1)$$

Fig. 2 shows that H_2 consumption reaches its peak at ~30 min and then gradually returns to its initial concentration, indicating that reduction of NiO in the discharge has gone to completion. Similar profiles for H_2 consumption have been obtained for plasma-reduction of Pt and Co based catalysts by Kim et al. [27]. The time