Atmospheric pressure cold plasma driven Ni/γ-Al_2O_3 catalytic reactor for methanation of CO_2

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Hydrogenation of CO_2 to CH_4 was carried out using Ni/γ-Al_2O_3 catalysts coupled with non-thermal plasma dielectric barrier discharge reactor (NTP-DBD). The effect of gas temperature (22-400°C), plasma input power (25-35 W), and CO_2 to H_2 ratio on CO_2 conversion rate and CH_4 selectivity has been studied. It was evidenced that, compared to conventional thermal catalysis, plasma-catalysis coupling decreased the catalyst activation temperature, *i.e.* the CO_2 conversion, by 50°C. Furthermore, 10 wt% Ni/γ-Al_2O_3 catalyst has shown about 40% CO_2 conversion and 70% CH_4 selectivity**.**

Modernization, deforestation and overwhelmingly increasing world population are significantly increasing the atmosphere CO_2 level. Consequently, several methods have been developed to reduce the atmospheric CO_2 level. The conversion of CO_2 in other products has attracted much more attention, especially non-thermal plasma (NTP) for CO_2 conversion [1] and methanation [2].

In this study, thermal catalysis, plasma, and plasma-catalysis processes have been investigated for direct hydrogenation of CO_2 in a wide range of temperature, plasma input power and CO_2 to H_2 ratio. The NTP-catalytic reactor is a cylindrical DBD powered by sub-ns HV pulses with an amplitude up to 20 kV at frequency up to 500 Hz.

The nickel metal is doped on γ-Al_2O_3 beads (1.8 mm diameter, Sasol Germany GmbH) by wet impregnation method. Before each experiment, the Ni/γ-Al_2O_3 catalyst (1.5 g) was activated for 20 min at 400°C under H_2 (5%)/N_2 flow. The catalyst was placed in the centre of the plasma discharge volume. This configuration, stated as In-Plasma Catalysis (IPC), leads to two distinguished discharge configurations: gas phase streamer discharge before and after the catalyst bed, and surface discharge on the catalyst.

For all the experiments, the total gas flow rate was fixed as 620 ml.min^{-1}, unless otherwise mentioned. CO_2, CH_4, CO, and O_2 concentrations were followed using gas chromatography (μGC, MyGC-SRA).

An example of data obtained for plasma alone, catalysts alone (γ-Al_2O_3, 10 wt% Ni/γ-Al_2O_3), and plasma-catalyst systems is shown in Fig. 1. For the investigated temperature range γ-Al_2O_3 catalyst, whether used alone or coupled with plasma, has shown less than 2% CO_2 conversion. Indeed, Ni doping on γ-Al_2O_3 has significantly increased the CO_2 conversion. Thermal catalytic activity of 10 wt% Ni/γ-Al_2O_3 catalyst begins above 250°C, and about 55% of CO_2 conversion is reached at 300°C. Under the similar operating conditions, when 10 wt% Ni/γ-Al_2O_3 is coupled with plasma, the CO_2 conversion starts at lower temperature and 45% CO_2 conversion is reached at 250°C. The decrease in catalyst activation temperature can be correlated to synergetic effect of plasma-catalyst coupling.

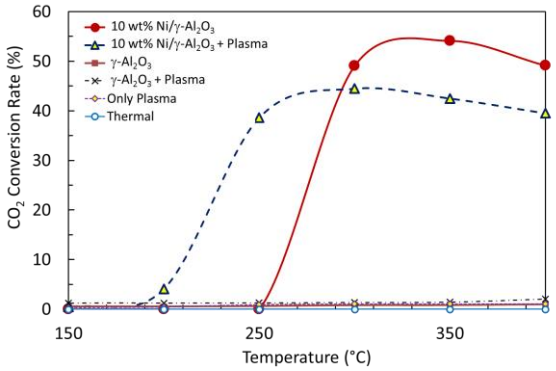

Fig. 1. CO_2 conversion rate as function of temperature (plasma conditions: 15 kV and 100 Hz).

It was evidenced that, without Ni doping on γ-Al_2O_3, CH_4 is not produced for all the investigated temperatures as reported in literature [3]. This implies that Ni doped on Al_2O_3 are mainly involved in CO_2 hydrogenation processes. It can be suggested that although plasma dissociates CO_2 but it does not induce the hydrogenation reaction. At 250°C, with or without plasma, 10 wt% Ni/γ-Al_2O_3 catalyst has shown 70% CH_4 selectivity. The decrease in CO_2 conversion and CH_4 production can be attributed to the catalytic partial oxidation of CH_4 to CO_2, CO, and H_2O at high temperature. In that case and at 300°C, the CO selectivity increased by a factor 2 when the combined plasma-Ni/γ-Al_2O_3 system is used compared to the Ni/γ-Al_2O_3 catalyst used alone (from 8 to 4%).

At a fixed temperature, the increasing of the plasma input power increase slightly the CO_2 conversion and CH_4 selectivity. However, the CO selectivity rapidly increases up to 10% (at 20 kV) evidenced the fact that the injected excess power probably promotes the CO formation from CO_2 and CH_4.

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