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Catalytic nonthermal plasma assisted co-processing of methane and nitrous oxide for methanol production

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ABSTRACT

The objective of the present study is the direct conversion of potential greenhouse gases methane (CH_4) and nitrous oxide (N_2O) into value added products like methanol, syngas, etc. in a nonthermal plasma reactor operated under ambient conditions. Typical results indicated that co-processing of the reactants has an advantage of *in-situ* decomposition of N_2O into N_2 and atomic oxygen that favors methane partial oxidation to methanol. In order to improve the selectivity to methanol, plasma reactor was operated by integrating CuO/CeO_2, NiO/CeO_2 and Cu-Ni (5-5)/CeO_2 catalysts. Among the studied catalysts, Cu-Ni (5:5 wt%) supported on ceria showed the best selectivity of ~36% to methanol.

1. Introduction

For decades, methane (CH_4) has been the feed stock for chemical industry, especially for the production of valuable chemicals and fuels, such as hydrogen, higher hydrocarbons, syngas (a mixture of CO and H_2), methanol (CH_3OH) and formaldehyde (HCHO). Development of efficient natural gas conversion processes is therefore essential for a sustainable feedstock for the chemical industry [1]. Methane conversion to methanol is a challenging process that is traditionally carried out in a two-step process, where CH_4 is converted into syngas, which on further reaction leads to CH_3OH. However, direct conversion of CH_4 into CH_3OH is very much desired, as it offers interesting opportunities for the production of liquid fuels and chemicals. Hence, co-processing CH_4 with a suitable chemical like nitrous oxide (N_2O) may be tested for this purpose. In addition, CH_4 and N_2O are long-lived in the atmosphere and are major contributors to the global warming and hence, co-processing of these reactants is beneficial [1,2]. In this direction, various attempts have been made to convert CH_4 into CH_3OH [3–5]. Lunsford and co-workers demonstrated that molybdenum supported on silica as an excellent catalyst for partial oxidation of CH_4 with N_2O [6–8]. As CH_4 is a stable compound due to high C–H bond strength and perfect symmetry, reactions with methane, especially partial oxidation to methanol (MPOM) demands severe reaction conditions [7]. Metal catalysts, e.g. Ni, Co, Pt, Rh, etc., are active for catalytic partial oxidation of methane (CPOM). However, the selectivity to methanol is not promising. Conventional thermal methods for CPOM typically require a high temperature (up to 1000 °C) and pressure (>10 atm), which limit the industrial applications. In addition, the stability of catalysts is still a matter of concern, despite intense investigation of CPOM over metallic catalysts [9–11]. The general observation is that metallic catalysts suffer from deactivation due to sintering and metal loss via the formation of volatile metal oxides [12–16].

Decomposition of CH_4 by using nonthermal plasmas (NTP) under ambient conditions is an alternate to the thermo catalytic techniques. NTP is characterized by high electron temperatures with the bulk gas temperature remains under ambient conditions. NTP offers highly energetic electrons that induce the reactions, ease of operation, etc. [17–21]. Experiments performed by Shepelev et al. with CH_4 and O_2 in a dielectric barrier discharge (DBD) reactor showed methanol selectivity 20% [22]. A pulsed corona/DBD discharge was also investigated in CH_4 diluted in small amounts of oxygen [23]. Even in a mixture of CH_4 and air (7:3), CH_3OH concentration of 0.6 vol% was reported when the reactor was operated under ambient conditions. Small amounts of methanol were also observed in a pulsed streamer corona operating in a mixture of CH_4 with CO_2 or water vapor. Okazaki et al. and Mizuno et al. have investigated the direct conversion of CH_4 to CH_3OH using silent electric discharge at 250 Hz and voltages up to 25 kV, where it was observed that the selectivity of methanol was better at lower oxygen concentrations, and dissociation of oxygen was noted as the pre-requisite for CH_3OH formation [24–26]. Another interesting aspect is that addition of catalyst to the plasma reactor also improved the activity

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and selectivity [26–33]. With this background, present study deals with NTP assisted co-processing of nitrous oxide (N_2O) and methane (CH_4) aiming at methanol production. The influence of the catalyst combination was tested to achieve the best selectivity towards CH_3OH. For this purpose, Cu doped Ni supported on the CeO_2 was developed, characterized and integrated with NTP.

2. Experimental

2.1. Catalyst synthesis

The ceria catalysts were prepared by solution combustion synthesis using citric acid as the fuel. In a typical synthesis, appropriate amounts of $(NH_4)_2Ce(NO_3)_6{\cdot}6H_2O$, $Cu(NO_3)_2$, $Ni(NO_3)_2{\cdot}H_2O$ and citric acid (oxidant/fuel = 1) were dissolved in minimum amount of distilled water at room temperature and sonicated for 30 min and transferred into an alumina crucible. The alumina crucible was then placed in a preheated furnace maintained at ~450 °C for 5 min. The solution undergoes dehydration and a spark appears at one corner, which spreads throughout the mass yielding a voluminous solid product. Prior to the activity test, the samples were calcined at 600 °C for 4 h. The final catalysts were denoted as 10Cu/Ce, 10Ni/Ce and Cu-Ni(5-5)/Ce, respectively.

2.2. Characterization techniques

Formation and identification of the designed catalysts was done with powder X-ray diffraction (XRD) by using a PANalyticalX'pert pro X-ray diffractometer using Cu K_α (λ = 1.541 Å radiation, 30 mA, 40 kV). Crystallite size was calculated by using the Scherrer's equation [34]. The textural properties were studied by N_2 adsorption/desorption measurements at liquid nitrogen temperature (at 77 K) in a Quantachrome autosorb automated gas sorption analyzer (NOVA 2200e). Before analysis, the samples were degassed at 250 °C for 6 h in vacuum.

The size and morphology of the nanoparticles were examined by using an FEI model TECNAI-G-220 S-Twin TEM instrument. Raman spectra of CeO_2 and ceria supported bimetallic catalysts were recorded on a Bruker senterra dispersive Raman microscope with laser excitation of wavelength of 532 nm. X-ray Photoelectron Spectroscopy (XPS) data were recorded by using Axis Ultra instrument under ultra-high vacuum condition ($<10^{-8}$ Torr) and a monochromatic Al Kα X-ray source (1486.6 eV). Temperature Programmed Reduction (TPR), temperature programmed decomposition (TPD) studies were carried out in a flow system (Quantachrom eautosorb-IQ automated gas sorption Analyzer) equipped with a thermal conductivity detector (TPR-TCD). The data was reconfirmed with an in-built mass spectrometer (RGA Prisma plus-200) controlled by the software Quadera and the second confirmation was done with a pre-calibrated ULTRAMAT 23 multi-gas Analyzer (SIEMENS) that measures CO, CO_2 and O_2. For TPR measurements, 50 mg of the sample was sandwiched between quartz wool plugs in a U-shaped quartz reactor and flushed with He for 30 min. The TPR profiles were obtained by heating the sample from room temperature to the desired temperature (600 °C) in 10% H_2 in Ar, (gas flow rates 40 ml/min and heating rate of 10 °C/min) and the gaseous products were sampled through a control valve to TCD after passing through a cold tarp to remove H_2O. Quantitative analysis was done by integrating the reduction signal and comparison was made by pre-calibrated signals.

2.3. Plasma reactor

A detailed description of the DBD reactor was reported elsewhere [35]. In a slightly modified configuration, the discharge was generated in a cylindrical quartz tube with an inner diameter of 20 mm. A copper wire rolled on the outer surface of the quartz tube acts as the outer electrode, whereas a stainless steel rod was used as the inner electrode (Fig. 1). The discharge length was 15 cm and discharge gap was fixed at 3.5 mm. The inner electrode was connected to AC high voltage source (Yaskawa varispeed F7 AC inverter, AC voltage 0–40 kV and frequency 50–1000 Hz variable), whereas the outer electrode was grounded. The discharge was ignited by applying AC high voltage in the range 12–20 kV (peak–peak) at 50 Hz. The flow rate of gas was controlled with mass flow controllers (GFC-17, Aalborg-USA). The energy dissipated during one period of voltage is calculated from the *V*–*Q* Lissajous diagram, as shown in Fig. 2 (Shown for feed ratio of CH_4/N_2O-5:1 from 12 to 22 kV). The electrical power used by the discharge was measured by using the *V*–*Q* Lissajous diagram, where the charge *Q* (i.e., time integrated current) was recorded by measuring the voltage across the capacitor (C = 1.5 μF) connected in series to the ground electrode. Applied voltage was measured with a 1000:1 high voltage probe (Agilent 34136A) and the *V*–*Q* wave forms were recorded by a digital oscilloscope (Tektronix TDS 2014 B). The area of Lissajous figure (Fig. 2) characterizes the energy dissipated during one period of voltage, from which power was calculated by multiplying with frequency. Specific input energy (SIE) of the discharge was calculated by following relation,

$$\text{SIT}\,(\text{J/l}) = \frac{\text{Power}\,(\text{W})}{\text{Gas flow rate}\,(\text{l/s})}$$

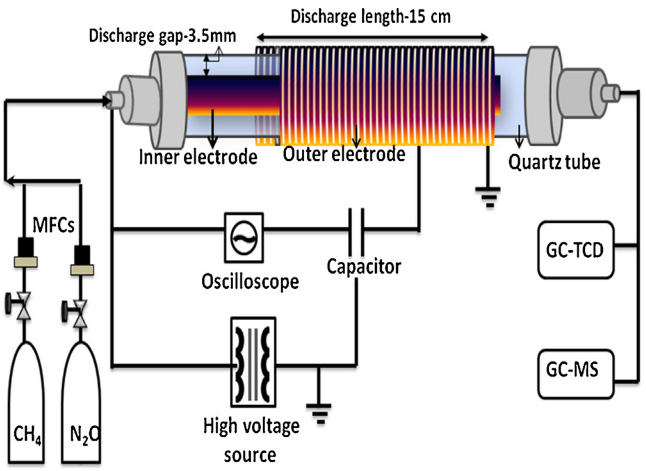

Fig. 1. Schematic representation of NTP-DBD reactor.

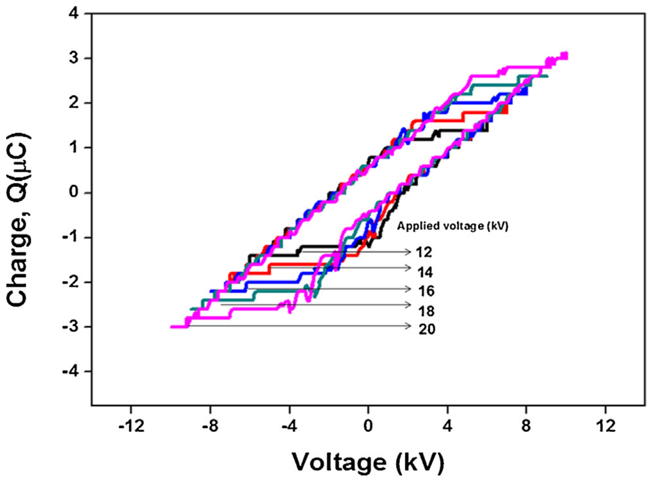

Fig. 2. *V*–*Q* Lissajous diagrams of 12–22 kV taken at 3.5 mm discharge gap and 50 Hz.