Partial oxidation of methane to synthesis gas over Ni-supported ceria catalyst

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Partial oxidation of methane to synthesis gas (a mixture of H₂ and CO) over 5 wt.% Ni/CeO₂ catalysts has been studied in a fixed bed down flow reactor. The catalyst has been characterized by XRD, N₂-sorption, SEM, TEM, ICP-AES and XPS data. It is found that the Ni-CeO₂ catalyst can activate methane at 500 ºC, and with increase in temperature the conversion increases up to 86.1% at 800 ºC. The H₂/CO mole ratio is almost constant at 1.9 in the temperature range from 500–800 ºC. The activity of the catalyst remains constant till 30 h, which is the main advantage of the present catalyst. Various reaction parameters like temperature, time-on-stream and GHSV are studied in detail.

Keywords: Catalysts, Supported catalysts, Oxidation, Partial oxidation, Methane, Synthesis gas, Nickel, Ceria, Carbon monoxide, Hydrogen

Methane, the most abundant and predominant component of the natural gas is forecast to outlast oil by a significant margin.¹ Its plentiful abundance in many locations around the globe has driven the researchers to work on the utilization of methane by its activation to other value added chemicals. Natural gas can be utilized for the purpose of producing fuel.² The current mean projection of remaining recoverable resources of natural gas is 16,200 trillion cubic feet (Tcf), 150 times than that of the current annual global gas consumption. Natural gas contains about 85–95% of methane,³ with other impurities such as ethane, propane, nitrogen, sulphur and carbon dioxide. In recent time it is uneconomical to use natural gas as a feedstock to synthesize chemicals or fuels because of the costly storage process and transportation system from the remote areas of the globe where it is most available.⁴⁷ Hence, in recent years, researchers have been investigating various methods to enhance the value addition of the methane either by synthesizing more valuable chemicals or more easily transportable fuels.⁸ However since the desired products are more reactive than methane itself, it is found that the yields are too low and is therefore unable to compete with the oil.⁹¹¹ Synthesis gas can be produced by steam reforming of methane, CO₂ reforming of methane, partial oxidation of methane and decomposition of methanol (mainly used in hydrogen production in fuel cells because methanol is high in energy density and easy to transport). Till date, steam reforming is the only large scale syngas production process.¹² Steam reforming is highly endothermic and nickel based catalysts are used in the current industrial processes. However, nickel promotes carbon formation which deactivates the catalyst and leads to reactor plugging.² The H₂/CO ratio produced in steam reforming is 3, whereas the desired ratio for producing hydrocarbon liquids (in gas-to-liquid process) is lower than that. Therefore, an alternative process can be applied such as partial oxidation of methane where the H₂/CO ratio is 2, which is suitable for the downstream processes, particularly for methanol synthesis and Fischer-Tropsch process.

Partial oxidation of methane is expected to become more important in the near future. The work reported in this paper discusses the catalytic partial oxidation of methane to get high yields of synthesis gas above 550 °C; below this temperature non-equilibrium product distribution is obtained. Studies revealed that ruthenium supported lanthanide oxide catalyst has excellent activity for the partial oxidation of methane and there is no carbon formation. According to thermodynamic calculations higher temperature is favorable for partial oxidation of methane and H₂, CO selectivity where high pressure is unfavorable.¹³ The conventional supported nickel catalysts used for methane reforming are very active for carbon formation that leads to rapid deactivation of the catalyst. While the coke-resistance alternative catalysts based on Rh, Ru, Pt etc. are excellent¹⁴⁻¹⁶ their use is discouraged due to their limited availability and high cost.
The drawback of the partial oxidation of methane processes reported so far is that although they exhibit sufficiently high conversions of methane for high selectivity of syngas of $\text{H}_2/\text{CO}$ ratio almost 2, the temperature reported for those results are very high at around 800 °C. To overcome the drawback of high temperatures, researchers are working on new catalysts using cheaper transition metals like Ni over expensive metals like Pt, Ru, etc. We report herein the partial oxidation of methane to synthesis gas over Ni supported on CeO$_2$ catalyst which does not deactivate even after 30 h on stream.

Materials and Methods

Catalyst preparation

Cerium oxide (ceria) was prepared by modifying a reported method. In a typical synthesis procedure, 20.3 g cerium nitrate hexahydrate, 10 mL H$_2$O and 75 mL ethanol was mixed and precipitated with 30% NH$_3$ solution. The resulting mixture was stirred for 3 h at 80 °C. Finally, the entire mixture was evaporated to dryness at 100 °C for 12 h. The dry solid obtained was calcined at 550 °C for 4 h in air.

Nickel loading was carried out using the following method. Cetyltrimethylammonium bromide (CTAB, 1.2 g) was dissolved in 5 mL ethanol. Then 0.8 g nickel nitrate hexahydrate dissolved in 5 mL distilled water was added to the CTAB solution. Then the Ni containing solution was added with 3 g previously prepared cerium oxide dispersed in 50 mL ethanol. The resulting mixture was stirred for 30 min and hydrazine hydrate was added to the mixture slowly. The resulting mixture was evaporated to dryness at 80 °C overnight. Finally, the obtained solid was dried at 100 °C for 3 h followed by calcination at 550 °C for 6 h.

Catalyst characterization

Powder X-ray diffraction patterns were recorded on a Rigaku-Geigerflex X-ray diffractometer fitted with a Cu Kα radiation source. Diffraction patterns in the 5º–80º region were recorded with a 0.04 step size (step time = 4 s). SEM images were taken on a FEI Quanta 200 F, using a tungsten filament doped with lanthanum hexaboride (LaB6) as the X-ray source, fitted with an ETD detector with high vacuum mode, using secondary electrons and an acceleration tension of 10 or 30 kV. Samples were analyzed by spreading them on a carbon tape. Energy dispersive X-ray spectroscopy (EDX) was used for the elemental analysis. The elemental mapping was also carried out using the same spectrophotometer. TEM images were collected using a Jeol JEM 2100 microscope. The samples were prepared by mounting an ethanol-dispersed sample on a lacey carbon Formvar coated Cu grid. The surface area was analyzed at ~180 °C with a Belsorbmax (BEL, Japan) using the BET equation. X-ray photoelectron spectra (XPS) were recorded on a Thermo Scientific K-Alpha X-ray photoelectron spectrometer and binding energies (±0.1 eV) were determined with respect to the position of the C 1s peak at 284.8 eV. EXAFS measurements of the Cu K-edge were carried out at the High Energy Accelerator Research Organization (KEK-IMMS-PF). The measurement was made in transition mode and spectra were taken at BL-7C and BL-9C. The electron storage ring was operated at 2.5 GeV and 450 mA and synchrotron radiation from the storage ring was monochromatized by a Si(111) channel cut crystal. The ionized chambers, which were used as detectors for the incident X-ray ($I_0$) and transmitted X-ray ($I$), were filled with N$_2$ gas mixture, respectively. The angle of the monochromators was calibrated with Cu foil. The EXAFS raw data were analyzed with UWXAFS analysis package, including background subtraction program AUTOBK and curve fitting program FEFFIT. The amplitude reducing factor, $S_0^2$ was fixed at 1.0. The backscattering amplitude and phase shift were calculated theoretically by FEFF 8.4 code. ATOMS was used to obtain the FEFF input code for the crystalline materials. TPR experiments were carried out in a Micromeritics, Auto Chem II 2920 instrument connected with a thermal conductivity detector (TCD). All samples were subjected for TPR in the temperature range of 40–1000 °C with an increment of 10 °C min$^{-1}$, using helium as carrier.

Catalytic activity

The partial oxidation of methane was carried out in a fixed-bed, tubular down-flow reactor under atmospheric pressure. Typically, 200 mg of catalyst was placed between two quartz wools plugged in the center of the 6 mm quartz reactor. Conventionally, the catalyst was used instantly in partial oxidation reaction. The gas hourly space velocity (GHSV or the volume of gasses pass through 1 g of catalyst in 1 h) was varied between 5000 and 30,000 h$^{-1}$ with a molar ratio of O$_2$:CH$_4$:He = 1:2:7. The entire reaction product was analyzed by an online gas chromatograph (Agilent GC-7890A) fitted with a TCD detector. The reaction products were analyzed using two different
columns; molecular sieves (for analyzing H₂) and PoraPack-Q (for analyzing CH₄, O₂, CO₂ and CO). Typical mass balance was measured using individual calibration curves in some of the experiments and this value was found to be within the error limit (±10%). H₂ was calculated in molecular sieves columns and for the rest of the gases, the PoraPack-Q column was used.

**Result and Discussion**

**Characterization of the catalyst**

The X-ray diffraction patterns of Ni-CeO₂ catalysts along with commercial CeO₂ are shown in Fig. 1. The peaks at 2θ value of 28.5º, 33.1º, 47.6º, 56.4º show the characteristic cerium oxide formation. The peaks of NiO appear at 2θ values of 37.6º and 43.1º, corresponding to (222) and (400) crystal planes respectively of NiO. The XRD of the spent catalyst (after 24 h of time-on-stream) 5%Ni-ceria catalyst shows characteristic peaks of CeO₂ at 28.5º, 47.6º, 56.4º without changing its phase, thus confirming the thermal stability of the support material. The morphology of the 5%Ni-CeO₂ catalyst was determined by scanning electron microscopy (SEM). The representative SEM image of 5%Ni-CeO₂ catalyst is shown in Fig. 2, which shows the spherical nature of the catalyst. The presence of Ni was also confirmed by EDX (Fig. 2) and detailed characterization of the distribution of the elements was carried out by means of elemental mapping which shows the homogeneous

![Fig. 1 – XRD patterns of ceria and nickel-supported ceria catalysts. [1, commercial CeO₂; 2, prepared CeO₂; 3, 5%Ni-CeO₂; 4, 10%Ni-CeO₂; 4, spent catalyst (5%Ni-CeO₂)].](image1)

![Fig. 2 – SEM of (a) 5%Ni-CeO₂ and (b) spent catalyst (5%Ni-CeO₂); (c) Elemental mapping of Ni; (d) TEM image of 5%Ni-CeO₂; (e) EDX pattern of 5%Ni-CeO₂ catalyst.](image2)
distribution Ni. The 2p XPS spectra of 5%Ni-CeO$_2$ catalyst is shown in Fig. 3. The binding energy values of Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ peaks at 854.2 eV and 872.8 eV confirm the presence of Ni$^{2+}$ in the catalyst. However, the spent catalyst shows the presence of both metallic Ni and the NiO. This is due to the in situ reduction of the NiO in the presence of the produced H$_2$. The TPR profile of 5%Ni-CeO$_2$ catalyst shows the presence of easily reducible NiO (Supplementary Data, Fig. S1). NiO will be reduced to metallic nickel using same number of mole of hydrogen since one Ni$^{2+}$ will use one mole hydrogen to be reduce to metallic nickel. In the TPR analysis, 100 mg sample was used and the consumed hydrogen was $8.5 \times 10^{-5}$ mole, which supports the presence of NiO in the sample.

**Catalyst performance**

Table 1 shows the activities of the different Ni-supported catalyst for partial oxidation of methane. Catalysts with ZrO$_2$ (entry 2) and TiO$_2$ (entry 4) supports show lower methane conversion as compared to the catalyst with CeO$_2$ support. Ni supported on CeO$_2$ (5%Ni-CeO$_2$) shows methane conversion of 86.1% (entry 1), whereas 5%Ni-ZrO$_2$ (entry 2) shows only 23.1% conversion at 800 ºC. 5%Ni-CeO$_2$/ZrO$_2$ (entry 3) shows 68.8% methane conversion and 5%Cu-CeO$_2$ shows 38.4% methane conversion at 800 ºC. It was also found that the methane conversion decreases with increasing GHSV. The catalyst shows 86.1% methane conversion when GHSV was 50,000 mL g$^{-1}$ h$^{-1}$ and the conversion of methane decreased to 82.6% when GHSV was increased to 500,000 mL g$^{-1}$ h$^{-1}$ (entry 6). The H$_2$/CO ratio was in the range of 1.9–2.

The effects of temperature and metal loading are shown Fig. 4. Methane conversion increases rapidly from 500–800 ºC, and then it remains constant (not shown in the figure). However, it was found that the methane conversion on Ni-CeO$_2$ increases initially up to 5% then decreases with increasing Ni loading above 5%. We believe that with increasing Ni loading above 5%, the agglomeration of Ni occurs which leads to decrease in methane conversion. The H$_2$/CO ratio is found to increase with increasing temperature during the course of this study.

The TOS studies indicate that the catalyst shows no deactivation till 30 h, which is the main advantage of the present catalyst. We believe that due to the high dispersion of Ni on CeO$_2$ support, the catalyst does not show any deactivation.

**Conclusions**

In the present study 5% Ni-CeO$_2$ catalyst shows very good catalytic activity for partial oxidation of methane to synthesis gas with H$_2$/CO ratio of ~2. The catalyst has been characterized by XRD, SEM, TEM, XPS, and N$_2$ adsorption/desorption studies. The catalyst shows 86.1% methane conversion and 87.2% selectivity with H$_2$/CO ratio of ≥1.97 at 800 ºC. With the increasing of Ni loading (>5%), agglomeration of Ni occurs and the activity decreases.
The catalyst is very stable till 30 h time-on-stream, which is the main advantage of this catalyst.

Supplementary Data

Supplementary data associated with this article, i.e., Fig. S1 available in the electronic form at http://www.niscair.res.in/jinfo/jica/IJCA_53A(4-5)467-471_SupplData.pdf.

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