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# Effect of metal-support interaction on activity and stability of Ni-$CeO_2$ catalyst for partial oxidation of methane

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ABSTRACT

The objective of the current study was to synthesize a nickel based catalyst with high activity at low temperature for partial oxidation of methane (POM). Ni-nanoparticles supported on $CeO_2$ nanoparticles were synthesized by two step preparation method. First, 30–50 nm $CeO_2$ was synthesized by solvo-thermal method and then Ni- nanoparticles were deposited over it following a newly developed procedure, where cetyltrimethylammonium bromide (CTAB) acted as morphology controlling agent and polyvinylpyrrolidone (PVP) as size controlling agent for nickel nanoparticles. The characterizations of synthesized catalysts were done by BET-Surface area, XRD, SEM, TEM, TPR, $H_2$-chemisorpton, TGA and XPS analysis. The catalysts showed excellent coke resisting ability during POM and produces synthesis gas with $H_2$/CO ratio almost 2. The catalyst activated methane at 400 °C with 10% methane conversion and converts methane almost completely at 800 °C. The catalyst showed above 98% methane conversion at 800 °C during 90 h of time on stream (TOS) reaction with $H_2$/CO ratio 1.98. Average 5.5 nm Ni particles, use of $CeO_2$ as a support played a very crucial role for methane activation at such lower temperature. The synergistic effect between small Ni-nanoparticles and $CeO_2$ nanoparticles of Ni-$CeO_2$ catalyst is the main reason for such activity. Detailed study of other reaction parameters like temperature, Ni loading, weight hourly space velocity (WHSV) was also carried out and reported.

## 1. Introduction

Methane, the predominant component of natural gas, is considered to be a major energy source for the future [1–3]. Methane is a major greenhouse gas with much higher greenhouse potential than $CO_2$ [4]. It is gas in normal atmospheric condition and its storage and transportation problems prompted researchers to find out an alternative to utilize this huge energy source. Methane can be converted directly into HCHO, $CH_3OH$, $C_2H_4$ etc. but low conversion and low selectivity to these products are the main problems as the products are more reactive than methane itself [5,6]. Nowadays, methane is industrially used to produce synthesis gas (a mixture of CO and hydrogen), the basic raw material for many industrial processes to produce other chemicals and synthetic fuels [6]. Steam reforming of methane (SRM) is the major large scale synthesis gas production process, which produces $H_2$/CO ratio 3 [7]. Again, the major problem with $CO_2$ reforming of methane is reverse water gas shift (RWGS) reaction and coking on catalyst surface [4,8], which reduces hydrogen selectivity and deactivates catalyst. POM efficiently produces synthesis gas with $H_2$/CO ratio 2 and it is the exact requirement for methanol synthesis [9]. Presence of oxygen in the reaction feed of POM reduces carbon deposition problem by removing the coke as CO and/or $CO_2$ [10,11]. Now, as POM provides so many advantages, it has its own problems too. First of all, it is an exothermic reaction, and the hot spot generation during the process raises some safety issues. Another issue is the requirement of pure oxygen, which is a problem from economic point of view. Because of potential of the production of synthesis gas via POM, researchers are trying to establish this process with the help of a suitable catalyst.

Decades of extensive research revealed that noble metal like Pt, Ru, Rh, Ir [1,5,12] and transition metals like Ni, Fe, Co [1,13–16] are very reactive for the POM process. Noble metals have very high activity and much more coke resistive during POM but the abundance and high cost limited its commercial application. From the reactivity point of view, Ni is the only transition metal with comparable activity to the noble metals. Low cost and high abundance of Ni makes it Holy Grail for methane activation. The problem with Ni catalysts is its coke sensitivity. Carbon accumulation on Ni surfaces during catalysis deactivates the catalysts rapidly and also causes reactor plugging [2]. Nano regime supported Ni catalysts are reported to be very much coke resistive [8] and efficiently pro-

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duce synthesis gas with $H_2$/CO ratio 2 during POM. Type of support is very crucial for obtaining resistance towards coking. Numerous reports showed applications with oxide supports like $SiO_2$, $Al_2O_3$, MgO, $ZrO_2$, $CeO_2$ etc [1,3,5,17]. $CeO_2$ is a suitable support for POM with high thermal stability, coke resisting behavior and very good redox properties [1,3,5,18,19]. $CeO_2$ is very well known for its oxygen storage property [20] and decreases coke formation by modifying the structural and electronic properties of catalysts [3,5]. Surface oxygen from cerium oxide reacts with carbonaceous species deposited on catalyst surface and again it gets re-oxidized by the gaseous oxidants in reaction system [10,11].

Metal-support interaction plays very significant role in controlling particle size, oxygen availability and coke resistance property of the catalyst. Strong metal-support interaction helps in formation of small and highly dispersed particles, resists sintering of catalysts particles during catalysis [4,21,22] and improves oxygen availability of the catalyst. The oxygen species at the metal-support interface are easily reducible [23,24] and during catalysis the oxygen species near the active metal removes the deposited carbon from catalyst surface improving the coke resistant property of catalyst [23–25]. Now, mechanism of POM reaction is highly dependent on catalyst properties. Eiras et al. [26] reported that POM reaction via direct route is theoretically possible. Recently we have reported Pt-$CeO_2$ catalyst for POM reaction at 350 °C [5]. At this much lower temperature $CO_2$ reforming or steam reforming of methane is not possible as much higher temperature is needed for these two reactions [21]. So, the formation of syngas at this temperature (350 °C) can only take place via direct route only. Choudhary et al. [1] reported that at very short contact time, if the POM reaction proceeds through indirect mechanism, there should be only combustion product present in the product gas, no POM product should be present because $CO_2$ reforming and Steam reforming of methane follows very slow kinetics.

Ni-MgO catalyst was reported by Kirillov et al. for POM with 75% of methane conversion with drastic decrease in conversion to 55% only after 24 h of time on stream (TOS) at 800 °C [27]. Asencios et al. reported NiO-MgO-$ZrO_2$ catalyst for POM with ≥90% of methane conversion at 750 °C but catalyst was deactivated by coking [10]. Green and his group [6] also reported costly molybdenum carbide catalyst for POM at very low gas hourly space velocity (GHSV) (2000 $h^{-1}$) and high pressure with 96% methane conversion at 900 °C. 96% methane conversion at 800 °C was reported by Li et al. over lanthanum doped Ni-$SiO_2$ core shell catalyst for POM with 65 h of time on stream stability at 700 °C [28]. Ni/$CeZrO_2$ catalyst with 7 h of TOS stability at 700 °C was reported by Larimi et al. with methane conversion above 80% [29]. Özdemir et al. [30] reported 89% methane conversion at 800 °C using air as oxidant over Ni/$MgAl_2O_4$ catalyst. Recently, Venezia and her group reported Ni-CeLa oxides [31] and Ni-$CeO_2$ catalysts prepared by different methods [32] for POM with above 90% of methane conversion at 800 °C. Oliveira et al. [33] recently reported 1.5% Rh-$CeO_2$ catalyst for POM. They reported 83.4% methane conversion at 800 °C.

Synthesis of a suitable catalyst with suitable support, which is thermally stable, coke resistant and exhibits excellent redox properties are the major challenge for methane activation purpose. Here, we are reporting synthesis of highly active and coke resistant Ni nanoparticles supported $CeO_2$ catalyst for the production of synthesis gas by POM.

## 2. Experimental

### 2.1. Catalyst preparation

Ni nanoparticle supported $CeO_2$ catalyst was synthesized by following two step preparation methods. First, 30–50 nm $CeO_2$ nanoparticles was synthesized by a surfactant free solvo-thermal method, then Ni nanoparticles was deposited on nano-crystalline $CeO_2$. In a typical synthesis procedure, 4.3 g cerium nitrate hexahydrate [$Ce(NO_3)_2{\cdot}6H_2O$] was dissolved in 125 ml ethanol by continuous stirring. After 2 h of stirring, 2% $NH_3$ solution was added very slowly to maintain pH at 7. Then after 1 h stirring of the whole mixture solution, it was autoclaved at 180 °C for 24 h. The autoclave was then cooled at 35 °C and a dry solid precipitate was obtained by evaporating the solvent by gradually increasing the temperature to 80 °C. The dried solid was then calcined at 700 °C for 6 h in air. The prepared cerium oxide was denoted as $CeO_2$*.

In the second step, Ni nanoparticles were deposited on $CeO_2$* by the following method. 10 ml ethanol was added with 0.4 g cetyltrimethylammonium bromide (CTAB) and 0.05 g polyvinylpyrrolidone (PVP) and dissolved the material. Then 0.25 g of nickel nitrate hexahydrate [$Ni(NO_3)_2{\cdot}6H_2O$] dissolved in 20 ml $H_2O$ was added slowly to the CTAB and PVP solution. The nickel salt solution was then added drop wise to 1 g of $CeO_2$* dispersed in 100 ml ethanol and continued stirring for 2 h. Then 200 μl of hydrazine hydrate [$NH_2NH_2{\cdot}H_2O$] was added with whole mixture solution to maintain the pH of the solution to 8 and continued stirring for 1 h. After 1 h of stirring the mixture solution was evaporated to dryness by gradual increase in temperature to 100 °C. The dried material was then finally calcined at 600 °C for 6 h in air and it was denoted as 5Ni-$CeO_2$*. 2.5 Ni-$CeO_2$* and 10Ni-$CeO_2$* catalysts were also prepared for comparison. Here in the depicted method, CTAB controls Ni species morphology, PVP controls the size of Ni species and hydrazine acted as a reducing agent, capping agent and a base also. For comparison purpose Ni was also deposited by the here described method over commercial cerium oxide and it was denoted as 5Ni-$CeO_2^{Com}$ (Supporting information).

Ni impregnated $CeO_2$ catalyst was synthesized using cerium oxide ($CeO_2$*) for comparison (Supporting information). All the catalysts are designated as xNi-$CeO_2$, where 'x' is the wt% of Ni present in the catalyst.

### 2.2. Catalyst characterization

Characterizations of the synthesized catalysts were performed by BET-Surface area, XRD, SEM, TEM, $H_2$-Chemisorption, XPS and TGA/DTG. The detailed process is given in Supporting information.

### 2.3. Catalytic procedure

Catalysts activity tests were performed in a fixed-bed down flow reactor. Before the reaction, the catalysts were reduced with 20%$H_2$ balance He gas for 2 h at 600 °C. Due to exothermic nature of the reaction, catalyst was diluted with inert γ-$Al_20_3$ and inert material (ground quartz) was used to dilute catalyst bed [34] and the reaction was performed at 350–800 °C, atmospheric pressure. The catalyst to diluent ratio 100:500 showed almost no temperature difference between the catalysts zones in the reactor. Typically, in a 6 mm quartz reactor, 60 mg of catalyst diluted with inert material was placed at the centre of two quartz wool plugs. WHSV was varied between 5000 and 200,000 ml $g^{-1}$ $h^{-1}$ with feed ratio of $O_2$:$CH_4$:He = 1:2:8.5 (mole ratio). The experimental set up to measure reaction temperature is discussed in detail in the Supporting information (Fig. S1). Analysis of the products were performed by online gas chromatography (Agilent 7890A) fitted with a TCD detector. Molecular sieves column was used for analyzing $H_2$ and PoraPack-Q column for analyzing $CH_4$, $CO_2$ and CO.