Catalysis Communications 92 (2017) 19–22

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Low temperature dry reforming of methane over Pd-CeO_2 nanocatalyst

Rajib Kumar Singha, Aditya Yadav, Astha Shukla, Manoj Kumar, Rajaram Bal *

Nanocatalysis Area, Refining Technology Division, CSIR-Indian Institute of Petroleum, Dehradun 248005, Uttarakhand, India

ARTICLE INFO

Article history:
Received 3 October 2016
Received in revised form 14 December 2016
Accepted 19 December 2016
Available online 21 December 2016

Keywords:
Pd-nanoparticles
CeO_2
Dry reforming
Methane

ABSTRACT

Pd-CeO_2 nanocrystals were prepared using a simple surfactant induced method, which initiated dry reforming of methane reaction only at 350 °C. Low temperature activity of the prepared catalyst was due to high Pd-dispersion and very good redox property of support Ceria (20–50 nm) nanocrystals (32.8% Ce^{+3} concentrations). The catalyst was found to be very good coke resisting and inhibited deactivation by coke formation during catalysis. Time on stream (TOS) study was carried out for 12 h and slight decrease in conversion was observed due to sintering, re-oxidation and hydroxylation of the active Pd-nanoparticles.

1. Introduction

Dry reforming of methane (DRM) or methane reforming with CO_2 is an extensively studied methane reforming reaction to produce much valuable synthesis gas by utilizing two major greenhouse gasses (CH_4 and CO_2) [1–5]. DRM is a highly endothermic reaction and is one of the better processes to utilize methane and carbon dioxide for synthesis gas production but the reaction requires very high temperature [6–10]. Decades of studies revealed that both noble metals (Rh, Ru, Pt, Pd) and non-noble metals like Co and Ni are highly active for DRM but only Ni is comparable with the noble metals in terms of reactivity [3–7,11,12]. Problem with DRM is intense coking during catalysis due to methane decomposition and Boudouard reaction [1–10]. Non-noble metals are highly coke sensitive but noble metals are reported to be quite good coke resisting elements [2,6,11,12]. So, from the reactivity and stability point of view, noble metal catalysts are better for catalytic DRM reaction. Now, deactivation of DRM catalysts can also occur by re-oxidation or hydroxylation of the active species of the reaction or by sintering of catalyst particles, which is mainly caused by low metal-support interactions between active metal particles and support particles [3–5]. Another problem of DRM is reverse water gas shift (RWGS) reaction, which highly affect H_2/CO ratio by consuming the produced hydrogen ($CO_2 + H_2 \rightarrow CO + H_2O$) [1–10,13].

For the advantage of utilizing two greenhouse gasses and production of highly valuable syngas, which is the basic raw material for Fischer-Tropsch synthesis for the production of various synthetic fuels [2,3,7], researcher are still involved in making the process much more effective. Researchers are still developing different noble and non-noble metal catalysts for the purpose. It has been found that catalysts in nano-regime show very high activity for different catalytic processes due to its unusual and advantageous behavior [3,4,14–17]. Low metal loading facilitates high chemical potential of the small Pd particles that are bound to Ceria. CeO_2 itself is reducible support and provides active surface oxygen during oxidation reduction reaction but addition of small amount of active metal like Pd highly enhances oxygen vacancy [18–20]. Farmer and Campbell reported that smaller active particles supported on partially reduced CeO_2 has much higher stability than its larger counterparts [18]. Smaller particles have more interactions with the support as these particles provide much more interfacial surface area than its larger counterparts [3,4,14–23]. Cargnello et al. reported that enhanced metal-support interaction between very small Pd and CeO_2 nanoparticles led to exceptionally high methane conversion even below 400 °C [20]. Liu et al. reported that strong metal-support interactions and created oxygen vacancies in the catalyst can enhance the reactant activation during DRM process even at room temperature (at 27 °C) [24]. Here, we are reporting a Pd-CeO_2 catalyst, active for DRM even at low temperature as 350 °C, which is theoretically possible [2,25].

2. Experimental

2.1. Synthesis of Pd-CeO_2 nanocrystals

In a typical synthesis procedure of Pd-CeO_2 catalyst, 1 g cetyltrimethylammonium bromide (CTAB) was dissolved in 100 ml distilled water by vigorous stirring for 30 min. After a homogeneous CTAB solution was formed, 6.5 g of cerium chloride heptahydrate ($CeCl_3 \cdot 7H_2O$) was added to it. The whole mixture was stirred for 2 h to form a homogeneous solution. After that, 0.05 g palladium chloride ($PdCl_2$) dissolved in 20 ml acetonitrile was added drop-wise to the

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* Corresponding author.
E-mail address: raja@iip.res.in (R. Bal).

http://dx.doi.org/10.1016/j.catcom.2016.12.019

cerium salt solution. The whole solution was kept on stirring at 50 °C for 30 min. to mix the precursors well (homogeneous solution). 25% NH_3 was then used to precipitate the salts maintaining pH at ~9. After 1 h of continuous stirring, 10 μl borane triethylammine complex was added to the mixture (Supporting information). The whole mixture was then stirred for 30 min and aged for 4 days (~96 h). After filtering and washing the precipitate with excess water to remove the chloride ions, it was dried at 100 °C for 6 h and then calcined at 600 °C for 6 h in air. The prepared catalyst was denoted as 0.86Pd-CeO_2, where 0.86 was the wt% of Pd in the catalyst obtained from ICP-AES analysis.

2.2. Characterization and activity measurements

Provided in Supporting information of the manuscript (Figure and Table numbers are designated as S1, S2 etc.).

3. Results and discussions

3.1. Characterizations

Surface area analysis of prepared 0.86Pd-CeO_2 catalyst was carried out, which showed 63 m^2/g surface area of it, whereas surface area of the spent catalyst was found to be 38 m^2/g. The observed result could be due to sintering of catalyst particles [4,15,16]. H_2-chemisorption analysis was carried out for determination of Pd dispersion in the catalyst. The analysis showed 33.9% Pd dispersion and about 2.9 nm average Pd-particles size. XRD analysis of the fresh catalyst showed only characteristics peaks for cubic CeO_2 but no peaks for any Pd-species was observed. The observation indicated about good dispersion of Pd-species but the absence of any Pd-species peaks can also be due to very low loading (0.86 wt%). CeO_2 particles size of fresh catalyst calculated from XRD using Scherrer equation was found to be 37.1 nm. XRD pattern of the spent catalyst showed much more intense CeO_2 peaks but still there was no peak for Pd-species observed. Increase in XRD peak intensity indicated increase in crystallinity of CeO_2 particles [4] but absence of any Pd-species peak indicated that small amount of Pd-species was not detectable as XRD is a bulk sensitive technique [4,15]. Absence of peak for graphitic carbon also revealed an important feature of the catalyst i.e. coke resistibility. Surface analysis to determine the Pd species present in the catalyst was carried out by XPS technique. From the binding energy (B.E.) values, the analysis revealed that fresh Pd-CeO_2 catalyst contain both metallic Pd (B.E. 334.8 eV) and Pd-oxide (PdO) (B.E. 336.7 eV) species. Presence of metallic Pd could be due to presence of CTAB during calcination (Supporting Information) [15]. XPS analysis of the spent catalyst showed metallic Pd (B.E. 334.9 eV), PdO (B.E. 336.6) and PdO_2 and/or $Pd(OH)_4$ (B.E. 337.5 eV) species. Presence of $Pd(OH)_4$ species was due to hydroxylation of the active Pd particles by produced water during catalysis [4]. To be sure about the hydroxide species in the spent catalyst we also analyzed the O 1S XPS pattern. The peak at B.E. value 531.4 eV confirmed the presence of hydroxide species in the spent catalyst [4]. XPS survey and Ce 3d core level spectra is also provided in Supporting information (Fig. S1). We have calculated Ce^{+3} concentration form XPS analysis [26,27], which was found to be 32.8% (Fig. S2). H_2-TPR profile of 0.86Pd-CeO_2 catalyst showed 4 peaks in the temperature range 50–800 °C. First peak at 110 °C was due to reduction of easily reducible very small Pd-oxide nanoparticles, second peak at 140–280 °C was due to little bit larger Pd-oxide particles, third peak (300–500 °C) was due to reduction of surface oxygen of support CeO_2 [15]. Normally the peak shows at about ~500 °C but the presence of Pd-species on the CeO_2 surface makes the oxygen at the metal-support interface much easily reducible [16]. The last peak at above 600 °C was due to bulk reduction of CeO_2 [15] (see Fig. 1).

To analyze the morphology of the prepared catalyst we have carried out both SEM (Fig. S3) and TEM analysis (Fig. 2) of the fresh catalyst catalyst, which revealed that CeO_2 particles were about 20–50 nm size and 1–15 nm of Pd-species deposited on the surface of CeO_2. Pd-dispersion analysis showed much lower size of Pd-nanoparticles. The high value of Pd-size measured from TEM analysis was due to the fact that the technique was not capable of detecting ultrasmall particles, which also contributed during H_2-chemisorption analysis. Fig. 2 (inset) shows the fringes of PdO nanocrystal. The d-spacing of 1.66 Å and 2.63 Å was attributed to (112) and (101) plane of PdO. We also carried out TEM analysis for the spent catalyst (Fig. S4), which showed sintered catalyst particles. TGA/DTG analysis of uncalcined and spent catalyst was performed to check thermal stability and carbon deposition on the catalyst surface (Figs. S5, S6).

3.2. Catalytic performance

Catalytic activity of the prepared catalyst was tested in the temperature range 300–800 °C at optimized weight hourly space velocity (WHSV) value 70,000 $ml \cdot g^{-1} \cdot h^{-1}$. Observed results for heat transfer and mass transfer (HT-MT) limitations experiments showed negligible HT-MT limitations (Figs. S7, S8). Carbon and material balance for the experiments was in between 98 and 102% (or $\pm 2\%$). Thermodynamic analysis says, DRM is highly endothermic reaction and requires very high temperature (800–1000 °C) to obtain high conversions as both the molecules are highly stable at normal condition [2,25,28].

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \Delta H_{298K} = 247\ \mathrm{kJ/mol}$$

With increasing pressure, reactant conversions and H_2/CO yields drops drastically. So, according to thermodynamics, it is essential to operate DRM at lower pressure [2,25,28]. At these conditions carbon deposition is inevitable [2,25,28]. These problems can be overcome by operating the reaction at lower temperatures and with the catalysts which are resistant towards coking during DRM [2,25,28]. Rate of reaction over 0.86Pd-CeO_2 catalyst was also calculated and reported (Table S1).

Fig. 3a shows reactant conversions and H_2/CO ratios at different temperature. It was found that experimental conversions values are lower than equilibrium conversion values (Fig. S9). Fig. 3b shows TOS stability of the catalyst at 800 °C. It can be seen from Fig. 3a that the reaction was initiated at 350 °C with methane and CO_2 conversions 3.56% and 1.96% respectively and very slow increase in conversions were observed up to 500 °C. In our recent articles, we have showed that use of CeO_2 as support or promoter and strong metal-support interactions activates methane at lower temperatures [3,4,14–17]. Initiation of DRM reaction at such a low temperature was the main advantage of the catalyst (Table S2) and it could be due to high activity of highly dispersed Pd-nanoparticles and high metal (Pd)-support (CeO_2) interactions [3,4,14–16]. High concentration (32.8%) of Ce^{+3} in 0.86Pd-CeO_2 was highly influential for activating methane at low temperature [2,5,8,12,15]. Deposition of Pd particles on the surface of CeO_2 created oxygen vacancies and these oxygen vacancies highly improved the anchoring of Pd-nanoparticles and increased Pd-dispersion [28]. Methane dissociates over Pd-nanoparticles and produced carbon and hydrogen. The produced carbon is then reduced the oxygen species of CeO_2 adjacent to the Pd-nanoparticles producing CO [29]. Produced carbon can also take part in CO formation by dissociative adsorption of CO_2, thereby removing the deposited carbon and initiating the DRM reaction. Very slow increase in reactant conversions up to 500 °C could be due to the inherent endothermic nature of DRM reaction. It could also be a reason that methane can be dissociated over Pd-oxide nanoparticles in an oxidizing environment created by CeO_2 by its oxygen storage property but CO_2 requires metallic Pd particles to dissociate and in the oxidizing environment its conversion was low at lower temperatures [3,4]. With increasing temperature and production of hydrogen by methane dissociation led to a reducing environment, which facilitated CO_2 dissociation and increase in CO_2 conversions was observed. After 550 °C, sharp increase in reactant conversions were observed may be due to favorable