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Synthesis effects on activity and stability of Pt-CeO_2 catalysts for partial oxidation of methane

Rajib Kumar Singha, Astha Shukla, Aditya Yadav, Sumit Sain, Chandrasekhar Pendem, L.N. Siva Kumar Konathala, Rajaram Bal*

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

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ABSTRACT

The objective of this study is to explore the effect of catalyst synthesis procedure on the activity of catalysts for partial oxidation of methane. In this aspect, Pt-nanoparticles supported CeO_2 catalysts were prepared by Hydrothermal, co-precipitation, impregnation and by controlled deposition of platinum nanoparticles on hydrothermally prepared cerium oxide. Prepared catalysts were characterized by BET-surface area, X-ray diffraction, H_2-Chemisorption, Transmission electron microscopy, Temperature programmed reduction, Inductively coupled plasma atomic emission spectroscopy and X-ray photoelectron spectroscopy. The study revealed that the catalyst preparation procedure plays a very crucial role on morphology, catalyst particle size, metal support interaction and activity of the catalysts. Catalytic activities were tested for partial oxidation of methane in the temperature range 350–800 °C. The study revealed that the catalyst prepared by controlled deposition of Pt-nanoparticles on hydrothermally prepared cerium oxide showed better activity for partial oxidation of methane compared to the catalysts prepared by other conventional methods. Controlled deposition of Pt-nanoparticles generated better metal-support interaction compared to the catalysts prepared by conventional hydrothermal, co-precipitation and impregnation methods. All the catalysts showed excellent coke resisting ability but the deactivation of most of the catalyst was found to be caused by catalyst particles sintering and re-oxidation of the Pt particles during catalysis.

1. Introduction

Conversion of methane to valuable chemicals like methanol, formaldehyde, ethane, ethylene and synthesis gas attracted researchers because of the high abundance of methane [1–5]. Direct production of methanol, formaldehyde and coupled products are highly desirable but low conversion and low selectivity to these products limited the application [4,6–8]. Methane is also considered to be one of the major energy sources present on earth and industrially used mainly for synthesis gas (a variable mixture of carbon monoxide and hydrogen gas) production, by reforming reactions [9–15] Methane is the basic raw material for these synthesis gas production processes and highly available in the remote areas, from where its transportation is very much difficult due to gaseous state in normal atmospheric conditions [16–19]. Industrially synthesis gas is produced by steam reforming of methane, which is a highly endothermic reaction and very high temperature is required (>850 °C) [15,20]. On the other hand, partial oxidation of methane (POM) is a slightly exothermic reaction, which minimizes energy requirement for the process [14,15,21]. POM is considered to be one of the most promising processes for synthesis gas production with very high efficiency [16,22–24]. As partial oxidation of methane has some advantages over steam reforming, like it is thermodynamically more favorable, produces syngas with H_2/CO ratio 2 and it is slightly exothermic, which makes the process more energy saving [12,15]. The process has some disadvantages too. The main problem is catalyst deactivation and hot spot generation during catalysis, which raises some safety concerns. The reason for catalyst deactivation during catalysis for POM was reported to be coking, which blocks the active sites for the reaction to take place and it causes reactor plugging also.

Decades of research revealed that noble metals (Pt, Rh, Ru etc.) [24–28] and 1st row transition metals (Ni, Fe, Co etc.) [12,14,15,19,29–33] are active for POM. Noble metals are highly active and far more stable during catalysis due to its coke resisting properties [24–26]. High costs of the noble metals are the main

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* Corresponding author.
E-mail addresses: raja@iip.res.in, rajab_73@yahoo.com (R. Bal).

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drawback for their application in the process. In terms of activity, only nickel (Ni) is comparable to noble metals for POM but nickel is highly coke sensitive [12,34,35]. Therefore, it is a very important and tough task for the researchers to develop a suitable catalyst with very high activity and stability for POM. For catalysts activity and stability catalyst supports are reported to play a major role [28,36–41]. Supports which are capable of suppressing coke deposition, highly thermally stable and much more active in lower temperature are favored for the process. Supports like CeO_2 and CeO_2-ZrO_2 are favored because of its redox property and high OSC (oxygen storage capacity) [42–45]. These materials are prone to get reduced at reducing environment and oxidized at oxidizing environment [24,46,47]. High OSC of these materials are helpful for catalysts activity, as the property enhances coke removal mechanism at the catalysts surface during catalysis [24,42,47].

Metal supports like Al_2O_3, SiO_2, MgO, La_2O_3, CeO_2, ZrO_2, CeO_2-ZrO_2 and different mixed oxides are extensively studied by the researchers for POM [12,14,15,25,27,39,48–50]. Lanza et al. reported Rh/ZrO_2 and Rh/CeO_2-ZrO_2 catalysts for POM, where they showed that addition of CeO_2 lowered the ignition temperature by 60 °C [38]. Hori et al. reported Pt/$CeZrO_2$/Al_2O_3 catalysts and claimed that the catalyst showed 24 h of time on stream stability at 800 °C, whereas significant decrease was observed in case of Pt/Al_2O_3 catalyst [51]. They reported that higher oxygen mobility in Pt/$CeZrO_2$/Al_2O_3 catalyst played the part for catalysts time on stream stability. Bueno et al. [28] reported that Cerium oxide modifies structural and electronic properties of a catalyst, which increases reducibility of noble metals and increases catalyst activity. Recently, Kondratenko et al. reported the dependence of catalytic activity on Rh particles size supported over γ-Al_2O_3 and explained that smaller Rh particles were much more active than the larger ones for synthesis gas production by POM [52]. Our very recent report described the synthesis and activity of Pt-CeO_2 catalyst for POM with 100 h of time on stream stability at 800 °C [21].

Catalyst preparation methods reported to have great influence on catalytic activity of the catalysts [14,17,53]. Here, we are reporting a comparative study of Pt-CeO_2 catalysts prepared by different methods, which showed variable activities for POM depending on their physicochemical properties controlled by preparation methods.

2. Experimental

2.1. Catalyst synthesis

2.1.1. Controlled deposition of Pt on CeO_2^{HT} (2Pt-CeO_2^{CD})

The catalyst was prepared by a two-step method. First, Cerium oxide nanocrystals were prepared by solvo-thermal method and then Pt nanoparticles were deposited over prepared CeO_2 by controlled deposition approach.

In a typical synthesis process, 5.02 g of Polydiallyldimethylammonium chloride (PDADMAC) was dissolved in 100 ml ethanol by stirring it for 1 h at room temperature (35 °C). 6.53 g of Cerium nitrate hexahydrate [$Ce(NO_3)_2.6H_2O$] dissolved in 20 ml distilled water was added slowly to the polymer solution and continued stirring for 1 h. After 1 h of stirring, pH of the solution was maintained to 12 by 5 (M) NaOH solution (in water). The whole mixture was stirred for 5 h, until a thick gel was formed. The mixture gel was then put into a stainless steel autoclave and kept at 180 °C for 48 h. The autoclave was then cooled at room temperature and the precipitate was washed with excess water to remove sodium. Obtained precipitate was then dried at 100 °C for 12 h and calcined at 600 °C for 6 h in air. The prepared cerium oxide was denoted as CeO_2^{HT}.

In second step of the method, Pt nanoparticles were deposited over the prepared CeO_2^{HT} nanocrystals by a controlled deposition approach in presence of cetyltrimethylammonium bromide (CTAB). First, 0.04 g of tetraamineplatinum(II) nitrate [$Pt(NH_3)_4(NO_3)_2$] was dissolved in a solution containing 0.04 g of CTAB dissolved in 10 ml of ethanol and 10 ml distilled water mixture. The Pt salt solution was then added drop wise to 1 g of CeO_2^{HT} dispersed in 100 ml ethanol. The whole mixture was kept on stirring for 1 h and 0.5 ml of $NH_2NH_2.H_2O$ (reducing agent) was added slowly to the mixture solution and continued stirring for 2 more h at room temperature (30–35 °C). Here both CTAB and hydrazine can act as capping agent also [54,55]. The temperature of the solution was raised to 60 °C after 2 h of stirring and the whole mixture was evaporated to dryness by gradual increase in temperature up to 100 °C. Obtained solid was then calcined at 600 °C for 6 h in air. The catalyst was denoted as 2Pt-CeO_2^{CD}.

2.1.2. Hydrothermal method (1.8Pt-CeO_2^{HT})

In a typical hydrothermal method 5.03 g Polydiallyldimethylammonium chloride (PDADMAC) was dissolved in 100 ml distilled water by stirring it for 1 h at room temperature (30–35 °C). Then 5.04 g of cerium nitrate hexahydrate [$Ce(NO_3)_2.6H_2O$] dissolved in 20 ml water was added drop wise to the polymer solution and continued stirring for 1 h followed by the addition of Pt salt solution containing 0.08 g of tetraamineplatinum(II) nitrate, dissolved in a solution containing 0.08 g of CTAB, 10 ml of ethanol and 10 ml distilled water. The whole mixture solution was then continued stirring at room temperature for 2 h and then 0.4 ml of $NH_2NH_2.H_2O$ was added and continued stirring for 1 more hour. pH of the solution was maintained to 12 using 5 (M) NaOH solutions (in water). After 1 h of stirring, whole mixture was put into a stainless steel autoclave and treated at 180 °C for 48 h. Obtained precipitate after cooling the autoclave at room temperature was washed with excess water and dried at 100 °C for 12 h. The dried material was then calcined at 600 °C for 6 h in air and the prepared catalyst was denoted as 1.8Pt-CeO_2^{HT}.

2.1.3. Co-precipitation method (1.9Pt-CeO_2^{CoPre})

In a typical co-precipitation method, both the precursor salt of cerium [5.04 g cerium nitrate hexahydrate] and Pt [0.08 g tetraamineplatinum(II) nitrate] was dissolved in 100 ml distilled water and dissolved well by continuous stirring at room temperature. After 1 h of stirring, the salt solution was precipitated completely, using 5 (M) NaOH solutions (in water). The precipitate was then washed with excess water to remove sodium and dried at 100 °C. The dried material was then calcined at 600 °C for 6 h in air and the catalyst was denoted as 1.9Pt-CeO_2^{CoPre}.

2.1.4. Impregnation method (2Pt-CeO_2^{Imp})

Impregnated catalyst was prepared by adding 0.04 g of tetraamineplatinum(II) nitrate [$Pt(NH_3)_4(NO_3)_2$] dissolved in 10 ml H_2O into 1 g of previously prepared CeO_2^{HT} dispersed in 100 ml distilled water. After 1 h of stirring at room temperature, the whole solution was evaporated to dryness by gradual increase in temperature up to 100 °C. The dried solid was then calcined at 600 °C for 6 h in air and the catalyst was denoted as 2Pt-CeO_2^{Imp}.

2.2. Characterization

Surface area analysis of the prepared samples were done at −196 °C with a Mircromeritics ASAP (2020) using the BET equation. Degasification of the sample was done at 350 °C for 6 h before analysis. Powder X-ray diffraction patterns of the samples were recorded on a Proto Analytical X-ray Diffraction System (AXRD) fitted with a Cu Kα radiation source. X-ray diffraction patterns of all the samples were recorded in 10°–80° region with 0.04 step size