



TiO₂ Supported gold–palladium catalyst for effective syngas production from methane partial oxidation

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ABSTRACT

The CO and H₂ (syngas) production from methane partial oxidation (MPO) using TiO₂ supported Au–Pd bimetallic catalysts are discussed. The supported Au, Pd and Au–Pd bimetallic nanoparticles were prepared by an incipient wetness impregnation or co-impregnation method and were characterized. The supported Au–Pd catalyst was selective for reforming and was more active compared to bare TiO₂, TiO₂ supported Au only, or Pd only catalysts. The catalyst properties before and after MPO reaction were investigated, including the stability of the TiO₂ support, and the stability of Au and Pd nanoparticles. The supported Au–Pd catalyst has the highest TON (TON_{H₂} = 23 at 650 °C), compared to supported Au catalyst (TON_{H₂} < 1) and supported Pd catalyst (TON_{H₂} < 1). Based on the analysis of outlet gases from the MPO reaction in a flow reactor, synergetic effects between Au and Pd, where Pd activates C–H bonds while gold modulates the behavior of oxygen at the catalyst surface, are shown to contribute to MPO. Additionally, the Au–Pd/TiO₂ material shows long-term activity (> 12 h) for the MPO reaction at 600 °C.

1. Introduction

Syngas (a mixture of H₂ and CO) is an important precursor for producing liquid hydrocarbon fuels and chemicals in the chemical industry. The production of syngas generally is based on one or more of the following fundamental processes: steam reforming, catalytic partial oxidation, dry reforming, and autothermal reforming (Scheme 1) [1,2]. In industrial production, steam reforming of methane is the most widely used method.

Catalytic partial oxidation of methane to syngas represents a potential strategy for syngas production [3]. It offers several advantages including low energy requirements, low operational temperature, and the possibility to regulate the H₂/CO molar ratio [4,5]

Previous studies have shown that reaction conditions can strongly influence the catalytic activity and product distribution of MPO systems. In general, with stoichiometric reactant mixtures (CH₄:O₂ = 2:1), significantly high temperatures (up to 1200 K) are often required to achieve high conversion and selectivity to partial oxidation products [6]. If the feed stream instead contains a CH₄:O₂ ratio of 1:2, total oxidation products become favored. Fortunately, H₂ and CO become

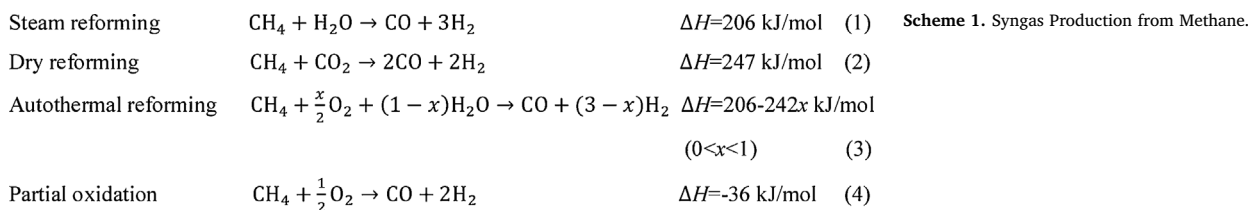
major products in a broad range of ratios higher than 1:2. A variety of reaction equilibria involving methane, oxygen, carbon monoxide, hydrogen, carbon dioxide, water, and surface species such as carbon and various oxygenates can exist simultaneously within the reactor, and in this case MPO can occur via an indirect pathway. With long contact times, oxidation reactions dominate in the entrance zone of the reactor, where molecular oxygen is abundant. Downstream from here, steam reforming, dry reforming, and water-gas shift reactions can occur. Further, the exothermic nature of many oxidation pathways can lead to hotspots and heterogeneity within the catalyst bed. The experiments conducted herein therefore focus on relatively low temperature ranges at ambient pressure to favor the production of partial oxidation products, and a rapid flow rate (GHSV = 40,000 h⁻¹) and short packed catalyst bed provides minimal gas residence time and promotes a homogeneous reaction environment. Such conditions favor a direct partial oxidation pathway to CO and H₂ and minimize complicating side-reactions.

Transition metals from groups 8, 9, and 10 (Ni, Co, Fe, Ru, Rh, Pd, Ir, Pt) have been reported as active catalysts for methane oxidation [7,8]. Among these metals, nickel based catalysts have been intensively

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studied as suitable catalysts for methane reforming, due to its relative low cost [9–11]. However, the Ni based materials are easily deactivated by carbon formation and sintering phenomena [12]. The use of noble metals is capable of effectively inhibiting carbon formation during the methane oxidation process. Pt, Pd, Rh, and Ru catalysts have been shown to exhibit better performances than Ni with higher resistances to coke formation [13,14]. In particular, the metal oxide (TiO₂, ZrO₂, Al₂O₃ et al.) supported noble metal materials have shown high activity and stability for the partial methane oxidation reaction [15]. Simultaneously, the use of supports significantly decreases the overall cost due to more efficient utilization of catalytic sites of metals.

Titanium dioxide (TiO₂) has been widely used as a catalyst support in many studies due to its high chemical and thermal stability. The size and nature of the interaction of a metal nanoparticle with the TiO₂ support can strongly influence the catalytic activity and selectivity of the heterogeneous catalyst [16]. The effect of TiO₂ supports with different metals (Rh, Ru, Pd, Pt et al.) on the conversion of methane to syngas has been given a great deal of attention [17–19]. TiO₂ supported Au and Pd materials have been intensively studied by Hutchings et al., as active catalysts for a variety of reactions such as alcohol oxidation, methane to methanol conversion, organic pollutant decomposition and H₂O₂ synthesis [20–23]. To the best of our knowledge, the synergistic role of Au, Pd in gas phase methane partial oxidation has not been studied.

TiO₂ supported Au materials are active catalysts for a wide range of gas phase oxidation reactions such as CO oxidation, olefin epoxidation, and the water-gas shift reaction [24]. In a study of CO oxidation, Stiehl et al. showed that molecular oxygen can be adsorbed on both Au (111) and Au nanoparticles supported on TiO₂ [25]. Further, more studies reported the interface of the Au cluster and TiO₂ are the active sites for molecularly adsorbed oxygen species [26–29]. The excellent oxygen adsorption ability makes TiO₂ supported Au materials potential catalysts for partial methane oxidation. TiO₂ supported Pd materials are reportedly able to completely oxidized methane at low temperatures (typically below 600 °C) [19,30]. Felvegi et al. had observed the adsorption and dissociation of CH₄ on TiO₂ supported Pd materials at temperatures as low as 200 °C. Moreover, the production of hydrogen and small amount of methanol was also observed [31]. Recently, Weaver et al. reported the activation of primary C–H bonds on PdO (101) [32]. Therefore, by combining the catalytic abilities of Au and Pd nanoparticles on a TiO₂ support, it is reasonable to expect a high activity of such a material for methane partial oxidation.

Herein, we report a TiO₂ supported gold and palladium catalyst (Au-Pd/TiO₂) for the partial oxidation of methane to CO and H₂. The catalytic activity of Au-Pd/TiO₂ was compared with Au/TiO₂ and Pd/TiO₂ to study the synergetic effect between gold and palladium. The as-synthesized Au-Pd/TiO₂ material was able to activate methane at low temperature (> 500 °C) and produce H₂ and CO with high selectivity. The stability of Au-Pd/TiO₂ material was investigated under different temperatures (500–700 °C) and the catalyst was able to maintain activity even after 12 h.

2. Experimental

2.1. Catalyst preparation

TiO₂ supported Au and Pd nanoparticles were synthesized by the

following impregnation method. First, a Au precursor solution was prepared by dissolving 5 g of HAuCl₄·3H₂O in 100 mL distilled water. Second, a solution of Pd was prepared by dissolving 0.17 g PdCl₂ in 4.15 mL distilled water. Diluted nitric acid was added to the Pd solution to improve solubility. The support (TiO₂, Degussa P25) was pretreated with 50 mL, 5% HNO₃ for 3 h, followed by washing with a large amount of distilled water and drying in an oven at 80 °C overnight. The Au and Pd solutions were simultaneously added to 3.8 g of pretreated TiO₂ while stirring. The obtained homogeneous paste was dried in an oven overnight at 80 °C and then calcined at 400 °C for 3 h to obtain TiO₂ supported Au and Pd nanoparticles. The amounts of Au and Pd were calculated as 2.5% for each. The prepared sample is labeled as 5%Au-Pd/TiO₂. Other samples containing only one noble metal (5%) were prepared by a similar method.

2.2. Characterization

Powder X-ray diffraction (XRD) analyses were performed using a Rigaku Ultima IV X-ray diffractometer (Cu Kα radiation, λ = 1.5406 Å) with an operating voltage of 40 kV and a current of 44 mA. Nitrogen (N₂) sorption experiments were conducted on a Quantachrome Autosorb-1-1C automated sorption system. The powders were degassed at 150 °C for 6 h prior to the measurements. The surface areas were calculated by the Brunauer–Emmett–Teller (BET) method, and the pore size distributions were calculated by the Barrett–Joyner–Halenda (BJH) method from the desorption isotherms. Morphological characterization was done using an FEI Nova NanoSEM 450 with an accelerating voltage of 2.0 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed in a PHI model 590 spectrometer with multiprobes (Physical Electronics Industries Inc.), using Al Kα radiation (λ = 1486.6 eV) operated at 250 W. The shift of binding energy due to relative surface charging was corrected using the C 1s level at 284.6 eV as an internal standard. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were obtained using a JEOL 2010 UHR FasTEM operating at an accelerating voltage of 200 kV. The samples were prepared by dispersing the material in ethanol. A drop of the dispersion was placed on a holey carbon coated copper grid and allowed to dry under ambient conditions. High-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) measurements were carried out using a Talos F200X microscope operating at 200 kV equipped with an energy dispersive X-ray spectroscopy (EDS) detector. Samples for IR spectroscopy were mixed with KBr and pressed at 5 T for 10 s. A Nicolet 8700 FT-IR with MCT detector was used to collect data from 400 to 4000 cm⁻¹ with a resolution of 2 cm⁻¹. A blank KBr pellet was used as background and 64 scans were averaged to give the final spectrum. The software suite Specta was used for baseline correction and normalizing the spectra. The zeta (ζ) potential measurements were carried out using a Zetasizer Nano ZS 90 (Malvern Instruments).

2.3. Catalytic activity tests

The catalytic activity of each material was evaluated in a continuous flow reactor operating at atmospheric pressure. A 50 mg sample of each material being investigated was packed into a 7 mm inner diameter quartz tube between quartz wool. The reactor tube was housed inside an electrically heated tube furnace connected to a programmable

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