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High catalytic stability of Pd-Ni/Y₂O₃ formed by interfacial Cl for oxy-CO₂ reforming of CH₄

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ABSTRACT

The effect of chloride in Pd precursors on catalyst activity and stability of Pd-Ni/Y₂O₃ catalyst was investigated for oxy-CO₂ reforming of methane. A series of Pd-Ni/Y₂O₃ catalysts with different Pd precursors (PdCl₂ and Pd(NO₃)₂) was prepared using wet-impregnation method over Y₂O₃ support. The presence of chloride in the Pd(Cl)-Ni/Y₂O₃ catalyst (PdCl₂ as precursor) aids in formation of Pd-Y₂O₃ compound which can interact with Ni to form bilayer Pd-Ni and prevent agglomeration at high temperature reaction condition. The presence of Pd-Y₂O₃ compound is of very importance for superior catalytic stability of Pd(Cl)-Ni/Y₂O₃ catalyst. The catalytic activity of Pd(Cl)-Ni/Y₂O₃ catalyst is much better than Pd(Ni)-Ni/Y₂O₃ catalyst (Pd(NO₃)₂ as precursor) due to smaller metal particle size and synergy between Pd and Ni to form bimetallic particles on the Pd(Cl)-Ni/Y₂O₃ catalyst. The effect of metal particle size on catalytic activities is clearly shown in Pd(Cl)-Ni/Y₂O₃ catalyst with various Pd/Ni ratios. A formation mechanism of bilayer Pd-Ni formed by interfacial chloride is proposed for Pd(Cl)-Ni/Y₂O₃ catalyst.

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1. Introduction

In recent years, the rapid increase of CO₂, which is the largest amount of greenhouse effect gas causing global warming, has been attracting a great interest from academic and industrial researchers. Enormous efforts are currently being undertaken to utilize CO₂. One of the potential ways to utilize CO₂ is via catalytic CO₂ (dry) reforming with methane (DRM) [1–6]. This reaction is attractive for industry as it yields low H₂/CO ratio, which is preferable for hydroformylation and carbonylation reactions [7,8]. In addition, methane is also reported as the second largest amount of greenhouse effect gas [9–11].

A variety of catalysts for the DRM reaction, such as Rh, Ru, Pt, Pd, Ir [12–14], Ni [15–24], and Co [25–28] catalysts, has been extensively investigated. The catalysts made from noble metals, such as Rh, Ru, Pt, Pd, and Ir have comparable activity than the Ni catalyst, but they have lower carbon deposition rate than the Ni catalyst. Generally, the carbon deposition rate decreases in the order as follows: Ni » Rh > Ir = Ru > Pt = Pd at 773 K and Ni > Pd = Rh > Ir > Pt » Ru at 923 K [29,30].

Even though high carbon deposition rate causing deactivation on the Ni catalyst is commonly observed, the Ni catalyst

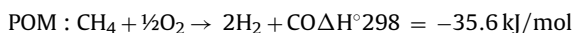
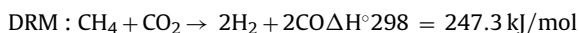
appears to be the most suitable catalyst as the noble metal catalyst is expensive. However, the Ni catalyst has to be modified to improve the performance and coke resistance. Numerous studies on catalyst modification [31] show that choosing the suitable catalyst support [32–35] and/or adding other metal as a promoter [36–39] can improve the performance and coke resistance of the nickel catalyst. For example, Zhang and Verykios [40] studied the effect of catalyst supports and reported that the Ni/La₂O₃ catalyst showed higher activity and stability than the Ni/Al₂O₃ and Ni/CaO catalysts. In addition, many promoters also showed improvement on the Ni catalyst. Horiuchi et al. [41] found that addition of basic metal oxides (Na₂O, K₂O, MgO, and CaO) to the Ni catalyst enhanced CO₂ adsorption, resulting in more adsorbed oxygen atoms (O_{ad}). The higher amount of adsorbed oxygen atoms (O_{ad}) prevented adsorbed hydrogen-deficient hydrocarbon species (CH_{x,ad}) to decompose to surface carbon since the adsorbed oxygen species could easily react with the adsorbed hydrogen-deficient hydrocarbon species (CH_{x,ad}) to form CO. Alipour et al. [42] reported that MgO-promoted-Ni/Al₂O₃ catalyst has higher catalytic activity than other alkaline earth promoters (CaO and BaO) on Ni/Al₂O₃ catalysts due to increase in nickel reducibility and decrease in reduction temperature of NiO species. Xu et al. [43] also reported that Ni/CaO-Al₂O₃ catalyst prepared using ordered mesostructured of Al₂O₃ and CaO basic promoter enhances the catalytic activity and stability as well as suppressing carbon formation compared to conventional supported catalyst.

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Beside high carbon deposition rate, sintering of Ni particles causing rapid deactivation has also been observed on Ni catalyst. Extensive studies on various catalyst support showed that formation of metal-support compound was important for preventing Ni sintering [32]. For example, Li et al. [44] reported that combination of NiCo bimetallic nanoparticles and a $Mg_x(Al)O$ support exhibits high coke resistance and long-term on-stream stability due to strong metal-support interaction. However, the current publication by Wang et al. [45] found that the Ni-CaO-ZrO₂ catalyst has high activity and stability due to strong metal-support interaction. However, the carbon formation rate is the highest among all tested catalysts, indicating that the type of deposited carbon could play more important role than the amount of deposited carbon. The presence of metal-support interaction was also found to play an important role in high catalyst activity and stability in other reactions [46–48].

Even though the catalyst modification can reduce the carbon deposition rate and prevent metal sintering, the energy requirement for the DRM reaction is very huge due to its high endothermicity. The high energy requirement is the drawback to prevent commercialization of the DRM reaction in industries. One way to overcome this drawback is to introduce exothermic reaction such as partial oxidation of methane (POM), resulting in a reaction called oxy-CO₂ reforming of methane (OCRM). The OCRM reaction can reduce not only the amount of carbon deposition since the oxygen can easily oxidize the deposited carbon on the catalyst, but also the total energy requirement since the OCRM reaction combines both the exothermic (POM) and endothermic (DRM) reactions [49–51]. The energy required from the DRM and released from the POM reactions are shown as follows:



Pd-Ni/Y₂O₃ catalyst has been reported to have the highest activity and stability in the OCRM reaction compared to other Pd-Ni catalysts on different supports due to the formation of metal-support compound resulting in small metal particle size, the presence of surface β -oxygen species promoting the cracking of C–H bond in CH₄ and the ability of Y₂O₃ to form oxycarbonate species to oxidize the surface carbon on the Pd-Ni/Y₂O₃ catalyst [52]. All those Pd-Ni catalysts were synthesized using PdCl₂ as the Pd precursor. It has also been reported in the literature that Rh/Fe₂O₃/ZrO₂ catalyst prepared from rhodium nitrate precursor has better activity in water gas shift reaction than the one from rhodium chloride due to the presence of residual chlorine [53]. The use of chlorine-containing-metal precursor hindered the reduction of the Rh³⁺ to metallic Rh on the Rh/CeO₂ catalyst, but the effect of metal precursors on catalyst performance was still unclear [54]. The similar results in the literature were observed for Pd-Ni catalyst in various reactions. For example, Yoshida et al. [55] showed that the Pd-Ni/Al₂O₃ catalyst synthesized from Pd(Ac)₂ precursor had higher bed temperature than the one from PdCl₂ precursor in oxidative steam reforming of methane reaction, even though the CH₄ conversion was similar. In addition, Dias and Assaf [56] also showed similar catalytic performance between Pd-Ni/Al₂O₃ catalysts synthesized from PdCl₂ and Pd(NO₃)₂ precursors in autothermal reforming of methane reaction. However, they observed formation of compound between Pd, Cl and the support, with the general formula Pd_xO_yCl_z on the Pd-Ni/Al₂O₃ catalyst synthesized from PdCl₂ precursor. The presence of this compound prevented the occurrence of reaction without H₂ reduction prior to the reaction. Moreover, they also observed that the difference in catalytic activity of the Pd-Ni/Al₂O₃ catalyst was mainly due to the difference in the metal surface area.

Since the characterization results of Pd-Ni catalysts synthesized from various Pd precursors showed significant different profiles but the catalytic performance of those catalysts are similar, the conclusion is still unclear. Therefore, in this study, the effect of chloride in Pd precursors on catalyst performance of the Pd-Ni/Y₂O₃ catalyst is investigated in the OCRM reaction. The interaction between Pd, Ni, and support is also studied to facilitate better understanding of the catalyst activity and stability in the OCRM reaction.

2. Experimental

2.1. Catalyst synthesis

A series of Pd-Ni catalysts with different ratios and nominal total loading of 5 wt% was synthesized by wet-impregnation method over Y₂O₃. The Pd precursor was either PdCl₂ or Pd(NO₃)₂, which was purchased from either Strem chemicals or Sigma-Aldrich, respectively, while the Ni precursor was obtained from Strem Chemicals in the form of Ni(NO₃)₂·6H₂O. Y₂O₃ purchased from Strem Chemicals was chosen as the catalyst support as it showed good performance in OCRM reaction in our previous study [52]. The Pd solution was prepared by either dissolving PdCl₂ in 2 M HCl solution or Pd(NO₃)₂ in deionized water. For bimetallic Pd-Ni catalyst preparation, the PdCl₂ powder was initially dissolved in 2 M HCl solution prior to addition of Ni(NO₃)₂·6H₂O. The Y₂O₃ support was then added to the Pd-Ni solution for impregnation process at room temperature. The catalysts were dried in oven at 100 °C for 12 h and calcined under air at 800 °C for 4 h. The catalysts synthesized from PdCl₂ are named as Pd(Cl) and those from Pd(NO₃)₂ as Pd(N). The synthesized Pd-Ni catalysts are named as xPd-yNi, with the Pd/Ni ratio as x/y. For example, 1Pd(Cl)-1Ni stands for the Pd-Ni catalyst prepared from PdCl₂ with Pd/Ni ratio of 1/1.

2.2. Catalyst characterization

2.2.1. Specific surface area measurement

The specific surface area of each catalyst was measured by adsorption and desorption of N₂ at –196 °C on the Micromeritics ASAP 2020. Prior to the surface area measurement, the catalyst was outgassed at 250 °C for a minimum of 12 h. The specific surface areas of catalyst were determined from the linear portion of BET plot.

2.2.2. FESEM

The morphology of each catalyst before and after catalytic test was visually observed using a field emission scanning electron microscope (FESEM: JEOL JSM-6700F). Prior to the analysis, the sample was coated using Pt-sputtering for 60 s at 20 mA.

2.2.3. TPR measurement

Temperature-programmed reduction (TPR) measurement for the fresh catalyst was performed on ThermoScientific TPDRO System 1100 Series. Prior to the TPR measurement, 0.05 g of catalyst was outgassed in He for 1 h at 350 °C to remove any impurities and then cooled down to room temperature. 5% H₂/N₂ gas was then introduced to the catalyst while the temperature of the furnace was increased at a heating rate of 10 K/min to 900 °C. The reduction degree was calculated with the assumption of hydrogen/metal ratio of 1.

2.2.4. X-ray diffraction

The X-ray diffraction pattern of each catalyst was measured on a Shimadzu XRD-6000 diffractometer using Cu K α radiation. The catalyst was placed on an aluminum slide and scanned from 2 θ of

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