Effect of a second metal (Y, K, Ca, Mn or Cu) addition on the carbon dioxide reforming of methane over nanostructured palladium catalysts

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ABSTRACT

The CO_2 reforming of CH_4 to synthesis gas was investigated over nanostructured Pd/Al_2O_3 catalysts promoted by various additives (K, Ca, Y, Mn and Cu) using a stoichiometric feedstock mixture. In order to understand the effect of the additives on the surface properties and catalytic performance of the catalysts, fresh and spent samples were characterized by a number of techniques, such as N_2 adsorption-desorption isotherms, XRD, CO-chemisorption, H_2-TPR, TPO, Raman and TEM. Additives strongly modified the reduction properties of Pd species and metal surface dispersion. The results showed that the addition of Y or Ca to Pd/Al_2O_3 slightly increased the initial activity expressed as CH_4 and CO_2 conversions, which is attributed to decreased reducibility of Pd species and enhanced Pd dispersion. In contrast, while the addition of K, Mn and Cu similarly reduced the reducibility of Pd species, their surface metal dispersions apparently decreased owing to decoration effect or alloy formation. This leads to lower initial activities for the modified catalysts than Pd/Al_2O_3. On the other hand, stability of catalysts activity during the long-term tests was associated with Pd sintering resistance as well as carbon deposition. The CO_2 reforming of CH_4 was ceased over Pd/Al_2O_3 after around 4.5 h of reaction due to catalyst bed blockage caused by the large amount of carbon deposition. The carbon formation was accelerated by Pd sintering. Among all catalysts, Y-modified Pd/Al_2O_3 showed the best stability with almost no activity loss in 20 h of reaction. This is probably because that the addition of Y to Pd/Al_2O_3 notably suppresses carbon formation and metal sintering and maintains Pd particle size below 10 nm. This particle size is crucial, below which carbon formation can be completely avoided under the present reforming conditions. For catalysts with other additives the catalytic activities decreased to different degrees after long-term tests, due to metal sintering and carbon deposition.

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1. Introduction

Recently reforming of methane with carbon dioxide (also known as dry reforming of methane: $CH_4 + CO_2 \rightarrow 2H_2 + 2CO$, $\Delta H_{298°} = +247$ kJ mol^{-1}) has attracted increasing attention as it consumes two of the most important greenhouse gases to produce synthesis gas (syngas), a mixture of CO and H_2, which is industrially useful for making various value-added liquid hydrocarbons and oxygenates through the well-known Fischer–Tropsch (FT) synthesis process [1,2]. The reforming process is also regarded as the most cost-effective way to obtain H_2 source [3]. Most group VIII metals are more or less active for the reaction [1,2]. However, no successful industrial application in large scale has been reported so far due to

the lack of development of appropriate catalysts. A major drawback of the dry reforming of CH_4 is the requirement of high operation temperature, usually above 800 °C, to achieve high enough conversions of both CH_4 and CO_2 due to the strong endothermic nature of the reaction. Supported Ni and Co catalysts have been extensively investigated for this reaction due to their low cost and availability in large scale. Yet mono-component Ni or Co catalysts require high reaction temperature for high conversion. The harsh reaction conditions usually lead to the sintering of active metal component and the occurrence of a large amount of carbon deposition on the catalyst surface, resulting in catalyst deactivation, reactor blocking and catalyst breakdown [1,2,4,5].

In order to overcome the drawbacks, a promising approach is the addition of various promoters to Ni or Co catalysts to improve their catalytic performance. K, Ca, Mn, Fe, Cu, Y, La and Ce were frequently added to supported Ni or Co catalysts for improving metal dispersion, decreasing carbon deposition and/or enhancing activity stability [6–10]. Nevertheless, catalyst deactivation remains as a serious problem, and a high reaction temperature

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(above 750 °C) is still needed to achieve high conversions of CO_2 and CH_4. Therefore, development of catalysts with good catalytic performance at lower reaction temperature is of great interest for the process.

Depending on supports and promoters, Rh, Pt and Pd catalysts have demonstrated excellent activity, selectivity and stability with strong resistance to carbon deposition for the drying reforming of CH_4 [1,2,11,12]. In particular, Pd-based catalysts with low metal loading are very attractive, because Pd is much less inexpensive than other noble metals such as Pt and Rh. It also has a very strong capability to activate CH_4 as well as excellent activity for CH_4 reforming by CO_2 at lower temperatures [13–16]. Yamaguchi and Iglesia [16] have reported that supported Pd catalyst is most active for the C—H bond activation of CH_4 compared to other Group VIII metal catalysts. The C—H bond activation is suggested as the rate limiting step for CH_4 reforming reaction [1]. SiO_2-supported Pd catalyst was observed to decompose CH_4 to H_2 and carbon deposit at around 250 °C [14]. The catalytic activity of Al_2O_3 and TiO_2-supported Pt group metal catalysts were investigated for CO_2 reforming of CH_4, and Pd and Rh showed close activities at 500 °C [13]. In addition, there are reports in the literature that Al_2O_3-supported Pd catalysts are very active and selective in the range of 400–730 °C for the reforming reaction [15,17]. However, unpromoted Pd catalysts suffered rapid deactivation at elevated reaction temperature (>600 °C) due to serious metal sintering and significant carbon formation during long-term stability test [17]. Supports and promoters have been, therefore, adopted to effectively suppress carbon formation [16–18], as they can effectively activate CO_2 and remove carbon species at the metal/support interface via reaction between produced active oxygen and chemisorbed carbon. On the other hand, exposed small Pd particle size, i.e. high Pd dispersion, could play a key role in obtaining high activity, selectivity and stability for the reforming reaction since CH_4 decomposition is a sensitive reaction on metal surface. It was demonstrated that additives of La and Ce effectively retarded Pd and Pt metal sintering and enhanced the active metal surface for the dry reforming of CH_4 [11,17,19]. And small metal particle size also tends to increase CO_2 activation on support [20]. In addition, nanostructured γ-Al_2O_3-supported Pt catalyst has been shown to be highly stable and active catalyst in CO_2 reforming of CH_4 [21].

We thus envision that low Pd loading catalyst, combined with excellent promoter and industrially available inexpensive support, could be an optimal candidate as effective and efficient catalyst of dry reforming of CH_4. In this study, effect of various additives, i.e. K, Ca, Y, Mn and Cu, on activity, selectivity and stability of nanostructured γ-Al_2O_3-supported 1 wt.% Pd catalyst for dry reforming of CH_4 is investigated at atmospheric pressure. To our best knowledge, these modified Pd catalysts for dry reforming of CH_4 have not been reported in the literature. Additives are expected to modify the surface properties of Pd active component, resulting in different performance of catalysts. Fresh and spent catalysts were characterized thoroughly by BET surface area, chemisorption, H_2-TPR, XRD, TPO, Raman and TEM to obtain insight of both initial activity and stability of catalysts.

2. Experimental

2.1. Catalyst preparation

Commercially available nanostructurd γ-alumina (Alfa Aesar, 1/8 in. pellet) was crushed and sieved to obtain particles of 20–40 mesh sizes. Additive-added Pd catalyst precursors were prepared by equal volume co-impregnation technique in one step using an aqueous solution of Pd and additive nitrates, i.e. $Pd(NO_3)_2 \cdot xH_2O$ (containing 38 wt.% metallic

Pd), KNO_3, $Ca(NO_3)_2 \cdot 4H_2O$, $Y(NO_3)_3 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ (all from Alfa Aesar), to obtain metallic Pd and additive loadings of 1 and 5 wt.%, respectively. After impregnation, the catalyst was kept at room temperature for 12 h, followed by drying at 120 °C for another 12 h and calcining at 500 °C for 3 h in static air. Catalysts are designated as Pd5 M/Al_2O_3 where M = Y, K, Ca, Mn or Cu.

2.2. Catalyst characterization

The surface textural properties of samples were tested at liquid nitrogen temperature using a Micromeritics ASAP-2020 instrument. The samples were degassed at 300 °C for 4 h prior to testing to remove any adsorbed moisture. The specific surface area was determined using the standard Brunauer–Emmett–Teller (BET) method in the pressure interval of 0.03–0.3 $P/P°$, and the pore distribution was calculated using the Barrett–Joyner–Halenda (BJH) method from the adsorption branch of the N_2 isotherm.

X-ray powder diffraction patterns of samples were recorded on a Philips X'Pert diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å) in θ–2θ scan mode, operated at 45 kV and 40 mA. Step size and step scan time are 0.02° and 3 s, respectively. The average crystallite size of metallic Pd was calculated using the Scherrer equation.

The CO chemisorption of samples reduced before reaction was measured using the Micromeritics ASAP-2020 instrument to determine the Pd dispersion and surface metal area. The sample was first degassed at 400 °C for 4 h and then cooled down, weighted and moved to a U-shape measurement tube. Prior to CO chemisorption, the sample was evacuated at 100 °C for 1 h, followed by in situ reducing in hydrogen at 400 °C for 2 h and then evacuating at 100 °C for another hour. Finally, the isotherm of CO chemisorption was measured at 35 °C. The Pd dispersion and surface metal area were calculated assuming the stoichiometry of Pd/H = 1.

The reducibility of sample was performed by a hydrogen temperature-programmed reduction (H_2-TPR) method. Approximately 100 mg of sample was loaded into a quartz tube reactor with a K-type thermocouple contacting the bottom of sample layer. Prior to hydrogen reduction, the sample was purged with UHP nitrogen flow of 30 ml/min for 1 h at room temperature. The H_2-TPR run was carried out by heating the sample in 5% H_2/N_2 atmosphere at a ramp rate of 10 °C/min. The hydrogen consumption was monitored by a QSM200 mass spectrometer (SRS, Inc.).

Carbon species deposited on the catalyst during dry reforming reaction was studied by temperature-programmed oxidation (TPO) method. Approximately 50 mg of sample was loaded into the aforementioned quartz micro-reactor. After purged in a dry air flow (25 ml/min) for 30 min, the sample was heated in same air flow from room temperature to 850 °C at a ramp rate of 10 °C/min. The reaction product, CO_2 ($m/e = 44$), was monitored using the aforementioned mass spectrometer. The amount of carbon deposition was estimated from the obtained CO_2 peak area, which was quantified by using the peak area of known volumes of CO_2.

Raman spectra of spent catalyst was obtained using a LabRAM Raman microscope (HORIBA Jobin Yvon Inc.) with the following operation parameters: a He–Ne laser of 632.8 nm as excitation source, laser intensity of ~2 mW, 10 s acquisition time and a total of 30 accumulation per spectrum. Before sample measurement, Raman spectrum was calibrated using a silicon wafer peak at 520.7 cm^{-1}. All the samples were analyzed under an atmospheric condition without pre-treatment.

TEM images of spent catalysts were obtained on a JEOL 2010 instrument operated at an accelerating voltage of 200 kV. The sample was prepared by dropping and drying the spent catalyst, which was dispersed in anhydrous ethanol by sonication, on holey carbon-coated Cu grids.