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Enhanced methane combustion performance over $NiAl_2O_4$-interface-promoted Pd/γ-Al_2O_3

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ABSTRACT

Poor durability and low Pd utilization efficiency are the main drawbacks of supported Pd catalysts for low-temperature methane combustion. Here, we present a facile way to stabilize the performance of Pd/Al_2O_3 by introducing a spinel $NiAl_2O_4$ interface as a promoter at no cost to the activity. The $NiAl_2O_4$ interface is formed by impregnation of alumina supports in the nickel-containing solution, followed by high-temperature calcination. A series of 0.4 wt.% $Pd/x NiO/\gamma$-Al_2O_3 with NiO loading varying among 0.0, 0.5, 1.0, and 9.0 wt.% is investigated. The formation of a $NiAl_2O_4$ interface promotes the distribution and crystallization of PdO, suppresses PdO particles aggregation and surface OH^- species accumulation during the reaction, and finally leads to the excellent performance of $Pd/0.5NiO/\gamma$-Al_2O_3. $Pd/0.5NiO/\gamma$-Al_2O_3 demonstrates higher Pd utilization efficiency than the state-of-the-art Pd-based catalysts and better stability than Pd/Al_2O_3. Such a spinel interface promotion strategy may bring new insight into the design of highly efficient Pd-based catalysts and their potential technological applications.

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1. Introduction

Catalytic combustion of methane at a low temperature (typically below 873 K) has been a topic of interest for decades [1–3]. Its main applications include the ignition of gas turbine combustors and the abatement of methane from internal combustion engines/natural gas-powered vehicles for emission control [2,3]. For gas turbine combustors, the inlet temperature of the honeycomb catalyst layer is determined by the lightoff characteristics of the catalyst. Since the preburner with flame to heat up a catalyst releases NO_x in the exhaust, the lowering of the ignition temperature is required for this high-temperature application [1]. For the elimination/control of methane emission from natural gas vehicles/power plants and the petroleum industry, one of the obstacles is the requirement for an efficient catalyst at a low temperature, typically less than 500–550 °C [2] and at best less than 300 °C [1]. As more stringent methane emission regulations are expected or now in force in many countries, there is renewed interest in this topic [4–11].

Supported Pd catalysts have been widely accepted among the most active materials in the total oxidation of methane under CH_4-lean conditions [2–8]. The performance of a Pd catalyst is related to the nature of the support through the dispersion of Pd and Pd–support interaction. In practice, alumina is adopted as a support in order to maintain favorable dispersion of active metal and thereby achieve valid utilization of precious metal [8,12]. Although the Pd/Al_2O_3 catalyst has been demonstrated to be active at temperatures above 400 °C, maintaining low-temperature Pd stability and improving Pd utilization efficiency due to the high cost of precious metals remain a challenging subject of continuous research effort [12–17]. The addition of various promoters, such as CeO_2 [4,17], NiO [6,12,13,18–20], CoO [12,20,21], ZrO_2 [16], FeO_x [12,20], MnO_x [12,15], and Pt [8,22–24], has been widely accepted as a promising way to increase the activity and stability of Pd/Al_2O_3. Among these, the addition of Pt into PdO/Al_2O_3 catalyst was found to be effective not only in improving the catalytic activity, but also in preventing the catalyst's deactivation in methane catalytic combustion [8,22–24]. However, the high loading and cost of precious metals have driven the search of non-noble additives. Gorte and co-workers reported using encapsulated PdO in a CeO_2 matrix to design a core–shell type catalyst, $1\%Pd@9\%CeO_2/Al_2O_3$, for lean CH_4 combustion; excellent low-temperature activity with complete CH_4 conversion around 400 °C and good stability under thermal conditions were obtained [4]. However, the follow-

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ing study of this group showed that this hierarchically structured catalyst exhibited more severe deactivation in the presence of water than the conventional impregnated catalyst [17], and the choice of Pd@ZrO_2/Si–Al_2O_3 was proposed [16].

Promotion by nickel oxide has also received particular attention because of improved Pd catalyst stability in methane combustion. The enhancement is ascribed to the Pd-dispersion-stabilizing effect of $NiAl_2O_4$ spinel [18–20], and the least lattice mismatch between the supported Pd nanoparticles and spinel of nickel has been shown to be responsible for the enhanced nanoparticle stability toward sintering [18]. However, some observations claim the opposite effect of the formation of $NiAl_2O_4$ spinel on activity because of the lowered surface area of the alumina support [12,18,19]. Thus, the Ni content in the alumina support must be extremely high to achieve a notable improvement in the Pd activity [12,13,18]. For example, in the work of Widjaja et al. [12], the addition of 36:1 NiO to the alumina support was required to obtain an optimum CH_4 oxidation performance. The large amounts of the second metal not only bring complexity to the large-scale support production and increase the price of the material [6], but also deteriorate the advantages of the alumina support, i.e., high surface area and good thermal stability [19]. Several attempts have been made to directly decorate the Pd particles by the formation of Pd–Ni bimetallic catalysts [6,22]. However, this approach usually requires careful nanoparticle structure control to yield catalytic performance improvement [6].

To profit from the textural properties of alumina and the stabilizing effect of $NiAl_2O_4$ spinel as a support for Pd catalysts, in this work, we present a facile way to stabilize the performance of Pd/Al_2O_3 for lean CH_4 catalytic combustion by introducing spinel $NiAl_2O_4$ interface as a promoter at no cost to the activity and morphology degradation of the support. A series of Pd/xNiO/γ-Al_2O_3 with NiO loadings varying from 0.5 to 9.0 wt.% is investigated. Pd/0.5NiO/γ-Al_2O_3 with a low Pd loading of 0.4 wt.% demonstrates higher Pd utilization efficiency than state-of-the-art Pd-based catalysts, with a >99% initial CH_4 conversion and a remaining >94% conversion after reaction for 50 h at 400 °C. The relation between the catalytic activity and the effect of NiO additives and spinel $NiAl_2O_4$ interface formation is discussed. Against the background of this study, the cost efficiency, high activity, and good stability of the minor nickel-promoted Pd/xNiO/γ-Al_2O_3 catalysts make them of potential interest for the ignition of a natural gas combustor and low-temperature CH_4 exhaust treatment.

2. Experimental

2.1. Preparation of catalysts

The support used in this work was obtained by calcining commercial γ-Al_2O_3 (Sinopharm Chemical Reagent Co., China) in air at 900 °C for 6 h. Nickel oxide was introduced into the γ-Al_2O_3 support by the incipient wetness impregnation method, with the support impregnated in an aqueous solution containing the requisite amount of $Ni(NO_3)_2 \cdot 6H_2O$ (98.0%, Tianjin Damao Chemical Reagent Factory, China) for 1 h under ultrasonication. Three different nickel oxide loadings, 0.5, 1.0, and 9.0 wt.%, were adopted. The as-impregnated samples were dried at 100 °C overnight and then calcined at 800 °C for 6 h in air with a heating rate of 10 °C/min. Pd catalysts were prepared over xNiO/Al_2O_3 by the wetness impregnation method, using $Pd(NO_3)_2 \cdot 2H_2O$ (Pd $\geqslant$ 39.0%, Aladdin, China) as the starting material in order to get 0.4 wt.% of palladium. The as-prepared catalysts were dried at 100 °C overnight and then calcined at 600 °C for 6 h in air with a heating rate of 10 °C/min before characterization and reaction testing. As references, 0.4 wt.% Pd/Al_2O_3 and 0.5 wt.% NiO/Al_2O_3 were prepared following the same procedure mentioned above. For simplicity, the samples were designated according to the nickel oxide loading. For example, Pd/0.5NiO/Al_2O_3 represents the catalyst with 0.5 wt.% of NiO and 0.4 wt.% Pd supported on γ-Al_2O_3. The final concentration of Ni and Pd in the samples was confirmed by inductively coupled plasma (ICP, IRIS (HR)) element analysis.

2.2. Characterization

Transmission electron microscopy (TEM, FEI Tecnai G2 Spirit) was used for the observation of supported palladium particles and their size distribution. High-angle annular dark-field (HAADF) imaging in the scanning transmission electron microscopy (STEM) mode was performed on the same electron microscope tilting the sample about a single axis using a Fischione ultra-narrow gap tomography holder. The phase purity and crystal structure of the catalysts were examined by X-ray diffraction (XRD, D-MAX 2200 VPC) using monochromatic CuKα radiation. X-ray photoelectron spectra (XPS) were recorded on an ESCALAB 250 spectrometer (Thermo Fisher Scientific, AlKα, $h\nu$ = 1486.6 eV, h refers to Planck's constant and ν refers to frequency of the incident wave) under a vacuum of $\sim 2 \times 10^{-7}$ Pa. Charging effects were corrected by adjusting the main C1s peak to a position of 284.8 eV. Smoothing, background removal, and peak fitting were carried out with a least-squares fitting program (Peak FIT, Sea Solve Software). The Brunauer–Emmett–Teller (BET) surface area, pore volume, and pore size distribution of the samples were measured with a Micromeritics ASAP 2020 instrument using adsorption of N_2 at 77 K. Prior to adsorption analyses, the catalysts were degassed in a flowing N_2 at 300 °C for 3 h. CO chemisorption measurements were performed at 193 K by a dynamic pulse method on samples prereduced in H_2 at 393 K. A CO/Pd average stoichiometry of unity was assumed to calculate the Pd dispersion. Temperature-programmed desorption of oxygen (O_2 TPD) was performed in a fixed-bed apparatus. The sample was first calcined in a 50 ml/min oxygen stream at 500 °C for 1 h and then cooled to 100 °C with a heating/cooling rate of 10 °C/min. A flow of He (purity 99.999%) was then introduced to purge away the adsorbed oxygen at 100 °C for 1 h, and the oxygen desorbed from the oxidized samples upon heating from 100 to 950 °C at a rate of 10 °C/min. The effluent species were monitored by mass spectrometry (MS, Hidden HPR 20). The O_2 signal was measured at $m/e = 32$. Raman spectra were recorded on a laser micro-Raman spectrometer (Renishaw In VIA). An Ar-laser excitation source at 514.5 nm with a power of 20 mW was used. The resolution was 1 cm^{-1}. In situ DRIFTS analyses were carried out with an EQVINOX-55 FFT instrument (Bruker) equipped with a diffuse reflectance accessory and an MCT detector. During each analysis, a finely ground sample (ca. 10 mg) was placed in a ceramic crucible within the in situ chamber. First, the sample was cleaned with 100 mL/min He at 120 °C for 1 h. The total reaction gas flow rate was 100 mL/min with a composition of CH_4:O_2:N_2 = 1:20:79. The spectra under reaction conditions were recorded after 64 scans with a resolution of 4 cm^{-1}.

2.3. Activity test

The catalytic oxidation of methane was performed using a continuous-flow quartz fixed-bed reactor (i.d. 7 mm) under atmospheric pressure. Approximately 200 mg catalyst with particle size 177–250 μm was packed to make up a 0.8-cm-long (0.31 cm^3 volume) catalyst bed. Experiments were performed at GHSV (gas hourly space velocity) of 30,000 (or 60,000 and 120,000 for the effect of GHSV study) ml h^{-1} g^{-1}. The feed concentration of CH_4 was 1.0 vol.% in the synthetic air. The temperature was raised by steps of 25 or 50 °C from 150 to 400 °C and then cooled by steps of 25 or 50 °C from 400 to 150 °C to obtain curves of methane con-

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