



Deactivation behavior of Pd-based SBA-15 mesoporous silica catalysts for the catalytic combustion of methane

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ABSTRACT

A series of Pd/SBA-15 and Pd/5% Ce_{1-x}Zr_xO₂/SBA-15 ($x = 0-1$) catalysts with Pd content ranging from 0.05% to 1% were prepared. The activity and stability of the catalysts for the combustion of methane were evaluated. The catalysts were characterized by X-ray diffraction (XRD), N₂ adsorption-desorption, CO chemisorption, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and temperature-programmed reduction (TPR). Deactivation behavior of the catalysts for the catalytic combustion of methane was investigated. The results show that all of the catalysts retained the SBA-15 mesoporous structure, with PdO and Ce_{1-x}Zr_xO₂ being confined in the channels. It is proposed that deactivation of the catalysts is associated with accumulation of Pd⁰, which cannot be efficiently reoxidized to PdO or PdO₂, due to the limited oxygen-transfer ability of the catalysts. The incorporation of the ZrO₂ as a promoter leads to an increase in the oxygen storage capacity and oxygen mobility of the catalysts, which in turn increases the rate of oxidation of Pd⁰ and mitigates deactivation of the catalyst.

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1. Introduction

Catalytic combustion of methane has been found to be more environmentally friendly than conventional flame combustion due to lower emissions of NO_x, CO, and unburned hydrocarbons as well as higher energy efficiency, and thus it has attracted increasing attention in recent years [1,2]. In addition, catalytic combustion of lean methane gas to abate methane emission from natural gas combustion devices or engines also has wide-ranging applications [2]. Supported palladium catalysts have been shown to have excellent activity toward methane oxidation, and PdO is generally considered the active species [3–5]. Of the different supports used for palladium, alumina has been reported to give the most active catalysts for methane combustion and has been studied extensively [1,2,6]; however, its poor durability hinders the development of viable catalytic combustors [2]. Various reasons have been suggested for the rapid deactivation of such Pd/Al₂O₃ catalysts; for example, it has been reported that deactivation results mainly from the sintering of γ -alumina [7] and the transformation of PdO \rightarrow Pd [8], whereas Ozawa et al. [9,10] concluded that PdO/Al₂O₃ catalysts are rapidly deactivated due to the transformation of PdO to metallic Pd and more slowly deactivated due to the growth of PdO particles. Euzen et al. [11] have suggested that the deactivation of PdO/Al₂O₃ catalysts is due mainly to the transformation of PdO \rightarrow Pd. Based on the general consensus in the literature, it

can be concluded that catalyst stability can be increased by increasing the stability of the support, retarding the transformation of PdO \rightarrow Pd, and suppressing the growth of PdO particles.

It is well known that ceria is an effective promoter for noble metal-based combustion catalysts, especially Pd/Al₂O₃ catalysts, and that ceria acts both as a phase-stabilizer for γ -alumina and to increase the dispersion and stability of the active form of the metal by means of a strong metal-support interaction [12,13]. But at high reaction temperatures, ceria is readily sintered, resulting in deactivation of the catalyst. It has been reported that formation of a solid solution by adding ZrO₂ to ceria leads to improved oxygen storage capacity (OSC), redox properties, and thermal resistance and to better catalytic activity at lower temperatures. Consequently, CeO₂-ZrO₂ solid solutions are widely used in three-way catalysts for treating automobile exhaust gas [14,15]. Although ZrO₂-based supports are stable at high temperature, they have the drawbacks of high cost and relatively low surface area [16,17]. Recently, mesoporous silica SBA-15 [18,19], which has a highly ordered hexagonal structure with high surface area (600–1000 m² g⁻¹), adjustable pore sizes of 4.6–30 nm, and wall thickness of 3.1–6.4 nm, has attracted wide attention as a new material for catalysts and catalyst supports. Pd-based catalysts supported on SBA-15 have been reported to exhibit excellent activity both for the catalytic combustion of methane [20,21] and for Heck reactions [22,23], which has been attributed to the high dispersion of Pd within the channels of SBA-15. The influence of solvents on the formation of metal and its oxide nanoparticles in SBA-15 also has been investigated [24].

Before these catalysts can be considered for actual practical applications, their long-term stability must be evaluated. No such

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study has been reported to date, however. In the present work, a series of catalysts with varying Pd content, based on SBA-15 as the support and $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ as the promoter, were prepared by the impregnation method, and their catalytic activity and stability during lean-methane combustion were investigated. The main goal was to explore the deactivation behavior of the catalysts for the complete oxidation of methane at low temperature.

2. Experimental

2.1. Catalyst preparation

SBA-15 was prepared as described previously [18]. In brief, 4 g of triblock poly (ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, $M = 5800$) was added to a mixture of 90 ml of deionized H_2O and 60 g of HCl (4 M), and stirred at 40°C for 2 h. Then 8.5 g of tetraethyl orthosilicate (TEOS) was slowly added, and the mixture was stirred for another 22 h. The gel mixture was transferred to Teflon bottles and aged at 100°C for 24 h under static conditions. After aging, the resulting solid was filtered, washed with deionized water until neutral, dried at room temperature, and finally calcined in flowing air at 500°C for 6 h to remove the organic template.

The Pd/SBA-15 samples were prepared by the impregnation method using an aqueous solution of $\text{Pd}(\text{NO}_3)_2$. The 5% $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ /SBA-15 ($x = 0$ –1) samples were prepared by coimpregnation of pure SBA-15 with a mixed aqueous solution of Ce and Zr nitrates. The Pd/5% $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ /SBA-15 samples were prepared by subsequent impregnation of these materials with an aqueous solution of $\text{Pd}(\text{NO}_3)_2$. The Pd content was varied from 0.1 to 1 wt%. All catalyst samples were dried at room temperature and then calcined in air at 500°C for 4 h.

2.2. Characterization

XRD patterns were obtained on a Rigaku D/Max 2500 VB2+ /PC diffractometer using $\text{CuK}\alpha$ radiation with the following operating parameters: 200 mA, 40 kV, 2θ scanning from 10° to 90° for wide-angle XRD and 50 mA, 40 kV, 2θ scanning from 0.7° to 5° for low-angle XRD. N_2 sorption isotherms were obtained at liquid nitrogen temperature using a Thermo Electron Sorptomatic 1990 instrument. Before each analysis, the sample was degassed for 5 h at 250°C under vacuum. BET and BJH analysis were used to determine the surface area and pore size distribution, respectively, of the samples. TEM images were obtained using a JEM2010 microscope operated at 200 kV. XPS experiments were carried out on an Thermo Electron Escalab250 instrument using $\text{AlK}\alpha$ as the exciting radiation at a constant pass energy of 50 eV. Binding energies were calibrated using the carbon present as a contaminant ($\text{C1s} = 285.0$ eV). The surface atomic compositions of all samples were calculated from photoelectron peak areas for each element after correction for instrument parameters.

The TPR experiments were performed using a Thermo Electron TPD/R/O 1100 series catalytic surface analyzer equipped with a thermal conductivity detector. The samples were heated under N_2 to 400°C at a rate of $20^\circ\text{C}/\text{min}$, then cooled in flowing N_2 to room temperature, and finally reduced with 5 vol% H_2/N_2 mixtures by heating to 900°C at a rate of $20^\circ\text{C}/\text{min}$. Water produced by sample reduction was condensed in a cold trap before reaching the detector. Only H_2 was detected in the outlet gas, confirming the effectiveness of the cold trap.

Pd dispersion, Pd surface area, and Pd crystallite size were evaluated by pulse chemisorption measurements with a Thermo Electron TPD/R/O 1100 series catalytic surface analyzer at 25°C using CO as probe molecules. Before the chemisorption measurements, the catalyst samples were treated at 500°C in a hydrogen flow

for 2 h. A CO/Pd ratio of 1 was assumed for the Pd dispersion calculation.

2.3. Catalytic activity and stability

Catalytic activity evaluation and stability tests were carried out in a quartz microreactor (8 mm i.d., 300 mm long) at atmospheric pressure under steady-state conditions. The catalysts were pressed into tablets and then crushed and sieved to 60–80 mesh. A 0.1-g catalyst sample was loaded into the reactor for each run. A gas mixture of 2 vol% CH_4 in air with a gas hourly space velocity (GHSV) of $6000\text{ ml g}^{-1}\text{ h}^{-1}$ was used to choose the catalysts to study for deactivation behavior and to carry out stability tests. A series of preliminary experiments was carried out to check for the lack of mass- and heat-transfer limitations. On testing two different catalyst loadings of 0.1 and 0.2 g and seven different GHSVs from 6000 to $72,000\text{ ml g}^{-1}\text{ h}^{-1}$, the influence of external mass transfer was found to be negligible at a GHSV $> 36,000\text{ ml g}^{-1}\text{ h}^{-1}$. Internal mass and heat transfer limitations also were ruled based on the results of experiments with four different particle sizes (20–40, 40–60, 60–80, and 80–100 mesh) and two different temperatures (400 and 450°C), as shown in Fig. S1 in the supplementary material. Thus, the intrinsic activity and activation energy of the catalysts can be obtained under our experimental conditions with particle sizes of 60–80 mesh and GHSV of $72,000\text{ ml g}^{-1}\text{ h}^{-1}$. The outlet products were measured by a gas chromatograph with a thermal conductivity detector (Beijing East and West Electronics Institute, GC-4000A). The reaction temperature was controlled with a K-type thermocouple placed in the vicinity of the catalytic bed. In every case, carbon dioxide and water were the only reaction products detected throughout the entire experiment. The stability tests for all samples were carried out at 450°C . To confirm the repeatability of the data, the repeat runs were implemented for the study of intrinsic activity. Tests were considered valid when carbon balance was between 95% and 105%. The turnover frequency (TOF), defined as the number of reactant molecules converted to products per surface metal atom, was calculated based on the data from pulse chemisorption measurements using CO.

3. Results

3.1. Catalyst activity

The effect of Pd loading content on the observed activities of the Pd/SBA-15 catalysts was studied. The results of observed activity evaluation for Pd/SBA-15 catalysts are shown in Fig. S2 in the supplementary material. These are the temperatures at which conversion of 10%, 50%, and 90%, respectively, were obtained. The values of T_{10} , T_{50} , and T_{90} are listed in Table 1. The results of physicochemical properties and CO chemisorption measurements of the samples are listed in Table 2. It is shown that for the Pd/SBA-15, the observed activity of the catalyst increased substantially with an increase in Pd content from 0.05% to 0.5%, with a more modest increase with further increasing Pd content up to 1%. The TOF of the 0.5% Pd/SBA-15 catalyst was $13.2 \times 10^{-3}\text{ s}^{-1}$ at 450°C , as reported in Table 2.

Because the catalyst exhibited only a marginal increase in observed activity when the Pd content was increased from 0.5% to 1%, the catalysts with a Pd loading of 0.5% were used to study the effect of CeO_2 , ZrO_2 , and Ce–Zr mixed oxides as promoters of catalyst performance. Fig. S3 in the supplementary material shows the observed activities of the 0.5% Pd/ $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ /SBA-15 ($x = 0, 0.5, 1$) catalysts with different $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ contents. It can be seen that when CeO_2 , $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$, or ZrO_2 was used as a promoter, the catalyst had a maximum observed activity at a promoter loading of 5%. The TOF of the 0.5% Pd/ $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ /SBA-15 ($x = 0, 0.5, 1$) catalyst

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