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Co₃O₄/HZSM-5 catalysts for methane combustion: The effect of preparation methodologies

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ABSTRACT

A series of Co₃O₄/HZSM-5 catalysts with different Co₃O₄ loadings were prepared by incipient wetness impregnation followed by thermal calcination or dielectric barrier discharge (DBD) plasma decomposition. Their catalytic performances for the complete combustion of methane were evaluated from 300 to 700 °C. The plasma decomposed samples exhibit much higher catalytic activity than the calcined ones. Among all the samples tested, the plasma decomposed catalyst with 20 wt.% loading of Co₃O₄ possesses the highest catalytic activity with T₁₀ (10% CH₄ conversion) at 300 °C and T₁₀₀ (complete conversion) at 550 °C. The excellent catalytic activity of the DBD plasma decomposed samples would attribute to well-dispersed Co₃O₄, enhanced low-temperature reducibility, high content of lattice oxygen and adsorbed oxygen species, as well as the low formation tendency of the intermediate of Co-formate.

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1. Introduction

With the environment-friendly advantages of lower carbon intensity and much lower emission of NO_x, hydrocarbons and CO during combustion, nature gas has been more widely used as fuel in vehicles [1] and others. However, the advantages are partly counteracted by the release of unburned methane, because methane has been recognized to have approximately 25 times higher greenhouse effect than CO₂ [2]. Therefore, abating unburned methane is critical. In consideration of the low temperature (<550 °C) and low CH₄ concentration (about 1000 ppm) of the exhaust [3], catalytic combustion technology is a promising strategy for the complete oxidation of the unburned methane [1–3]. Although supported noble metal catalysts, especially the supported Pt and Pd catalysts, exhibit excellent catalytic performance at low temperatures, their commercial application is limited due to the high cost of the noble metals [4,5]. Transition metal-based catalysts are increasingly attractive to be substitutes for methane combustion owing to their much lower cost and relatively abundant resources [1,4–6]. Cobalt oxide (Co₃O₄) has been considered to be one of the best candidate for methane combustion among all the transition metal oxides [1,4,6–8]. However, sintering during methane combustion

is a noticeable problem for Co₃O₄, which drastically decreases its catalytic performance for methane combustion. In order to deter the sintering of Co₃O₄, many efforts have been made by distributing Co₃O₄ on various supports, such as SiO₂, ZrO₂, MgO, TiO₂, Al₂O₃ and zeolites [8–11]. The research results showed that properties of Co₃O₄, like surface area, stability, reducibility and subsequent reactivity, can be improved after its deposition on the support. Different support has different pore structure, thermal stability, surface area and acidity, which cause different effect on the catalytic activity of Co₃O₄. However, some could have negative effects. For example, in the case of Al₂O₃ supported Co₃O₄ catalysts, the interaction between Co₃O₄ particles and Al₂O₃ support is strong because of the formation of the Co–O–Al linkage, resulting in a decline in the reducibility and activity of the catalysts [12]. Therefore, an appropriate metal oxide support to deposit Co₃O₄ for catalytic combustion of CH₄ is important. ZSM-5 zeolite has been widely used as catalyst or support as well as the hydrocarbon trap for reducing cold-start emissions of engines, owing to its high thermal stability, large specific surface area, high acidity, and well-defined pore structure [13–16]. ZSM-5 zeolite should be a promising support for Co₃O₄ catalyst for complete catalytic combustion of unburned methane from engines of natural gas vehicles and others. In addition, ZSM-5 zeolite can also be the trap of unburned methane when the emission temperature is below the light-off temperature of supported Co₃O₄ catalysts, which is also in favor of abating unburned methane in the exhaust. However, to the best of the authors' knowl-

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edge, there is still no reported work on ZSM-5 zeolite supported Co_3O_4 catalysts for the catalytic combustion of methane.

It is well known that the preparation methods have great influences on the structural and textural properties of catalysts, such as specific surface area, the dispersion of active species and the strength of interaction between active component and support. These properties in turn determine the performance of catalysts [1]. The conventional incipient wetness impregnation (IWI) method is commonly used for the synthesis of heterogeneous catalysts. However, for the supported Co_3O_4 catalysts, prepared with this IWI method, the active component, Co_3O_4 , cannot be well dispersed on the support surface, especially when the Co_3O_4 loading is relatively high [1,11]. Recently, the IWI method, combining with combustion synthesis as a two-stage process, has been employed by An et al. [1] and Zavyalova et al. [8] to prepare $\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ catalysts. They found that the catalysts had higher Co_3O_4 dispersion, relatively lower Co_3O_4 crystallization, greater oxygen non-stoichiometry, higher $\text{Co}^{3+}/(\text{Co}^{2+} + \text{Co}^{3+})$ ratios, and easily reducible surface Co^{3+} , compared with the ones prepared by the conventional IWI method.

On the other hand, the decomposition of catalyst precursor is a basic operation step for catalyst preparation. The decomposition is normally conducted thermally. Recently, the decomposition using dielectric barrier discharge (DBD) plasma attracts more and more attentions [17]. DBD is a conventional cold plasma phenomenon. It is normally applied for ozone generation, gas treatment, glass surface modification, plastic treatment and UV lighting. The characteristic of the DBD setup is the use of the dielectric layer on the electrode. DBD can be initiated at room temperature. Under the influence of DBD, the decomposition of catalyst precursor can be carried out more quickly *via* the reactions between the precursor and the energetic plasma species (like electron, excited species and others). Smaller catalyst particle size can be achieved with different crystal structure, compared with the catalyst prepared by the thermal treatment [17–23]. However, to our knowledge, the DBD plasma decomposition has not been employed to decompose the precursor of ZSM-5 supported Co_3O_4 catalysts.

Herein, we report $\text{Co}_3\text{O}_4/\text{HZSM-5}$ catalysts prepared by IWI method followed by DBD plasma decomposition. The obtained catalysts possess much higher catalytic activity for methane complete combustion compared with the ones synthesized by IWI method followed by thermal calcination.

2. Experimental

2.1. Catalyst preparation

HZSM-5 zeolite powder (Si/Al molar ratio: 25, BET surface area: $350.2\text{ m}^2\text{ g}^{-1}$) was obtained from the Catalyst Plant of Nankai University (Tianjin, China). The supported catalysts with 10 wt.%, 20 wt.%, and 30 wt.% of nominal Co_3O_4 loading were prepared by an incipient wetness impregnation using cobaltous nitrate hexahydrate (>99%, Kemiou Chemical Reagent Co., Ltd., Tianjin, China). After impregnation, the samples were placed at room temperature for 12 h, and then dried at 70°C for another 12 h. The as-prepared samples were denoted as x-F, where x = 10, 20 and 30, respectively, based on their nominal Co_3O_4 loadings, 10 wt.%, 20 wt.% and 30 wt.%. Subsequently, all the three dried samples were separated into two parts. One part was calcined at 700°C for 4 h in a furnace. The other part was decomposed by DBD plasma. The three calcined samples were designated as x-C, and the three plasma treated ones were denoted as x-P.

The DBD plasma decomposition has been described in detail elsewhere [20–23]. Briefly, a chamber was constructed by two pieces of quartz plate with thickness and diameter of 2 mm and 90 mm, respectively, as upper and lower surfaces. A quartz ring

with height, thickness and internal diameter of 8 mm, 2 mm and 50 mm was respectively placed between the two quartz plates as the wall of the chamber. The chamber was fixed by two steel plate electrodes through squeezing the two quartz plates during the plasma decomposition process. The voltage used to generate plasma during the decomposition was supplied by a CTP-2000K voltage generator (Corona Laboratory, Nanjing, China). The average voltage applied was 14 kV, with a sinusoidal waveform at a frequency of about 22 kHz. The average power was 179 W. Air was directly used as the medium gas of the plasma generation.

2.2. Catalyst characterization

Thermal-gravimetric analysis (TGA) for the samples was carried out with a Netzsch STA 449 F3 system with a heating rate of $10^\circ\text{C min}^{-1}$ in flowing air ($25\text{ cm}^3\text{ min}^{-1}$) from 35°C to 1000°C .

The specific surface areas of the samples were measured on a Nova Automated Gas Sorption System (Quantachrome Corporation, USA) by N_2 adsorption at -196°C . Before the measurement, the samples were degassed at 200°C for 4 h. BET method was used to calculate the specific surface areas. Horvath–Kawazoe (HK) method was employed to determine the micro-pore size distributions.

Fourier transform infrared (FT-IR) absorption spectra in transmission mode were collected at room temperature using a Nicolet 6700 spectrometer (Thermo-Nicolet) with 64 scans at a resolution of 4 cm^{-1} .

Powder X-ray diffraction (XRD) patterns of the samples were collected on a Rigaku D/MAX-2500 V/PC diffractometer equipped with a Ni-filtered $\text{Cu K}\alpha$ radiation source ($\lambda = 1.54056\text{ \AA}$). The scanning range and speed are $10^\circ < 2\theta < 90^\circ$ and 4° min^{-1} , respectively. Phase identification was performed by comparison with the X-ray spectrum cards from the Joint Committee on Powder Diffraction Standards (JCPDSs).

Transmission electron microscopy (TEM) images were recorded on a TEM Philips Tecnai G2F20 instrument operated at 200 kV. Prior to measurement, the sample was ultrasonic dispersed in pure ethanol for 30 min followed by deposition on a copper grid, and then the suspension was dried under air.

Hydrogen temperature-programmed reduction (H_2 -TPR) study was conducted by using a TPDRO 1100 apparatus (Thermo Finnigan, LLC) equipped with a thermal conductivity detector (TCD). About 50 mg of the sample was pretreated in N_2 ($30\text{ cm}^3\text{ min}^{-1}$) at 50°C for 1 h. The pretreated sample was then reduced in 5 vol.% H_2/N_2 at the flow rate of $30\text{ cm}^3\text{ min}^{-1}$ by ramping from 50 to 800°C at $10^\circ\text{C min}^{-1}$.

X-ray photoelectron spectroscopy (XPS) analyses were performed on a Perkin-Elmer PHI-1600 spectrometer using monochromatic $\text{Mg K}\alpha$ (1253.6 eV) as radiation source. The carbonaceous C1s line (284.6 eV) was used as reference for the calibration of binding energies (BEs).

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments for methane combustion were carried out on a Tensor 27 spectrometer (Bruker) equipped with a liquid N_2 cooled MCT detector and a high temperature reaction chamber (Praying Mantis, Harrick). DRIFT spectra were collected by accumulating 64 scans at 4 cm^{-1} resolutions. All gases, 3.98 vol.% $\text{CH}_4/\text{helium}$, 3 vol.% O_2/helium , and ultrahigh purity helium were purchased from Air Liquide. Prior to each test, approximately 100 mg sample was loaded in a sample cup and was held at 300°C under flowing Ar at $30\text{ cm}^3\text{ min}^{-1}$ for 1 h followed by collecting an appropriate background. After that, methane adsorption was carried out in 3.98 vol.% CH_4/He at a rate of $3\text{ cm}^3\text{ min}^{-1}$ for 15 min. Sample was then exposed to 3 vol.% O_2/He ($30\text{ cm}^3\text{ min}^{-1}$) for 30 min. All the background-subtracted spectra were expressed as Kubelka-Munk units.

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