



Morphology-dependent performance of Co_3O_4 via facile and controllable synthesis for methane combustion

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ABSTRACT

Spinel type cobalt oxide (Co_3O_4) nanocrystals were controllably synthesized with different morphologies (cubical, hexagonal and flower-like) via a facile hydrothermal method. The properties of the nanostructured Co_3O_4 were characterized by XRD, SEM, TEM, HRTEM and XPS techniques. The performance of the catalysts in methane combustion was evaluated under lean methane atmosphere. Superior catalytic activities for methane combustion were observed over these oxides. The performances seemed to depend on their morphologies. The catalytic activities of flower-like Co_3O_4 and hexagonal plate-like Co_3O_4 were comparable to those of noble metal catalysts due to the preferred exposure of more active $\{111\}$ crystal plane. In case of cubical Co_3O_4 the $\{001\}$ plane is the dominantly exposed crystal plane. The results may provide significant insights for the development of nanostructured metal oxide catalysts for the catalytic combustion of methane.

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1. Introduction

The known reserves of natural gas have doubled in the last decade due to the increased usage of shale gas, coal bed methane, and low-permeability gas found in sandstones (tight gas). It is promising to substitute the petroleum-based transportation fuel for methane. Compared to gasoline and diesel vehicles, natural gas vehicles (NGVs) are more environmentally friendly. However, unburned methane exhausted from NGVs has more significant greenhouse effect. The global warming potential of methane is 21 times greater than that of carbon dioxide. Lean methane is vented directly to the atmosphere during coal mining due to the lack of proven technologies. Hence there is a potential emission reduction if methane emitted can be converted to CO_2 . However, methane is difficult to be oxidized due to the strongest C–H bond among hydrocarbons. The catalytic oxidation of methane has also been used as a probe reaction to evaluate the performance of combustion catalysts. So the studies on methane combustion catalyst can contribute to promote the development of the relevant technologies. Supported noble metals such as Pd and Pt have been widely studied in catalytic oxidation due to their superior perfor-

mance [1,2]. However, the use of noble metals is limited to some extent in commercial applications because of their high cost and inferior anti-sintering. It is crucial to develop cost-effective and active substitute catalysts. Transition and rare-earth metal oxide catalysts have appealed considerable attention owing to their relatively high catalytic activity and low cost [3–5]. Among these metal oxides, cobalt oxide is known as the most active catalyst for CO oxidation due to its weak oxygen bond strength and high turnover frequency for redox reaction [6]. Studies have shown that its performance in catalytic combustion is strongly morphology-dependent. Currently, there is an explosive growth on the research on the morphology-dependent nanocatalysis. Nanoparticles exhibit peculiar characteristics due to the presence of numerous exposed corner and edge atoms accessible for catalysis, while the nanocrystals with various morphologies are enclosed by certain index facets. They provide different abilities of electron transfer and amounts of active sites responsible for the catalytic activity and selectivity. For this reason, Co_3O_4 nanocrystals with different morphologies have been synthesized such as sphere [7–9], nanorod [10–13], nanobelt [14], nanocube [13,15,16], nanowire [17], nanoplate [13,18], hollow [19,20], hierarchical [21] and so forth. Studies showed that their catalytic behaviors are strongly dependent on their morphologies and possibly attributed to the electron transfer properties of different Co_3O_4 nanomaterials [13,22,23]. Additionally the $\{110\}$ crystal plane in Co_3O_4 nanorods is more active than the $\{111\}$ one over Co_3O_4 particles for CO oxidation [24,25]. More specifi-

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cally, Co^{3+} is regarded as the active site for CO oxidation, whereas the Co^{2+} is almost inactive [6,26,27]. The {001} and {111} planes contain only Co^{2+} cations, while the Co^{3+} cations are dominant on the {110} plane. Therefore the rod-shaped Co_3O_4 with active sites of Co^{3+} is more active than Co_3O_4 particles containing only Co^{2+} sites for the CO oxidation. Similar results were also found by Li and et al. [14] that the activity in methane combustion was dependent on the Co_3O_4 morphology. Co_3O_4 nanosheets exhibit the highest activity due to the dominant presence of high index crystal plane {112}. The morphology-dependent nanocatalysis was also found over other metal oxides such as CeO_2 [28]. According to the studies, superior catalytic performance can be obtained by tuning the morphology of Co_3O_4 . However, most studies have been focused on the CO catalytic oxidation. Only few pioneering studies have been done to verify the morphology- or plane-dependence in methane combustion over Co_3O_4 nanocrystals, especially under lean fuel atmosphere. Furthermore, the synthesis schemes reported previously for Co_3O_4 nanocrystals are very complicated and require additional organic solubilizing agents [29–32]. In this study a facile and “green” synthesis routine was developed. The Co_3O_4 synthesized with specified morphologies (such as cubical, hexagonal sheet-like, hexagonal plate-like, and flower-like) were evaluated in methane combustion under lean-fuel conditions. Morphology-dependent performance of Co_3O_4 is studied based on the structural and morphological properties determined by BET, XRD, SEM, TEM, HRTEM and XPS characterizations.

2. Experimental section

2.1. Synthesis materials

All the reagents were analytic grade and used as received without further purification: Cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), absolute ethanol, polysorbate20, triethylamine, ethanolamine. All chemical reagents are from Sinopharm Chemical Reagent Beijing Co., Ltd.

2.2. Catalyst synthesis

Flower-like Co_3O_4 ($\text{Co}_3\text{O}_4\text{-F}$) was synthesized by dissolving 20 mmol of cobalt nitrate in 100 mL of deionized water. Then 20 mL of ethanolamine was dissolved in 50 mL of deionized water forming a transparent solution. Two solutions obtained were mixed under vigorous stirring for at least 30 min. Then the suspension was transferred into a Teflon-lined stainless steel autoclave, and aged 28 h at 200 °C. Aged suspension was filtered and washed by deionized water and absolute ethanol several times. The obtained solids were dried under vacuum at 80 °C overnight. The samples were calcined in air at 350 °C for 3 h. For preparation of hexagonal plate-like Co_3O_4 ($\text{Co}_3\text{O}_4\text{-P}$), synthesis conditions were identical to those of $\text{Co}_3\text{O}_4\text{-F}$ with two exceptions. Firstly, the transparent solution consisted of 2.5 mL of triethylamine, 2.25 g of polysorbate20 and 50 mL of deionized water. Secondly, the suspension was aged 24 h at 160 °C. For synthesis of hexagonal sheet-like Co_3O_4 ($\text{Co}_3\text{O}_4\text{-S}$) [33] and cubical Co_3O_4 ($\text{Co}_3\text{O}_4\text{-C}$) [16], synthesis conditions were identical to those of $\text{Co}_3\text{O}_4\text{-P}$ with only some exception. For $\text{Co}_3\text{O}_4\text{-C}$ catalyst, the 20 mmol of cobalt nitrate was dissolved in 100 mL of absolute ethanol and 20 mL of triethylamine was dissolved in 50 mL of absolute ethanol. While for the $\text{Co}_3\text{O}_4\text{-S}$ catalyst, the 20 mmol of cobalt nitrate was dissolved in 50 mL of deionized water and 5 mL of triethylamine was dissolved in 100 mL of absolute ethanol.

2.3. Characterization

BET specific surface areas (S_{BET}) of the catalysts were measured according to the Brunauer-Emmett-Teller (BET) method by

nitrogen adsorption at 77 K using a Quantachrome NOVA2200e instrument. Prior to analysis, the samples were degassed under vacuum at 300 °C for at least 2 h. The pore size distribution and total pore volume were determined from the desorption branch of the isotherms using the Barrett-Joyner-Halenda (BJH) desorption method.

Phase of the samples was identified by Powder X-ray Diffraction (XRD) with a Rigaku RINTD/MAX-2500PC X-ray diffractometer using $\text{Cu K}\alpha$ radiation at 200 mA and 40 kV. The samples were scanned from 20° to 80° with a step size of 0.02°. Phase identification was done using the reference JCPD database.

X-ray photoelectron spectra (XPS) were measured using an ESCALAB 250Xi spectrometer with an aluminum anode for $\text{K}\alpha$ ($h\nu = 1484.6$ eV) radiation. Detailed spectra were recorded for the region of Co 2p, O1s photoelectrons with a 0.1 eV step at a pressure 1×10^{-10} mBar. Analysis was performed by the XPSPEAK41 software, and charging effects were corrected by adjusting binding energy (B.E.) of C1s to 284.5 eV.

CH_4 temperature programmed reduction ($\text{CH}_4\text{-TPSR}$) experiments were performed on a flow system at a Quantachrome CHEMBET3000 adsorption instrument equipped with a TCD detector and a MS detector. The moisture was removed from the TPR effluent stream in a water trap before the TCD and MS detector. During each analysis, the as-prepared catalyst (ca. 20 mg) was placed into a quartz reactor. First, the sample was pretreated in 3% vol. O_2/He mixture (20 mL/min) at 350 °C for 60 min, and cooled to 35 °C. Then the sample was heated up to 900 °C at a ramp rate of 10 °C/min in a flow of 20 mL/min of 10 vol.% CH_4/Ar mixture.

The surface morphologies of sample were observed by an FEI Quanta 200F scanning electron microscopy (SEM) equipped with energy dispersive spectrometry (EDS).

The transmission electron microscopy (TEM) measurement was carried out with an FEI Tecnai G2 Spirit equipment operated at an accelerating voltage of 120 kV. The catalyst powder was ultrasonically dispersed in ethanol and dropped onto a copper grid coated with amorphous carbon film, then dried in air.

The high resolution transmission electron microscopy (HRTEM) measurement was performed with an FEI Tecnai G2 F30 S-Twin equipment at an accelerating voltage of 300 kV. The sample preparation procedure for HRTEM was identical to the one for TEM.

2.4. Catalytic tests

The catalytic performance for CH_4 combustion was tested in a fixed-bed quartz reactor (i.d. 6 mm) packed with 0.2 g catalyst (40–60 mesh). The reaction temperature was controlled by a PID temperature regulator. The dry feed gas containing 0.2 vol.% CH_4 in air was supplied to the catalyst bed through a mass flow controller at a gas hourly space velocity (GHSV) of 110,000 h^{-1} . Additionally the catalytic performance was also evaluated under the proximately real exhaust atmosphere but having higher water content. The feed gas containing 0.4 vol.% CH_4 and 10 vol.% H_2O in air was supplied to the catalyst bed at a GHSV of 80,000 h^{-1} . The compositions of the dry feed gas and the combustion flue gas were analyzed by an on-line infrared gas analyzer from ONUUE Electronics Ltd. The gas compositions were also analyzed by an Agilent 7890 gas chromatograph equipped with FID and TCD detectors.

3. Results and discussion

3.1. X-ray diffraction study

Fig. 1 shows the wide-angle XRD patterns of the precursors of all Co_3O_4 samples. The precursor of $\text{Co}_3\text{O}_4\text{-C}$ showed only the peak of Co_3O_4 *Fd-3m* with lattice constant $a = 0.8050$ Å (JCPDS PDF

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