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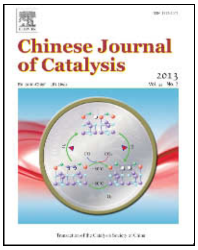

Article

Influence of calcination and pretreatment conditions on the activity of Co_3O_4 for CO oxidation

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ABSTRACT

The influence of calcination and pretreatment conditions on the structure of Co_3O_4 and its activity for CO oxidation were studied. TG analysis indicated that the precursor of Co_3O_4 prepared by a precipitation method was present in the form of cobalt hydroxide carbonate, calcination of which within the temperature range of 150–400 °C in air resulted in the formation of cubic phase Co_3O_4. N_2 adsorption-desorption, powder X-ray diffraction, transmission electron microscopy, and activity test results showed that the prepared Co_3O_4 samples were comprised of nanoparticles, with the specific surface area and size distribution closely related to the calcination temperature. Over these samples, a size dependence of the catalytic activity for CO oxidation was clearly observed. As identified by positron annihilation lifetime spectrum, low temperature oxygen temperature-programmed desorption, and durability testing for CO oxidation, pretreatment of Co_3O_4 in N_2 within the temperature range 150–250 °C favors the formation of surface oxygen vacancy clusters, the occurrence of which would be beneficial for the adsorption and activation of O_2, and also for the catalytic oxidation of CO. Meanwhile, the reconstruction of oxygen vacancies on the surface of Co_3O_4, induced by the pretreatment process, was also discussed.

1. Introduction

Tricobalt tetraoxide (Co_3O_4) has been attracting much attention in heterogeneous catalysis due to its excellent performance in the catalytic oxidation of CO and hydrocarbons [1,2]. Typically, Co_3O_4 has a spinel structure which consists of Co^{3+} cations in octahedral sites and Co^{2+} cations in tetrahedral sites. In this structure, accordingly, there are two kinds of oxygen ion: one is bonded to three Co^{3+} ions, while another is bonded to one Co^{3+} and one Co^{2+} ion as the nearest neighbors [3,4]. It has been demonstrated that the catalytic activity of Co_3O_4 for CO oxidation is closely related to the ratio of Co^{3+}/Co^{2+} on the predominantly exposed planes, and the adsorption and activation of molecular oxygen [1]. With this in mind, there are two strategies to design and synthesize Co_3O_4 with high catalytic performance. Firstly, precise tuning of Co^{3+}/Co^{2+} on the surface of Co_3O_4 was successfully realized using controlled synthesis of nano materials, thus creating desired catalysts with excellent activity. By using a hydrothermal method, recently, Co_3O_4 nanorods preferentially exposing the reactive (110) planes were prepared by Xie et al. [5], on which Co^{3+} cations are solely present. This feature of Co_3O_4 nanorods is favorable for the adsorption of CO and its further reaction with neighboring oxygen to produce CO_2, and finally resulting in complete oxidation of 1% CO even at temperatures as low as –77 °C. Similarly, Hu et al. [6] prepared Co_3O_4 nanobelts and nanocubes by a hydro-

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thermal method. The former had predominant exposure of (011) planes while the latter had a predominance of exposed (001) planes. Such features provide Co^{3+} sites with different activities for CO oxidation. By using KIT-6 as hard template, Ren et al. [7] created crystalline mesoporous Co_3O_4, on which completely oxidation of 1% CO was realized at the temperature of –50 °C after pretreatment in 8% O_2 at 400 °C. Considering the crucial roles of oxygen vacancies in the activation of oxygen and the catalytic oxidation of CO over Co_3O_4 [8,9], on the other hand, substitution of Co with hetero-atoms or pretreatment under suitable conditions has been employed to create cobalt oxide-based catalysts with high efficiency. Cerium-substituted Co_3O_4 catalysts were prepared by Luo et al. [10], among which a sample with Co/(Co + Ce) atomic ratio of 0.3 gave the largest amount of oxygen vacancies, and exhibited the highest activity for low temperature CO oxidation. Lou et al. [11] also found that doping of Co_3O_4 with Bi_2O_3 promoted the formation of oxygen vacancies, accelerating the adsorption and activation of oxygen, thus enhancing its performance in CO oxidation. Indeed, 20% Bi_2O_3-Co_3O_4 could completely oxidize CO (1%) even at a temperature of –89 °C. Over this catalyst, meanwhile, complete CO conversion was maintained at –75 °C for 600 min. By using $Co(NO_3)_2$ as a precursor of cobalt and $(NH_4)_2CO_3$ serving as a precipitant, Co_3O_4 catalysts were prepared by Wang et al. [12]. Over these samples, the O_2^- and O^- species were responsible for low temperature CO oxidation, which was confirmed by activity testing and oxygen temperature-programmed desorption (O_2-TPD) analysis. As suggested by Sadykov and co-workers [9], the surface reconstruction of Co_3O_4 induced by He pretreatment at 350 °C was favorable for the formation of oxygen species weakly bound on the surface, and thus enhanced CO oxidation at low temperatures. More recently, Yu et al. [13] found that pretreatment of Co_3O_4 in an atmosphere of air, or nitrogen, or CO/air promoted the formation of surface oxygen vacancies, on which the adsorption and activation of molecular oxygen were triggered. This feature induced by pretreatment was beneficial for low temperature CO oxidation over Co_3O_4, enabling complete oxidation of 1% CO at –80 °C.

In order to optimize the conditions employed for Co_3O_4 preparation, herein, the influence of calcination temperature on the activity of Co_3O_4 for CO oxidation was intensively studied. Meanwhile, positron annihilation lifetime spectrum (PALS) and O_2-TPD analyses were carried out to identify the impacts of pretreatment conditions on the formation of surface oxygen vacancies and on the adsorption and activation of oxygen.

2. Experimental

2.1. Co_3O_4 preparation

Co_3O_4 was prepared by a precipitation method as reported in previous studies [13,14]. Typically, an aqueous solution of Na_2CO_3 with a concentration of 0.15 mol/L was heated to 70 °C and quickly poured into an aqueous solution of $Co(NO_3)_2$ (0.12 mol/L, also heated at 70 °C), followed by further aging at 60–70 °C for 1 h under vigorous stirring. After cooling down to room temperature and standing for another 2 h, the precipitate was repeatedly washed with distilled water (heated below 70 °C) and centrifugally separated, until the pH value of the solution was ~8.0. The solid obtained was dried at 100 °C overnight and calcined in air within the temperature range of 120–400 °C for 4 h. Before measurement, the sample was crushed and sieved to ensure particles were between 60–90 mesh in size.

2.2. Activity test

The catalytic tests for CO oxidation were carried out in a fixed-bed quartz reactor (i.d. = 5 mm), containing 150 mg of catalyst samples. A standard reaction gas containing 1.0 vol% CO, 20 vol% O_2, and 0.018 vol% H_2O was fed at a total flow rate of 50 ml/min (GHSV = 20000 ml/(h·g)). In all cases, pretreatments were performed at the desired temperatures (120–250 °C) for 40 min in a stream of N_2 or dry air at a flow rate of 50 ml/min. The concentrations of CO in the inlet and outlet streams were measured by using an automatic sampling gas chromatograph (GC8A, Shimazu Corporation), and then the conversion of CO was calculated based on the changes of CO concentrations. The temperature was typically lowered from room temperature using a methanol/liquid nitrogen mixture contained in a vacuum bottle.

2.3. Co_3O_4 characterization

BET surface areas were determined by nitrogen adsorption at –196 °C by using a Quantachrome Autosorb (IQ) instrument. Prior to N_2 physisorption, the catalysts were degassed at 120 °C for 4 h. Powder X-ray diffraction (XRD) measurements of the catalysts were carried out on a X'Pert PRO MPD instrument using Cu K_α radiation. The patterns were measured over the 2θ range from 10° to 90° at a scan step of 0.02°. Thermal gravity (TG) analysis of an uncalcined sample was performed on a TGA-50 analyzer (Shimazu Corporation). The morphology and the particle size distribution of the prepared samples were examined by a Hitachi H-7500 transmission electron microscope (TEM) with 80 kV acceleration voltage.

O_2-TPD experiments were performed at Automated Catalyst Characterization System (Autochem 2920, Micromeritics, USA) equipped with a mass spectrometer (QIC 20, Hiden, UK) by using 200 mg catalyst powder [13]. After pretreatments at different conditions, the sample was cooled down to –70 °C, and then exposed to O_2 at the same temperature. After 60 min, the feed gas was switched to He for purging the system for 60 min and then the temperature was raised at a ramp of 10 °C/min from –70 to 600 °C in a stream of He at 30 ml/min. During this process, the mass signal of O_2 (m/z = 32) was recorded.

PALS measurements were carried out on a positron annihilation lifetime spectrometer at the Key Laboratory of Nuclear Analytical Techniques, Institute of High Energy Physics, CAS. It consists of a BaF_2 scintillation crystal detector coupled with nuclear electronic plug-in components and a fast-slow coincidence system, with a time resolution of 190 ps full-width at half-maximum (FWHM). During the measurement, two pieces of the same Co_3O_4 samples were set in front of and behind the ^{22}Na source, respectively, which was also located at the axial