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Full Length Article

The influence on the structural and redox property of CuO by using different precursors and precipitants for catalytic soot combustion

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ABSTRACT

To gain fundamental understanding on the catalytic property of individual CuO for soot combustion, a series of CuO samples have been prepared with a simple precipitation method by using different Cu precursors and precipitants. Pure monoclinic CuO crystalline phase has been detected by XRD and Raman for all the samples. However, by changing the precursors and precipitants, the morphology and texture property of the CuO samples can be influenced. Furthermore, the redox property of the CuO catalysts can also be altered. Soot-TPR results have testified that four types of active sites with varied activity are present on the surface of all the samples, but only the two types of active sites that can be reduced by soot particles below 500 °C are believed to contribute effectively to soot combustion. It has been discovered that the surface oxygen mobility and abundance are the crucial factors to determine the soot combustion activity of CuO catalysts. Because of the optimal balance of these two factors, CuO-Cu$(NO_3)_2$-Na_2CO_3, a CuO catalyst prepared by the combination of Cu$(NO_3)_2$ precursor and aqueous Na_2CO_3 precipitant, displays the highest soot combustion activity among all the catalysts.

1. Introduction

Soot particulates emitted from diesel engines are one of the major air pollutants, which can cause severe environmental and health problems [1]. Filtering it with a DPF trap and followed by catalytic combustion is a feasible way to eliminate their pollution for atmosphere. Since the temperature of the exhaust gas of a diesel engine is generally below 400 °C [2], it is still a great challenge to develop highly active and stable catalyst to effectively combust the emitted soot particulates at relatively low temperature region. Up to now, many catalysts, such as supported noble metal catalysts [3–5], alkaline metal oxides [6–9] and transition metal oxide catalysts [10–13], have been studied for this reaction. Among these catalysts, Pt catalysts are the most active for diesel soot oxidation under practical conditions so far [14]. However, due to the limited source and high cost of precious metals, people have made many attempts to develop cheaper catalyst formulations for this reaction. Transition metal oxides such as CuO-based [15], CeO_2-based [16–19], MnO_x-based [20], Co_3O_4-based [21], spinels [22,23], perovskites [24,25] and pyrochlores [26,27] have been widely investigated for soot combustion over recent decades.

CuO is a typical p-type semiconductor metal oxide, which has played an important role in the history as catalysts for various redox reactions due to its highly active Cu-O bonds [28,29]. For instance, the famous Hopcalite catalyst, which was invented at the beginning of last century and consists of CuO and MnO_x, displays superior activity for CO oxidation at room temperature and has been practically used [30,31]. Over the past decades, the application of CuO as an active component of catalyst has also been extended to environmental catalysis for soot removing. As early as 1995, Huang and co-authors reported that γ-alumina-supported CuO shows very high activity for the combustion of motorcycle soot particulates [32]. The addition of noble metals such as Pt and Pd can induce the dissociative adsorption and spillover of oxygen, thus strengthening the activity of CuO significantly. Nakagawa and co-workers supported CuO on CeO_2 with different morphologies and found that the CeO_2 morphology influences the soot combustion activity of the catalysts evidently [33]. In comparison with CuO/CeO_2 with uncontrolled morphology, those samples with controlled morphologies such as rod shape display improved activity, because of the presence of larger external surface areas, mesopore volumes and better surface reducibility. Reddy and co-workers also found that copper oxide can promote ceria-zirconia based bimetallic catalysts for low temperature soot oxidation [34]. Chen and co-workers supported

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CuO_x/CeO_2 active species onto ZrO_2-TiO_2 supports with well-defined mesoporous and hierarchical meso/macroporous structures, and found that the best catalysts can achieve 90% soot oxidation at 404 °C [35]. López-Suárez and co-workers prepared potassium-copper perovskite catalysts for mild temperature diesel soot combustion, and revealed that the addition of CuO can suppress the volatilization loss of potassium, thus stabilizing the activity of the catalysts [36]. Wang and co-workers found that CuO is very active for soot combustion, and the addition of some chlorides such as KCl can further enhance the activity [37].

For the preparation of the above-mentioned catalysts, CuO is generally used as one of the components to get improved activity. However, with the major purpose to understand the fundamental catalytic properties of CuO, pure CuO has also been prepared as catalysts and probed by CO oxidation [28,29,38,39]. As early as 1994, Somorjai and co-workers compared the CO oxidation activity on copper with different oxidation states and found that the intrinsic rates followed the sequence of $Cu^0 > Cu_2O > CuO$, and the activation energy showed a reversed trend [28]. Their kinetic data testified that metallic Cu^0 showed a comparable activity to a Pt foil catalyst, and the reaction followed a Langmuir-Hinshelwood mechanism. Upon oxidizing the metallic Cu^0 to Cu_2O and CuO, there is a loss of the active sites and thus decreasing the activity gradually. Later on, Kakuta and co-workers [29] found that for CO oxidation on CuO, surface Cu valence cycles between Cu^{2+} and metallic Cu^0, and the reaction rates nearly agree to the bulk reduction rate of $CuO \rightarrow Cu^0$. In contrast, on Cu_2O, it will be oxidized first into metastable CuO* and then the Cu valence cycles between Cu^{2+} and Cu^+. Adsorption of $O_2{}^-$ and/or O^- is characteristic of CuO*, in contrast with that of O_2 and/or O of CuO. Boronnin and co-workers [38] confirmed that an O^- species with a binding energy of 531.3 eV is responsible for the high CO oxidation activity of CuO nanopowders. Based on the CO pulse kinetic data, Tikhov and co-workers [39] revealed that Cu^+ cation clusters located at outlets of extended defects, which are paths for fast oxygen diffusion from the CuO bulk, are the major active sites responsible for the CO oxidation activity. All these works, indeed, have provided valuable information for people to understand the catalytic properties of individual CuO catalysts.

Moreover, different Cu precursors, precipitants and methods have been tried by people to prepare CuO materials for varied purposes. Deevi and co-workers [40] reported for the first time that a pure CuO catalyst prepared by precipitating 0.5 M $Cu(NO_3)_2$ aqueous solution using an 15% ammonia solution at a pH of 7.5, which was dried at room temperature for 48 h and followed by calcination in air at 250 °C for 2 h shows superior activity, on which CO complete oxidation can be achieved at room temperature. Drying and calcination of the precipitated $Cu(OH)_2$ are critical to obtain an active CuO catalyst. Shin and and co-workers [41] used different precipitants, such as ammonium hydroxide, sodium hydroxide, sodium carbonate and sodium hydrogen carbonate to precipitate copper nitrate aqueous solution to synthesize CuO catalysts, and found that varying precipitants affect the morphology, crystallinity and catalytic activity of CuO evidently. A CuO sample prepared with sodium hydrogen carbonate shows the best activity for CO oxidation, because of its higher oxygen mobility and surface area. The Cu precursor effect on preparing CuO materials has also been investigated by quite a lot of researchers [42–44]. Using a hydrothermal method and CTAB hydrolysis agent, Rabbani and co-workers [42] prepared CuO catalysts with copper nitrate, copper acetate and copper sulfate for photocatalytic oxidation of methylene blue by hydrogen peroxide. It was found that the sample prepared with copper nitrate displays the best activity due to its highest surface area and most abundant surface hydroxyl groups. Some researchers also found that the change of Cu precursors can alter the morphology, crystallinity, surface area and the optical energy band gap of CuO significantly [43,44]. For example, Chand and co-workers [44] revealed that with copper acetate as the precursor, a CuO sample with the best optical and dielectric properties for industrial applications can be achieved.

Despite all the above mentioned work on CuO as catalysts for different catalytic reactions and as other functional materials, the study on the structure and redox property of individual CuO for soot combustion has been rarely profiled. In 1990s, Neefts and co-workers [45,46] compared the soot combustion activity of single component oxides under loose contact, tight contact and diesel soot collected on catalyst condition, and found that CuO showed only medium activity. MoO_3 and PbO displayed the highest activity among all the individual oxides. It is suggested that the mobility of a catalyst material, which influence the contact between soot and catalyst, is important for the loose contact activity. More recently, Meng and co-workers reported that they have synthesized monolithic lawn-like individual CuO-based nanorods array for diesel soot combustion to simulate the real application conditions, and found that the nanorods array demonstrates much higher activity than CuO particles under intimate contact mode [47]. It was concluded by them that the monolithic macroscopic structure of the catalyst on the copper substrate makes it practical for large scale preparation and application.

In order to achieve CuO-based catalysts with better performance for soot combustion, it is of great necessity to gain deeper fundamental understanding on the structure and reactivity relationship of pure CuO. Therefore, in the present study, a series of CuO catalysts have been prepared systematically with an easy precipitation method by using different copper salts as precursors and different base solutions as precipitants. It has been found that the morphology, texture and redox property of CuO samples can be altered by using different precursors and precipitants. A CuO sample with the the best activity for soot combustion can be tuned by the combination of a $Cu(NO_3)_2$ precursor and a Na_2CO_3 aqueous solution precipitant. With various characterization techniques, the bulk structure and surface properties of the CuO samples have been investigated, and the major factors controlling the reaction performance of CuO for soot combustion have been elucidated.

2. Experimental

2.1. Chemical suppliers and purities

All the chemicals used to prepare CuO samples are listed here, together with their suppliers and purities:

$Cu(NO_3)_2 \cdot 3H_2O$, Tianjin Fengchuan Chemical Reagent Co. Ltd., China, ≥99.0%; $Cu(Ac)_2 \cdot H_2O$, Aladdin Shanghai, China, 99.0%; $CuSO_4 \cdot 5H_2O$, Tianjin Damao Chemical Reagent Co. Ltd., China, ≥99.0%; $CuCl_2 \cdot 2H_2O$, Tianjin Hengxing Chemical Reagent Co. Ltd., China, 99.0%;
Na_2CO_3, Tianjin Damao Chemical Reagent Co. Ltd., China, ≥99.8%; $NaHCO_3$, Sinopharm Chemical Reagent Corporation, China, ≥99.5%;
NaOH, Sinopharm Chemical Reagent Corporation, China, ≥96.0%; NH_4OH, Guangdong Fine Chemical Engineering Technology Research Center, China, A.R. grade, 25–28 wt%

2.2. Catalyst preparation

All the CuO catalysts were prepared by an easy precipitation method. With the preparation of a CuO sample by precipitating $Cu(NO_3)_2$ solution with Na_2CO_3 participant as an example here, 0.03 mol $Cu(NO_3)_2 \cdot 3H_2O$ was dissolved into a certain amount of distilled de-ionised (DDI) water to form 0.3 mol L^{-1} stable solution. Then aqueous Na_2CO_3 solution (0.5 mol L^{-1}) was dripped slowly into it until the pH reached about 8. Afterwards, the precipitate was vacuum-filtered and washed thoroughly with DDI water, with a total dissolved solid (TDS) less than 20 ppm. The precipitate was dried at 110 °C overnight, and subsequently calcined at 500 °C in air atmosphere for 4 h to get the final catalyst, which was named CuO-$Cu(NO_3)_2$-Na_2CO_3. All the other CuO