



Research Paper

Indium-doped Co_3O_4 nanorods for catalytic oxidation of CO and C_3H_6 towards diesel exhaustLei Ma^a, Chang Yup Seo^a, Xiaoyin Chen^a, Kai Sun^b, Johannes W. Schwank^{a,*}^a Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109, USA^b Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109, USA

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ABSTRACT

Platinum-group metals are widely used as diesel oxidation catalysts (DOCs) for exhaust control. It is a challenge to improve performance and reduce the cost of DOCs, while also to avoid interference of hydrocarbons and sintering of platinum metals at high temperatures. We present here an indium-doped Co_3O_4 uniform nanorod catalyst whose catalytic performance in CO, C_3H_6 , and even NO oxidation is comparable to platinum-group DOCs in diesel exhaust. No obvious deactivation was observed in long-term stability tests under simulated diesel exhaust conditions. These indium-doped Co_3O_4 nanorods might open a promising pathway towards low-cost efficient diesel exhaust control systems. Characterization results indicated that lattice oxygen could be much more easily abstracted by hydrogen or carbon monoxide from indium-doped Co_3O_4 than from Co_3O_4 and the physical mixture Co_3O_4 and In_2O_3 . The presence of indium with its large cation radius could influence the chemical status of surface/chemisorbed oxygen in Co_3O_4 - In_2O_3 nanorods, thereby increasing the mobility of lattice oxygen involved in the catalytic oxidation reaction. The reaction mechanism of catalytic oxidation of CO and C_3H_6 were evaluated based on kinetic and FTIR studies. For CO oxidation, activated CO_3^* reduced by adsorbed CO^* in an irreversible step to generate the final product of CO_2 could be considered as the kinetically-relevant step. DRIFT spectroscopy confirmed that only stable carbonate species were observed over Co_3O_4 - In_2O_3 nanorods that might be further reduced by CO to form CO_2 . For C_3H_6 oxidation, the incorporation of activated oxygen (O^*) into anion vacancy of catalyst surface was the kinetically-relevant step, while the active sites on catalyst surface should be totally covered by the intermediates of C_3H_6 or its generated species, which actually acted as the most abundant surface intermediates (MASI). DRIFT spectroscopy confirmed that C_3H_6 and its related intermediates like formate, acetate, and acetone species would be formed over Co_3O_4 - In_2O_3 nanorods.

1. Introduction

Diesel oxidation catalysts (DOCs), usually comprised of supported platinum (Pt) metals, are principally used to oxidize carbon monoxide (CO) and hydrocarbons (HCs) in diesel emissions [1]. In addition, catalytic oxidation of nitrogen oxide (NO) to nitrogen dioxide (NO_2) over DOCs also plays a key role in the effectiveness of NO_x removal including lean NO_x trap (LNT), selective catalytic reduction of NO_x with ammonia (NH_3 -SCR) at low temperatures, and passive regeneration of downstream diesel particulate filters (DPF). Although platinum-group metals are currently the predominant catalyst components in commercial DOCs, there are still some problems with the usage of them [1]. For example, trace amounts of platinum could migrate from heated DOCs to downstream zeolite SCR catalysts, and cause severe performance loss on the zeolite [2], although adding palladium (Pd) could to some extent alleviate this problem. Furthermore, CO oxidation would be severely

inhibited by hydrocarbons due to the strong chemisorption of hydrocarbons on active Pt sites [3]. Pt-group metals are susceptible to sinter causing activity loss at high temperatures [4]. Additionally, the high cost of platinum group metals provides a strong incentive to look for replacements of platinum metals in advanced aftertreatment systems. Therefore, there is substantial interest in developing active DOCs with low noble metal loadings or even noble metal-free DOCs that address the exhaust system cost and meet the target emission regulations.

Several significant studies have been undertaken for developing new generations of noble metal-free DOCs like NO oxidation catalysts comprised of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ [5] and Mn-Mullite [6], but these kinds of catalysts might still have to be combined with Pt or Pd to achieve effective oxidation of CO and HCs in diesel exhaust. Cobalt oxide (Co_3O_4) spinels might be one of the most active oxidation catalysts in automotive emissions control [7–9]. Binder et al. [10] reported that Co_3O_4 doped with copper and ceria could outperform Pt catalysts in CO

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oxidation at low temperatures in simulated diesel emissions. The advantage of the cobalt ternary oxide catalysts was that CO oxidation would not be significantly inhibited in the presence of propylene (C_3H_6). Yet, the C_3H_6 oxidation performance was still significantly lower than that of as-prepared Pd catalysts and commercial DOCs. In view of these results, the challenge still remains to develop a noble metal-free catalyst capable of effectively handling all the pollutants in diesel exhaust gas mixtures.

It turns out that Co_3O_4 nanorods could maximally expose the effective lattice planes for catalytic oxidation. The surface of Co_3O_4 nanorods exposing (110) lattice planes predominately comprised of Co^{3+} sites, which are generally recognized as the active sites for catalytic oxidation reaction [11]. It is also possible to modify the textural and redox properties of Co_3O_4 and facilitate the formation of oxygen vacancies by introducing metal dopants with different cation radius, which would be much more beneficial for catalytic oxidation [12,13]. Herein, we present a platinum-free catalyst based on indium-doped Co_3O_4 nanorods, which could effectively oxidize CO, propylene, and even NO in simulated diesel exhausts and also exhibit a good long-term stability in the presence of stream. This new class of catalysts might open a promising pathway towards low-cost efficient diesel exhaust control systems that are entirely free of noble metals.

2. Experimental

2.1. Preparations of catalysts

The synthesis of the SBA-15 template followed the procedures reported in the literature [14–16]. The SBA-15 template was prepared in aqueous solution using Pluronic P123 (Sigma Aldrich, average $M_n \sim 5800$) as structure-directing agent and tetraethyl orthosilicate (TEOS, Sigma Aldrich, 98%) as the silicon source. Typically, 10 g P123 was dissolved in 374 mL deionized water and 16 mL HCl (Sigma Aldrich, 37 wt%). The aqueous mixture was heated to 35 °C and vigorously stirred for one hour, after which 21 g TEOS was added into the solution and further left vigorously stirring at 35 °C for 24 h. The solution was subsequently aged at 100 °C for 24 h in autoclaves under static conditions. The solid product was filtered and washed with a mixture of 20 mL HCl and 200 mL ethanol, followed by deionized water wash. It was then finally calcined in static air at 550 °C for 4 h to remove the copolymer template.

Co_3O_4 and In_2O_3 nanorod samples were prepared using SBA-15 silica as a hard template. In a typical synthesis, 1 g of SBA-15 was dispersed in 5 mL of 0.8 M $Co(NO_3)_2 \cdot 6H_2O$ (Sigma Aldrich, ACS reagent, $\geq 98\%$) or 0.8 M $In(NO_3)_3 \cdot xH_2O$ (Sigma Aldrich, 99.99% trace metals basis) in ethanol solution and vigorously stirred at room temperature for at least 4 h. Subsequently, the samples were dried at 60 °C overnight, after which they were transferred to quartz boats without cover followed by a calcination process in static air at a ramp rate of 1 °C/min to 200 °C and held for 4 h. The composite powders were impregnated by metal precursors one more time using the same procedure as that in the first impregnation process, dried at 60 °C overnight, and then calcined at 600 °C for 6 h at a ramp rate of 1 °C/min with an intermediate temperature plateau at 200 °C for 4 h. The silica template was removed by rinsing with 2 M NaOH hot aqueous solution (ca. 80 °C) for at least three times. The solid products were filtered and washed with deionized water until neutralization, dried in an oven at 60 °C overnight, and then treated in flowing nitrogen ($1.67 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$) with a ramp rate of 1 °C/min to 300 °C and held for 1 h.

Indium-doped Co_3O_4 nanorods, coded as $Co_3O_4-In_2O_3$, were prepared following the same procedure as Co_3O_4 nanorods. During the impregnation process, both $Co(NO_3)_2 \cdot 6H_2O$ and $In(NO_3)_3 \cdot xH_2O$ precursors were dissolved in ethanol solution. The total concentration of metal nitrate precursors was kept at 0.8 M, and the expected mole ratio of Co/In was 5.8. To confirm the synergistic roles between cobalt oxides

and indium oxides, a physical mixture of Co_3O_4 and In_2O_3 nanorods was also prepared and coded as $Co_3O_4 \& In_2O_3$ (26 wt% In_2O_3). The catalyst was used for catalytic oxidation of CO tests and temperature-programmed reduction by hydrogen to examine what role the proximity of cobalt and indium played in $Co_3O_4-In_2O_3$ nanorods. The quantitative results of different elements on $Co_3O_4-In_2O_3$ were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) in Galbraith Laboratories, Inc.

All the nanorod powder samples were pressed into pellets and sieved with mesh sizes of 180–250 μm before performing catalytic activity tests and kinetic studies. Before the catalytic tests, all the nanorod samples were pretreated at 300 °C in a flow of nitrogen ($33.3 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$) for 1 h at a ramping rate of 2 °C/min.

The commercial diesel oxidation catalyst (DOC) contains alumina-supported Pt, which is one of the most active elements for CO, C_3H_6 and NO oxidation [1,17]. A Pt/ Al_2O_3 model DOC catalyst was prepared for catalytic performance tests. Generally, $\gamma-Al_2O_3$ (Alfa Aesar) support powder was pretreated at 700 °C for 4 h in flowing dry air ($1.67 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$) to prepare 2.0 wt% Pt/ Al_2O_3 by incipient wetness impregnation with $Pt(NH_3)_4(NO_3)_2$ (Sinopharm) precursor aqueous solution. The impregnated sample was dried at 120 °C overnight and treated in static air at 600 °C for 5 h. This preparation procedure led to the Pt/ Al_2O_3 catalyst having a surface area of 97.3 m^2/g and an average Pt particle size of 1.1 nm (as shown Fig. S1). The powder Pt/ Al_2O_3 model catalyst was pressed into pellets and sieved with mesh sizes of 180–250 μm , and reduced in a flow of 2.5% H_2/N_2 ($33.3 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$) at 400 °C for 1 h at a ramping rate of 2 °C/min prior to the catalytic tests.

2.2. Catalytic reaction tests

Reactant gases (2% CO/N_2 , 1% NO/N_2 , 3% O_2/N_2 , 20% O_2/N_2 , 5% H_2/N_2 , high-purified N_2) were purchased from PurityPlus Specialty Gases. Reactant gas (1% C_3H_6/N_2) was obtained from Airgas, Inc. The gas flow rates were controlled and metered by mass flow controllers from MKS Instruments, Inc.

Light-off tests of carbon monoxide (CO) and propylene (C_3H_6) oxidation were carried out in a fixed-bed quartz tube reactor (4 mm inner diameter) with a ramp rate of 2 °C/min. The catalyst temperature was electronically controlled and measured by two K-type thermocouples located upstream and downstream of the catalyst bed. Since inlet and outlet temperatures were identical for all the runs, it can be assumed that the reactor was sufficiently controlled in an isothermal status. The catalysts (50 mg, 180–250 μm) were diluted with the same size silica gel (80 mg, Davisil Grade from Sigma Aldrich) that was pretreated at 800 °C for 4 h in static air prior to mixing. For typical CO only oxidation tests, a gas mixture containing 1% CO, 1.5% O_2 balanced with N_2 was fed into the reactor. For simulated diesel emissions of CO and C_3H_6 oxidation tests, a gas mixture containing 0.4% CO (when used), 0.1% C_3H_6 (when used), 0.05% NO (when used), 10% O_2 , and 5% H_2O (when used) with N_2 as balance was passed through the reactor. Deionized water was controlled and injected by a D-Series syringe pump from Teledyne Isco. To make liquid water fully vaporized, the main gas lines were wrapped by heating tapes and isolation materials to maintain the downstream lines isothermal at 120 °C up to the FTIR gas analyzer. The total flow rate for all the tests was fixed at 200 mL/min under standard temperature and pressure, corresponding to a weight hourly space velocity (WHSV) of 240, 000 $\text{mL g}^{-1} \text{ h}^{-1}$. An Antaris™ IGS Gas Analyzer from Thermo Fisher Scientific Inc. was used to analyze the gas reactants and products (CO, C_3H_6 , CO_2 , NO, NO_2 , N_2O , and H_2O). The conversion of CO, C_3H_6 , and NO to NO_2 are defined by the following equations, respectively.

$$X_{CO} = (C_{CO,in} - C_{CO,out}) / (C_{CO,in}) \times 100\% \quad (1)$$

$$X_{C_3H_6} = (C_{C_3H_6,in} - C_{C_3H_6,out}) / (C_{C_3H_6,in}) \times 100\% \quad (2)$$

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