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Tuning chemical bonding of MnO_2 through transition-metal doping for enhanced CO oxidation

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A B S T R A C T

Replacing a small fraction of cations in a host metal oxide with a different cation (also known as doping) provides a useful strategy for improving the catalytic activity. Here, we report transition metal (Fe, Co, Ni, and Cu)-doped α-MnO_2 nanowires synthesized by a one-step hydrothermal method as CO oxidation catalysts. The as-prepared catalysts displayed morphology, crystal structure, and specific surface area similar to those of the pure MnO_2 nanowires. A catalytic activity test showed that all doped MnO_2 nanowires exhibited much enhanced CO oxidation activity, with the Cu-doped ones being the most active (TOF of $9.1 \times 10^{-3}\,s^{-1}$ at 70 °C). The Cu-doped MnO_2 nanowires showed nearly 100% conversion of CO at 100 °C at an hourly gas space velocity of 36,000 mL $g^{-1}\,h^{-1}$, which could last for 50 h without obvious deactivation even in the presence of 2% water vapor. Density functional theory calculations suggested that Cu doping could make the formation of oxygen vacancies in MnO_2, which is the rate-determining step for CO oxidation reaction, easier than for Fe-, Co-, and Ni-doped and pristine MnO_2. Our work demonstrates a facile and promising strategy for improving the catalytic activity for oxide-based catalysts, which should be applicable for a variety of different chemical reactions.

1. Introduction

Low-concentration carbon monoxide (CO) emission from industrial and/or domestic activities is harmful to both human health and the environment. Catalytic oxidation of toxic CO into nontoxic CO_2 offers a major solution for CO removal in air pollution treatments. Precious metals such as Au [1,2], Pt [3,4], Pd [5–7], and Rh [8] dispersed on specific metal oxides with high oxygen storage capacity such as CeO_2, $Ce_xZr_{1-x}O_2$, and Fe_2O_3 are highly active for catalytic CO oxidation. However, because of the increasing price of noble metals, it is necessary to develop low-cost catalysts with comparable catalytic activity. Over the past few years, various transition metal oxides have been reported to be active for CO oxidation, such as Co_3O_4 [9,10], CuO [11], MnO_2 [12], and CeO_2 [13]. Among these, MnO_2 has been widely studied due to its low cost, environmental friendliness, and relatively high activity [14,15]. For example, Liang et al. [15] synthesized MnO_2 nanorods with four different phases and found that the activity for CO oxidation

decreased in the order $\alpha \approx \delta > \gamma > \beta$-$MnO_2$. The activity of MnO_2 could be further improved by dispersing more active components such as Ag [16] and Cu [17,18] on its surface or mixing with cobalt to form spinel oxide [19].

It is known that replacing a small fraction of cations in a host metal oxide with a different cation (also known as doping) can change the catalytic performance of the metal oxide catalyst [20]. The doping can modify the chemical bonding at the surface of the host oxide, which may in turn modify its catalytic activity favorably. The active centers in such systems could be either the oxygen atoms near the dopant or the dopant itself. For example, Li et al. [21] reported much enhanced CO oxidation catalytic activity for Ni-doped CeO_2 catalyst compared with pure CeO_2. Cu-doped CeO_2 nanoparticles also exhibited increased CO oxidation activity [22]. Recently, Zhou and co-workers [23] reported enhanced catalytic CO oxidation activity over Co_3O_4 nanowires by replacing Co^{2+} with Cu^{2+}. However, the activity improvement is not obvious, since Co_3O_4 itself is very active for CO oxidation. Here, we report that transition-metal-doped MnO_2 nanowires synthesized by a one-step hydrothermal method exhibit greatly enhanced catalytic activity for CO oxidation. A 100% conversion of CO can be reached over Cu-doped MnO_2 nanowires at about 100 °C, which is 150 °C

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lower than over pristine MnO_2 nanowires. Density functional theory (DFT) calculations suggest that Cu doping could make the formation of oxygen vacancies in MnO_2, which is the rate-determining step for the CO oxidation reaction, easier than in pristine MnO_2, which explains the much enhanced CO oxidation activity of Cu-doped MnO_2 nanowires.

2. Experimental

2.1. Synthesis

Potassium permanganate ($KMnO_4$, ⩾99%), copper(II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$, ⩾99%), cobalt(II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, ⩾98%), iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, ⩾98%), and nickel(II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, ⩾99%) were purchased from Sigma-Aldrich. Ammonium chloride (NH_4Cl, ⩾99.5%) and sodium carbonate (Na_2CO_3, ⩾99%) were received from TCI. Deionized water was obtained from a Millipore Q water purification system. All chemical reagents were used directly without further purification. Transition-metal-doped MnO_2 nanowires were synthesized using a modified hydrothermal method [24]. In brief, 40 mL of aqueous solution containing 0.8 mmol $KMnO_4$, 0.8 mmol NH_4Cl, and 0.08 mmol transition metal nitrate (Fe, Co, Ni, and Cu, separately) was put into a 45 mL Teflon-lined stainless steel autoclave. The hydrothermal synthesis was conducted at 200 °C for 48 h in an electric oven. Afterward, the brown cottonlike product was collected by filtration and fully rinsed several times with deionized water to remove K^+, followed by drying overnight at 120 °C. The obtained samples were denoted as $Fe_{0.1}MnO_x$, $Co_{0.1}MnO_x$, $Ni_{0.1}MnO_x$, and $Cu_{0.1}MnO_x$, respectively. In addition, Cu-doped MnO_2 with different doping amounts (0.04 mmol and 0.16 mmol $Cu(NO_3)_2 \cdot 3H_2O$ were used) was synthesized by the same method and denoted as $Cu_{0.05}$-MnO_x and $Cu_{0.2}MnO_x$, respectively. Pure MnO_2 nanowires without doping were synthesized as a reference under the same conditions and denoted as MnO_2. MnO_2 nanowires-supported CuO catalysts with a $CuO:MnO_2$ molar ratio of 1:10 were also prepared by a deposition–precipitation method to compare with Cu-doped MnO_2. In detail, 1 mmol of MnO_2 nanowires were dispersed in 50 mL of 0.002 M $Cu(NO_3)_2$ solution. Subsequently, 0.01 M Na_2CO_3 solution was added dropwise under stirring until the pH of the solution reached 8–9. The mixture was then collected by filtration and fully rinsed several times with deionized water, followed by drying overnight at 120 °C, and then calcined at 200 °C for 5 h. The obtained catalyst was denoted as $CuO_{0.1}/MnO_2$.

2.2. Characterization

Powder X-ray diffraction (XRD) analysis was carried out on a Bruker D2 Phaser using Cu Kα radiation ($\lambda = 0.15418$ nm) with a LYNXEYE detector at 30 kV and 10 mA. X-ray absorption spectroscopy (XAS) measurements were collected using a synchrotron radiation light source of the National Synchrotron Radiation Research Center, Taiwan, and the measurements were made at the Mn K-edge (6539 eV) and Cu K-edge (8979 eV) with the sample held at room temperature. Inductively coupled plasma (ICP, Prodigy) was used to determine the transition metals:Mn molar ratio in the doped MnO_2 nanowires series catalysts. Aqua regia was used to dissolve the samples. Standard solutions for ICP purchased from Sigma-Aldrich were used as the external standard. N_2 adsorption–desorption was performed on an Autosorb-6 (Quantachrome) at 77 K. Before analysis, the samples were degassed at 200 °C for 5 h. The Brunauer–Emmett–Teller (BET) surface area was calculated in the P/P_0 range of 0.05–0.2. Temperature-programmed reduction with H_2 (H_2 TPR) or CO (CO TPR) was carried out on an automated chemisorption analyzer (ChemBET Pulsar, Quantachrome). Prior to the measurement, about 50 mg of catalyst placed in a quartz U-tube was pretreated in a He stream at 200 °C for 0.5 h and then cooled to room temperature. H_2 TPR was conducted with a gas mixture of 5 vol.% H_2 in Ar, while CO TPR was conducted with a gas mixture of 10 vol.% CO in He at a flow rate of 30 mL/min. The temperature was raised to 500 °C at a heating rate of 10 °C/min. The amount of H_2 or CO consumption was quantified by a thermal conductivity detector (TCD). Temperature-programmed desorption of CO (CO TPD) was conducted in the same equipment. Prior to the measurement, about 50 mg of catalyst placed in a quartz U-tube was pretreated in a 5 vol.% O_2 in a He stream at 200 °C for 0.5 h and then cooled to room temperature. The sample was saturated with CO by flowing 10 vol.% CO in He for 30 min, then purged with He for 30 min. Subsequently, the sample temperature was increased to 400 °C at a ramping rate of 20 °C/min. The TCD signal was recorded along with sample temperature. The morphological and elemental information were studied with field-emission scanning electron microscopy (FESEM, JEOL JSM-6700F) and transmission electron microscopy (TEM, JOEL JEM-2100) in conjunction with energy-dispersive X-ray spectroscopy (EDX). It should be noted that Ni TEM grids with holey film instead of Cu grids were used to probe Cu elemental distribution in $Cu_{0.1}MnO_x$ nanowires. XPS measurements were carried out on an ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific) using a monochromatic Al Kα X-ray beam (1486.6 eV). All binding energies were referenced to the C1s peak (284.6 eV) arising from the adventitious hydrocarbons.

2.3. Catalytic activity test

CO oxidation reaction was carried out in a homebuilt continuous-flow fixed-bed quartz reactor (internal diameter 4 mm) under atmospheric pressure. Briefly, 50 mg of catalyst powder diluted with 250 mg SiC (200–400 mesh) was loaded into the reactor and pretreated with purified air at 200 °C for 30 min, followed by cooling to room temperature (RT) and switching to reaction gas mixture. The catalyst temperature was controlled by a K-type thermocouple positioned inside the catalyst bed. A mixture gas of 1% CO and 20% O_2 balanced with N_2 was controlled using a mass flow controller (Alicat Scientific Inc.) at 30 mL/min (standard temperature and pressure), corresponding to an hourly gas space velocity (GSV) of 36,000 mL g^{-1} h^{-1}. The reaction temperature range is RT–350 °C with a ramp rate of 1 °C/min. Mass and heat transfer limitations were examined by conducting a Weisz–Prater analysis [25] and a Mears analysis [26]; the details are given in the Supplementary Materials (SM). The reaction rates at 70 °C were measured with the same mixture gas and the hourly gas space velocity was in the range of 18,000–500,000 mL g^{-1} h^{-1}, through which the conversion of CO was adjusted to below 5% in order to calculate the reaction rates under differential reactor conditions. The turnover frequency (TOF) values were estimated based on the surface metal atoms [9], and the calculation details are depicted in the SM. For the stability tests with moisture, the reaction mixture gas was bubbled in deionized water at 25 °C (the volume fraction of moisture determined by GC is about 2%) before passing through the reactor. The concentrations of CO, CO_2, O_2, and N_2 in the inlet and outlet streams were measured by an online gas chromatograph (7890B, Agilent) equipped with a TCD and a FID detector. CO_2 were separated using a Hayesep Q column, while CO, O_2, and N_2 were separated by a Molsieve 5A column. CO conversion (X_{CO}) was calculated as $X_{CO} = (F_{CO,in} - F_{CO,out})/(F_{CO,in}) \times 100\%$, where $F_{CO,in}$ and $F_{CO,out}$ are the molar flow rates of CO at the inlet and outlet of the reactor, respectively.

For all of the experiments, CO_2 was the only CO oxidation product detected, and the difference of total carbon mole fraction