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Insight into the function of alkaline earth metal oxides as electron promoters for Au/TiO_2 catalysts used in CO oxidation

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ABSTRACT

Introduction of alkaline earth metal oxide (AEMO) into TiO_2 was found to promote CO oxidation (in the order BaO > SrO > CaO > MgO) over Au nanoparticles supported on TiO_2. From experimental (electron-transfer reaction, CO electrochemical oxidation, CO adsorption and Mott–Schottky plots) and theoretical (density functional theory) calculations, it is proposed that AEMO may act as an electron promoter for CO oxidation, but not as an exclusive structural promoter as widely regarded. Introduction of AEMO raises the Fermi level of the TiO_2 support, resulting in an enhanced electron transfer from the support to the Au sites and promoting activation of CO adsorbed at Au sites. Moreover, the enhanced catalytic activities induced by AEMO depend on the increase in the Fermi level of the support in the order: TiO_2–BaO > TiO_2–SrO > TiO_2–CaO > TiO_2–MgO. This investigation provides a new insight to understand the role of the electron promoters in the thermocatalytic reactions.

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1. Introduction

Over the past three decades, studies on the supported Au catalysts for CO oxidation at low temperatures have resulted in unexpected observations [1,2]. It is generally accepted that the catalytic activities of Au catalysts depend on the nature of Au nanoparticles (NPs) and properties of the supports [3,4]. In this context, the Au deposited typical reducible TiO_2 support is one of the most intensively studied systems [5,6]. Several attempts have been made to improve the catalytic activity of Au/TiO_2 at room temperature, such as doping with nitrogen [7], addition of sulfur [8,9], packing a thin layer of alumina [10], and introducing FeO_x [11], Co_3O_4 [12], and In_2O_3 [13] to the TiO_2 support. These improvements are attributed to the role of the perimeter between Au NPs and supports. Alkaline earth metal oxide (AEMO), usually regarded as structural promoters, can also promote the catalytic activity of Au/TiO_2 for CO oxidation at low temperatures by stronger interactions of low-coordinated Au atoms and Ti cations [14–16]. Some studies [17–19] also indicate that the AEMO incorporated into Au/TiO_2 mainly benefits in stabilizing the Au NPs size, thus promoting CO oxidation. However, to the best of our knowledge, charging of the supported clusters [20] plays a very important role in promoting the catalytic activity of Au NPs. Previous studies [21–23] have reported that even if the oxide itself had no catalytic activity, charge transport at the oxide–metal interface was one of the major factors accounting for the enhanced activity and selectivity of heterogeneous catalysts. In our previous studies [24–26], we have demonstrated that an increase in the surface electron densities of Au sites induced by electron transfer between the Au NPs and support enhanced the preferential oxidation of CO in the presence of H_2. In fact, Au NPs and supports undergo charge equilibration to drive the energetics of the composites by raising the Fermi level (E_F) to more negative potentials, resulting in a strong electron-donating ability of the composites and an enhanced interfacial charge-transfer efficiency [27,28]. This role of electron transfer or the increase in E_F of the support leads to an increase in the surface electron densities of Au sites and subsequently to the activation of the adsorbed reactant molecules at Au sites (i.e., high electron densities of Au sites lead to a red shift of the C—O vibration of electron back-donation to the CO antibonding orbital) [20].

Based on the aforementioned considerations, we believe that the construction of binary mixed oxides such as AEMO with TiO_2 as a support may also enhance the electron-donating ability of the support. This should promote the catalytic activity of Au NPs for oxidizing CO. To prove this hypothesis, we prepared a series of Au catalysts supported on AEMO (MgO, CaO, SrO and BaO; 10 mol%)-

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modified TiO_2 microspheres with a similar size distribution of Au NPs and tested their catalytic performance for oxidizing CO at room temperature. We herein demonstrated that the intrinsic driving force for the improved catalytic activity of Au/TiO_2, activated by the irreducible AEMO, mainly originated from the stronger electronic interactions between Au and AEMO-modified support rather than solely due to the Au NP size effects. Because of a weak change in the valence state in alkaline earth metals, an in-depth understanding of electron promoters was achieved. These findings are also helpful in a comprehensive understanding of CO oxidation on the Au/TiO_2 system and in designing new Au catalysts with a high catalytic performance.

2. Experimental

2.1. Preparation of catalysts

All the chemicals were of analytical grade and were used as received without further purification. The TiO_2 and TiO_2–AEMO microsphere supports were prepared by precipitation and hydrothermal procedures. Tetrabutyl titanate (6 mL) was dissolved in ethylene glycol (150 mL). After stirring this solution for 8 h, acetone (300 mL) and deionized water (13.5 mL) were added, and the formed precipitates were filtered, washed with ethanol, and dried at 80 °C. Subsequently, to prepare TiO_2–AEMO microspheres, the above precursor and a calculated amount of alkaline earth metal nitrate (molar ratio of alkaline earth metal and TiO_2 was 1/10) were dispersed in deionized water (60 mL). The resulting slurry was transferred to a 100 mL Teflon-lined autoclave and placed in an oven for hydrothermal treatment at 180 °C for 10 h. The produced solid precipitates were separated from the solution by centrifugation, the reside was washed several times with distilled water, and finally dried at 80 °C for 12 h in an oven (denoted as TiO_2, TiO_2–MgO, TiO_2–CaO, TiO_2–SrO, and TiO_2–BaO based on the used type of alkaline earth metal salt). The actual weight content of Mg, Ca, Sr and Ba elements measured by ICP-MS were 2.57%, 4.32%, 8.13% and 14.06%, respectively.

Au NPs were deposited onto TiO_2 or TiO_2–AEMO microspheres by a deposition–precipitation process with a theoretical Au loading of 1.0 wt%. Based on the weight of the microspheres, 100 mL suspension including a suitable amount of $HAuCl_4 \cdot 3H_2O$ and the support {the actual weight percentage of Au NPs measured by inductively coupled plasma-mass spectrometry (ICP-MS) over Au/TiO_2, Au/TiO_2–MgO, Au/TiO_2–CaO, Au/TiO_2–SrO, and Au/TiO_2–BaO were 0.93%, 0.91%, 0.93%, 0.91% and 0.92%, respectively} was poured into a beaker, and the pH value was adjusted to 10.0 by 1.0 M NaOH under vigorous stirring for 12 h at room temperature. This was followed by washing with water, until the $AgNO_3$ test no longer showed the presence of residual Cl^-, and drying overnight at 80 °C. The obtained products were dispersed in 20 mL deionized water and reduced using a 1.0 M $NaBH_4$ aqueous solution at room temperature. The products were washed with water and dried at 80 °C. Finally, the Au catalysts were activated at 350 °C for 2 h at a heating rate of 3 °C min^{-1} in air atmosphere.

2.2. Characterization of catalysts

The X-ray diffraction (XRD) patterns of the catalysts were collected using a Bruker D8 Advance powder X-ray diffractometer using Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm) operated at 40 kV and 40 mA. The actual Au contents of the catalysts were determined by ICP-MS. Particle morphology was investigated using an SU8000 (Hitachi) field-emission scanning electron microscope (SEM). The nanostructure and Au NP size distribution of the synthesized materials were determined by high-resolution transmission electron microscopy (TEM) and an electron diffraction image using a JEOL JEM-2010 EX with the field emission gun operating at 200 kV. UV–vis diffuse reflectance spectra (UV–vis DRS) of the catalysts were measured using a Varian Cary 5000 UV–vis–NIR spectrophotometer. Raman spectra were recorded on a LabRAM HR UV–NIR microscope (HORIBA Jobin Yvon) at 532 nm using an Ar^+ ion laser. The laser beam intensity and spectrum slit width were 2 mW and 3.5 cm^{-1}, respectively. X-ray photoelectron spectroscopy (XPS) was performed using a Quantum2000 system and the data were collected using an Al Kα X-ray beam (1486.6 eV) operated at 25 W. The C 1s signal of 284.6 eV was used to calibrate the XPS data.

2.3. Measurement of electron transfer reaction

The electron-transfer reactions were monitored by UV–vis spectroscopy. Tetracyanoethylene (TCNE) adsorption and reactions were carried out as follows: A TCNE solution of 1.0 g L^{-1} was prepared in a 100 mL calibrated flask. Fresh catalyst (0.1 g) and a magnet were placed in a 10 mL flask and pretreated with a N_2 flow for 30 min, and then 1 mL TCNE solution was added. The reaction reached equilibrium after 30 min. For visible light reaction, visible light ($490\ nm \le \lambda \le 760\ nm$) was introduced into the container. An absorption peak was observed at ~300 nm, indicating that the reaction between Au catalysts and electron acceptor proceeded in the acetonitrile solution, i.e., TCNE was reduced to generate an electron–TCNE complex ($TCNE^-$). Therefore, TCNE was used as a probe to better understand the electronic effects on the Au catalytic systems.

2.4. Electrochemical measurements

A three-electrode-compartment electrochemical cell with a platinum wire was used as the counter electrode, and an Ag/AgCl electrode in a saturated KCl solution (+0.24 V vs. normal hydrogen electrode (NHE)) was used as the reference electrode. The catalysts were used as the working electrode, and the electrochemical experiments were performed using an IM6eX electrochemical workstation system (Zahner, Inc., Germany) at room temperature. For CO stripping voltammograms, the solutions were prepared from $HClO_4$ (0.1 M) and deionized water. First, nitrogen (99.99%) was used to deoxygenate all the solutions, and then 99.99% CO was used to dose CO. The data were recorded at 0.05 V s^{-1} by first scanning negatively until 0.0 V and then scanning positively until 1.9 V. To obtain the flat band potential of Mott–Schottky plots, the solution was prepared from Na_2SO_4 (0.1 M) and deionized water. Three Mott–Schottky plots were obtained at different frequencies of 0.5 kHz, 1 kHz, and 1.5 kHz. The working electrodes were prepared as follows: First, 10 mg ground sample was added to 5 mL absolute ethanol to prepare the slurry, and then the slurry was injected into a $2.5 \times 1.0\ cm^2$ indium-tin oxide (ITO) glass with a cell size of $5 \times 5\ mm^2$ and finally, dried at 100 °C for 300 min.

2.5. CO adsorption of catalysts

Fourier transform infrared spectra (FT-IR) of CO adsorption at room temperature were recorded at atmospheric pressure using an infrared cell reactor (Nicolet Nexus, Model 670) after exposing the samples to CO for 30 min until a steady state was reached. Prior to the admission of CO, an IR background transmission spectrum for sample was recorded. The samples were pressed using a holder fitted with an aluminum foil and placed in a vacuum cell. The samples were pretreated for 2 h at 150 °C.

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