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Influence of cerium modification methods on catalytic performance of Au/mordenite catalysts in CO oxidation

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ABSTRACT

This work investigated influence of cerium modification methods (impregnation and ion-exchange) on the gold dispersion, surface chemical states, synergistic effect between gold and cerium and CO oxidation activity of Au catalysts supported on Ce modified mordenites. The supports and catalysts were characterized by XRF, ICP, XRD, N_2 adsorption–desorption, UV–vis spectroscopy, HRTEM, in situ FT-IR and XPS. In general, Ce-containing Au catalysts were found to be more active in CO oxidation than the Ce-free counterpart, with the impregnation method of cerium modification being more effective than the ion exchange method. The different catalytic performance of Ce-containing catalysts was related to multiple factors: (1) the impregnation method of cerium modification was more favorable to form Au particles with smaller mean size than the ion-exchange method, due to the higher ratio of surface Lewis acid sites; (2) the interface between Au and CeO_2 particles produced by impregnation method was more beneficial for the redox equilibrium of $Au^0 + Ce^{4+} \leftrightarrow Au^{3+} + Ce^{3+}$ to shift to right to form more active Au^{3+} species than the interface between Au particles and Ce cations produced by ion-exchange method, which enhanced the synergistic effect between gold and cerium and the catalytic performance of CO oxidation.

1. Introduction

Since Haruta and co-workers found that CO oxidation could be achieved at a low temperature if gold nanoparticles were formed on suitable supports [1,2], catalysis by gold nanoparticles has attracted much attention because of their high activity. Previous studies have demonstrated that the nature of support plays a significant role in the stabilization and dispersion of the active phase [3]. Furthermore, the reducible metal oxide support can supply reactive oxygen to the active gold sites in the reaction process [4]. From this point of view, it is of great importance to investigate the interaction between gold nanoparticle and the support.

Recently, with the advantages of its adjustable acidic property [5], zeolite has been used as a superior support for loading gold nanoparticles [6]. Mohamed et al. [7] prepared the dealuminated and nondealuminated mordenite to support gold, and found that the dealuminated support was responsible for the stability of CO coordinated Au^+. Wan et al. [8] adjusted surface acidity of Y-type zeolite prior to the preparation of gold catalysts. They found that the gold particles on the surface acidity modified Y support are smaller and more uniformly distributed than those on the support without any surface pretreatment. In the light of these literatures, the distribution, charge and stability of the gold species supported on the zeolite depend on the concentration and strength of acid centers of the zeolite [8]. Modification of zeolite by different metal ions, such as Fe, Ce and Ti [8–10], is one of the methods of improvement of acidic property of zeolite, stabilization of gold species and catalytic performance of supported gold catalysts. Among these additives, due to the unique properties of ceria, such as high oxygen storage capacity and well redox cycles between Ce^{3+} and Ce^{4+} [11], ceria has become one of the most interesting active oxide materials employed for the modification of gold catalysts. Some studies demonstrated that the use of cerium to modify zeolite could increase oxygen mobility in the oxidation reaction and improve reaction activity [9,12]. However, little information on the Au catalysts supported on cerium modified mordenite has been reported. Other than these, the role of interface between gold and cerium species has been regarded as adsorption and reaction sites for CO

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oxidation [3]. Several theoretical studies have shown that O_2 can be absorbed at the gold–cerium interface and that the reaction barrier for CO oxidation is very low at the interface [13,14]. Liu et al. [15] proposed that a charge transfer from Au atom to a neighboring Ce cation would occur during the catalysis process, which promoted the reaction. Flytzani-Stephanopoulos et al. [16] recently studied the CO oxidation reaction on a well-controlled Au/CeO_2 multilayered structure (called nanotower), and found that the reaction rate scaled with the total length of the Au/CeO_2 interface for nanotowers with the same total Au and CeO_2 surface areas. Thus, different morphologies and properties of gold–cerium interfaces can lead to distinct catalytic activities. However, to our knowledge, little attention has been paid to comparing the effect of different gold–cerium interfaces, i.e. interface between Au and CeO_2 particles or between Au particles and Ce cations, on the synergistic effect and catalytic performance. Modification of mordenite with cerium by different methods can in turn provide different cerium species, such as CeO_2 particles and Ce ions [9], which is a suitable route to investigate this effect.

In this work, supported Au mordenite catalysts were modified with Ce by impregnation and ion-exchange methods to obtain different gold–cerium interfaces. The as-prepared Au catalysts were characterized by means of XRF, ICP, XRD, UV–vis, N_2 adsorption–desorption, HRTEM, XPS, in situ FT-IR and CO oxidation model reaction. This study mainly focuses on the influences of difference support surfaces on the dispersion, dimension and charge of Au particles, and the contribution from different gold–cerium interfaces to the catalytic properties of CO oxidation.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of supports

Acid zeolite mordenite (HMOR) with a silicon to aluminum ratio of 7.1 and $Ce(NO_3)_3 \cdot 6H_2O$ were used as received. The Ce-supported material was prepared by incipient wetness impregnation method with $Ce(NO_3)_3$ solution. The CeO_2 loading amount was 3 wt%. The mixture was kept stirring for 3 h and was evaporated at 110 °C. The resultant material was calcined at 500 °C in the flowing air for 5 h. This support was denoted as CeM_{imp}.

Another Ce-containing support was prepared by liquid-phase ion-exchange of HMOR with 0.5 mol L^{-1} $Ce(NO_3)_3$ solution at 80 °C for 6 h. This ion-exchange procedure was carried out twice. After completion of ion-exchange, the sample was washed thoroughly with deionized water and dried overnight at 110 °C. Subsequently, the support was calcined at 500 °C for 5 h in air atmosphere. This support was referred as CeM_{ie}.

2.1.2. Preparation of Au catalysts

The supported Au catalysts were prepared via the deposition–precipitation method using $HAuCl_4 \cdot 4H_2O$ as gold precursor. $HAuCl_4$ solution was added dropwise to a stirred suspension of 1 g support in water. The pH of the solution was kept close to 8.5 with NaOH (0.05 mol L^{-1}), and the solution thermostated at 70 °C was aged for 1 h. The catalyst was washed repeatedly with distilled water, dried in air overnight at 100 °C and calcined at 300 °C for 3 h in flowing air atmosphere. The resulted samples were designated as Au/M, Au/CeM_{imp} and Au/CeM_{ie}, respectively.

2.2. Catalyst characterization

The Si/Al molar ratios and Ce contents of pure supports and Au catalysts were analyzed by X-ray fluorescence spectrometer (ARL-9800).

The actual Au contents of Au catalysts were derived from a Jarrell-Ash 1100 inductively coupling plasma (ICP) atomic emission spectrometer. The samples were completely dissolved in suitable acid before analysis.

XRD patterns were recorded on a Philips X'pert Pro diffractometer using Ni-filtered Cu Kα radiation (0.15418 nm). The X-ray tube was operated at 40 kV and 40 mA. The instrumental line broadening was measured using a silicon standard. The grain sizes of the prepared materials were determined by the Scherrer equation. Lattice volumes of the samples were calculated by full curve fitting, using Jade 5 software.

The total surface areas of these supports and Au catalysts were determined via nitrogen adsorption at −196 °C with the Brunauer–Emmett–Teller (BET) method using a Micrometrics ASAP-2020 apparatus. The surface areas and volumes of micropores were obtained from the *t*-plot method.

UV–vis diffuse reflectance spectra were recorded in the range of 200–900 nm by a Shimadzu UV-2401 spectrophotometer with $BaSO_4$ as reference for baseline emendation. The spectrum of the support was subtracted from the spectrum of the corresponding Au catalyst.

HRTEM images of these samples were obtained by a JEM-2100 microscope at an acceleration voltage of 200 kV, equipped with energy dispersive X-ray spectrometer (EDX).

FT-IR spectra were collected on a Nicolet 5700 FT-IR instrument (Thermo Electron Corporation, USA) with a resolution 4 cm^{-1}. For the transmission IR experiments under ambient condition, the measured wafer was prepared by using KBr as diluent.

In situ FT-IR spectra of ammonia adsorption were collected on a Nicolet 5700 FT-IR instrument. The nature of acid sites was investigated using ammonia as the probe molecule. A thin, but intact, self-supporting wafer (≈15 mg) of the adsorbents was prepared and mounted inside a high temperature cell (HTC-3, Harrick Scientific Corporation, USA). The wafer was pretreated by N_2 (99.999%) at 300 °C for 1 h. After cooling to ambient temperature, NH_3 (99.999%) was introduced into the HTC at atmospheric pressure for 30 min, then the cell was flushed by N_2 for 30 min. After that, the HTC was heated to 300 °C under N_2 atmosphere at a rate of 10 °C min^{-1}, and the spectra were recorded at various target temperatures.

In situ FT-IR spectra of CO adsorption were collected on a Nicolet 5700 FT-IR instrument. The self-supporting wafer mounted in HTC-3 was pretreated for 1 h at 300 °C in the flowing N_2 atmosphere. After cooled to room temperature, the sample was conducted to a controlled stream of 2 vol% CO/N_2 for 30 min. In situ CO adsorption FT-IR spectra were recorded at various target temperatures with subtraction of the corresponding background reference.

X-ray photoelectron spectroscopy (XPS) analysis was performed on a PHI5000 Versaprobe high performance electron spectrometer, using Al Kα radiation (1486.6 eV) operating at an accelerating power of 25 W. All binding energies (BE) were referenced to the C 1s peak at 284.6 eV to account for the charging effect. This reference gave BE values with an accuracy at ±0.1 eV.

2.3. Catalytic activity measurements

The CO oxidation activities of Au catalysts were measured in a flow micro-reactor with a gas composition of 1.6 vol% CO, 20.8 vol% O_2 and 77.6 vol% N_2 at a space velocity of 30,000 mL g^{-1} h^{-1}, and 50 mg catalyst was used for each measurement. The catalyst was pretreated in a N_2 stream at 200 °C for 1 h and then cooled to room temperature, after that, the mixed gases were switched on. Two columns and thermal conductivity detector (TCD) were used for the purpose of analyzing the production, column A with 13× molecular sieve for separating O_2, N_2 and CO, and column B, packed with Porapak Q for separating CO_2.