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Insights into support effects on Ce-Zr-O mixed oxide-supported gold catalysts in CO oxidation

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Abstract

Au/$Ce_{1-x}Zr_xO_2$ catalysts (x = 0–0.8) were prepared by a deposition-precipitation method using $Ce_{1-x}Zr_xO_2$ nanoparticles as supports with variable Ce and Zr contents. Their structures were characterized by complimentary means such as X-ray diffraction, Raman, scanning transmission electron microscopy and X-ray photoelectron spectroscopy (XPS). These Au catalysts possessed similar sizes and crystalline phases of $Ce_{1-x}Zr_xO_2$ supports as well as similar sizes and oxidation states of Au nanoparticles. The oxidation state of Au nanoparticles was dominated by Au^0 especially in CO oxidation. Their activities were examined in CO oxidation at different temperatures in the range of 303−333 K. The CO oxidation rates normalized per Au atoms increased with the increasing Ce contents, and reached the maximum value over Au/CeO_2. Such change was in parallel with the change in the oxygen storage capacity values, i.e. the amounts of active oxygen species on Au/$Ce_{1-x}Zr_xO_2$ catalysts. The excellent correlation between the two properties of the catalysts suggests that the intrinsic support effects on the CO oxidation rates is related to the effects on the adsorption and activation of O_2 on Au/$Ce_{1-x}Zr_xO_2$ catalysts. Such understanding on the support effects may be useful for designing more active Au catalysts, for example, by tuning the redox properties of oxide supports.

Key words

gold catalyst; ceria-zirconia support; CO oxidation; oxygen storage capacity; support effect

1. Introduction

Gold nanoparticles supported on oxides are active for catalyzing a broad range of reactions including low-temperature CO oxidation, water gas shift reaction, oxidation of volatile organic compounds, selective oxidation of alcohols and selective hydrogenation [1−12]. Intensive studies on the supported Au catalysts in CO oxidation as a probe reaction have demonstrated that their activities strongly depend not only on Au particles including their sizes, shapes [13−15] and oxidation states (Au^0, Au^+ or Au^{3+}) [4,16−18] but also on the underlying supports [19−22]. However, unlike the effects of Au particles, the origin of the support effects remains unclear or even controversial, which may be due to the variations of many properties of the supports employed for comparison, such as their surface areas, particle sizes, crystalline phases and surface contaminations (e.g. by residual Cl^-). Such variations lead to the change in the activities of Au catalysts, and accordingly to the difficulty in identifying the intrinsic support effects, as reflected by the reported large variations of the activities for Au on any given support in the literature. Clearly, the choice of the supports is of primarily importance to get insights into the intrinsic support effects on Au catalysts.

In this work, we chose homogeneous Ce-Zr mixed oxides, $Ce_{1-x}Zr_xO_2$, with well-defined structures as supports [23] and examine the activities of Au catalysts in CO oxidation. Recently, Dobrosz-Gomez et al. [24] reported that the activity of Au/$Ce_{1-x}ZrO_x$ (x = 0.25, 0.5, 0.75) catalysts increases with the increasing Ce/Zr molar ratio. These catalysts are much more active than Au/ZrO_2, and the activity of Au/CeO_2 is in between the activity of Au/$Ce_{0.75}Zr_{0.25}O_2$ and Au/$Ce_{0.5}Zr_{0.5}O_2$. Such difference in the activity is related to the effect of the support compositions on the reducibility of Au catalysts. However, such correlation was made by referring to the temperatures at which the catalyst reduction is initially detected and given CO conversions (e.g. 10% conversion) are reached, which appears to be more qualitative than quantitative. Meanwhile, they did not provide the Au particle sizes for all the studied catalysts, which, due to

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the aforementioned effects of Au particle size, are crucial for rigorous comparison of Au activity deposited on different supports.

Here, we synthesize a series of Au catalysts deposited on different $Ce_{1-x}Zr_xO_2$ ($x = 0, 0.2, 0.4, 0.6, 0.8$) supports with a similar Au nanoparticle size (~3 nm) and oxidation state (Au^0), in addition to the similar size and crystalline phases of $Ce_{1-x}Zr_xO_2$ supports. Their catalytic activities are examined in CO oxidation and then related to their active oxygen atoms normalized per Ce atom. The linear correlation between the two properties sheds lights on the origin of the support effects on Au catalysts.

2. Experimental

2.1. Preparation of $Ce_{1-x}Zr_xO_2$ oxide supports

$Ce_{1-x}Zr_xO_2$ ($x = 0-0.8$) oxide supports were prepared by a mild urea hydrolysis based on hydrothermal method [23]. In brief, $(NH_4)_2Ce(NO_3)_6$ (>99.0%, AR, Sinopharm Chemical Reagent Co. Ltd), $ZrO(NO_3)_2$ (AR, Beijing Chem. Corp.), and urea (>99.0%, AR, Beijing Chem. Corp.) in the molar ratio of $Ce^{4+} : ZrO^{2+} : \text{urea} = (1-x) : x : 15$ ($x = 0$, 0.2, 0.4, 0.6 and 0.8) were dissolved in 80 mL deionized water by keeping the total cation concentration at $0.1\ mol\cdot L^{-1}$ in a Teflon-lined stainless steel autoclave (inner volume of 100 mL). Then the autoclave was sealed tightly, and placed in a temperature-controlled oven for hydrothermal treatment at 413 K for 24 h. After the hydrothermal treatment, yellow precipitates were centrifugally separated, washed with deionized water and ethanol several times, and subsequently dried at 353 K in air overnight. The as-prepared $Ce_{1-x}Zr_xO_2$ powders were then calcined in air at 773 K for 4 h.

2.2. Preparation of $Ce_{1-x}Zr_xO_2$-supported gold nanoparticle catalysts

$Au/Ce_{1-x}Zr_xO_2$ catalysts were prepared by a deposition-precipitation (DP) method [25]. The typical preparation procedure was described briefly below. $HAuCl_4$ (AR, Beijing Chem. Corp.) was dissolved in 250 mL deionized water to form a solution at a Au concentration of $1.46\times10^{-3}\ mol\cdot L^{-1}$, into which an aqueous solution of NaOH ($0.1\ mol\cdot L^{-1}$) was added dropwise over 4 h to adjust the pH value of the gold solution to 10. At such constant pH (maintained by adding $0.1\ mol\cdot L^{-1}$ NaOH solution), 2 g $Ce_{1-x}Zr_xO_2$ oxide powders were ultrasonically dispersed in Au solution for about 0.5 h, which then kept at room temperature under vigorous agitation for 2 h. Afterwards, the oxide powders were filtrated and washed with deionized water until no Cl^- ions could be detected in the effluent by a $AgNO_3$ solution. The resulting solids were dried under vacuum of 0.4 Pa overnight at 308 K, which were then crushed and sieved (60−80 mesh) for use in CO oxidation and in measurement of oxygen storage capacity (OSC).

2.3. Characterization of $Ce_{1-x}Zr_xO_2$ supports and Au catalysts

Bulk Zr and Ce compositions were measured by X-ray fluorescence (XRF) on a Bruker S4 Explorer spectrometer, using a power of 1 kW. The actual contents of Au in catalysts were determined by inductive coupled plasma atomic emission spectrometry (ICP-AES) (PROFILE SPEC) after the catalysts were dissolved in nitric acid and refluxed for 12 h. BET specific surface areas (*S*) were measured by nitrogen adsorption at 78.3 K using an ASAP 2010 analyzer (Micromeritics) after samples were outgassed at 423 K for at least 4 h under dynamic vacuum (<1.3 Pa).

Powder X-ray diffraction (XRD) patterns were recorded in 2θ range of 20^o-80^o at a scanning rate of 4 ^{o}/min on a Rigaku D/Max-2000 diffractometer with a slit of 0.5^o using Cu K_α radiation ($\lambda = 1.5406$ Å) with a Nickel filter operated at 40 kV and 150 mA. The lattice parameters were calculated from XRD data by Cohens method [23]. The average grain sizes (D) were estimated by Scherrer equation, $D = 0.90\ \lambda/\beta \cos\theta$, where θ is the diffraction angle of (1 1 1) peak of the cubic phase or (1 0 1) peak of the tetragonal phase, and β is the full width at half-maximum (FWHM) of (1 1 1) or (1 0 1) peak that is calibrated from high purity silicon. A slow step scan (0.02 ^{o}/step, 2 s) in the range of 36^o–40^o was carried out to measure the particle sizes of Au particles.

High-angle annular dark-field scanning Transmission electron microscopy (HAADF-STEM) images were taken on a Philips Tecnai F30 FEGTEM equipped with a field emission source at an accelerating voltage of 300 kV with a point resolution of 0.2 nm. Samples were prepared by uniformly dispersing them in ethanol and then placing them onto carbon-coated copper grids. The average particle diameters were calculated from the mean diameter frequency distribution with the formula: $d = \Sigma n_i d_i / \Sigma n_i$, where n_i is the number of particles with particle diameter d_i in a certain range. For such calculation, more than 100 particles of Au or 200 particles of oxides were measured.

Raman spectra were collected on a Senterra confocal microscope spectrometer (Bruker) with an Ar ion laser of 514.5 nm excitation wavelength and a resolution of $4\ cm^{-1}$ at a laser power of 2 mW. X-ray photoelectron spectroscopy (XPS) measurements were performed on an Axis Ultra spectrometer (U. K.) equipped with a focused monochromatized X-ray source (Al K_α, $h\nu = 1486.6$ eV) at a power of 225 W. The binding energies (BE) were calibrated by referring to the measured BE of C 1s at 284.6 eV.

Fourier transform infrared (FT-IR) spectra for CO adsorption on supported Au catalysts were recorded on a Bruker Tensor 27 spectrophotometer equipped with a LCT detector. The resolution was set at $4\ cm^{-1}$. Au catalysts were pressed into self-supporting discs and placed in a quartz IR cell with CaF_2 windows. Before measurements, the samples were pretreated in the IR cell in flowing air ($30\ mL\cdot min^{-1}$) at 573 K for 4 h, and then evacuated at 573 K for 2 h. After cooling to 298 K, spectra were taken as background references, and then CO or a mixture of CO and O_2 was introduced into the IR cell. All