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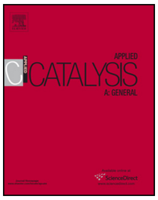

Coupling reaction between α,β-unsaturated aldehyde and methanol catalysed by gold-supported on mesostructured cerias

Kanae Tsutsumi, Hideaki Yoshitake*

Division of Materials Science and Chemical Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

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ABSTRACT

In this study, in order to examine the effects of the nanostructure of the support oxide on the reaction between α,β-unsaturated aldehyde and methanol, we prepared three kinds of ceria supports for gold catalysts. The three types consisted of nano particles (CeO_2-nano), rod-like particles (CeO_2-rod) and cubic particles (CeO_2-cube). Although the BET surface areas of these cerias correspond roughly with their estimated particle sizes, the loading of gold was the largest on CeO_2-cube, which has the largest crystallite size and lowest surface area of the three oxides, and while no significant differences were found in the gold particle sizes in the TEM photographs, the surface density of gold particles was estimated to be the largest on Au/CeO_2-cube. The high intensity of the (2 0 0) line compared to the (1 1 1) line in XRD diffraction implies that the (1 0 0) surface was selectively grown in the crystallites of CeO_2-cube. Ce L_3-edge XANES spectra of the cerias reveal that the population of Ce(III) was larger in CeO_2-nano and CeO_2-rod than in CeO_2-cube. Au 4f XPS showed that there was a higher population of Au(I) on Au/CeO_2-nano and Au/CeO_2-rod than on Au/CeO_2-cube. In the acrolein–methanol reaction, both methyl acrylate and 3-methoxy propanal were formed and comparison of the catalysts revealed that the differences in selectivity to methyl acrylate were small. In contrast, using crotonaldehyde instead of acrolein, the selectivity to methyl 2-butenoate was 100% on Au/CeO_2-nano and Au/CeO_2-rod and that to 3-methoxybutanal was 100% on Au/CeO_2-cube. The differences in activity and selectivity are discussed based on the structures of the catalysts and the α,β-unsaturated aldehyde.

1. Introduction

The properties of ceria as a catalyst material are often attributed to the mobility of oxygen in the solid, its reduction–oxidation reactivity and its oxygen storage capacity [1–3]. Its application in automotive exhaust catalysts, for which it is generally believed that ceria works as an "oxygen reservoir," has been very successful [4]. Various catalytic oxidations stimulated by the redox properties of this oxide, have been reported [5], while its use as a support material has inspired researchers engaged in studies on metal catalysis [2,6,7]. The reactions explored include water–gas shift reactions [8,9], combustion of volatile organic compounds [10], CO oxidation in hydrogen [11–17], selective oxidation of alcohol [18,19], and the oxidation of aldehyde [20]. It is well known that metal catalyses are considerably influenced by interactions with the support material, though the effects due to structural variations of the material have not been thoroughly elucidated in most of the support oxides.

The morphology-controllable syntheses of nanostructured transition metal oxides have been stimulating the development of new solid catalysts. Ceria is potentially one of the most important such oxides. Various synthetic methods have been proposed for the preparation of nanoparticle [21–23], nano-fibre [22,24] nano-belt [24] nano-rod [22,25] cubic [26] spindle [22,24] and mesoporous [22,24,27–29] cerias. Cerias with other complex nanostructures can also be prepared using different surfactants or by changing the pressure and temperature [30–34]. The precise control of the nanostructure has stimulated studies on the size-dependent properties of ceria, such as phonon confinement [35,36], their electronic structure [37–39] and oxygen reactivity [39]. However, the preparation of these cerias has often been accompanied by low temperature calcination and structure directing process by surfactants; therefore, the degree of crystallisation and the density of oxygen defects are dependent not only on the particle size but also on the method of preparation. This implies the importance of structural analyses in relation to their oxidation number and lattice structure as well as their morphological characteristics when they are used as catalyst materials.

Methyl acrylate, which is one of the most important precursors in the chemical industry, is produced through the Reppe reaction

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* Corresponding author. Tel.: +81 45 339 4359; fax: +81 45 339 4378.
E-mail address: yos@ynu.ac.jp (H. Yoshitake).

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with acetylene, carbon monoxide and methanol in the presence of a nickel bromide catalyst. However, nickel is a carcinogenic element. (Its amount in drinking water is limited to less than 20 ppb in the European Union.) Thus the replacement of the catalyst or process is highly desirable. The alkoxylation of α,β-unsaturated aldehyde can occur when using a proper catalyst [40,41], which deals with the formation of methyl acrylate. However, the formation of acrylate is accompanied with a side reaction in which alkoxyalcohol is formed, thus the selectivity between these products is critically important. The formation of the former product involves intermolecular hydrogen abstraction with oxygen, while the latter product is formed through a simple addition to the C═C double bond. Thus active oxygen species on the surface may be important for increasing the selectivity for forming methyl acrylate. In the present study, we prepared gold catalysts using various nanostructured ceria as their support. Although gold has intensively been studied as an oxidation catalyst for CO and organic molecules, oxidation without the formation of a new C—O bond has been rarely explored [42–61]. The mode of H abstraction is clearly different from the oxidation reactions widely exploited on gold catalysts. In addition, the affinity of oxygen is changed depending on the structure of the ceria surface. In this study, we intend to shed light on a new aspect of the oxidation catalysis of gold and the effects of the ceria support as a reservoir for oxygen, using various nanostructured cerias.

2. Method

2.1. Materials

Cerium (III) nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$, 98%), n-heptane (C_7H_{16}, 97.0%), 1-hexanol ($C_6H_{13}OH$, 99.0%), sodium hydroxide (NaOH, 93.0%), cerium oxide (IV) (CeO_2-ref, 99.9%), hydrogen tetrachloroaurate (III) tetrahydrate ($HAuCl_4{\cdot}4H_2O$, 99.9%) and sodium carbonate (Na_2CO_3, 99.8%) were purchased from Wako Pure Chemical Industries. The 25% aqueous solution of tetramethylammonium hydroxide pentahydrate ($TMAOH_{aq}$, $(CH_3)_4NOH{\cdot}5H_2O$, 97%) and Triton X-100 were reagent grade and were supplied by Aldrich. Diethylene glycol diethylether (diglyme, $C_6H_{14}O_3$, 98.0%, Tokyo Chemical Industry Co., Ltd.) was also commercially available. The reactants (acrolein, methacrolein and crotonaldehyde) for the catalytic reactions were purchased from Tokyo Chemical Industry Co., Ltd. except methanol (99.8%, Wako Pure Chemical Industries). These reagents were used without further purification.

2.2. Preparation of nanoparticle ceria (CeO_2-nano)

A mixture of 0.868 g of cerium nitrate hexahydrate dissolved in 7.13 g of deionized water, 58 g of n-heptane, 11.84 g 1-hexanol and 15 g of Triton X-100 stirred until it became a homogeneous liquid, was mixed with a second mixture of 6.40 g of $TMAOH_{aq}$, 1.60 g of deionized water, 58 g of 1-heptane, 11.84 g 1-hexanol and 15 g of Triton X-100. The liquid mixture thus obtained was stirred for 24 h at room temperature. The precipitate formed was collected by filtration, washed with a mixture of 2.5 g of diglyme and 12.5 g n-heptane, dried at room temperature for 24 h, heated at 373 K for 24 h and finally calcined at 773 K for 2 h.

2.3. Preparation of rod-like ceria (CeO_2-rod) and cube-shaped ceria (CeO_2-cube)

10 mL of 0.45 M cerium (III) nitrate aqueous solution was added dropwise to 80 mL of 6 M sodium hydrate. After stirring for 10 min at room temperature, the solution was transferred to a teflon reactor in order to complete hydrothermal syntheses at 373 K or 453 K for rod-like ceria or cube-shaped ceria, respectively. The duration of heating was 24 h. The solids were filtrated, washed with deionized water, dried at 355 K and finally calcined at 673 K for 4 h.

2.4. Preparation of gold/ceria catalysts

Gold was loaded onto CeO_2-ref, CeO_2-nano, CeO_2-rod and CeO_2-cube by a conventional deposition precipitation method. These cerium oxides were soaked in aqueous solutions of hydrogen tetrachloroaurate (III), in which the pH was adjusted to be 10, with continuous stirring at room temperature. The amount of gold in the solution was 3 wt%-Au after being fully deposited on the ceria. After heating at 333 K for 6 h, the solid was filtrated, washed with deionized water and dried at 373 K for 1 h, followed by increasing the temperature to 473 K. The aurate was decomposed for 3 h at this temperature. The catalysts are denoted as Au/CeO_2-ref, Au/CeO_2-nano, Au/CeO_2-rod and Au/CeO_2-cube, respectively.

2.5. Structural analysis

The Au loadings, determined by ICP-AES using an ICPE-9000 Multitype Inductively Coupled Plasma Emission Spectrometer (Shimadzu), were 1.1, 1.9, 2.5 and 2.8 wt% for Au/CeO_2-ref, Au/CeO_2-nano, Au/CeO_2-rod and Au/CeO_2-cube, respectively. The structural periodicity of the catalysts was confirmed by X-ray diffraction (XRD) using a RINT 2200 diffractometer (equipped with a Cu target, Rigaku Co.) operated at 40 kV and 40 mA. Nitrogen adsorption and desorption were carried out for the ceria solids after drying at 453 K for 2 h using a Quantachrome NOVA 4200e sorptometer. X-ray photoelectron spectra of the catalysts were measured using a Quantera SXM spectrometer (Ulvac-Phi, Inc.) Raman spectra of the ceria supports were measured under atmospheric conditions with an inVia Reflex Raman microscope (Renishaw) using a green light laser (532 nm). The powder particles were observed by transmission electron microscopy with a JEM-2100F field emission microscope (200 kV, JEOL) equipped with an EDS analyser. The Ce K-edge XANES spectra were measured at BL-7C beamline, Photon Factory (2.5 GeV), High Energy Accelerator Research Organization (Proposal 11G093) using a Si(1 1 1) double crystal monochromator.

2.6. Catalytic reactions

Typically, α,β-unsaturated aldehyde (acrolein, methacrolein and crotonaldehyde) was mixed with methanol. The solution was then stirred with the catalyst (50 mg) in a sealed reactor with an Ar-O_2 gas flow (25 mL/min at a temperature of 273 K). After 3 h, the solution was filtered off and analysed using a gas chromatograph.

3. Results

The XRD patterns of the nanostructured cerias are depicted in Fig. 1. No significant difference in the positions of the (1 1 1), (2 0 0), (2 3 0), (3 1 1), (2 2 2), (4 4 0), (3 3 1), (4 2 0) and (4 2 2) lines from those of CeO_2-ref can be found in any of the patterns. The clear line broadening in CeO_2-nano and CeO_2-rod allows us to estimate the crystallite size using the Scherrer equation. The estimate of the crystallite size is also applicable to CeO_2-cube. The results of the calculations are listed in Table 1. Since anisotropic crystal growth is possible when the crystallite has a certain nanostructure, we calculated the ratio of the intensities of the (1 1 1) and (2 0 0) diffractions. The results are also shown in Table 1. This parameter indicates the difference in crystal growths between (1 1 1) and (2 0 0) orientations. We do not find a large difference (>10%) in this ratio, $I(1\,1\,1)/I(2\,0\,0)$, between CeO_2-ref (3.5), CeO_2-nano (3.2) and