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Article

Activity promotion of anti-sintering Au/MgGa₂O₄ using ceria in the water gas shift reaction and catalytic combustion reactions

Guo-Qing Ren^{a,b}, Guang-Xian Pei^{a,b}, Jing-Cai Zhang^{a,c}, Wei-Zhen Li^{a,c,*}^a Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China^b University of Chinese Academy of Sciences, Beijing 100049, China^c Dalian National Laboratory for Clean Energy, CAS, Dalian 116023, Liaoning, China

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ABSTRACT

Heterogeneous gold nanocatalysts have both inspired researchers with their unique catalytic performance and frustrated them due to the contradictions observed in their activities and stabilities. A recent breakthrough has shown that gold nanoparticles (NPs) can retain their catalytically active size over a MgGa₂O₄ spinel support upon sintering at high temperatures. Herein, we report the catalytic activity of anti-sintering Au/MgGa₂O₄ for use in water gas shift reaction (WGS) and catalytic combustion reactions, and the promoting effect of ceria. Upon adding ceria to 800°C-aged Au/MgGa₂O₄, the CO conversion in the WGS was increased from ~1.5% to ~34.0% at 450 °C, and the “light-off” temperatures (*T*₅₀) for methane combustion and CO oxidation were decreased by ~80 and ~100 °C, respectively. Characterizations using XRD, HAADF-STEM, EDS mapping, H₂-TPR, XPS, and DRIFTS confirmed the proximate contact of Au with ceria and their significant synergistic effect, which thereby combined the benefits of ceria toward the dissociation of H₂O or O₂ and the Au NPs toward activating CO or CH₄. These results show that this stepwise stabilization-activation strategy is efficient for rationally constructing stable and active gold nanocatalysts, which may open up possibilities for the wide application of gold nanocatalysts at elevated temperatures.

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1. Introduction

Since the discovery of the surprisingly high activity of Au nanoparticles (NPs) in low temperature CO oxidation and acetylene hydrochlorination in the 1980s [1,2], gold has no longer been regarded as an inert noble metal in catalytic reactions. With further “gold rush” research, it has been widely acknowledged that the size and support sensitivities are the intrinsic characteristics of gold nanocatalysts [3–11], while also the barriers for their practical application. Au NPs can exhibit excellent catalytic activity over a certain particle size range (2–5 nm) and

when supported on “active” supports [6,7]. Thus, stabilizing supported gold NPs in their “active” sizes and constructing a synergistic effect between the gold NPs and “active” support are necessary to exert these advantages. Recently, we have reported that MgGa₂O₄ spinel can be used to stabilize Au NPs within a particle size of 2–5 nm at temperatures above the melting point of bulk gold (1064 °C) [12], which solves the long-term problem of gold nanocatalysts from the aspect of their thermal stability. Unfortunately, the MgGa₂O₄ support is an irreducible support, which limits the application of these supported Au NPs in redox reactions.

* Corresponding author. Tel: +86-411-84379738; Fax: +86-411-84685940; E-mail: weizhenli@dicp.ac.cn

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The strong dependence of gold nanocatalysts on the support is mainly due to the presence of a synergistic catalytic effect between the Au NPs and supports. For example, the water-gas shift reaction (WGS: $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$), which is an important reaction for tuning the CO/H_2 ratio in syngas and upgrading H_2 , prefers reducible supports or alkali metal ions, such as CeO_2 and Fe_2O_3 or Na^+ and K^+ , respectively. This results in the intimate contact between the support and Au NPs in which CO activation occurs on the Au NPs and O–H bond cleavage occurs on the reducible support or alkali metal ion [13–16]. Catalytic combustion reactions, such as CO oxidation and methane combustion, also prefer Au NPs supported on reducible supports because the Au NPs are efficient toward CO/ CH_4 activation, but do not dissociate molecular O_2 [17–20]. In order to realize the activation of Au NPs on an inert support, reducible metal oxides have been widely used as additives. Tao *et al.* [21] have reviewed that reducible metal oxides as promoters can adjust the redox properties of the support and create surface defects/oxygen vacancies, which benefit the dissociation of certain reactants. Among them, CeO_2 is an excellent reducible support, which shows high oxygen mobility and storage capacity [22]. It has been reported that oxygen vacancies can be created in the ceria lattice at moderate temperatures and under reductive atmospheres, and these oxygen vacancies can provide active sites for H_2O or O_2 dissociation [23,24]. Reina *et al.* [25] have designed highly efficient Au/ Al_2O_3 WGS catalysts by introducing CeO_2 as a promoter in the water activation step and MO_x ($\text{M} = \text{Fe}, \text{Cu}, \text{Zn}$) as dopants. Similarly, the introduction of redox supports can also improve the activity of Au NPs in catalytic combustion reactions. Gluhoi *et al.* [17] and Zhang *et al.* [26] have reported that CeO_2 can significantly improve the activity of Au/ Al_2O_3 for CO oxidation, and also proved that CeO_2 acts as an oxygen supplier via the Mars and van Krevelen mechanism.

Herein, we present an example of modulating the activity of anti-sintering Au MgGa_2O_4 catalyst for use in the WGS and catalytic combustion reactions by incorporating CeO_2 as a promoter. Characterizations using HAADF-STEM, X-ray diffraction (XRD), Energy dispersive X-ray spectroscopy (EDS) mapping, Hydrogen temperature-programmed reduction (H_2 -TPR), and X-ray photoelectron spectroscopy (XPS) proved that after impregnating CeO_2 on the severely aged Au MgGa_2O_4 catalyst, the MgGa_2O_4 stabilizes the Au NPs intimate contact with CeO_2 , which results in a strong synergistic effect. This stable matrix shows significantly improved activity in both the WGS and catalytic combustion reactions. *In-situ* Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was also used to clarify the possible promotion mechanism of CeO_2 using the WGS as an example.

2. Experimental

2.1. Synthesis of the catalysts

The magnesium gallate spinel support precursor was prepared via the homogeneous co-precipitation of stoichiometric magnesium and gallium nitrate with urea in methanol, as pre-

viously reported [12].

The Au MgGa_2O_4 catalyst was prepared by soaking 8 g of MgGa_2O_4 powder in 150 mL of an aqueous solution of chloroauric acid ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, Au content >47.8%, Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd) with nominal 2% weight loadings and stirred for 24 h. The suspension was then filtered and washed with concentrated ammonia (25%–28%, Tianjin Damao Chemical Reagent Factory). The filter cake was dried at 80 °C, and then calcined in ambient air at 300 or 800 °C for 5 h at a heating rate of 5 °C·min⁻¹. The samples were denoted as Au MgGa_2O_4 -T-5h, where T is the thermal treatment temperature used. The as-obtained catalysts have Au weight loadings of 1.09 wt%, as-determined using ICP-AES analysis.

The CeO_2 -modified Au MgGa_2O_4 catalyst was prepared via an incipient wetness impregnation process using the Au MgGa_2O_4 -800°C-5h catalyst and an aqueous solution of cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, >99.0%, Sinopharm Chemical Reagent Co., Ltd). The impregnated sample was dried at 80 °C and then calcined at 400 °C for 5 h. The resulting catalyst was denoted as $\text{CeO}_2/[\text{AuMgGa}_2\text{O}_4\text{-800}^\circ\text{C-5h}]$ and has a CeO_2 weight loading of 20.7 wt%, as-determined using ICP-AES analysis. A Au/ CeO_2 -RRCe-2 benchmark catalyst with a gold weight loading of 0.98 wt% was purchased from Haruta Gold Incorporated, which was calcined at 300 °C for 2 h and used as the reference.

2.2. Catalyst characterization

The actual loadings of Au and CeO_2 were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES) on an IRIS intrepid II XSP instrument (Thermo Electron Corporation). Prior to the measurements, all the samples were dissolved using aqua regia.

XRD patterns were recorded on a PANalytical PW3040/60 X' Pert PRO diffractometer equipped with a $\text{Cu K}\alpha$ radiation source ($\lambda = 0.15432$ nm) operated at 40 kV and 40 mA.

High-resolution transmission electron microscopy (TEM) analysis was performed on a JEOL JEM-2100F operated at 200 keV with a specified point-to-point resolution of 0.19 nm and a lattice resolution of 0.10 nm. This instrument was equipped with a high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) detector and the resolution was 0.2 nm. EDS was recorded on an Oxford Instruments ISIS/INCA EDS system equipped with an Oxford Pentafet ultrathin window (UTW) detector in HAADF-STEM mode. To obtain the particle size distribution, we analyzed no less than 100 particles.

H_2 -TPR experiment was performed on an automated absorption apparatus TP-5080 equipped with a thermal conductivity detector (TCD) (Tianjin Xianquan Co. Ltd). About 50 mg of the catalyst was loaded into a quartz reactor and pretreated at 400 °C in air at a flow rate of 30 mL·min⁻¹ for 30 min. After cooling to room temperature under a He atmosphere, the flow gas was switched to 5 vol% H_2/N_2 at a flow rate of 30 mL·min⁻¹. Finally, the catalyst was heated to 900 °C at a ramping rate of 10 °C·min⁻¹ and the TCD signals were recorded.

DRIFTs was recorded on a Bruker EQUINOX 55 spectrometer equipped with an MCT detector and operated at a resolution of 4 cm^{-1} for 32 scans. Before each experiment, the sample (~40 mg) was calcined *in situ* in air at 400 °C in a DRIFTs cell (HC-500, Pike technologies). Then under a flow of He, the temperature was cooled to 200 °C and held at this temperature for 30 min. Subsequently, a background spectrum was recorded for the sample, which was then subtracted automatically from the subsequent spectra. The corresponding gas for H_2O adsorption and dissociation (10 vol% $\text{H}_2\text{O}/\text{He}$) was introduced into the reaction cell and the spectra recorded as a function of time until saturation. The gas was then switched to He to purge the gaseous H_2O molecules and 2 vol% CO was introduced into the reaction cell to detect the reaction between CO and the adsorbed H_2O . The spectra were recorded as a function of time until no obvious changes were observed. The flow rate involved in these steps was 20 $\text{mL}\cdot\text{min}^{-1}$.

XPS data were collected on a Thermofisher ESCALAB 250 spectrometer using a monochromatized Al K_{α} X-ray source (1486.6 eV) and applied power of 150 W. The C 1s peak (284.8 eV) was used as the reference.

2.3. Catalytic reactions

All the reactions were carried out at atmospheric pressure in a fixed-bed micro-reactor. The catalyst powders (~50 mg) were diluted with 0.5 g quartz sand and placed in a U-shaped quartz reactor. A k-type thermocouple in a thin quartz tube was inserted into the catalyst bed to measure and control the temperature. The reactants and products were analyzed using an on-line gas chromatograph (Agilent 7890 B) equipped with a 5A molecular sieve and Parapak Q packed column, and a thermal conductivity detector. The feed gas used for the WGS was 2 vol% CO + 10 vol% H_2O balanced with He. The feed gases used for CO oxidation and CH_4 combustion were 1 vol% CO + 20 vol% O_2 balanced with He and 1 vol% CH_4 + 20 vol% O_2 balanced with N_2 , respectively. The flow rate used was 30 $\text{mL}\cdot\text{min}^{-1}$, which results in a space velocity of 36000 $\text{mL}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$. The conversion of CO was calculated using $\text{Conv}_{(\text{CO})} = C_{\text{CO}_2}/(C_{\text{CO}} + C_{\text{CO}_2}) \times 100\%$, in which C_{CO_2} and C_{CO} are the concentration of CO_2 and CO in the effluent gas, respectively. The conversion of

CH_4 was calculated using $\text{Conv}_{(\text{CH}_4)} = (C_{\text{CH}_4, \text{in}} - C_{\text{CH}_4, \text{out}})/C_{\text{CH}_4, \text{in}} \times 100\%$, in which $C_{\text{CH}_4, \text{in}}$ and $C_{\text{CH}_4, \text{out}}$ are the concentration of CH_4 in the feed and effluent gases, respectively.

3. Results and discussion

3.1. Characterization of the pristine and CeO_2 promoted $\text{Au}/\text{MgGa}_2\text{O}_4$ catalysts

3.1.1. Dispersion of Au and CeO_2

HAADF-STEM and XRD were used to estimate the dispersion and thermal stability of the Au NPs before and after the addition of CeO_2 as a promoter. Fig. 1 shows the HAADF-STEM images obtained for the $\text{Au}/\text{MgGa}_2\text{O}_4$ -300°C-5h, $\text{Au}/\text{MgGa}_2\text{O}_4$ -800°C-5h, and $\text{CeO}_2/[\text{Au}/\text{MgGa}_2\text{O}_4$ -800°C-5h] samples. The fresh $\text{Au}/\text{MgGa}_2\text{O}_4$ -300°C-5h sample is made up of highly dispersed Au particles with high particle density (Fig. 1(A)). Most of the Au particles were below 2 nm with some in the range of 3–5 nm, resulting in a mean particle size (D_m) of 1.6 nm and a standard deviation of 0.6 nm. This indicates that the Au NPs could be readily dispersed on the MgGa_2O_4 support via the simple impregnation method. After the aging process, the resulting $\text{Au}/\text{MgGa}_2\text{O}_4$ -800°C-5h also displayed small Au NPs (~3.1 nm with a standard deviation of 1.0 nm) and a few larger Au particles in the range of 20–30 nm (Fig. 1(B) and inset). This indicates that most of the well-dispersed Au NPs were stabilized by the MgGa_2O_4 support, as previously reported [12]. After further modification with ~20% CeO_2 , $\text{CeO}_2/[\text{Au}/\text{MgGa}_2\text{O}_4$ -800°C-5h] is still made up of lots of small Au NPs (~3.1 nm with a standard deviation of 1.6 nm) and well-dispersed CeO_2 NPs (~5 nm) on the MgGa_2O_4 surface (Fig. 1(C)). These results indicate that the addition of CeO_2 did not influence the thermal stability of the Au NPs. Furthermore, CeO_2 was well-dispersed on the MgGa_2O_4 support, which may form an interface with the Au NPs.

XRD was also carried out to estimate the dispersion and crystallinity of the Au and CeO_2 in $\text{Au}/\text{MgGa}_2\text{O}_4$ -300°C-5h, $\text{Au}/\text{MgGa}_2\text{O}_4$ -800°C-5h, and $\text{CeO}_2/[\text{Au}/\text{MgGa}_2\text{O}_4$ -800°C-5h] with the MgGa_2O_4 and $\text{CeO}_2/\text{MgGa}_2\text{O}_4$ supports used as the reference samples (Fig. 2). Accordingly, only the distinct peaks of MgGa_2O_4 spinel (PDF#00-010-0113) were observed in the

Fig. 1. HAADF-STEM images and the corresponding particle size distribution of the $\text{Au}/\text{MgGa}_2\text{O}_4$ -300°C-5h (A), $\text{Au}/\text{MgGa}_2\text{O}_4$ -800°C-5h (B), and $\text{CeO}_2/[\text{Au}/\text{MgGa}_2\text{O}_4$ -800°C-5h] (C) catalysts.

Fig. 2. XRD patterns of the Au/MgGa₂O₄ and CeO₂/[Au/MgGa₂O₄] catalysts.

fresh Au/MgGa₂O₄-300°C-5h sample, indicating that Au was readily dispersed below the detection limit of XRD via the simple wetness impregnation method. After the aging process of the Au/MgGa₂O₄-300°C-5h sample at 800 °C for 5 h, the distinct peaks of Au (PDF#00-004-0784) appeared and the corresponding particle sizes of the sintered Au NPs were estimated to be 19.9 nm according to the Scherrer equation, which correspond to the large Au NPs observed in the HAADF-STEM images (Fig. 1(B)). Meanwhile, the peaks of the MgGa₂O₄ support become much sharper and the crystal sizes of MgGa₂O₄ estimated by Scherrer equation increased from ~5 to ~12 nm, which indicates that sintering of the MgGa₂O₄ support occurred during the aging process at 800 °C for 5 h. The distinct peaks of Au still exist in the CeO₂/[Au/MgGa₂O₄-800°C-5h] sample and the particle sizes of the sintered Au crystals remained at ~19 nm. Both the HAADF-STEM and XRD results illustrate that the Au NPs in the Au/MgGa₂O₄-800°C-5h and CeO₂/[Au/MgGa₂O₄-800°C-5h] samples exhibit bimodal size distributions with small-sized particles (~3 nm) and large-sized branches (~20 nm), which is in accordance with our previous report [12]. Meanwhile, the Au particle sizes were not influenced by the addition of the CeO₂ promoter. For the CeO₂/[Au/MgGa₂O₄-800°C-5h] catalyst, the distinct peaks of CeO₂ (PDF#00-034-0394) appeared and the corresponding particle size of the CeO₂ crystals was estimated to be 6.0 nm, which is similar to that observed in CeO₂/MgGa₂O₄ (6.5 nm).

3.1.2. Synergistic effect between the Au NPs and CeO₂

Due to the heavy Ce atoms, the contrast observed in the HAADF-STEM image shown in Fig. 1(C) is not good enough to distinguish CeO₂ from the MgGa₂O₄ support and Au NPs. Thus, EDS analysis was performed on the CeO₂/[Au/MgGa₂O₄-800°C-5h] catalyst to confirm whether there was geometrically intimate contact between the Au NPs and CeO₂. As shown in Fig. 3(A) and (B), the signals of the Au NPs were surrounded by the signals of Ce, which indicate that the Au NPs are in contact with the CeO₂ promoter geometrically over the MgGa₂O₄ support. Fig. 3(C) shows the elemental analysis of the spots with (a) and without (b) visible Au particles. All

Fig. 3. HAADF-STEM images and EDS analysis of the CeO₂/[Au/MgGa₂O₄-800°C-5h] catalyst.

of the Mg, Ga, Ce, and Au elements are present in both spots with varied intensities (Fig. 3(D)), which further confirms the close proximity between CeO₂ and the Au NPs. The geometrically intimate contact between the Au NPs and CeO₂ may induce a synergistic effect to enhance the catalytic performance, which will be discussed in the following section.

H₂-TPR was used to detect the reducibility of the CeO₂/[Au/MgGa₂O₄-800°C-5h] catalyst with CeO₂/MgGa₂O₄ and Au/MgGa₂O₄-800°C-5h as the reference samples. No obvious reduction peaks were detected over the Au/MgGa₂O₄-800°C-5h catalyst below 500 °C, which suggests that the Au NPs remain in their metallic state and is consistent with the fact that AuO_x species are not stable [27,28]. For CeO₂/MgGa₂O₄, two major peaks ($T_H = 423$ °C, $T_L = 357$ °C) were observed in the detected region (30–900 °C), which can be attributed to the different surface capping oxygen atoms (O²⁻ or O⁻ anions) in CeO₂ [29,30]. It is noteworthy that the corresponding reduction peaks for CeO₂ at T_H and T_L in the

Fig. 4. H₂-TPR profiles of the CeO₂/[Au/MgGa₂O₄-800°C-5h], Au/MgGa₂O₄-800°C-5h, and CeO₂/MgGa₂O₄ samples.

$\text{CeO}_2/[\text{Au}\text{MgGa}_2\text{O}_4\text{-}800^\circ\text{C-}5\text{h}]$ catalyst were significantly decreased to 205 and 156 $^\circ\text{C}$, respectively. It was also observed that the reduction temperatures of CeO_2 in $\text{CeO}_2/[\text{Au}\text{MgGa}_2\text{O}_4\text{-}800^\circ\text{C-}5\text{h}]$ decreased upon increasing the Au loading (Fig. S1). The obvious decrease in the reduction temperatures observed for CeO_2 in $\text{CeO}_2/[\text{Au}\text{MgGa}_2\text{O}_4\text{-}800^\circ\text{C-}5\text{h}]$ may be attributed to the strong interactions formed between the Au NPs and CeO_2 . A good synergistic effect between the Au NPs and CeO_2 is attractive for catalysis.

Furthermore, the electronic states of Au/(Ce)/O/Mg/Ga in the $\text{Au}\text{MgGa}_2\text{O}_4\text{-}800^\circ\text{C-}5\text{h}$ and $\text{CeO}_2/[\text{Au}\text{MgGa}_2\text{O}_4\text{-}800^\circ\text{C-}5\text{h}]$ samples were detected using XPS. As shown in Fig. 5(A), the Au $4f_{7/2}$ XPS spectra of $\text{Au}\text{MgGa}_2\text{O}_4\text{-}800^\circ\text{C-}5\text{h}$ shows a binding energy peak at ~ 83.0 eV, which can be assigned to the metallic Au NPs. After adding the CeO_2 promoter, the signals for both Au $4f$ and Mg $2s$ became much weaker due to the coverage of CeO_2 , and the binding energy for Au $4f_{7/2}$ shifted to 84.5 eV (Au^+) [31]. This indicates that there are strong interactions between Au and CeO_2 , which in turn confirms that the Au NPs are in close contact with the CeO_2 promoter. In regard to the electronic states of Ce in the $\text{CeO}_2/[\text{Au}\text{MgGa}_2\text{O}_4\text{-}800^\circ\text{C-}5\text{h}]$ sample, there are four doublets observed in the Ce $3d$ XPS spectra (Fig. 5(B)). In accordance with the literature [32], the peaks labeled 'u' correspond to the $3d_{3/2}$ spin-orbital states and those labeled 'v' correspond to the $3d_{5/2}$ states. The u'''/v''' , u'/v' doublets are the primary photoemission from Ce(IV) and Ce(III), and the u''/v'' , u/v doublets are shake-down features resulting from the transfer of one or two electrons from a filled O $2p$ orbital to an empty Ce $4f$ orbital. Thus, the appearance of both u'''/v''' and u'/v' doublets indicates the coexistence of Ce(IV) and Ce(III) in the $\text{CeO}_2/[\text{Au}\text{MgGa}_2\text{O}_4\text{-}800^\circ\text{C-}5\text{h}]$ sample. The existence of Ce(III) can be used as an indicator for oxygen vacancies, which are widely acknowledged to be the activation sites for water or oxygen molecules in the WGS and combustion reactions [33]. In addition, the O $1s$ signals of the $\text{Au}\text{MgGa}_2\text{O}_4\text{-}800^\circ\text{C-}5\text{h}$ and $\text{CeO}_2/[\text{Au}\text{MgGa}_2\text{O}_4\text{-}800^\circ\text{C-}5\text{h}]$ samples were also collected (Fig. 5(C)). For the $\text{Au}\text{MgGa}_2\text{O}_4\text{-}800^\circ\text{C-}5\text{h}$ sample, there are two kinds of O species with binding energy peaks at 530.6 and 532.2 eV, which can be assigned to the lattice O and surface under-coordinated O atoms in the spinel support [34]. In addition to the O species corresponding to MgGa_2O_4 , two signals with binding energy peaks at 528.9 and 529.5 eV were observed in the $\text{CeO}_2/[\text{Au}\text{MgGa}_2\text{O}_4\text{-}800^\circ\text{C-}5\text{h}]$ sample, which can be ascribed to lattice and surface O atoms in the CeO_2 promoter. It is noteworthy that the binding energies of O $1s$ for the CeO_2 promoter in the $\text{CeO}_2/[\text{Au}\text{MgGa}_2\text{O}_4\text{-}800^\circ\text{C-}5\text{h}]$ sample were similar to or lower than that of CeO_2 with abundant oxygen vacancies reported in the literature [35], which, when combined with the appearance of Ce(III), confirms that oxygen vacancies exist in the $\text{CeO}_2/[\text{Au}\text{MgGa}_2\text{O}_4\text{-}800^\circ\text{C-}5\text{h}]$ sample. Mg and Ga were both detected to be Mg^{2+} and Ga^{3+} in the $\text{Au}\text{MgGa}_2\text{O}_4\text{-}800^\circ\text{C-}5\text{h}$ and $\text{CeO}_2/[\text{Au}\text{MgGa}_2\text{O}_4\text{-}800^\circ\text{C-}5\text{h}]$ samples, indicating that the addition of CeO_2 little effect on the electronic structure of the MgGa_2O_4 spinel support (Fig. 5(D) and (E)) [36,37].

3.2. Catalytic performance of the pristine and CeO_2 promoted $\text{Au}\text{MgGa}_2\text{O}_4$ catalysts

3.2. Catalytic performance of the pristine and CeO_2 promoted $\text{Au}\text{MgGa}_2\text{O}_4$ catalysts

The catalytic performance of the as-synthesized catalysts were investigated using the WGS and catalytic combustion (methane combustion and CO oxidation) reactions. A benchmark catalyst, $\text{Au}/\text{CeO}_2\text{-RRCe-}2$ with a Au loading of 0.98 wt% purchased from the Haruta Gold Incorporated, was used as a reference for comparison.

Fig. 6A presents the catalytic performance of the catalysts at various temperatures in the WGS. Over the $\text{Au}\text{MgGa}_2\text{O}_4\text{-}300^\circ\text{C-}5\text{h}$ catalyst, the CO conversions increased from 3.2%, to 5.4%, 8.8%, and 17.9% upon increasing the temperatures from 250 to 350, 450, and 550 $^\circ\text{C}$, respectively, while $\text{Au}\text{MgGa}_2\text{O}_4\text{-}800^\circ\text{C-}5\text{h}$ was much less active. This can be ascribed to the sintering of MgGa_2O_4 because the XRD and HAADF-STEM results (Figs. 1 and 2) show that most of the Au NPs remain stable. These activities were inferior to those observed over the $\text{Au}/\text{CeO}_2\text{-RRCe-}2$ reference catalyst, which were 8.8%, 12.2%, 23.2%, and 63.9%, respectively. These are consistent with the reported results, which show that a reducible oxide support is favorable for the WGS [13,14]. Upon the addition of CeO_2 to the low activity $\text{Au}\text{MgGa}_2\text{O}_4\text{-}800^\circ\text{C-}5\text{h}$ catalyst, the catalytic activity of the resulting $\text{CeO}_2/[\text{Au}\text{MgGa}_2\text{O}_4\text{-}800^\circ\text{C-}5\text{h}]$ was significantly enhanced with

Fig. 5. XPS signals of Au $4f$ (A), Ce $3d$ (B), O $1s$ (C), Mg $2p$ (D), and Ga $2p$ (E) of the $\text{Au}\text{MgGa}_2\text{O}_4\text{-}800^\circ\text{C-}5\text{h}$ and $\text{CeO}_2/[\text{Au}\text{MgGa}_2\text{O}_4\text{-}800^\circ\text{C-}5\text{h}]$ samples.

Fig. 6. Catalytic performance of the pristine and CeO₂ promoted AuMgGa₂O₄ catalysts and the Au/CeO₂-RRCe-2 benchmark catalyst obtained from Haruta Gold Incorporated at various reaction temperatures in the WGS (A), CO oxidation (B), and CH₄ combustion (C). (WGS: 2 vol% CO + 10 vol% H₂O + He; CH₄ combustion: 1 vol% CH₄ + 20 vol% O₂ + N₂; CO oxidation: 1 vol% CO + 20 vol% O₂ + He; Space velocity: 36,000 mL g_{cat}⁻¹ h⁻¹).

CO conversions of 5.1%, 19.3%, 50.0%, and 69.6% at 250, 350, 450, and 550 °C, respectively, demonstrating the benefit of the intimate contact between the stabilized Au NPs and CeO₂. Interestingly, when compared with the Au/CeO₂-RRCe-2 reference catalyst, the CeO₂/[AuMgGa₂O₄-800°C-5h] was also more active at higher temperatures. These observations are consistent with the support effect of Au nanocatalysts in the WGS [13]. The excellent synergistic effect between the Au NPs and CeO₂ occurs due to the formation of CeO₂/Au perimeters via appropriately intimate contact with each other in geometry and the promotion of the reducibility of CeO₂, which were confirmed by the EDS analysis and H₂-TPR results shown in Figs. 3 and 4, respectively. Thus, the stabilized Au NPs on MgGa₂O₄ spinel support retain their catalytic functions and can be readily ignited once in contact with an appropriate oxide promoter for a specific reaction. It is noteworthy that the Au NPs in AuMgGa₂O₄ subjected to calcination at 800 °C with CeO₂ can display higher catalytic activity than that of the fresh benchmark Au/CeO₂-RRCe-2 catalyst, clearly showing the potential of AuMgGa₂O₄ as a thermally stable ensemble in the rational construction of highly active gold catalysts. In addition, we also investigated the long-term catalytic stability of CeO₂/[AuMgGa₂O₄-800°C-5h] in the WGS at 450 °C (Fig. S2). During the 48 h test, CeO₂/[AuMgGa₂O₄-800°C-5h] showed a deactivation period of ~5 h and then a stable plateau at least for 40 h. The average CO conversion during the plateau observed for the CeO₂/[AuMgGa₂O₄-800°C-5h] catalyst was 34.5%. XRD, HAADF-STEM, and EDS-mapping were used to characterize the spent catalyst. Both the XRD and HAADF-STEM results (Figs. S3 and S4) show that the particle size of the Au NPs remained almost unchanged after long-term reaction, indicating that the Au NPs were rather stable over the MgGa₂O₄ spinel support. Furthermore, the Au NPs are still in contact with the CeO₂, as reflected in the EDS-mapping images (Fig. S4(B)). In regard to the CeO₂ promoter, the corresponding crystal size detected using XRD was slightly increased from 6.0 to 7.0 nm after the long-term reaction. Thus, the deactivation observed during the initial 5 h may be attributed to the slight increase in the crystal size of the CeO₂.

The catalysts were also investigated in the CO oxidation and CH₄ combustion reactions in which they showed various activities, but similar evolution trends (Fig. 6(B) and (C)). For CO

oxidation (Fig. 6(B)), the fresh AuMgGa₂O₄-300°C-5h catalyst provides good catalytic activity in which the reaction temperature for 50% CO conversion (T_{50}) was ~110 °C. For the aged catalyst, the AuMgGa₂O₄-800°C-5h becomes much less active, whose T_{50} increases to ~230 °C. However, upon introducing CeO₂ into the aged catalyst, the resulting CeO₂/[AuMgGa₂O₄-800°C-5h] catalyst presents enhanced activity and the T_{50} decreases to ~130 °C. Notably, the CeO₂/[AuMgGa₂O₄-800°C-5h] catalyst appears more active than the fresh AuMgGa₂O₄-300°C-5h catalyst at temperatures below 80 °C. The Au/CeO₂-RRCe-2 benchmark catalyst is more active than all the AuMgGa₂O₄ catalysts with a T_{50} of ~83 °C, and represents a highly active Au nanocatalyst in this reaction. Fig. 5(C) shows the catalytic performance of the catalysts observed during the combustion of methane. Unlike catalyzing the CO oxidation reaction at low temperature, meaningful CH₄ conversions occur at temperatures over 400 °C. The T_{50} for the fresh AuMgGa₂O₄-300°C-5h catalyst was ~614 °C and that for AuMgGa₂O₄-800°C-5h increased to 648 °C. The Au/CeO₂-RRCe-2 benchmark catalyst was also slightly more active than these AuMgGa₂O₄ catalysts with a T_{50} of 598 °C. However, the CeO₂/[AuMgGa₂O₄-800°C-5h] catalyst has a T_{50} of 570 °C and was more active than AuMgGa₂O₄-300°C-5h and AuMgGa₂O₄-800°C-5h as well as Au/CeO₂-RRCe-2. It is obvious that CeO₂ can also significantly promote the activity of the AuMgGa₂O₄ ensemble for both the CO oxidation and CH₄ combustion reactions.

3.3. Promotion mechanism of CeO₂

3.3.1. Experimental evidence

Here we take the WGS as an example to illustrate the promotion mechanism of CeO₂ for H₂O splitting on the CeO₂/[AuMgGa₂O₄] catalyst. In order to detect the ability to adsorb and dissociate water, *in-situ* DRIFTS of the H₂O adsorption experiment was recorded on both the AuMgGa₂O₄-800°C-5h and CeO₂/[AuMgGa₂O₄-800°C-5h] catalysts under 10 vol% H₂O at 200 °C. As shown in Fig. 7 (0 min), the typical bands for the O–H stretching vibration are observed after the adsorption saturation of H₂O. For the CeO₂/[AuMgGa₂O₄-800°C-5h] sample, the O–H stretching vibration of H₂O and the OH groups appeared between 3800 and

Fig. 7. *In-situ* DRIFTS of adsorbed H₂O reacted with 2 vol% CO over the Au/MgGa₂O₄-800°C-5h and CeO₂/[Au/MgGa₂O₄-800°C-5h] catalysts.

3000 cm⁻¹. The bands appearing in this region can be summarized as follows: (1) The bands at 3750, 3670 cm⁻¹, and 3494 cm⁻¹ are related to the stretching vibrations of the monodentate, bidentate and tridentate ceria hydroxyl groups [38], and (2) the broad band at ca. 3400 cm⁻¹ can be ascribed to physisorbed H₂O molecules bound by weak hydrogen bonds with each other [39]. For the Au/MgGa₂O₄-800°C-5h sample, only the band at ca. 3400 cm⁻¹ due to the O-H stretching vibration of physisorbed H₂O molecules was observed. These results indicate that CeO₂/[Au/MgGa₂O₄-800°C-5h] can dissociate H₂O molecules to form ceria hydroxyl groups, while this does not happen over the Au/MgGa₂O₄-800°C-5h catalyst.

In order to investigate the role of the dissociated H₂O molecules in the WGS, we performed the reaction between CO and adsorbed H₂O over the catalysts studied. After purging with He, 2 vol% CO in He was introduced into the reaction cell and the spectrum was recorded as a function of time. Fig. 7 shows the DRIFTS signals observed for both CeO₂/[Au/MgGa₂O₄-800°C-5h] and Au/MgGa₂O₄-800°C-5h during the first 10 min of the reaction. For the CeO₂/[Au/MgGa₂O₄-800°C-5h] catalyst, CO₂ bands appeared between 2280–2400 cm⁻¹ and their intensity sharply increased within the first 2 min and then decreased. Along with the changes observed for the CO₂ bands, the intensities of the bands corresponding to the ceria hydroxyl groups also obviously decreased during the first 2 min of the reaction and then remained stable, especially the tridentate ceria hydroxyl band observed at ca. 3494 cm⁻¹. These results indicate that CO reacts with the ceria hydroxyl groups to produce CO₂. For the

Au/MgGa₂O₄-800°C-5h catalyst, there were no obvious changes in the bands corresponding to the physisorbed H₂O molecules and CO₂. In combination with the above results, it was obvious that the addition of CeO₂ promoted the dissociation of water and the dissociated hydroxyl groups then reacted with CO to form CO₂.

3.3.2. Proposed mechanism

In view of the above analysis, the possible mechanism for the activity promotion of CeO₂ in anti-sintering Au/MgGa₂O₄ is illustrated in Fig. 8. It has been reported that Au NPs are efficient for CO activation at low temperature, while not efficient at dissociating water molecules [13,14]. The addition of CeO₂ makes up for the deficiency of Au/MgGa₂O₄ toward water dissociation. The formation of Ce-OH observed in the *in-situ* DRIFTS results illustrates that the H₂O molecules adsorbed on the surface of CeO₂ are dissociated and the resulting hydroxyl groups then react with CO to form CO₂, which allows the reaction to proceed smoothly. According to the well acknowledged mechanism of the WGS based on theoretical calculations [13,40], the possible reaction pathway that occurs on the CeO₂/[Au/MgGa₂O₄] catalyst is shown in Fig. 8. Firstly, the water molecule dissociates on the O vacancies of ceria to form -OH and -H, and CO is adsorbed on the Au sites located nearby. The adsorbed CO then reacts with the dissociated hydroxyl group to form carboxyl (-HOCO), which decomposes to CO₂ and adsorbed •H. Two adsorbed •H then combine to produce H₂ and thus, the reaction cycle is completed. In addition, CeO₂ is an excellent reducible support, which has high oxygen mobility and storage capacity [22]. Meanwhile, it has been reported that oxygen vacancies can be created on the ceria lattice at moderate temperatures and under reductive atmospheres, and these oxygen vacancies can also provide active sites for O₂ dissociation [23,25]. It has also been experimentally proven that the addition of CeO₂ supplies active oxygen for the oxidation reaction [17,26,41]. Thus, the promotion effect of CeO₂ in CeO₂/[Au/MgGa₂O₄-800°C-5h] in the CO oxidation and CH₄ combustion reactions is attributed to the improvement in the activation of oxygen. On the whole, the CeO₂/[Au/MgGa₂O₄] catalyst combines the advantages of MgGa₂O₄ and CeO₂ to stabilize the Au NPs and activate certain reactants, respectively, and can be used as a durable and active heterogeneous gold catalyst.

4. Conclusions

In this paper, we have reported that the catalytic activity of

Fig. 8. The proposed mechanism of CeO₂ for activity promotion of anti-sintering Au/MgGa₂O₄.

the anti-sintering Au NPs on MgGa_2O_4 can be further promoted by proximate contact with CeO_2 . Characterizations using XRD, HAADF-STEM, EDS mapping, XPS, and H_2 -TPR showed that the MgGa_2O_4 stabilized Au NPs were in intimate contact with the CeO_2 with strong synergistic effects in the CeO_2 -modified Au/ MgGa_2O_4 catalyst. Such a stable matrix exhibits significantly improved catalytic activity in the WGS, catalytic combustion of methane, and CO oxidation reaction. Specifically, severely aged Au/ MgGa_2O_4 together with the CeO_2 promoter presents even higher activity than that of the fresh Au/ CeO_2 -RRCe-2 benchmark catalyst in the WGS and reduces the “light off” temperature (T_{50}) for methane combustion and CO oxidation by 80 and 100 °C, respectively when compared with that of bare Au/ MgGa_2O_4 catalyst. The great promotion effect of CeO_2 on the catalytic activity of anti-sintering Au/ MgGa_2O_4 was derived from its excellent ability for the dissociation of H_2O or O_2 . This stepwise stabilization-activation strategy will be an effective way for rationally constructing stable and active heterogeneous gold catalysts.

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Graphical Abstract

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Activity promotion of anti-sintering Au/ MgGa_2O_4 using ceria in the water gas shift reaction and catalytic combustion reactions

Guo-Qing Ren, Guang-Xian Pei, Jing-Cai Zhang, Wei-Zhen Li *

Dalian Institute of Chemical Physics, Chinese Academy of Sciences; University of Chinese Academy of Sciences; Dalian National Laboratory for Clean Energy

The addition of CeO_2 to thermally stable Au/ MgGa_2O_4 significantly enhances its catalytic activity in the water-gas shift reaction, CH_4 combustion and CO oxidation reactions.

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CeO₂对抗烧结Au/MgGa₂O₄催化剂用于水汽变换和催化燃烧反应的促进作用

任国庆^{a,b}, 裴广贤^{a,b}, 张景才^{a,c}, 李为臻^{a,c,*}

^a中国科学院大连化学物理研究所, 辽宁大连116023

^b中国科学院大学, 北京100049

^c中国科学院洁净能源创新研究院, 辽宁大连116023

摘要: 自上世纪八十年代在多相催化研究领域兴起纳米金催化淘金热以来, 负载型纳米金催化剂的优越性和局限性都得到了广泛的研究。负载型纳米金催化剂活性强烈依赖于其晶粒尺寸和载体性质, 一般认为, 金纳米颗粒只有在一定的尺寸范围(2–5 nm)且负载在“活性”载体表面才能发挥出其优异的催化活性。然而, 小尺寸纳米金颗粒热稳定性差的弱点阻碍了其工业化应用的进程。因此, 如何实现小尺寸金纳米颗粒的高温稳定以及构筑金与“活性”载体间有效的接触界面是发挥纳米金优异催化性能的关键。我们曾利用MgGa₂O₄尖晶石载体与金纳米颗粒形成金属-氧化物“异质孪晶”结构, 从而实现了将~3 nm的金颗粒稳定在块体金的熔点(1064 °C)以上, 为小尺寸纳米金的高温稳定提供了新的思路。但MgGa₂O₄尖晶石是一种非氧化还原性载体, 对水分子或氧气分子的辅助活化作用较弱, 因而限制了具有优异高温抗烧结性能的Au/MgGa₂O₄催化剂在水汽变换和催化燃烧反应中的应用。

本文采用等体积浸渍法在高温800 °C焙烧5 h后的Au/MgGa₂O₄-800°C-5h样品上进行CeO₂助剂的修饰, 以提高其对水分子和氧气分子的活化能力。利用STEM, XRD和EDS-Mapping表征对CeO₂/[Au/MgGa₂O₄-800°C-5h]样品进行结构分析, 发现该样品中纳米Au具有优异的高温抗烧结性能, 800 °C焙烧5 h并经CeO₂修饰后其颗粒尺寸仍保持在3.1 nm左右, 样品中CeO₂的晶粒尺寸约为6 nm, 且Au纳米颗粒与CeO₂助剂间形成了有效的接触界面。利用H₂-TPR和XPS表征对该样品的氧化还原性能及电子性质进行分析, 发现CeO₂/[Au/MgGa₂O₄-800°C-5h]样品中CeO₂的还原温度相比于CeO₂/MgGa₂O₄对比样品显著降低, XPS结果显示CeO₂添加后Au的化学价态由金属态变为氧化态, 表明Au与CeO₂助剂间具有显著的电子转移。同时, CeO₂的添加显著提高了800 °C老化后Au/MgGa₂O₄催化水汽变换(CO转化率由~1.5%升到~34.0%, 450 °C)、甲烷燃烧(T₅₀降低80 °C)和CO氧化(T₅₀降低100 °C)等反应活性。为理解CeO₂对Au/MgGa₂O₄的催化性能促进机制, 我们选取水汽变换反应为例, 利用DRIFTS表征发现CeO₂促进了反应物H₂O的活化, 并结合小尺寸Au对CO的活化能力, 从而使水汽变换反应顺利进行。

本文在MgGa₂O₄尖晶石稳定纳米金的基础上, 利用具有优异氧传输性能的CeO₂作为助剂, 提高了该催化剂对水分子和氧气分子的活化能力, 从而获得了对水汽变换反应和催化燃烧反应具有高稳定性和高活性的CeO₂/[Au/MgGa₂O₄]催化剂。这种“先稳定-后活化”的催化剂设计思路也为今后高稳定性、高催化活性的纳米金催化剂的设计和制备提供了借鉴。

关键词: 纳米金催化剂; 氧化铈助剂; 镓酸镁尖晶石; 水汽变换; 催化燃烧

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*通讯联系人. 电话: (0411) 84379738; 传真: (0411) 84685940; 电子信箱: weizhenli@dicp.ac.cn

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