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Short Communication

Water–gas shift activity of ceria supported Au–Re catalysts

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ABSTRACT

Au–Re/ceria, Au/ceria and Re/ceria catalysts were prepared using deposition precipitation and impregnation techniques for Au and Re addition, respectively, except the sample prepared by sequential impregnation. Catalysts were characterized by HRTEM-EDS, SEM-EDS, XPS and XRD. WGS activity tests on the samples were performed in the temperature range 200–450 °C. The effects of Re incorporation, metal addition sequence, space velocity and H_2O/CO ratio on the catalytic performance were investigated. The novel Au–Re/ceria catalysts showed high activity in WGS reaction, especially at high H_2O/CO ratios, led by the presence of catalytically active and steam tolerant sites formed on the bimetallic catalysts.

1. Introduction

Water–gas shift (WGS) reaction, $CO + H_2O \leftrightarrow CO_2 + H_2$, is one of the key reactions in a typical fuel processor (FP) used in CO-free hydrogen production. WGS unit in an FP follows the reforming unit and reduces the CO concentration in the reformer effluent while increasing the hydrogen yield. Since reversible WGS reaction is moderately exothermic and equilibrium-limited, the desired CO levels can be achieved at low temperatures. In an FP, WGS is normally performed in two serial reactors, namely, high-temperature shift (HTS) reactor operating at 350–500 °C and low temperature shift (LTS) reactor operating at 180–240 °C for obtaining high activity and conversion simultaneously [1]. There has been great interest in the development of active, selective, thermally stable, poison resistant and *non-pyrophoric* noble metal based WGS catalyst formulations supported on metal oxide carriers since standard HTS (Fe_3O_4/Cr_2O_3 oxide) and LTS ($Cu/ZnO/Al_2O_3$) catalysts cannot be used in FPs due to their disadvantages such as thermodynamic limitations at high temperatures, sensitivity to air, the need of long pre-conditioning, and slow kinetics at low temperatures [1–4].

Catalyst formulations involving supported gold on ceria have shown to exhibit high WGS activity comparable to that of conventional catalysts [5–12]. Ceria has been emphasized as a reducible oxide support [5,13,14]; hence, a source of oxygen [13] and stabilizing agent for highly dispersed Au in the active nanostructured form [5,6,15] and a promoter for WGS reaction [6,15].

The reactivity of the gold–ceria catalysts is strongly influenced by the Au particle size and structure, which are sensitive to a number of variables, including preparation method [16], state and structure of the support [13,14,16], and catalyst pretreatment [3]. Among the employed methods of preparation, highly dispersed, low particle size gold is reported to be achieved via deposition precipitation (dp) method [5,10,17].

While ceria supported noble metal catalysts are promising candidates to be used in FP applications, efforts have been made to increase stability and catalytic activity of these catalysts further [18]. In our knowledge however, this is not the case for gold/ceria catalysts; only a few groups have tried to dope rare earth metals into ceria [19] or add another metal besides gold [17] to achieve better yields. Recently, Andreeva et al. [19] have investigated the influence of preparation method on structure and catalytic performance of gold supported on rare earth metal doped ceria catalysts. They concluded that higher WGS activity was achieved for catalysts promoted by Yb and Sm compared to the other gold/ceria based catalysts. Hurtado-Juan and his coworkers [17] have claimed to be the first ones to systematically study bimetallic, gold-on-ceria based promoted catalysts. They reported that the highest LTS activity belongs to Pt–Au/ceria in the group of Au–M/ceria (M: Pt, Pd, Ca, W, Ni) catalysts. They also proposed that the role of the Au–M system is to alter the local band structure of ceria facilitating its redox properties at low temperatures [17].

The addition of rhenium to TiO_2 and CeO_2–ZrO_2 supported Pt catalysts was shown to enhance the WGS activity [2,20]. Sato et al. reported for TiO_2 supported catalysts that catalytically active sites, which are effective for the activation of water and acceleration of WGS reaction, were formed between Re and Pt, Pd or Ir metals [20].

In the current study, impregnation and deposition precipitation (dp) techniques were employed to prepare Au–Re/ceria catalysts which were then characterized by HRTEM-EDS, SEM-EDS, XPS and XRD, and tested for WGS reaction. The effects of temperature, Re

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incorporation, metal addition sequence, GHSV and H_2O/CO ratio on the WGS activity were investigated and compared to those of Au/ceria catalysts.

2. Experimental

Ceria support was prepared by homogeneous precipitation of cerium nitrate using Na_2CO_3. It was then dried overnight at 105 °C and calcined at 400 °C for 4 h. Au/ceria catalysts were prepared by dp technique, which was carried out under fully controlled pH, stirring speed and temperature. Ceria was suspended in deionized (DI) water at a pH of 8.0–8.5. The pH was adjusted by adding aqueous ammonium carbonate solution. Subsequently, the desired amount of tetrachloro auric acid was added dropwise under vigorous stirring and then the precipitate was aged for 1 h., filtered and washed with DI water at 65 °C. The filtrate was then dried overnight at 75 °C under vacuum and calcined at air in a muffle furnace at 400 °C for 4 h. Re addition to all catalysts was conducted via an incipient-to-wetness impregnation technique using aqueous solution of ammonium perrhenate. The preparation methods of all catalysts tested for WGS activity are given in the text in brackets next to the catalyst as impregnation (imp), sequential impregnation (si) and deposition precipitation (dp). For example, 1% Au–0.5% Re/ceria (imp + dp) implies first the impregnation of Re on to ceria support and then the deposition precipitation of gold.

The characterization of the catalysts was carried out at Boğaziçi University R&D Center (SEM and XRD), TUBITAK MRC Materials Institute (HRTEM), and Middle East Technical University (XPS). The microstructure of the samples was examined using a Philips XL30 ESEM-FEG system. Quantitative elemental analyses were performed using energy dispersive spectroscopy (EDS). The crystalline phases of the catalyst samples were identified using Rigaku D/MAX-Ultima+/PC X-ray diffraction device equipped with Cu-Kα radiation operating at 40 kV and 40 mA with 2°/min scan speed. Further detailed characterization of the samples were performed by JEOL 2100 LaB6 HRTEM (200 kV) equipped with EDS; from which, bright-field images, diffraction patterns and semi-quantitative elemental analysis were obtained. In XPS tests, SPECS spectrometer equipped with a hemispherical electron analyzer and Al-Kα 282 W dual X-ray source was used. The XPS data analysis was performed with XPSPeak 4.1. The areas of peaks were estimated by calculating the integral of each peak after subtracting a Shirley background and fitting the experimental curve to a combination of Lorentzian/Gaussian lines.

Reaction tests were conducted in a down-flow, 55 cm long 1/4 in. OD, stainless steel tubular microreactor. The catalyst bed was fixed in the middle by glasswool. The height of the catalyst bed was ca. 0.4 cm. The temperature of the catalyst bed was controlled (±0.1 °C) via a programmable temperature controller (Eurotherm 3216P). The flow rates of high purity gases supplied from high-pressure gas cylinders (hydrogen, CO, nitrogen) and water were controlled by Brooks mass flow controllers and an Agilent 1100 HPLC pump, respectively; water fed to the system was evaporated before introducing it into the feed mixture.

The catalysts in reduced form (75 mg catalyst; in situ at 200 °C for 1 h under 100 ml/min of 5% H_2/N_2) were tested for their WGS activities in the temperature range 200–450 °C. No pre-conditioning was applied on freshly reduced samples prior to the reaction tests and all tests were conducted on freshly reduced samples. Blank tests confirmed inactivity of the reaction rig. All transfer lines in reaction and analysis parts of the system were kept at 125 °C to prevent possible condensation. Two ice traps were used to remove water vapor from the product stream prior to the analysis. Two Agilent Technologies 6850 gas chromatographs equipped with Porapak Q and Molecular Sieve 5A columns were used for analyzing feed and product streams. 1 h time-on-stream data were used while reporting the catalyst performance.

3. Results and discussion

3.1. Catalyst characterization

The XRD patterns of all calcined and reduced samples showed the presence of CeO_2 in the cubic crystal structure of fluorite-type. Rhenium impregnation and gold deposition did not influence the size of ceria crystallites to a great extent (Table 1); therefore, neither the extent of crystallization nor the structure of the support are the reasons for the differences observed in the catalytic activity of bimetallic catalysts. No detectable diffraction peaks of gold or rhenium crystallites were obtained, suggesting both metals are highly dispersed with very small particle sizes. The decrease in the calculated ceria lattice constants in the bimetallic catalysts (Table 1) can be attributed to the incorporation of Re^{+7}, which has smaller ionic radius (0.53 Å); into ceria lattice of ionic radius 0.97 Å [18]. This incorporation is evident in the case of 0.5% Re–1% Au/ceria (dp + imp) considering the shift in the XRD peaks towards higher diffraction angles.

Considering the redox properties of CeO_x, detailed analysis of Ce oxidation states is an important parameter. Fig. 1a represents the XPS spectra of Ce 3d core level electrons of the freshly reduced catalysts and catalysts used in WGS reaction as well. Ce 3d regions of the XPS spectra were evaluated and a relative amount of Ce^{3+} compound was estimated using the following equation [9,21]:

$$\left[Ce^{3+}\right] = I{-}Ce^{3+} / \left(I{-}Ce^{3+} + I{-}Ce^{4+}\right)$$

where $I{-}Ce^{3+}$ and $I{-}Ce^{4+}$ represent the sum of intensities of two doublets resulting from Ce_2O_3 and three doublets resulting from CeO_2, respectively. The higher Ce^{3+} content (Table 2) on 1% Au/ceria (dp) and 1% Au–0.5% Re/ceria (imp + dp) samples compared to that of 0.5% Re–1% Au/ceria (dp + imp) implies higher electron transfer ability from the support to metallic sites resulting in higher catalytic activity [7,22]. As a result of this electron transfer during reaction, the amount of Ce^{3+}decreased for 1% Au/ceria (dp) and 1% Au–0.5% Re/ceria (imp + dp), whereas for 0.5% Re–1% Au/ceria (dp + imp), low WGS activity level led to increased Ce^{4+} content on the surface due to limited oxygen utilization by the active sites. The O 1s spectra of the catalysts are shown in Fig. 1b. In all cases, the 1s peak is complex; the components observed after deconvolution of the O 1s peak are given in Table 2. For the freshly reduced samples, the low energy side of the O 1s binding energy scale (~529 eV) corresponds to the oxygen in the ceria lattice [23,24]. The other two peaks at ca. 531 and 533 eV are attributed to the chemisorbed water and hydroxyls, and to the weakly adsorbed water only on the ceria in oxidized state [22,25], respectively. Comparably higher amounts of adsorbed water and hydroxyls are evident for the freshly reduced 1% Au–0.5% Re/ceria (imp + dp) catalyst sample. Due to the water gas shift reaction, the intensity of the 531 eV peak decreased significantly for 1% Au/ceria (dp) and 1% Au–0.5% Re/ceria (imp + dp) implying the spent hydroxyls during reaction. This result is in agreement with the catalytic performance tests which run with the feed having $H_2O/CO = 5$; the most active catalyst is 1% Au–0.5% Re/ceria (imp + dp) which has the lowest amount of hydroxyls after the reaction. As a result of the WGS reaction, the peak related to the adsorbed water

Table 1
Ceria lattice constants and crystallite sizes of reduced catalysts.

Sample	Lattice constant, a[a] (nm)	Crystallite size[b] (nm)
1% Au–0.5% Re/ceria (imp + dp)	0.542	12.0
0.5% Re–1% Au/ceria (dp + imp)	0.540	13.8
1% Au/ceria (dp)	0.542	12.3
Ceria	0.542	11.6

[a] Calculated using $d^2 = a^2/(H^2 + K^2 + L^2)$.

[b] Calculated using the Scherrer Equation.