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COMMUNICATION

Low-Temperature Water-Gas Shift Reaction over Au/ZrO_2 Catalysts Using Hydrothermally Synthesized Zirconia as Supports

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Abstract: Au/ZrO_2 catalysts with a nominal gold loading of 1.0% were prepared by a deposition-precipitation method employing a series of ZrO_2 samples synthesized by a convenient hydrothermal route as supports. These catalysts were evaluated for low-temperature water-gas shift reaction under a model reformed methanol gas atmosphere. The effect of the hydrothermal synthesis temperature of zirconia on the catalytic activity of Au/ZrO_2 was investigated. The optimal hydrothermal synthesis temperature of ZrO_2 was 150 °C. The corresponding catalyst offers a CO conversion of 87% at a reaction temperature of 240 °C, which is significantly higher than that of the previously reported Au/Fe_2O_3, Au/CeO_2, and Au/$CeZrO_4$ catalysts. The Au/ZrO_2 catalysts were characterized by X-ray diffraction, atomic absorption spectrometry, N_2-physisorption, and scanning electron microscopy. The results indicate that the catalytic performance of the Au/ZrO_2 catalysts is mainly influenced by the morphology and pore structure of the ZrO_2 that was hydrothermally synthesized at different temperatures. A uniform nanodisk morphology and increase in the pore volume and pore diameter of the ZrO_2 particles lead to a higher catalytic activity of the Au/ZrO_2 catalyst.

Key words: hydrothermal method; hydrothermal synthesis temperature; gold; zirconia; supported catalyst; water-gas shift reaction

The water-gas shift reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$, ΔH = –41.2 kJ/mol, ΔG = –28.6 kJ/mol, WGS) is mainly used to purify the reformed gas and to supply pure H_2 for ammonia and other chemical synthesis processes. Recently, this reaction has attracted renewed attention because of its application in on-line H_2 production to fuel proton exchange membrane fuel cells (PEMFCs) [1,2]. Gold supported catalysts are regarded as the most promising low-temperature WGS catalysts for use under the harsh operating conditions of PEMFCs because of their superior low-temperature catalytic efficiency, wide operating temperature range, and excellent oxidation-tolerant and water-tolerant properties [3,4].

It has been established that gold supported catalysts such as Au/Fe_2O_3 [5–7], Au/CeO_2 [8–11], Au/TiO_2 [12], Au/ThO_2 [13], Au/$Cu_xMn_yO_z$ [14], Au/$CeZrO_4$ [15–17], and Au/ZrO_2 [5,18–23] give high catalytic activity in the low-temperature WGS reaction. The Au/ZrO_2 system has been of great interest because of its excellent catalytic performance. The physical properties of ZrO_2 such as its crystal phase [18], particle/crystallite size [19], density of surface hydroxyl groups [19], and specific surface area [20] were found to strongly influence the catalytic performance of Au/ZrO_2 catalysts for the low-temperature WGS reaction. For instance, Au nanoparticles supported on monoclinic zirconia exhibited higher WGS activity than that on tetragonal zirconia [18] and the increase in the particle size of ZrO_2 caused a significant decrease in Au-ZrO_2 contact boundaries i.e. active sites for the WGS reaction [19]. Considering that the physical properties of ZrO_2 are directly affected by the preparation method, it is critical to choose a suitable ZrO_2 preparation method to improve the catalytic efficiency of the Au/ZrO_2 catalyst to investigate the structure-property relation of the catalysts and to further guide the design of new catalysts. ZrO_2 supports for Au/ZrO_2 catalysts have been mainly synthesized by a reflux method [18,19], a precipitation method [5,20–22], and a template-directed hydrothermal method [23] while no reports have focused on

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the preparation of Au/ZrO_2 catalysts with ZrO_2 synthesized by a template-free hydrothermal method. In this paper, a series of ZrO_2 samples were prepared from a $ZrOCl_2$ aqueous solution by hydrolysis under hydrothermal conditions and used as supports for Au/ZrO_2 catalysts. The effects of hydrothermal synthesis temperature of zirconia on the structural properties and low-temperature WGS catalytic activity of Au/ZrO_2 were investigated.

A typical ZrO_2 hydrothermal synthesis was carried out as follows. $ZrOCl_2{\cdot}8H_2O$ aqueous solution (60 ml, 0.40 mol/L) was transferred into a 100 ml Teflon-lined stainless steel autoclave and this was maintained at different hydrothermal temperatures for 6 h. The resultant precipitate was then washed thoroughly with deionized water, dried at 120 °C for 8 h, and calcined at 450 °C in static air for 4 h. The support is denoted ZrO_2-*t*, where *t* refers to the hydrothermal temperature of ZrO_2. The Au/ZrO_2 catalysts with a nominal Au loading of 1.0% were prepared by a deposition-precipitation method using KOH as the precipitating agent. The catalyst samples are denoted Au/ZrO_2-*t*. X-ray diffraction (XRD) measurements for the structure determination were carried out with a PANalytical X'Pert Pro diffractometer using Co K_α radiation (λ = 0.1790 nm) and the scanning speed was 0.25°/s. The actual loading of gold in each catalyst was measured by atomic absorption spectroscopy (AAS) on a Varian SpectrAA-220 atomic absorption spectrometer. The specific surface area and pore structure of the samples were measured at –196 °C on a Micromeritics ASAP 2020 physical adsorption analyzer. A Hitachi S-4800 scanning electron microscope (SEM) was used to study the morphology of the catalysts.

The catalytic activity of the samples for the WGS reaction was measured from 150 to 300 °C on a CO-CMAT9001 apparatus that was equipped with a flow reactor. The preliminarily pretreatment of the samples was performed under a H_2 atmosphere at 300 °C over 2 h in a tubular-furnace and then the samples were quickly transferred to the reactor tube after cooling to ambient temperature under the H_2 flow. The following testing conditions were applied: atmospheric pressure; catalyst 0.5 g; space velocity = 10000 $cm^3/(g{\cdot}h)$; feed gas was a model reformed methanol gas containing 10% CO, 60% H_2, 12% CO_2, and balance was N_2; the ratio of vapor to feed gas was 1. The concentration of CO in the effluent was analyzed on-line using a gas chromatograph (Shimadzu GC-8A) equipped with a thermal conductivity detector (TCD).

The catalytic activity of the gold-zirconia catalysts for the low-temperature WGS reaction is shown in Fig. 1. As shown in this figure, significant differences in CO conversion were found for the samples over the whole testing temperature region. The catalytic activity decreased as follows: Au/ZrO_2-150 > Au/ZrO_2-170 > Au/ZrO_2-190 > Au/ZrO_2-130, i.e. with an increase in the hydrothermal synthesis temperature of ZrO_2, the catalytic activity of the resultant Au/ZrO_2 catalysts increased initially and then decreased and gave a maximum at the hydrothermal temperature of 150 °C. The influence of the hydrothermal temperature of ZrO_2 on the catalytic performance of the Au/ZrO_2 catalysts may be related to differences in the physical properties of the catalysts. Although the real gold loading is just 0.88% (Table 1), the Au/ZrO_2-150 sample gives a CO conversion of 87% at the reaction temperature of 240 °C, which is significantly higher than that of the reported 8.0% Au/Fe_2O_3 [7], 3.0% Au/CeO_2 [11], and 3.0% $Au/CeZrO_4$ [17] catalysts (conversion is 64%, 15%, and 69%, respectively). In other words, the Au/ZrO_2 catalysts with the ZrO_2 support prepared by the hydrothermal method can maintain high catalytic activity even though the gold content is very low, which is of great commercial value.

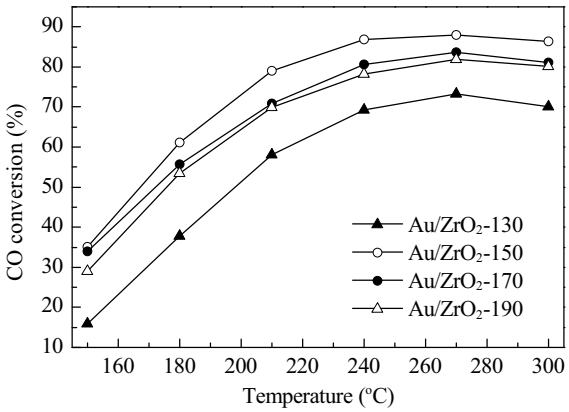

Fig. 1. Catalytic activity of Au/ZrO_2 catalysts for water-gas shift reaction. Reaction conditions: catalyst 0.5 g, feed 10%CO-60%H_2-12%CO_2-18%N_2, space velocity = 10000 $cm^3/(g{\cdot}h)$, steam/gas volume ratio = 1.

To investigate the reason for the difference in catalytic activity of the samples, several characterization methods were used. XRD patterns for the gold-based samples pretreated in hydrogen are shown in Fig. 2. All the diffraction peaks are related to the monoclinic phase of zirconia (JCPDS 01-089-9066) and no characteristic peaks of metallic gold are present (typical 2θ of 44.7°, JCPDS 01-089-3697), suggesting a high dispersion of gold particles on the support surface. With an increase in the hydrothermal temperature the XRD peaks of ZrO_2 become sharp and intense, indicating that the crystallization process is very effective. The corresponding crystallite size of the ZrO_2 particles calculated using the Scherrer equation increases from 3.0 to 7.4 nm (Table 1). Based on the catalytic activity results, the catalytic behavior of the catalysts correlates well with the crystallite size of the ZrO_2 particles for Au/ZrO_2-150, Au/ZrO_2-170, and Au/ZrO_2-190, i.e. smaller zirconia nanoparticles lead to a higher catalytic activity for the Au/ZrO_2 catalyst, which is consistent with the results reported by Li et al. [19] and Zhang et al. [24]. The improvement in activity upon reducing the ZrO_2 crystallite size is attributed to the increased Au-ZrO_2 contact boundaries in the catalysts [19,24], which are regarded as active sites in the WGS reaction.