



Uranium oxide-supported gold catalyst for water–gas shift reaction



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ABSTRACT

The orange yellow UO_3 and bottle green U_3O_8 phases were prepared by thermal decomposition of uranyl nitrate hexahydrate at 400 °C and 500 °C, respectively. Gold catalysts supported on two oxides were prepared by incipient wetness impregnation for water–gas shift reaction. The gold catalysts were characterized by the techniques such as nitrogen physical adsorption, X-ray diffraction, temperature-programmed reduction, and X-ray photoelectron spectroscopy. The Au/UO_3 catalyst has both microporous and mesoporous structures while the $\text{Au}/\text{U}_3\text{O}_8$ catalyst has only microporous structure. The presence of gold on the oxide surface greatly facilitates the reduction of uranium oxide support. The active sites for water–gas shift reaction are likely dominant metallic gold with a small portion of oxidized gold species due to $\text{UO}^{2+}/\text{U}^{4+}$ redox property. The Au/UO_3 catalyst shows higher activity with 55% conversion of CO in comparison with $\text{Au}/\text{U}_3\text{O}_8$. High activity on Au/UO_3 catalyst is attributed to facile the reducibility of UO_3 and its high surface gold atomic concentration.

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1. Introduction

Water–gas shift reaction (WGS) is one of the most important industrial processes for removing carbon monoxide impurity in hydrogen feedstock in ammonia synthesis, steam reforming of methanol and glycerol, and for adjusting the CO/H_2 ratio in syngas feeds [1,2]. Two types of industrial catalysts have been commercially available for this reaction: a high-temperature iron-based catalyst and a low-temperature copper-based catalyst. In recent years, many attentions have been paid to using supported gold catalysts for WGS. Most of them makes great struggle to improve its catalytic activity and understand the fundamental aspects related to the natures of active gold sites, role of support, and reaction mechanism [3–8]. It is known that the catalytic performance of gold catalyst depends highly on size and shape of gold nanoparticles, reducible property of oxide support, gold-oxide interface interactions, and so on. Andreeva et al. first used $\text{Au}/\alpha\text{-Fe}_2\text{O}_3$ catalyst for WGS and found that its activity is comparable with that of a conventional copper catalyst [9,10]. Fu et al. reported subsequently that Au/CeO_2 catalyst had higher activity than other oxides-supported gold catalysts [11–13]. The good reducibility of and high oxygen storage of ceria as well as a perturbation of the lattice constant of ceria caused by the diffusion of Au ions into ceria were considered to be responsible for its high activity [14–16]. Obviously, the selection of an efficient support is a decisive factor to provide good catalytic performance.

Uranium is an actinide element with six valence electrons. The ability to attain high coordination numbers makes it as a promising catalytic

material. Some studies have focused on uranium oxide as a catalyst or a catalyst support [17–22]. Many chemical processes can proceed efficiently due to participation of the catalysts containing uranium oxides. For example, Collette et al. [17] prepared uranium oxides supported on SiO_2 , TiO_2 , Al_2O_3 , and MgO carriers for destructive reaction of volatile organic compounds and suggested strong oxide–oxide interaction. Pollington et al. [18] and Campbell et al. [19] reported that $\text{UO}_x/\text{Al}_2\text{O}_3$ catalyst exhibited comparable activity and selectivity to that of conventional supported Pt catalysts in the catalytic reduction of NO. Berry et al. [20] found that uranium oxide component could maintain a high dispersion of metallic nickel in Ni/UO_x catalyst and inhibit its sintering. Gordeeva et al. [21] used porous U_3O_8 as a support to prepare very active Ni- and Ru-catalysts for steam reforming of methane. Taylor et al. [22,23] studied the activity and mechanism of uranium oxide catalysts for the oxidative destruction of volatile organic compounds and of short chain alkanes. Choudhary et al. [24,25] demonstrated that $\text{Au}/\text{U}_3\text{O}_8$ catalyst had higher selectivity and yield than other oxides-supported gold catalysts for selective oxidation of benzyl alcohols by molecular oxygen. Recently Ismagilov et al. [26] reviewed the synthesis and characterization of uranium-containing catalysts. The benefit of uranium oxide-based catalyst is high activity, thermal stability, and resistance to poisoning by coke. The facile uranium redox couple is responsible for high activity of uranium oxide catalyst. Therefore, uranium compounds form a notable class of efficient catalysts and further studies of this catalytic system can open a new vista.

In this study, we reported the preparation of uranium oxides and supported gold catalysts for the first time in water–gas shift reaction. The techniques such as nitrogen adsorption, X-ray diffraction (XRD), temperature-programmed reduction (TPR) and X-ray photoelectron spectroscopy (XPS) were employed to understand the structure and

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the catalytic performance of gold nanoparticles supported on uranium oxides.

2. Experimental procedure

2.1. Catalyst preparation

The most common uranium salt is uranyl nitrate hexahydrate $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. In this study a series of uranium oxides were obtained through thermal decomposition of the salt in static air at the range of 300–800 °C. The obtained uranium oxides were denoted as $\text{UO}_3\text{-T}$, in which T expresses the calcination temperature of uranium salt.

Gold catalysts supported on $\text{UO}_3\text{-T}$ were prepared by the impregnation method as the following procedures [27,28]. The solid $\text{UO}_3\text{-T}$ was first impregnated with a basic solution of HAuCl_4 overnight at room temperature. The pH value of the solution was controlled to be 7–8 with a 2 mol/L NaOH solution. The obtained wet sample was immersed in 6 mol/L $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution and thereafter washed with distilled water several times to remove residual chloride ions on the surface. After dried in a vacuum at 80 °C for 12 h, the sample was calcined in air at 300 °C for 3 h. For each sample, the theoretic Au loading is 1.0 wt.% and the actual loading was determined by atomic absorption spectroscopy to be 0.98 wt.%.

2.2. Catalytic activity testing

The water–gas shift reaction was carried out in a fixed-bed flow reactor at atmospheric pressure, as described in previous work [29]. The feed gases consisted of 99.99% CO at 10 mL/min and water vapor with 31.1 kPa partial pressure. Reaction temperature was controlled at the range of 150–350 °C. Prior to the reaction, 0.5 g gold catalyst was reduced in situ in pure H_2 at 200 °C for 2 h. The components in feed and effluent gases were analyzed by gas chromatography and then a QIC-20 quadrupole mass spectrometer (Hiden Analytical Ltd.). The following gas chromatography analysis conditions used: pure Ar as carrier gas, column temperature 50 °C, vaporization temperature 120 °C, detector temperature 120 °C, a thermal conductivity detector with carbon black molecular sieve as packed column (internal diameter 3 mm and length 2 m). The catalytic activity was expressed as CO conversion and calculated through the amount of H_2 in the effluent gas according to the following expression: $\text{CO conversion} = n(\text{H}_2)/n(\text{CO})_{\text{in}}$ in where $n(\text{H}_2)$ is the amount of H_2 produced by water–gas shift reaction and $n(\text{CO})_{\text{in}}$ is the initial amount of CO.

2.3. Catalyst characterizations

The phase analyses of uranium oxides and supported gold catalysts were performed on a Shimadzu-6100 X-ray powder diffractometer with a monochromatic copper $K\alpha$ radiation operated at 40 kV and 30 mA. The crystalline phase was identified according to the JCPDS powder diffraction file cards.

The textural property of each sample was measured by isothermal adsorption–desorption of nitrogen using a Quantachrome NOVA 3000e automated surface area and pore size analyzer. The specific surface area was determined by using nitrogen adsorption data from the relative equilibrium pressure interval of $0.03 < P/P_0 < 0.3$, where P is the equilibrium nitrogen pressure and P_0 is the saturation nitrogen pressure, according to Brunauer–Emmett–Teller method. The average pore radius and the pore size distribution were calculated from the corresponding nitrogen isotherm using Barret–Joyner–Halenda method.

The H_2 TPR profiles of UO_3 , Au/UO_3 and AuU_3O_8 samples were obtained in TP-5000 multifunction adsorption instrument. Prior to the reduction, 50 mg sample was baked at 60 °C for 2 h and then cooled down to room temperature in pure nitrogen and subsequently switched in the reducing gas of 10% hydrogen in argon at 20 mL/min. After the baseline became smooth, the temperature was linearly raised to

800 °C at 10 °C/min. The 5A molecular sieve was mounted in the gas line to remove water formed during the reduction prior to going into the thermal conductivity detector.

XPS analyses of Au/UO_3 and $\text{Au}/\text{U}_3\text{O}_8$ samples were finished on a VG ESCA 210 X-ray photoelectron spectrometer using Mg $K\alpha$ radiation with an energy of 1253.6 eV and a residual gas pressure of 2.7×10^{-6} Pa in the analysis chamber. The binding energy reference of Au 4f, U 4f, and O 1s was taken at 285.0 eV for the C 1s peak arising from adventitious carbon. The analyzer was operated in constant analyzer energy mode. The surface gold atomic concentration of each sample was derived from corresponding peak area.

3. Results and discussion

3.1. Phase analyses of uranium oxide and supported gold catalyst

The oxides of uranium including a few species in which UO_2 (brown), U_3O_8 (bottle green), and UO_3 (orange-yellow) have been well-characterized. The oxides readily interconvert at elevated temperatures. According to Heynen and Van der Baan [30], Mckee [31], the uranium salts such as uranyl nitrate and uranyl acetate can decompose to form hexagonal UO_3 phase at above 400 °C. Heating UO_3 in air to 650 °C and higher obtains orthorhombic U_3O_8 phase. It will obtain cubic face-centered UO_2 and intermediate phases with heating U_3O_8 or UO_3 in hydrogen stream at 700 °C and higher. In this experiment, uranium oxides were prepared by thermal decomposition of uranyl nitrate in air at 300–800 °C.

As shown in Fig. 1, the diffraction peaks at $2\theta = 18.4^\circ$, 24.8° , and 29.1° are assigned to monoclinic $\beta\text{-UO}_3$ phase (JCPDS 18-1428) and the diffraction peaks at $2\theta = 21.4^\circ$, 26.0° , 26.5° , 33.9° , and 34.3° come from orthorhombic $\alpha\text{-U}_3\text{O}_8$ phase (JCPDS 47-1493). Therefore, an orange yellow phase (UO_3) is observed between 300 and 400 °C. At above 400 °C, UO_3 begins to lose oxygen via the following reaction [32]: $3\text{UO}_3(\text{s}) \rightarrow \alpha\text{-U}_3\text{O}_8(\text{s}) + 1/2\text{O}_2(\text{g})$. A bottle green phase (U_3O_8) was obtained between 500 and 800 °C. However, the diffraction peaks of UO_2 phase (JCPDS 41-1422), i.e., $2\theta = 28.4^\circ$, 32.9° , 46.9° , 55.7° , and 58.3° , are not observed due to using calcination in air procedure during the preparation [21,26,32]. In addition to the phase transition from UO_3 to U_3O_8 , the increase of calcination temperature also causes the increase of the crystallization and particle size of uranium oxide.

The diffraction peaks of metallic gold (JCPDS 04-0784), i.e., $2\theta = 38.2^\circ$, 44.4° , and 64.6° , are not obviously observed in Fig. 2 for all supported gold catalysts, indicating the gold particles are probably either with small average size or highly dispersed on uranium oxide supports.

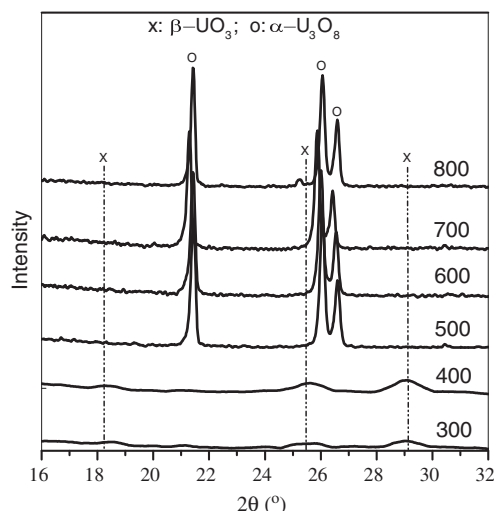


Fig. 1. XRD patterns of uranium oxides obtained at different temperatures (°C).

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