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Comparative study of Au/ZrO_2 catalysts in CO oxidation and 1,3-butadiene hydrogenation

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Abstract

This work investigates the effects of Au^{3+}/Au^0 ratio or distribution of gold oxidation states in Au/ZrO_2 catalysts of different gold loadings (0.01–0.76% Au) on CO oxidation and 1,3-butadiene hydrogenation by regulating the temperature of catalyst calcination (393–673 K) and pre-reduction with hydrogen (473–523 K). The catalysts were prepared by deposition–precipitation and were characterized with elemental analysis, nitrogen adsorption/desorption, TEM, XPS and TPR. The catalytic data showed that the exposed metallic Au^0 atoms at the surface of Au particles were not the only catalytic sites for the two reactions, isolated Au^{3+} ions at the surface of ZrO_2, such as those in the catalysts containing no more than 0.08% Au were more active by TOF. For 0.76% Au/ZrO_2 catalysts having coexisting Au^{3+} and Au^0, the catalytic activity changed differently with varying the Au^{3+}/Au^0 ratio in the two reactions. The highest activity for the CO oxidation reaction was observed over the catalyst of $Au^{3+}/Au^0 = 0.33$. However, catalyst with a higher Au^{3+}/Au^0 ratio showed always a higher activity for the hydrogenation reaction; co-existance of Au^0 with Au^{3+} ions lowered the catalyst activity. Moreover, the coexisting Au particles changed the product selectivity of 1,3-butadiene hydrogenation to favor the formation of more *trans*-2-butene and butane. It is thus suggested that for better control of the catalytic performance of Au catalyst the effect of Au^{3+}/Au^0 ratio on catalytic reactions should be investigated in combination with the particle size effect of Au.
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Keywords: Au/ZrO_2 catalysts; Gold catalyst; Cationic gold; CO oxidation; Hydrogenation; Catalytic sites; 1,3-Butadiene

1. Introduction

Despite that many investigations have been made for the elucidation of active sites in CO oxidation, the nature of active gold in the CO oxidation is still under debate [1–6]. For example, some publications showed that small metallic gold nanoparticles interacting strongly with support oxides were essential for the high catalytic activity [2,5,7,8]. And, the low-coordinated surface Au atoms at the steps, edges and corners of the Au particles were proposed as the catalytic sites [7]. However, other reports evidenced that the high catalytic activity of supported Au catalysts in CO oxidation had a relation to the presence of cationic gold [3,4,9–11]. Some reports even concluded that the oxidized gold species were more active than the metallic gold [9–11]. It has also been suggested that the real catalytic sites could be ensembles containing both cationic and metallic gold [3,4].

It could be interesting to mention that significantly higher activity for the CO oxidation were usually observed when nanosized oxides were used to "support" Au nanoparticles [5,12,13]. In particular, remarkable enhancement in the catalytic activity by gold was demonstrated if particles of the "supporting" oxide were sized to match the sizes of Au nanoparticles to make a metal/oxide nanocomposite as in Au/ZrO_2 [5] and Au/CeO_2 [13].

The selective hydrogenation of 1,3-butadiene has been an important model reaction in characterizing the catalysis by transition metals. Though theoretical calculation and hydrogen chemisorption experiments showed that the surface of metallic gold was inert for hydrogen activation [14,15], earlier investigations demonstrated that Au nanoparticles on oxide support were active for the hydrogenation reaction [16,17]. We discovered recently that the mass specific activity of isolated Au^{3+} ions on zirconia surface were two orders of magnitude higher than that of Au nanoparticles in catalyzing the selective

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hydrogenation of 1,3-butadiene to butenes [18]. And, when there were coexisting metallic Au nanoparticles, the activity of gold appeared to decrease with decreasing the Au^{3+}/Au^0 ratio of the catalyst [18].

In the present work, our study is extended to investigate the effect of Au^{3+} ions in Au/ZrO_2 catalysts on the CO oxidation reaction. The results are compared systematically with those of the 1,3-butadiene hydrogenation on the same catalysts to understand if there is any similarity in the properties of catalytically active sites in Au/ZrO_2 catalysts for both reactions. We intend to show that the distribution of gold oxidation states can be an essential aspect for better control of the catalytic performance of supported Au catalyst.

2. Experimental

2.1. Catalyst preparation and characterizations

ZrO_2 was prepared conventionally first by hydrolysis of $ZrOCl_2$ with an aqueous solution of ammonia to form a $ZrO(OH)_2$ hydrogel. After extensive wash by deionized water, the hydrogel was dried (393 K) overnight and then calcined (673 K, 5 h) in flowing air (60 mL min^{-1}) to produce the ZrO_2 support, which consisted of 55% monoclinic and 45% tetragonal phase by XRD analysis [5] and showed a BET surface area of 120 $m^2\ g^{-1}$ and a pore volume of 0.16 cm^3/g. The averaged crystal size of this support calculated from XRD line broadening was 5–6 nm and its particle size by TEM measurement was 10–30 nm. Au/ZrO_2 catalysts with 0.01, 0.05 and 0.76% Au by weight were prepared by deposition–precipitation method using $HAuCl_4$ for the gold precursor as described elsewhere [5,18,19]. Except for the 0.76% Au/ZrO_2 catalysts, the obtained samples were then calcined at 473 K in flowing air for 5 h and were denoted as *m*% Au/ZrO_2-473, *m*% denotes the percentage of Au loading (ICP-AES analysis). As the content of cationic gold varies with the final calcination temperature of supported gold catalyst [9,18,20], the calcination temperature (*T*) of the 0.76% Au/ZrO_2 sample was varied in the range of 393–673 K to make 0.76% Au/ZrO_2-*T* samples of different Au^{3+}/Au^0 ratios. A 0.08% Au/ZrO_2-473 catalyst was prepared by a treatment of the 0.76% Au/ZrO_2-473 sample with a 2% KCN solution as described earlier [18,20].

The gold content was determined by ICP-AES. BET measurements were carried out with nitrogen adsorption at 77 K on a Micromeritics ASAP 2010C instrument. The crystal phase of ZrO_2 was characterized with powder X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer using the Ni-filtered Cu Kα radiation source at 40 kV and 40 mA. TEM and HRTEM characterizations were performed on JEM-2010F (200 kV). The samples were dispersed in ethanol using an ultrasonic bath, and then deposited on a polymer coated copper grids. EDS was combined to differentiate the gold particles from zirconia particles. About 200 particles were chosen to determine the mean diameter of Au particles according to equation $d = \Sigma n_i d_i / \Sigma n_i$, where n_i and d_i are the number and diameter of Au particles, respectively.

Quantitative temperature-programmed reduction (TPR) of the Au/ZrO_2 catalysts was conducted from 293 to 1053 K on a homemade TPR apparatus equipped with a thermal conductivity detector (TCD) with 5% H_2/Ar at a flow rate of 30 mL min^{-1} as the reductant [18]. The temperature ramp was 10 K min^{-1}. Before the reduction, the sample was pretreated at 473 K for 30 min with flowing Ar. The H_2 consumption data was measured by integrating the area under the TCD signal and on the basis of the calibrations determining TCD responses at various weight of pure CuO.

X-ray photoelectron spectra (Au 4f) of the catalysts were recorded with a PHI-5300 ESCA spectrometer equipped with Mg Kα radiation. The residual pressure in the analytical chamber was maintained below 10^{-10} Torr during data acquisition. The binding energies of Au 4f were corrected for surface charging by referencing them to the energy of C 1s peak of contaminant carbon at 285.0 eV.

2.2. Catalytic tests

Catalytic activity of CO oxidation and 1,3-butadiene hydrogenation were measured in continuous flow fixed bed reactors (i.d. = 6 mm) under atmospheric pressure at the reaction temperature of 343 and 393 K, respectively [5,18]. The reactant of 1.0 vol% CO in dry air or 2.15 vol% 1,3-butadiene in H_2 was introduced to the catalyst at flow rates of 34.0 and 13.5 mL min^{-1} with space velocities of 20,400 and 8100 $mLh^{-1}(g\text{-cat.})^{-1}$, respectively. Before the reaction, the catalysts (100 mg, diluted with 500 mg quartz sand to ca. 0.6 mL) were in situ pretreated with flowing ultra-pure argon (Ar, 30 mL min^{-1}) at 473 K (393 K for 0.76% Au/ZrO_2-393) for 2 h. The pretreatment of 0.05% Au/ZrO_2-473 sample was changed also to include redox pretreatments with H_2 or O_2 at desirable temperatures. The reactor effluents of CO oxidation and 1,3-butadiene hydrogenation were on-line analyzed using an HP-6890 (TCD, molecular 5A as an adsorbent) and GC-8A (FID, GDX-501 as an adsorbent) gas chromatographs, respectively. No reaction of CO was detected when the reactor was loaded with the ''pure'' ZrO_2 support for blank reaction tests but the conversion of 1,3-butadiene was ca. 0.9% in the blank tests.

3. Results

3.1. Physicochemical properties of Au/ZrO_2 catalysts

Table 1 shows the BET surface area and pore volume of ZrO_2 and Au/ZrO_2 samples. The loading of no more than 0.08% Au on ZrO_2 resulted in no change in the sample texture properties when compared with ''pure'' ZrO_2. The BET surface area and pore volume decreased by ca. 20% for 0.76% Au/ZrO_2-*T* samples. These changes in texture properties could be attributed to some blocking of the support pores by Au nanoparticles in the 0.76% Au/ZrO_2 samples since the catalyst calcination temperature *T* was kept no higher than the calcination temperature (673 K) of the ZrO_2 support. As observed in our previous study using higher temperatures for

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