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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.

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

Table 1
BET surface area, pore volume, average Au particle size, and gold reducibility of Au/ZrO_2 catalysts

Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)	d_{Au} (nm)	TPR peak (K)	Au^{3+}/Au^0
ZrO_2	120	0.16	–	–	–
0.01% Au/ZrO_2-473	120	0.16	nd[a]	508	∞
0.05% Au/ZrO_2-473	120	0.16	nd	504	∞
0.08% Au/ZrO_2-473	120	0.16	nd	496	∞
0.76% Au/ZrO_2-393	100	0.13	3.5	483	0.45
0.76% Au/ZrO_2-473	100	0.13	4.1	483	0.33
0.76% Au/ZrO_2-573	100	0.13	6.7	488	0.20
0.76% Au/ZrO_2-673	90	0.13	8.0	nd	0

[a] nd: Not detected.

the calcination of zirconia support [5], XRD patterns of the Au/ZrO_2 samples were found similar to that of the support material and the presence of Au was uncertain in the XRD measurements.

The averaged Au particle sizes in Au/ZrO_2 catalysts obtained from the TEM/HRTEM analysis are also given in Table 1. Those samples containing 0.01, 0.05 and 0.08% Au showed TEM images very similar to that of the ZrO_2 support; no metallic Au particles were detected even when they were analyzed with HRTEM, indicating that the loaded gold were atomically dispersed on zirconia surface at such low loading levels [18]. Nearly spherically shaped metallic Au particles were detected in the 0.76% Au/ZrO_2-*T* samples. And, the measured sizes/diameters of Au particles were seen to increase with *T* [9,18,20]. When *T* = 393 and 473 (i.e., 0.76% Au/ZrO_2-393 and -473), Au particles were found narrowly sized and averaged to 3.5 and 4.1 nm, respectively. The averaged Au particle size grew to 6.7 and 8.0 nm and their size distribution became much broader when *T* was increased to 573 and 673 K, respectively.

Fig. 1 shows the XPS spectra of 0.76% Au/ZrO_2-*T* samples. According to a number of earlier reports [5,9,11,18,21–23], the binding energies of gold at 87.3–87.8 eV ($4f_{5/2}$) and 83.6–84.5 eV ($4f_{7/2}$) were characteristic of the metallic gold (Au^0) while those at 89.4–90.4 eV ($4f_{5/2}$) and 86.3–87.7 eV ($4f_{7/2}$) of Au^{3+} ions. It is seen that the 0.76% Au/ZrO_2-673 sample (*T* = 673 K) contains only Au^0 but the other 0.76% Au/ZrO_2-*T* samples of *T* < 573 K contain coexisting Au^0 and Au^{3+} ions. It is interesting to note that the relative intensity of the XPS signals for Au^{3+} ions increased clearly with decreasing the catalyst calcination temperature (*T*), indicating that the reduction degree of gold in the Au/ZrO_2 catalyst was enhanced by using a higher *T*.

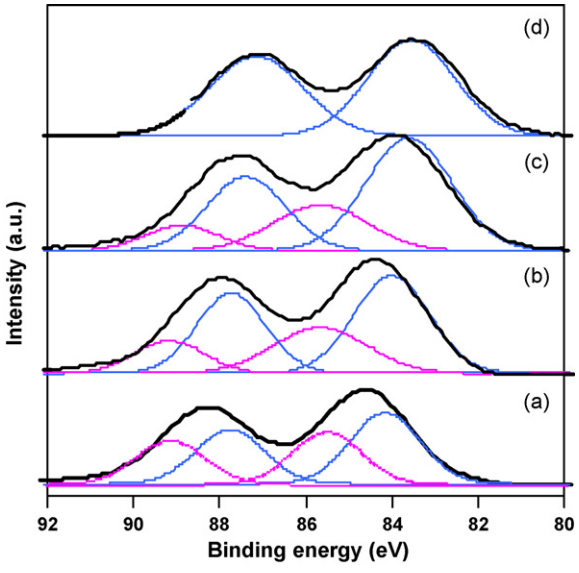

Fig. 1. XPS spectra of Au 4f in 0.76% Au/ZrO_2 catalysts calcined at 393 K (a), 473 K (b), 573 K (c) and 673 K (d).

Since the exposure of supported gold catalyst to photoelectrons during XPS measurement may effect a change in the oxidation state of gold [11,23], temperature-programmed reduction (TPR) technique was used to measure quantitatively the reduction and distribution of gold oxidation states in Au/ZrO_2 catalysts, as in our earlier work [18]. Hydrogen consumption peaks due to the reduction of gold was detected in the temperature range of 430–520 K [18,24] on the Au/ZrO_2 samples except 0.76% Au/ZrO_2-673. Partial (<3%) reduction of Zr^{4+} to Zr^{3+} at the support surface was also detected at much higher temperatures (above 773 K) [18,21,25]. No reduction of gold was detected in the TPR of the 0.76% Au/ZrO_2-673 catalyst agrees well with the XPS data (Fig. 1) that gold atoms in this catalyst were already reduced to Au^0 after it was calcined at *T* = 673 K, which is also consistent with earlier observations that high temperature calcination of supported gold catalyst would lead to complete reduction of gold to form metallic particles [5,9,20]. Calibration of the hydrogen consumption peak for the reduction of gold disclosed that the stoichiometric reduction molar ratio was H_2/Au (M) = 1.5 ± 0.2 for our Au/ZrO_2 samples containing no more than 0.08% Au, which evidenced that all of gold atoms existed as reducible Au^{3+} ions [18]. Note that the surface density of Au^{3+} ions in these samples of low Au loadings was no more than 0.02 nm^{-2}, which was sufficiently low to assure that the Au^{3+} ions were highly isolated at the surface of these samples [18]. Very recently, Liu et al. [26] claimed based on their DFT modeling of gold monomer on tetragonal ZrO_2 that isolated Au^{3+} ions are stable at temperatures below 500 K. This DFT calculation study based on tetragonal zirconia could be considered in support of our TPR identification of the Au^{3+} ions on the present ZrO_2 support containing ca. 45% tetragonal phase. Moreover, the modeling calculation seems also to suggest that the isolated Au^{3+} ions could be reduced to Au^+ ions under reductive conditions, such

as in hydrogen at 400 K [26]. Unfortunately, we have no evidence for such a predicted formation of Au^{+} in our samples as we observed only one TPR peak and the reduction stoichiometry was always H_2/Au (M) = 1.5 ± 0.2 for the samples containing only isolated Au^{3+} ions. Also, the reduction onset temperature of the isolated Au^{3+} appeared always higher than 455 K in the TPR measurement, which is significantly higher than the predicted temperature (400 K) in Ref. [26].

The reducible gold cations in the 0.76% Au/ZrO_2 catalysts are all assumed to be Au^{3+} ions as identified in the samples containing no more than 0.08% Au. This enables us to measure the Au^{3+}/Au^{0} ratio in each of the Au/ZrO_2 samples by calibrating the TPR hydrogen consumption peak, which are shown in the last column of Table 1. For the 0.76% Au/ZrO_2-*T* samples, the Au^{3+}/Au^{0} ratio decreased significantly with increasing *T*, showing again that the calcination temperature is crucial in regulating the Au^{3+}/Au^{0} ratio in oxide-supported gold catalysts [5,9,20].

The decrease in the TPR peak temperature of Au^{3+} ions with increasing the loading of gold (Table 1) would suggest that there are a number of types of gold binding sites on the zirconia surface. The addition of the gold titrates in a sense the stronger binding sites and then weaker ones. The TPR peak temperature characterized the binding strength of gold to the zirconia surface, thus at higher levels of gold, the reduction temperature of gold would be lower because a higher percentage of the gold would be sitting on the weaker binding sites.

3.2. Performance of Au/ZrO_2 catalysts in CO oxidation and butadiene hydrogenation

3.2.1. Effect of gold loading

Fig. 2 reports on the effect of gold loading on the catalytic performance of Au/ZrO_2-473 by showing the catalytic CO conversion against the reaction time on stream (TOS) in CO oxidation reaction at 343 K. The conversion levels of CO in the oxidation reaction were 1.1, 5.1, 8.3 and 59.3%, respectively, over the catalysts containing 0.01, 0.05, 0.08 and 0.76% Au. For the samples with the low Au loadings (i.e., ≤0.08%), which have only isolated Au^{3+} ions, it is easy to note that the CO conversion is just proportional to the number of Au^{3+} ions in the catalysts. The mass specific activities of gold in these catalysts, expressed by the reaction rate of CO over a gram of gold (mmol g-Au^{-1} s^{-1}), were found very close (0.232–0.246 mmol g-Au^{-1} s^{-1}). These data indicate that every Au^{3+} ion in the catalysts with the low Au loadings is equally active in the CO oxidation reaction. The high conversion of CO over the 0.76% Au/ZrO_2-473 catalyst could have relation to the much higher content of gold and the coexistence of Au^{3+} and Au^{0}; the mass specific activity of gold in this catalyst (0.177 mmol g-Au^{-1} s^{-1}) was even lower than that of the isolated Au^{3+} ions (0.232–0.246 mmol g-Au^{-1} s^{-1}) in the ones with low Au loadings.

The catalytic performance of *m*% Au/ZrO_2-473 catalysts in 1,3-butadiene hydrogenation at 393 K is shown in Fig. 3. The hydrogenation reaction was very selective for the "semi" hydrogenation of 1,3-butadiene to form butenes on these catalysts [18]. The major component of the butenes is 1-butene (ca. 60%) and the *trans*/*cis* ratio of 2-butenes is in the range of 0.3–0.5 (Table 2); the higher content of *trans*-2-butene and *trans*/*cis* ratio over the 0.01% Au/ZrO_2-473 catalyst could be due to a disturbance of the reaction over bare ZrO_2 [27], which produced butene isomers according to their thermodynamic equilibrium (80% *trans*-2-butene, 5% *cis*-2-butene, and 15% 1-butene; i.e., *trans*/*cis* = 16). Over the catalysts containing no more than 0.08% Au, the butadiene conversion in the selective hydrogenation also appeared in proportion to the number of Au^{3+} ions, which gave to very similar mass specific activities (2.01–2.15 mmol g-Au^{-1} s^{-1}) for the gold in these catalysts. It should be notified that the butadiene conversion over the 0.76% Au/ZrO_2-473 catalyst (75.2%) was significantly lower than the 0.08% Au/ZrO_2-473 catalyst (85.4%) having only isolated Au^{3+} ions. The mass specific activity of gold in this 0.76% Au/ZrO_2-473 catalyst (0.20 mmol g-Au^{-1} s^{-1}) was even one order of magnitude lower than that of those containing only isolated Au^{3+} ions (2.01–2.15 mmol g-Au^{-1} s^{-1}).

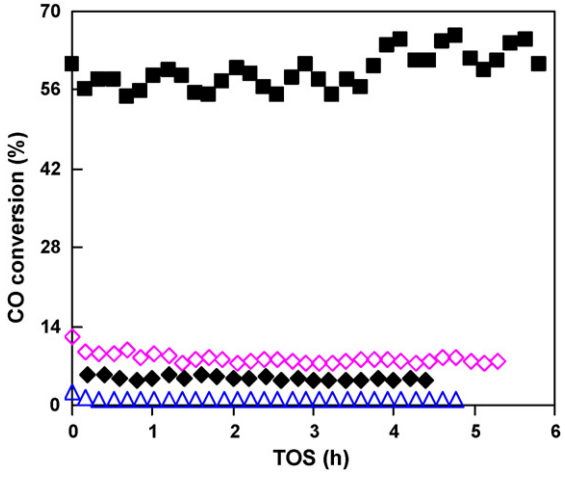

Fig. 2. Effect of gold loading (△) 0.01%; (◆) 0.05%; (◇) 0.08%; (■) 0.76% in Au/ZrO_2-473 catalysts on CO conversion in the catalytic CO oxidation reaction at 343 K.

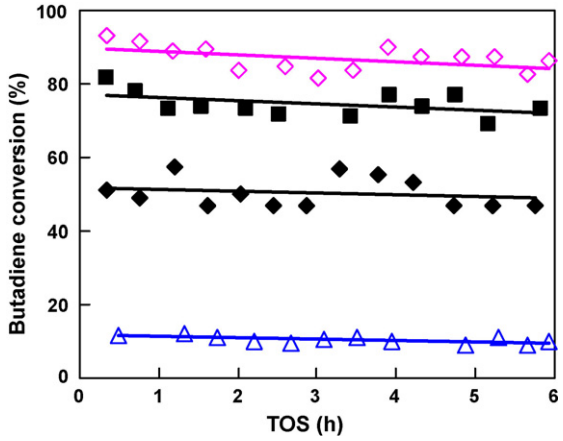

Fig. 3. Effect of gold loading (△) 0.01%; (◆) 0.05%; (◇) 0.08%; (■) 0.76% in Au/ZrO_2-473 catalysts on butadiene conversion in the hydrogenation reaction of 1,3-butadiene at 393 K.

Table 2
Product distribution of the catalytic hydrogenation of 1,3-butadiene at 393 K over Au/ZrO_2 catalysts

Sample	Butane	1-Butene	*trans*-2-Butene	*cis*-2-Butene	*trans*/*cis*
0.01% Au/ZrO_2-473[a]	0	52.6	20.7	26.7	0.78
0.05% Au/ZrO_2-473	0	64.7	9.4	25.9	0.36
0.05% Au/ZrO_2-473[b]	3.9	47.7	26.4	22.0	1.20
0.05% Au/ZrO_2-473[c]	13.8	20.3	50.2	15.7	3.19
0.08% Au/ZrO_2-473	0	63.7	10.0	26.3	0.38
0.76% Au/ZrO_2-393	0.3	64.0	9.4	26.3	0.36
0.76% Au/ZrO_2-473	0.4	60.6	11.6	27.4	0.42
0.76% Au/ZrO_2-573	0.7	59.6	14.0	25.7	0.54
0.76% Au/ZrO_2-673	2.6	56.9	16.7	23.8	0.70

[a] The product selectivity over this catalyst could be significantly affected by the reaction over the bare support surface (see the text).
[b] Before reaction, the catalyst was pretreated with flowing H_2 at 473 K for 60 min.
[c] Before reaction, the catalyst was pretreated with flowing H_2 at 523 K for 60 min.

3.2.2. *Effect of catalyst calcination*

Fig. 4 shows the effect of catalyst calcination temperature on the catalytic CO oxidation at 343 K over 0.76% Au/ZrO_2-*T* catalysts. In the oxidation reaction, the conversion of CO increased when the catalyst calcination temperature *T* was raised from 393 to 473 K. But, a further increasing of *T* up to 673 led to continued decrease in CO conversion (Fig. 4). The lowest CO conversion (ca. 4.2%) was found on the catalyst of $T = 673$ K (0.76% Au/ZrO_2-673, $Au^{3+}/Au^0 = 0$), and the highest CO conversion (ca. 59%) was obtained on the catalyst of $T = 473$ K (0.76% Au/ZrO_2-473, $Au^{3+}/Au^0 = 0.33$). The mass specific activities of gold in the 0.76% Au/ZrO_2-*T* catalysts was 0.177 mmol g-Au^{-1} s^{-1} at $T = 393$ K, it increased to 0.177 mmol g-Au^{-1} s^{-1} at $T = 473$ K and then decreased to 0.045 and 0.013 mmol g-Au^{-1} s^{-1}, respectively, at $T = 573$ and 673 K. These data suggest that there is no simple correlation between the CO oxidation activity and Au^{3+}/Au^0 ratio in the 0.76% Au/ZrO_2 catalysts.

An induction period was seen over the 0.76% Au/ZrO_2-*T* catalysts of $T = 393$ K. This induction period became less pronounced at $T \geq 473$ K. And, there was no induction period over the 0.76% Au/ZrO_2-673 catalyst that contains only metallic Au; it showed instead a slight deactivation in the initial three hours. The induction period observed with the 0.76% Au/ZrO_2-*T* of $T < 673$ K could be due to a formation of the so-called well-defined perimeter between gold and zirconia [9].

Shown in Fig. 5 is the effect of catalyst calcination on the performance of 0.76% Au/ZrO_2-*T* catalysts in the hydrogenation reaction, which is different from the case of the CO oxidation reaction (Fig. 4). The butadiene conversion declined continuously and dramatically with the continued increase in *T*; the average conversion of 1,3-butadiene was 98.4, 75.2, 53.4 and 39.0%, respectively, when *T* was increased from 393 to 473 K, then 573 K, and finally 673 K. The mass specific activity of gold in 0.76% Au/ZrO_2-*T* catalysts was 0.38 mmol g-Au^{-1} s^{-1} at $T = 393$ K, it decreased to 0.20, 0.14 and 0.10 mmol g-Au^{-1} s^{-1}, respectively, when *T* was raised to 473, 573 and then 673 K. Clearly, the catalyst having a higher Au^{3+}/Au^0 ratio exhibits a higher catalytic activity for the hydrogenation of 1,3-butadiene.

Trace to small amounts of normal butane, the complete hydrogenation product of 1,3-butadiene, was detected in the products of the hydrogenation reaction over the 0.76% Au/ZrO_2-*T* catalysts (Table 2). The amount of butane in the hydrogenation products was not significant (<1.0%) at $T \leq 573$ K, it increased to 2.6% at $T = 673$ K. The significantly

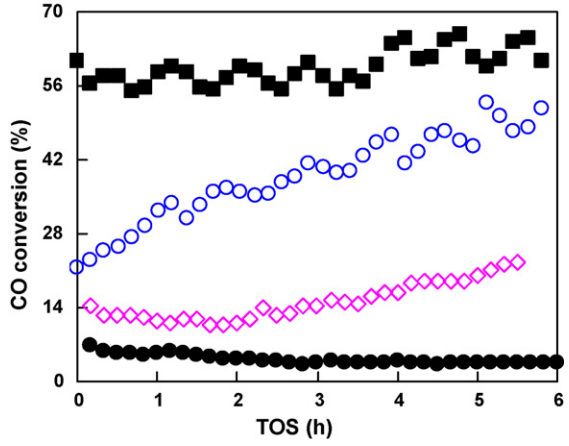

Fig. 4. Calcination temperature effect of the 0.76% Au/ZrO_2-*T* catalyst on CO conversion. $T = 393$ K (○), 473 K (■), 573 K (◇), and 673 K (●).

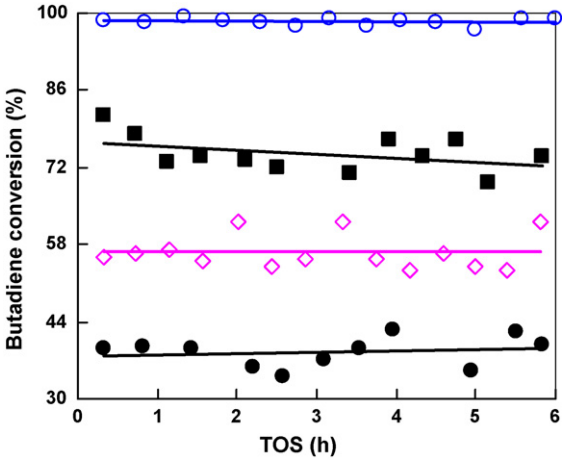

Fig. 5. Calcination temperature effect of the 0.76% Au/ZrO_2-*T* catalyst on butadiene conversion. $T = 393$ K (○), 473 K (■), 573 K (◇) and 673 K (●).

increased formation of butane over the 0.76% Au/ZrO_2-673 catalyst ($T = 673$) would be characteristic of metallic Au catalyst since its most discriminating feature from the other 0.76% Au/ZrO_2 is that it does not contain cationic gold but only metallic Au^0. A formation of n-butane (ca. 2%) was also reported earlier for 1,3-butadiene hydrogenation over metallic Au deposited on Al_2O_3 support [21].

3.2.3. Effect of hydrogen reduction

The 0.05% Au/ZrO_2-473 catalyst was chosen to study the pretreatment effect of hydrogen reduction on the catalytic performance of Au/ZrO_2-473. The pretreatments were conducted in flowing hydrogen at 473 and 523 K to induce, respectively, a partial and complete reduction of the Au^{3+} ions to metallic Au^0 atoms. Fig. 6 shows the effect of hydrogen reduction on the performance of 0.05% Au/ZrO_2-473 in the catalytic CO oxidation (A) and 1,3-butadiene hydrogenation (B). The H_2-reduction pretreatment at 473 K led to a distinct increase in the catalyst activity for CO oxidation; the CO conversion increased to ca. 12% from ca. 5% over the argon purged unreduced catalyst. However, the completely pre-reduced catalyst (i.e. after the pretreatment at 523 K) appeared less active than the catalyst pre-reduced at 473 K for the oxidation reaction (Fig. 6A). These data reveal that pre-reduction of a part of Au^{3+} ions in an Au/ZrO_2 catalyst with no metallic Au^0 is essential in effecting the highest possible catalyst activity but complete reduction of all the Au^{3+} ions to Au^0 atoms would make the catalyst less active for the CO oxidation reaction.

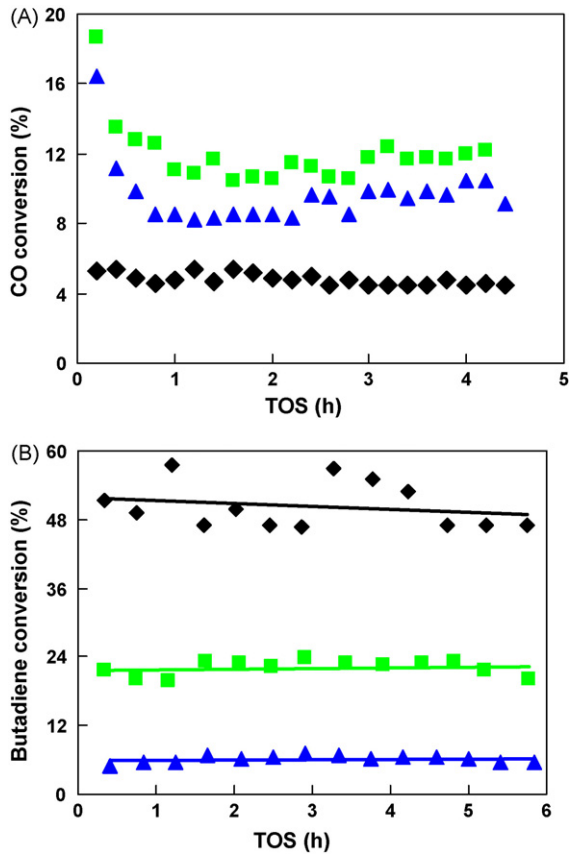

Fig. 6. Pretreatment effect of the 0.05% Au/ZrO_2-473 catalyst on CO oxidation (A) and 1,3-butadiene hydrogenation (B). The catalyst was pretreated with flowing hydrogen at 473 K (■) and 523 K (▲). The reference data (◆) were obtained over the catalyst pretreated with flowing argon at 473 K.

Different effect of hydrogen pretreatment was observed for the catalytic hydrogenation of 1,3-butadiene (Fig. 6B). The H_2-reduction pretreatment at 473 K led to a sharp decrease in the catalyst activity for the hydrogenation reaction; the butadiene conversion decreased to 22% from ca. 50% over the argon purged unreduced catalyst. Moreover, the completely pre-reduced catalyst was featured by a further sharp decline in the hydrogenation activity; the butadiene conversion became as low as 7% after the catalyst was pretreated with hydrogen at 523 K. These results clearly show that the catalyst activity for the hydrogenation reaction is steadily lost as a consequence of the pre-reduction of the Au^{3+} ions to form metallic Au^0 atoms.

Noticeably, H_2-reduction pretreatments of the 0.05% Au/ZrO_2-473 catalysts resulted also in significant changes of the product selectivity (Table 2). While no butane was detected over the argon purged unreduced catalyst, the H_2-reduction pretreatments led to significant formation of butane in the product. Also, the distribution of butene products changed to favor the formation of more 2-butenes. And, the *trans*/*cis* ratio of the 2-butenes increased from ca. 0.4 over the unreduced catalyst to 1.2 and 3.2, respectively, over the pre-reduced ones.

4. Discussion

The present catalytic data over Au/ZrO_2 catalysts show that either isolated Au^{3+} ions (like those in the catalysts containing 0.01, 0.05 and 0.08% Au) or metallic surface Au^0 atoms (like the ones of Au atoms in 0.76% Au/ZrO_2-673) are active for CO oxidation and 1,3-butadiene hydrogenation reactions. However, Au^{3+} ions coexisting with metallic Au nanoparticles at the surface of zirconia (like those in 0.76% Au/ZrO_2-393, -473, and -573) lead to some different consequences in the two reactions.

To understand the difference and similarity in the nature of catalytically active gold sites of Au/ZrO_2 catalysts for the two reactions, we summarized the reaction data in Table 3. The catalytic turn over frequency (TOF) data outside the parentheses were calculated on the basis of exposed Au^0 atoms while those inside the parentheses were based on the numbers of Au^{3+} ions. Although different in the gold loading (0.01–0.08%), all of the three catalysts containing only isolated Au^{3+} ions proved to show almost the same TOF numbers either in the CO oxidation (0.047 s^{-1}) or in the butadiene hydrogenation (0.41 s^{-1}). Thus, the isolated Au^{3+} ions are equally active not only in the selective hydrogenation of 1,3-butadiene [18], but also in the oxidation of CO. This conclusion could have important implication since the ability of Au^{3+} ions in catalytic CO oxidation over supported gold catalysts was seldom addressed [7,9–11,20].

The Au/ZrO_2 samples in Table 3 can be grouped into three categories. The samples with no more than 0.08% Au stand for zirconia-supported cationic gold (Au^{3+}) catalyst, which is one extreme in the categories. The 0.76% Au/ZrO_2-673 sample stands for zirconia-supported metallic gold (Au^0) catalyst,

Table 3
Summary of the catalytic reaction data of Au/ZrO_2 catalysts for the oxidation of CO at 343 K and hydrogenation of 1,3-butadiene at 393 K

Sample	CO oxidation			1,3-Butadiene hydrogenation		
	Conversion (%)	Reaction rate[a]	TOF[b] $\times 10^2$ (s^{-1})	Conversion (%)	Reaction rate[a]	TOF[b] (s^{-1})
0.01% Au/ZrO_2-473	1.1	0.246	(4.90)	10.3	2.08	(0.41)
0.05% Au/ZrO_2-473	5.1	0.232	(4.58)	49.9	2.01	(0.40)
0.08% Au/ZrO_2-473	8.3	0.235	(4.63)	85.4	2.15	(0.42)
0.76% Au/ZrO_2-393	39.1	0.117	9.39 (7.39)	98.4	0.38	0.31 (0.25)
0.76% Au/ZrO_2-473	59.3	0.177	15.0 (14.05)	75.2	0.20	0.17 (0.16)
0.76% Au/ZrO_2-573	15.1	0.045	5.39 (5.32)	53.4	0.14	0.17 (0.17)
0.76% Au/ZrO_2-673	4.2	0.013	1.47	39.0	0.10	0.12

[a] The unit is mmol g-Au^{-1} s^{-1}.
[b] The TOF data were calculated on the basis of exposed Au^0 atoms or Au^{3+} ions (data in the parentheses) in the catalyst.

which is the other extreme in the categories. And, between the two extremes are the other 0.76% Au/ZrO_2-*T* catalysts (*T* = 393, 473 and 573 K) that contain coexisting Au^{3+} ions and Au^0 atoms. The significant difference in the TOF of CO oxidation over the catalysts of the two extremes indicates that zirconia-supported isolated Au^{3+} ions (TOF: 0.047 s^{-1}) are much more active than the exposed Au^0 atoms (TOF: 0.015 s^{-1}) of Au particles with the average size of 8.0 nm in the 0.76% Au/ZrO_2-673 catalyst (Table 1).

The TOF numbers outside the parentheses, which were based only on exposed Au^0 atoms, for the catalysts categorized in the middle of the extremes (i.e., 0.76% Au/ZrO_2-393, -473 and -573), were not so different from those inside the parentheses that are based only on Au^{3+} ions of the same catalysts. Clearly, the two types of TOF data for CO oxidation over the 0.76% Au/ZrO_2 catalysts changes with the Au^{3+}/Au^0 ratio. In other words, the coexistence of Au^{3+} and Au^0 affects the catalytic activities of metallic as well as cationic gold in CO oxidation over the 0.76% Au/ZrO_2 catalysts. The maximum TOF (0.15 s^{-1}) over the exposed Au^0 atoms in 0.76% Au/ZrO_2-473 catalyst could imply that the most active 0.76% Au/ZrO_2 catalyst should be manipulated to have a proper Au^{3+}/Au^0 ratio (e.g., $Au^{3+}/Au^0 = 0.33$) for the oxidation reaction. In other words, the most active 0.76% Au/ZrO_2 catalyst should have a quarter of the gold remained as Au^{3+} ions. On the other hand, the maximum TOF over the 0.76% Au/ZrO_2-473 catalyst might hint an optimum Au particle size of ca. 4.1 nm (Table 1) for the oxidation reaction but further work would be needed for understanding the particle size effect of Au in Au/ZrO_2 catalyst.

It should be notified that similar effect of catalyst calcination on the CO oxidation reaction is also observed in earlier publications for other oxide-supported gold catalysts [7,9–11]. For example, a 1% Au/TiO_2 catalyst prepared by deposition-precipitation was calcined at 473, 573 and 873 K, respectively, by Haruta and co-workers [7]. The catalyst calcined at 573 K was found to exhibit the highest activity for CO oxidation. Since the average Au particle size was 2.4, 2.5 and 10.6 nm, respectively, in the catalysts calcined at 473, 573 and 873 K, the highest activity was accounted for by the specific particle size (2.5 nm) of Au in the catalyst calcined at 573 K. The authors explained that Au particles of 2.5 nm would have high concentrations of step Au^0 sites both at Au surfaces and the metal-support borderlines. However, the gold particle sizes in the catalysts calcined at 473 and 573 K (2.4 nm versus 2.5 nm) were basically the same but showed distinctly different catalytic activity for CO oxidation [7]. It was notified that the catalysts calcined at 473, 573 K contained also Au^{3+} ions but the authors made no attempt to relate their observed Au^{3+} ions with the catalyst activity [7]. It was also shown by others [9] that the activity for CO oxidation of Au/Al_2O_3, Au/TiO_2 and Au/Fe_2O_3 catalysts decreased with increasing the catalyst calcination temperature between 393 and 773 K. They observed that the decrease in catalyst activity can be correlated with the change of gold oxidation state from Au^{3+} in $Au(OH)_3$ and Au_2O_3 to Au^0 (metallic Au) as evidenced by XANES and XPS characterizations of the calcined catalyst and the catalyst activity decreased also with lowering the Au^{3+} ions [9]. Recently, catalytic sites incorporating cationic gold were also reported for Au/MgO and Au/α-Fe_2O_3 catalysts [10,11].

The observation that the butadiene conversion was always higher over the 0.76% Au/ZrO_2 (Fig. 5) or 0.05% Au/ZrO_2 (Fig. 6) catalysts with a higher number of unreduced Au^{3+} ions can be easily understood with the knowledge that the supported Au^{3+} ions are much more active than supported Au particles [18]. The TOF for the hydrogenation reaction over Au^0 at the surface of Au particles (8.0 nm) in the 0.76% Au/ZrO_2-673 catalyst (0.12 s^{-1}) is one third of that over the isolated Au^{3+} ions in the catalyst of low gold loadings (0.41 s^{-1}). Surprisingly, this TOF difference for the hydrogenation reaction is quantitatively the same as the difference for the CO oxidation reaction (Table 3). Despite that the coexisting exposed Au^0 atoms have also contributed, though less efficient, to the hydrogenation catalysis, the decrease in TOF based on Au^{3+} ions with the decrease in Au^{3+}/Au^0 ratio over the 0.76% Au/ZrO_2 catalysts indicates that the coexisting metallic gold (Au^0) lowers the catalytic activity of Au^{3+} ions in Au/ZrO_2 catalysts. Unlike in the CO oxidation reaction, regulation of Au^{3+}/Au^0 ratio in the 0.76% Au/ZrO_2 catalysts, therefore, cannot make the catalyst more active than the isolated Au^{3+} ions by TOF.

The performance of 0.05% Au/ZrO_2-473 catalyst in response to the H_2-reduction pretreatment (Fig. 6) is in further support of the above discussion on the functions of Au^{3+} ions and metallic Au^0 atoms in the catalytic reactions. The highest activity of the partially reduced catalyst (after the pretreatment with H_2 at 473 K) for CO oxidation demonstrates again that

small Au nanoparticles coexisting with a certain number of Au^{3+} ions in Au/ZrO_2 catalyst are more active for the oxidation reaction. Since the size of Au particles in the reduced 0.05% Au/ZrO_2 catalyst can be smaller due to the low loading of gold, the exact Au^{3+}/Au^0 ratio for maximizing the activity of this catalyst would be different from that in the case of 0.76% Au/ZrO_2 catalyst.

An important feature of Au/ZrO_2 catalysts in 1,3-butadiene hydrogenation is in the product selectivity [18]. The catalysts containing only Au^{3+} ions are 100% selective for the semi hydrogenation to form butenes. Moreover, the obtained butene product is rich in 1-butene (ca. 64%) and the *trans*/*cis* ratio in 2-butenes is as low as 0.4 (Table 2). The presence of metallic gold in the catalyst is reflected by an appearance of totally hydrogenated product (butane) of 1,3-butadiene, as well as a lowering of 1-butene and a raising of *trans*-2-butenes in the reaction product. The significantly different selectivity for butane formation between the completely reduced 0.05% Au/ZrO_2 and 0.76% Au/ZrO_2-673 catalysts, both of which have no Au^{3+} ions, but only metallic Au particles, can be an indication that the Au particle size in supported metallic Au catalyst is also important in affecting the product selectivity of 1,3-butadiene hydrogenation; the Au particle size in the completely reduced 0.05% Au/ZrO_2 catalyst, although not measured in the study, must be significantly smaller than that (8.0 nm, Table 1) in the 0.76% Au/ZrO_2-673 catalyst.

The above discussion made no consideration of the predicted possible reduction of the Au^{3+} to Au^+ ions during the hydrogenation of 1,3-butadiene [26]. The first reason was that the temperature for hydrogenation reaction (393 K) was made significantly lower than reduction onset temperature of the isolated Au^{3+} ions (>455 K). The second reason was that the Au/ZrO_2 catalysts showed quite stable activities during the hydrogenation reaction (Figs. 3 and 5); the activities would change significantly if reduction of gold happened during the reaction. Thirdly, the performance of the partially pre-reduced 0.05% Au/ZrO_2 catalyst (i.e., after the pretreatment with H_2 at 473 K) in the hydrogenation reaction (Fig. 6B; Table 2) was featured by a combined hydrogenation catalysis of the metallic Au (e.g., 0.76% Au/ZrO_2-673) and Au^{3+} ions, which was also not indicative of other active gold species. Co-existance of cationic Au^{3+} with metallic Au particles but without detectable Au^+ ions were also detected over other oxide supports [3,9,11,13,20]. It should be realized that the prediction of Au^{3+} to Au^+ reduction was done using tetragonal zirconia as the model surface, which was different from the zirconia support (55% tetragonal + 45% monoclinic) used in the present study.

5. Conclusions

Our present data show that either exposed Au^0 atoms or Au^{3+} ions in Au/ZrO_2 catalysts are active for the CO oxidation and 1,3-butadiene hydrogenation reactions but a combination of the gold oxidation states (i.e., Au^{3+} and Au^0) has different consequences on the two reactions. Proper tuning of the Au^{3+}/Au^0 ratio in Au/ZrO_2 catalyst can significantly improve the catalyst activity in CO conversion. High concentration of heterogenized isolated Au^{3+} ions at zirconia surface is most effective for the selective hydrogenation of 1,3-butadiene to form butenes. Co-presence of metallic gold with Au^{3+} ions would lower the catalytic activity by TOF for 1,3-butadiene hydrogenation and change the product selectivity for more *trans*-2-butene and butane. These findings could also have important implications for the development and performance enhancement of gold catalysts on other supports.

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References

[1] G.C. Bond, D.T. Thompson, Catal. Rev. Sci. Eng. 41 (1999) 319.
[2] M. Haruta, M. Daté, Appl. Catal. A 222 (2001) 427.
[3] G.C. Bond, D.T. Thompson, D. T. Gold Bull. 33 (2000) 41.
[4] H.H. Kung, M.C. Kung, C.K. Costello, J. Catal. 216 (2003) 425.
[5] X. Zhang, H. Wang, B.Q. Xu, J. Phys. Chem. B 109 (2005) 9678.
[6] R.J. Davis, Science 301 (2003) 926.
[7] F. Boccuzzi, A. Chiorino, M. Manzoli, P. Lu, T. Akita, S. Ichikawa, M. Haruta, J. Catal. 202 (2001) 256.
[8] M. Valden, X. Lai, D.W. Goodman, Science 281 (1998) 1647.
[9] E.D. Park, J.S. Lee, J. Catal. 186 (1999) 1.
[10] J. Guzman, B.C. Gates, J. Am. Chem. Soc. 126 (2004) 2672.
[11] G.J. Hutchings, M.S. Hall, A.F. Carley, P. Landon, B.E. Solsona, C.J. Kiely, A. Herzing, M. Makkee, J.A. Moulijn, A. Overweg, J.C. Fierro-Gonzalez, B.C. Gates, J. Catal. 242 (2006) 71.
[12] J.J. Pietron, R.M. Stroud, D.R. Rolison, NanoLett 2 (2002) 545.
[13] S. Carrettin, P. Concepción, A. Corma, J.L. Nieto, V.F. Puntes, Angew. Chem. Int. Ed. 43 (2004) 2538.
[14] B. Hammer, J.K. Norskov, Nature 376 (1995) 238.
[15] S. Lin, M.A. Vannice, Catal. Lett. 10 (1991) 47.
[16] G.C. Bond, P.A. Sermon, G. Webb, D.A. Buchanan, P.B. Wells, J. Chem. Soc., Chem. Commun. (1973) 444.
[17] M. Okumura, T. Akita, M. Haruta, Catal. Today 74 (2002) 265.
[18] X. Zhang, H. Shi, B.Q. Xu, Angew. Chem. Int. 44 (2005) 7132.
[19] X. Zhang, H. Wang, B.Q. Xu, Acta Chim. Sinica 63 (2005) 86.
[20] J.T. Calla, R.J. Davis, Catal. Lett. 99 (2005) 21.
[21] S. Schimpf, M. Lucas, C. Mohr, U. Rodemerck, A. Brückner, J. Radnic, H. Hofmeister, P. Claus, Catal. Today 72 (2002) 63.
[22] M.P. Casaletto, A. Longo, A. Martorana, A. Prestianni, A.M. Venezia, Surf. Interface Anal. 38 (2006) 215.
[23] N.A. Hodge, C.J. Kiely, R. Whymanb, M.R.H. Siddiqui, G.J. Hutchings, Q.A. Pankhurst, F.E. Wagner, R.R. Rajaram, S.E. Golunski, Catal. Today 72 (2002) 133.
[24] J. Guzman, B.C. Gates, J. Phys. Chem. B 107 (2003) 2242.
[25] L. Ilieva, J.W. Sobczak, M. Manzoli, B.L. Su, D. Andreeva, Appl. Catal. A 291 (2005) 85.
[26] Z.P. Liu, C.M. Wang, K.N. Fan, Angew. Chem. Int. 45 (2006) 6865.
[27] Y. Nakano, T. Yamaguchi, K. Tanabe, J. Catal. 80 (1983) 307.