Remarkable Nanosize Effect of Zirconia in Au/ZrO₂ Catalyst for CO Oxidation[†]

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Nanosize effect of ZrO_2 in Au/ZrO₂ catalyst was studied by deposition-precipitation of Au nanoparticles in similar sizes (4–5 nm) on ZrO₂ nanoparticles of varying sizes. The catalysts were characterized with XRD, TEM, XPS, and nitrogen adsorption to understand the effect of ZrO₂ particle size on the catalytic nanostructures. Nanocomposite Au/ZrO₂ catalysts consisting of comparably sized Au-metal (4–5 nm) and ZrO₂ (5–15 nm) nanoparticles are found advantageous over those containing similarly sized Au-metal but larger ZrO₂ (40–200 nm) particles for CO oxidation. This finding may have important implications on the designed preparation of advanced nanostructured catalysts and other chemical materials.

1. Introduction

The interest in oxide-supported Au catalysts has increased substantially since Haruta et al. discovered that small Au nanoparticles are exceptionally active for low-temperature CO oxidation.¹⁻⁵ Exploration of the catalytic performance of Au nanoparticles on the basis of sizes has been the main focus of most research in this field.¹⁻⁹ It was reported that the catalytic activity by turnover frequency (TOF) of Au catalyst on different oxide supports (TiO₂, α -Fe₂O₃, Co₃O₄) increases with decreasing the particle size of Au nanoparticles in the range of 2-10 nm.⁶ Goodman et al. found that Au nanoparticles of about 3.5 nm showed the highest activity in a series of Au/TiO₂ model catalysts.⁸ Although the active catalysts commonly contain small (2-5 nm) Au nanoparticles, the size of Au particles alone does not seem to be a sufficient factor for the high activity of nanosized Au catalysts.¹⁰⁻¹⁴ For instance, Bollinger and Vannice found that deposition of TiO_x overlayers onto inactive Au powders (10 μ m) can also produce very active TiO₂-Au catalyst for CO oxidation.¹⁰ In the attempt of Rolison et al., the loading of ca. 6 nm Au nanoparicles onto TiO₂ sized to 10-12 nm produced composite Au/TiO₂ catalyst that exhibited high activity for CO oxidation, while Au particles of similar sizes were found inactive on commercial TiO₂ powders.^{13,14} While the nature of active sites for CO oxidation on supported Au catalysts is still being elucidated, increasingly gained experimental evidence continues to show that the interaction between Au particles and the supporting oxide support at their contact boundaries plays an important role in determining the catalytic activity of the Au nanoparticles.^{3,5,6,10} It can be expected that such interaction at the metal-oxide boundaries can be properly tuned by systematically reducing the particle size of the support oxides.

With advances occurring in the synthesis of nanoparticle supports with controlled size, researchers should be encouraged to explore the size effect of oxide-support nanoparticles, as well as metal nanoparticles.¹⁵ For instance, our earlier exploration on the size effect of ZrO₂ on the catalysis of Ni metal has generated nanocomposite Ni/ZrO₂ catalysts consisting of com-

parably sized Ni-metal (10–15 nm) and ZrO₂ (7–25 nm) nanocrystals, which show excellent catalytic performance for the reforming reactions of methane (CH₄ + CO₂ = 2CO + 2H₂ and/or CH₄ + H₂O = CO + 3H₂).^{16–19} We are extending the work to study the effect of reducing oxide particle size on the catalysis of Au/oxide catalyst. Reported herein is our study on the nanosize effect of zirconia on the catalytic performance of Au/ZrO₂ catalysts for CO oxidation. We prove that the catalytic activity of Au nanoparticles (4–5 nm) in Au/ZrO₂ can be enhanced remarkably with reducing the particle size of zirconia "support" in the range of 5–100 nm, which unravels a new dimension in tailoring the performance of metal catalysts.

2. Experimental Section

2.1. Preparation and Catalytic Testing of Au/ZrO₂ Catalyst. ZrO₂ powders were derived from a single source of ZrO-(OH)₂ hydrogel according to the methods described previously.^{16,17} The hydrogel was obtained by conventional hydrolysis of zirconyl chloride in aqueous ammonia water of pH = 10. Following our earlier sample coding,^{16–19} ZrO₂-CP-973 is the sample prepared by calcination for 5 h in flowing air of the $ZrO(OH)_2$ hydrogel at 973 K. Also, ZrO_2 -AN-T(T = 673, 873, 73)973, and 1073 K) samples were prepared by thermal processing at temperature T in flowing nitrogen of an alcogel of $ZrO(OH)_2$, which was obtained by washing the hydrogel with anhydrous ethanol several times. The alcogel was digested in anhydrous ethanol under reflux (350 K) before it was processed to 973 K in flowing nitrogen to give the ZrO₂-AD-973 sample. Au/ZrO₂ catalysts were prepared by the well-established depositionprecipitation method.^{6,7} ZrO₂ powders were dispersed in a 0.1 wt % HAuCl₄ solution at room temperature, followed by deliberately adjusting with 0.2 M NH₄OH the solution pH to ca. 9.0 \pm 0.1. This aqueous dispersion was stirred for 6 h and aged for 2 h at the adjusted pH, and then suction filtered. Extensive washing with deionized water was then followed until it was free of chloride ions (i.e., until conductance of the washed solution in the final wash was less than 10^{-5} S m⁻¹). Vacuum drying at 383 K and air calcination at 673 K for 5 h of the sample finalized the preparation of Au/ZrO₂ catalysts.

The activity in catalytic CO oxidation was measured in a continuous flow, fixed-bed U-shape quartz reactor (i.d. 4 mm)

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Figure 1. Powder X-ray diffraction patterns of zirconia samples: (a) ZrO_2 -AD-973; (b) ZrO_2 -CP-973; (c) ZrO_2 -AN-1073; (d) ZrO_2 -AN-973; (e) ZrO_2 -AN-873; (f) ZrO_2 -AN-673.

under atmospheric pressure (0.1 MPa). The reaction feed (1.0 vol % CO in dry air) was introduced into the reactor with a space velocity of 20 400 mL/(h \times g-cat). Before the reaction, the catalysts (100 mg, diluted with 500 mg of quartz sand to ca. 0.6 mL) were in-situ pretreated with H₂ at 523 K for 2 h. The reactor effluent was on-line analyzed with an HP-6890 gas chromatograph equipped with a molecular 5A column and a thermal conductivity detector (TCD).

2.2. Sample Characterizations. The crystal structures of ZrO2 and Au/ZrO2 samples were characterized with powder X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer using the Ni-filtered Cu Ka radiation source at 40 kV and 40 mA. The percentage of monoclinic phase (M%) in the oxide "support" was measured according to the equation:²⁰ M% = $I_{M(\bar{1}11)}/(1.6I_{M(\bar{1}11)} + I_{T(111)})$, where $I_{M(\bar{1}11)}$ and $I_{\rm T}(111)$ are the diffraction intensities of the monoclinic (111) $(2\theta = 30.4^{\circ})$ and tetragonal (111) $(2\theta = 28.5^{\circ})$ planes, respectively. The average crystal size of ZrO₂ was measured with the X-ray broadening analysis (XLBA) by using the wellknown Scherrer equation: $d = 0.89\lambda/(B(2\theta)\cos\theta)$, where $B(2\theta)$ is the width of the XRD pattern line at half peak height in radians, λ is the wavelength of the X-ray, 0.15406 nm, θ is the angle between the incident and diffracted beams in degrees, and d is the crystal size of the powder sample in nanometers.

Surface areas of the samples were measured with nitrogen adsorption at 77 K on a Micromeritics ASAP 2010C instrument. The samples were dehydrated under vacuum at 523 K for 5 h before the adsorption measurement. TEM and HRTEM analyses were performed on JEM-2010F (200 kV) and Tecnai F30 (300 kV), respectively. The samples were first dispersed carefully in ethanol using an ultrasonic bath, and then deposited on a polymer coated copper grid. X-ray photoelectron spectra (Au 4f) of the catalysts were recorded with an SKL-12 spectrometer equipped with Mg K α radiation. The residual pressure in the analytical chamber was maintained below 10^{-8} 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. Au loading was determined by XRF analysis on an XRF-1700 instrument.

3. Results and Discussion

All of the ZrO₂ samples used in the preparation of Au/ZrO₂ catalysts were derived from the same source of $ZrO(OH)_2$ hydrogel. The thermal processing/calcination of ZrO₂ samples is known to produce crystals with two different phases, that is, monoclinic (M) and tetragonal phases (T). Figure 1 compares the XRD patterns of the alcogel derived ZrO₂-AD-973 and ZrO₂-AN-*T* samples with that of the conventionally prepared ZrO₂-

 TABLE 1: Size and Texture Properties of Zirconia

 Nanoparticles

sample	BET surface (m ² /g)	pore volume (cm ³ /g)	XLBA size ^a (nm)	TEM size (nm)	ZrO ₂ - phase ^b (%)
ZrO ₂ -CP-973	23	0.11	M22	40-200	M92/T8
ZrO ₂ -AN-973	36	0.26	M21/T20	20 - 25	M92/T8
ZrO ₂ -AD-973	58	0.32	M12/T11	10-15	M92/T8
ZrO ₂ -AN-673	162	0.36	M6/T5	5-10	M76/T24
ZrO ₂ -AN-873	61	0.28	M12/T11	12-17	M88/T12
ZrO ₂ -AN-1073	20	0.19	M30	25 - 40	M97/T3

^{*a*} Average crystal size obtained with the Scherrer equation by using the ($\overline{1}11$) diffraction ($2\theta = 28.5^{\circ}$) for monoclinic and the (111) diffraction ($2\theta = 30.4^{\circ}$) for tetragonal crystals; M and T represent the monoclinic and tetragonal phase, respectively. ^{*b*} Percentage of monoclinic phase = $I_{M(\overline{1}11)}/(1.6I_{M(\overline{1}11)} + I_{T(111)})$.

CP-973. The presence of diffraction at $2\theta = 30.4^{\circ}$ indicates the presence of tetragonal crystals, although the XRD patterns are dominated by monoclinic crystals. The indistinguishable difference in the XRD patterns of ZrO₂-AD-973, ZrO₂-AN-973, and ZrO₂-CP-973 samples in the figure clearly indicates that the crystal phase composition of ZrO₂ is independent of the sample history (CP, AN, or AD preparation) when the final calcination temperature was 973 K. For the ZrO₂-AN-*T* samples obtained by varying the calcination temperature (*T*), the percentage of the monoclinic phase increased from 76% of ZrO₂-AN-673 to 97% of ZrO₂-AN-1073, respectively.

The size and texture data of zirconia powders used for the preparation of Au/ZrO2 catalysts are given in Table 1. It is apparent that the particle sizes by TEM of ZrO₂-AN-973 and ZrO₂-AD-973 are much smaller, and their surface area and pore volumes are higher than that of ZrO₂-CP-973. The similar sizes obtained from XLBA and TEM measurements of the alcogel derived ZrO₂-AN-973 and ZrO₂-AD-973 samples verify our earlier observation that these samples are composed of discrete ZrO₂ nanocrystals.^{16–19} In contrast, the difference in the XLBA (22 nm) and TEM (40-200 nm) sizes of the conventional ZrO₂-CP-973 sample indicates that primary crystals in this sample have agglomerated more or less to form larger hard aggregates. In the preparation of ZrO₂-AN powders, the processing temperature in flowing nitrogen of the ZrO(OH)₂ alcogel was changed between 673 and 1073 K to vary the particle sizes of the powders, which produced the samples with particle sizes of 5-10 nm (ZrO₂-AN-673), 12-17 nm (ZrO₂-AN-873), 20-25 nm (ZrO₂-AN-973), and 25-40 nm (ZrO₂-AN-1073), respectively. Again, the agreement in XLBA and TEM sizes of these ZrO₂-AN samples indicates that they are composed of discrete ZrO₂ nanocrystals.

Shown in Table 2 are properties of the calcined Au/ZrO_2 catalysts. Nitrogen adsorption measurement indicated that the loading of ca. 0.7% Au by deposition-precipitation has little effect on the texture of zirconia. XRD patterns of the Au/ZrO₂ catalysts were found similar to those of the corresponding "pure" zirconia, and no diffraction for metallic Au was observed.

XPS study was carried out to obtain information on the state of Au in the calicined Au/ZrO₂ catalysts; the results are shown in Figure 2 for Au/ZrO₂-CP-973, Au/ZrO₂-AD-973, Au/ZrO₂-AN-673, and Au/ZrO₂-AN-973 catalysts. All of these Au/ZrO₂ catalysts showed two XPS signals with binding energies near 83.5 and 87.3 eV. According to ref 21, the binding energies of Au 4f electrons for Au, Au₂O₃, and Au(OH)₃ are at 83.9, 86.3, and 87.7 eV for 4f_{7/2} and 87.7, 89.6, and 91.4 eV for 4f_{5/2}, respectively. Thus, the XPS data in Figure 2 are characteristic of 4f_{7/2} and 4f_{5/2} electrons in the metallic Au of the catalysts. As compared to those of the bulk Au metal,²¹ the lower binding

TABLE 2: Properties and Catalytic Activities of Au/ZrO₂ Catalysts for CO Oxidation at 343 K

catalyst	BET surface (m ² /g)	Au-loading (wt %)	$D_{ m Au}{}^a$ (nm)	conv. (%)	rate ×10 ^{−7} mol/(s g-cat)	$\begin{array}{c} {\rm TOF}^b \\ \times 10^{-3} \ {\rm s}^{-1} \end{array}$
Au/ZrO2-CP-973	22	0.74	4.0	4.6	1.1	2.8
Au/ZrO2-AN-973	34	0.63	5.3	12.9	2.9	9.2
Au/ZrO ₂ -AD-973	55	0.71	4.7	29.9	6.8	18.9
Au/ZrO ₂ -AN-673	142	0.77	5.4	31.8	7.2	18.5
Au/ZrO ₂ -AN-873	53	0.70	4.7	18.5	4.2	11.9
Au/ZrO2-AN-1073	18	0.70	5.4	7.1	1.6	4.6

^{*a*} Au particle size was determined by TEM. At least 200 particles were chosen to determine the mean diameter of Au particles according to equation $d = \sum n_i d_i/n_i$; the size scattering was within 3–7 nm. ^{*b*} The turnover frequencies (TOF) were calculated on the basis of the number of Au atoms exposed at the surfaces, which were estimated from the mean diameters and actual loadings of the Au particles. In this calculation, the shape of Au particles was assumed to be closed-shell particles of nearly spherical shape.²



Figure 2. XPS spectra of Au 4f in Au/ZrO_2 catalysts: (a) Au/ZrO_2 -CP-973; (b) Au/ZrO_2 -AN-973; (c) Au/ZrO_2 -AD-973; (d) Au/ZrO_2 -AN-673.

energies of Au 4f in these catalysts may indicate a modification of the electronic structure of Au due to the interaction between the nanosized metallic Au and zirconia particles.

Figure 3 shows the representative TEM images of all of the Au/ZrO₂ catalysts tabulated in Table 2; Au particles in these catalysts are narrowly sized (scattering between 3 and 7 nm), and their average sizes are in the range of 4-5 nm. Noticeably, the particle sizes of ZrO₂-CP-973 (40-200 nm) are 1 order of magnitude larger than the sizes of Au nanoparticles (ca. 4.0 nm) in Au/ZrO₂-CP-973 (Figure 3A). The images of Figure 3A clearly show that a single particle of zirconia (ZrO₂-CP-973) is capable of holding/supporting a number of the Au particles and the chance is very low for the Au particles to make contact with more than one zirconia particle in Au/ZrO₂-CP-973. Obviously, the reduction in the particle sizes of zirconia from ZrO₂-CP-973 (40-200 nm) to ZrO₂-AN-973 (20-25 nm) and further to ZrO₂-AD-973 (10-15 nm) resulted in increased chance for Au particles (4-5 nm) to make contact with multiple zirconia particles in the Au/ZrO₂ catalysts (Figure 3A-C). Reduction of the particle size of ZrO₂-AN by changing the processing temperature of the alcogel also produced a similar effect in the Au/ZrO₂-AN samples (Figure 3D, E, B, and F). In fact, the Au/ZrO₂-AD-973 and Au/ZrO₂-AN-673 samples (Figure 3C and D) were evolving to show the feature for Au/ ZrO₂ nanocomposites because the sizes of Au particles (4-5 nm) were getting to match with the particle sizes of the zirconia "support" (ZrO₂-AD-973, 10-15 nm and ZrO₂-AN-673, 5-10 nm), allowing a factor of ca. 2 for the size deviation.^{13,14,16,17} Thus, the present attempt of reducing the particle size of zirconia to approach size comparability of the Au and zirconia nanoparticles has generated nanocomposite-like Au/ZrO2 catalyst, for example, Au/ZrO₂-AN-673, possessing a large amount of the Au-ZrO₂ contact boundaries or Au-ZrO₂ junctions.

The comparable sizes of Au nanoparticles in the catalysts make it possible to study the nanosize effect of ZrO_2 on the

catalysis of Au/ZrO₂. Also included in Table 2 are the catalytic activities for the CO oxidation reaction by CO conversion, specific mass reaction rate, and TOF based on the Au atoms exposed at the surfaces. Figure 4 shows the effect of reaction temperature (323-373 K) on CO conversion over Au/ZrO2-CP-973, Au/ZrO₂-AN-973, and Au/ZrO₂-AD-973 catalysts. Clearly, the catalyst activity can be ranked in the order of Au/ ZrO₂-AD-973 > Au/ZrO₂-AN-973 > Au/ZrO₂-CP-973, indicating that the smaller the size of zirconia nanoparticles in the Au/ZrO₂ catalyst, the higher the catalyst activity. We found that all of our Au/ZrO2 catalysts showed stable catalytic activity for the CO oxidation reaction (e.g., Figure 5). Under similar reaction conditions, the steady-state activity of the present Au/ZrO₂-CP-973 catalyst agreed well with that of the Au/ZrO₂ catalyst reported by Haruta et al.; for example, the present Au/ZrO₂-CP-973 catalyst produced a CO conversion of 47% at 373 K (Figure 5), while the CO conversion over the catalyst in Haruta et al.'s work was 50%.6 The differences in the catalyst activity are more pronounced when one compares the TOF in Table 2. To ensure accuracy, the TOF were calculated with the catalytic data at 343 K because at this temperature the CO conversion levels can be limited to less than ca. 30%. The TOF and the specific reaction rate over Au/ZrO₂-AD-973 are 6 times larger than that over Au/ZrO₂-CP-973 at 343 K.

Figure 6 shows the dependence of CO conversion on the reaction time-on-stream (TOS) at 343 K over the Au/ZrO₂-AN-T catalysts. Interestingly, the catalytic activity of Au/ZrO₂-AN-T was clearly seen to decrease with increasing the processing temperature of ZrO₂-AN. The specific reaction rates and TOF of the most active Au/ZrO2-AN-673 are about 4 times higher than that of the least active Au/ZrO₂-AN-1073 catalyst (Table 2). While there are differences in the phase composition and crystallinity, and consequently uncertainties in the surface properties of the ZrO₂-AN nanoparticles prepared with different processing temperatures, particle size effect of the oxide support (ZrO₂-AN) can still be crucial in determining the catalytic activity because a similar size effect of the oxide support also appeared in the Au/ZrO₂-CP-973, Au/ZrO₂-AN-973, and Au/ ZrO₂-AD-973 catalysts that contain differently sized zirconia particles of similar phase composition and crystallinity (Figure 1 and Table 1). Alternatively, the present data clearly indicate that the activity of Au/ZrO₂ catalyst is greatly improved with reducing the size of ZrO₂ nanoparticles.

A referee of the present paper considered that the activity difference between Au/ZrO₂-AN-973 and Au/ZrO₂-AD-973 was not very large and may also be explained by the size effect of Au particles. He/she might be correct if one just looks at these two data without considering comprehensively all of the catalytic data (Tables 1 and 2, and Figures 3, 4, and 6). The activity difference is actually significant: Au/ZrO₂-AD-973 is twice more active than Au/ZrO₂-AN-973 and 6 times more than Au/



Figure 3. TEM images of the Au/ZrO_2 catalysts: (A) Au/ZrO_2 -CP-973; (B) Au/ZrO_2 -AN-973; (C) Au/ZrO_2 -AD-973; (D) Au/ZrO_2 -AN-673; (E) Au/ZrO_2 -AN-873; (F) Au/ZrO_2 -AN-1073. The encircled particles are Au particles. Insets: HRTEM images of the selected areas.

ZrO₂-CP-973. The average size of Au in Au/ZrO₂-CP-973 (4.0 nm) is the smallest in comparison with those in Au/ZrO₂-AN-973 (5.3 nm) and Au/ZrO₂-AD-973 (4.7 nm); if the size effect of Au was more pronounced, the Au/ZrO₂-CP-973 catalyst would show the highest activity, but its activity is actually just one-sixth of Au/ZrO₂-AD-973. As shown in Table 2, Au/ZrO₂-AN-973 (Au: 5.3 nm), Au/ZrO₂-AN-673 (Au: 5.4 nm), and Au/ZrO₂-AN-1073 (Au: 5.4 nm) have basically the same size for Au particles, but the activity of Au/ZrO₂-AN-673 having

the smallest zirconia particles is 4 times that of Au/ZrO_2 -AN-1073, and twice that of Au/ZrO_2 -AN-973. More importantly, our data show that the activity of Au/ZrO_2 increases systematically/monotonically with the decrease of the "support" particle size for all of the samples in Figures 4 and 6 (also see Table 2), strongly suggesting that the "support" size effect is far more remarkable.

It seems unreasonable that the observed activity enhancement in the present study may be due to the size scattering of Au



Figure 4. Catalytic activity of Au nanoparticles supported on zirconia nanocrystals: (\blacktriangle) Au/ZrO₂-CP-973; (\Box) Au/ZrO₂-AN-973; (\bigcirc) Au/ZrO₂-AD-973.



Figure 5. Catalytic stability of Au/ZrO₂-CP-973 and Au/ZrO₂-AD-973 catalysts at 373 K: (\blacktriangle) Au/ZrO₂-CP-973; (\bigcirc) Au/ZrO₂-AD-973.



Figure 6. CO conversion at 343 K over Au/ZrO₂-AN-*T* catalysts: (\blacklozenge) Au/ZrO₂-AN-673; (\blacktriangle) Au/ZrO₂-AN-873; (\Box) Au/ZrO₂-AN-973; (\blacklozenge) Au/ZrO₂-AN-1073.

particles. Comprehensive reviews by Haruta^{5,7,25} on the catalytic CO oxidation over Au nanoparticles supported by various oxides (e.g., TiO_2 , Fe_2O_3 , Co_3O_4) have shown that the catalytic activity by TOF of Au changed slowly when the particle size of Au is larger than 4 nm (refer to Figure 9 in ref 6), although the rate increased sharply when the size of Au particles becomes smaller than 4 nm.⁶ For example, the TOF of Au/TiO₂ catalyst decreased by a factor of 2 (from 2.5 to 1.2 s^{-1}) when the average size of Au was increased from 4 to 6 nm (refer to Figure 2 in ref 4).^{4,8} Because ZrO₂ is, in comparison with TiO₂, a support of poorly active for Au nanoparticles,^{22,23} the effect due to the size scattering of Au particles can be much smaller when the average size of Au is changed between 4 and 6 nm. The average size of Au nanoparticles in the present Au/ZrO₂ catalysts is within the range of 4-6 nm, and their actual size scattering is reasonably narrow enough (i.e., between 3 and 7 nm). The activity difference among the present Au/ZrO2 catalysts goes up to 6 times (Table 2), as discussed in the last paragraph, and is clearly more significant than the size effect of Au nanoparticles in the even more active Au/TiO₂ catalysts with the average Au sizes

in the same range (4–6 nm). It is thus conclusive that the activity difference in our Au/ZrO₂ catalysts (Table 2, Figures 4 and 6) is mainly due to the size effect of the nanosized zirconia support particles rather than the size scattering of Au particles. The supporting material size effect on Au catalyst was also addressed by Rolison et al.^{13,14} and Corma et al.;²⁴ they showed only two extreme cases for Au/TiO₂^{13,14} and Au/CeO₂²⁴ catalysts, respectively. However, this present investigation seems more systematic and has provided a general trend for the support size effect in a series of zirconia samples.

It is unlikely that CO oxidation over Au/ZrO₂-AD-973 and Au/ZrO2-AN-673 catalysts involves a radically different chemical mechanism from that over Au/ZrO2-CP-973 and Au/ZrO2-AN-1073 catalysts. Although the nature of active sites and the reaction mechanism have not yet been clearly identified, many researchers agreed that the contact boundaries between Au and the support oxide should play an important role in the catalytic reaction.^{2-6,10-12,25} The Au-oxide boundaries or contact perimeters function most probably as active sites for the activation of the oxygen reactant; CO molecules adsorbed on Au may need to migrate to react with the activated oxygen at those boundaries.^{2-6,10-12,25} Thus, the main factors affecting the catalyst performance should be the properties of the Au-oxide contacts as well as the nature and particle size of the oxide support as reviewed by Haruta.5,25 Specific to the case of zirconia support, some recent studies have shown that zirconia nanoparticles can hold a lot of oxygen vacancies,²⁶⁻²⁸ and in particular the number of surface vacancies associated with the paramagnetic F-centers was found to increase with decreasing the size of zirconia nanoparticles smaller than 50 nm.²⁸ Such vacancy sites were found important in the formation of electronrich Au particles as active sites for the partial hydrogenation of acrolein over Au/ZrO2 catalysts.27 According to Corma et al.,24 increased oxygen vacancies in nanosized small (3-4 nm) ceria "support" were crucial in Au/CeO2 catalyst for the activation of oxygen in the CO oxidation reaction. We believe that a similar mechanism may prevail in the catalysis of CO oxidation over the present Au/ZrO₂ catalysts. The continuous reduction in the sample particle size of the ZrO₂ "support" not only leads to continuously increased Au-oxide contact boundaries in the Au/ZrO₂ catalyst but also modifies the chemical properties at such boundaries due to the presence of a larger number of oxygen vacancies at the surfaces of smaller ZrO₂ nanoparticles,^{26–28} creating a situation where oxygen can become easily activated²⁴ and then move more easily (the increased Auzirconia contact junctions mean minimized diffusion distances for the reactive surface species) to react with the adsorbed CO molecules, which accounts for the data that the activity of Au/ ZrO₂ catalyst is greatly enhanced with reducing the size of ZrO₂ nanoparticles.

It seems therefore that there are two approaches in increasing Au–oxide contact boundaries for the Au catalyst. The first approach is to reduce the size of Au nanoparticles as shown in many earlier reports;^{1–9} the second is to reduce the particle size of the oxide support as demonstrated in this work. In the second approach, the small spherical Au nanoparticles, having sizes of 4-5 nm in diameter (Figure 3), are composed of 2000-4000 Au atoms;^{2,29} about 24-32% of the atoms are exposed on the surface and can potentially have direct contact/interaction with ZrO₂. The increased contact boundaries between Au and ZrO₂ by reducing the sizes of ZrO₂ nanoparticles are mainly due to the generation of Au–ZrO₂ junctions with which a single Au nanoparticle can make contacts with multiple ZrO₂ particles (Figure 3). This approach is in contrast to the creation of more

metal—oxide boundaries by generating smaller metal particles on a single oxide-particle in the first approach.

In contrast to conventional oxide-supported metal catalysts with metal "flea" riding an oxide "boulder", as in the case of Au/ZrO₂-CP-973 and Au/ZrO₂-AN-1073, the similar sizes of the ZrO₂ (5-15 nm) and Au (4-5 nm) nanoparticles in the highly active Au/ZrO₂-AD-973 and Au/ZrO₂-AN-673 catalysts (Figure 3C and D) identify them as nanocomposites of Au and ZrO₂ nanoparticles.¹⁷ In addition to the effect of tailoring the activity of Au nanoparticles and the reactivity at the Au-ZrO₂ contact boundaries, the formation of multiple Au-ZrO₂ contact junctions for each of the Au nanoparticles in the nanocomposite catalysts can also lead to many more channels and minimized distances for the surface diffusion of reactive CO and/or oxygen species. The fact that both of the nanocomposite Au/ZrO₂ catalysts exhibit the highest activity for the CO oxidation (Table 2) proves again the feasibility of designing metal/oxide nanocomposite for advanced catalysts.^{16,17}

In conclusion, the present data indicate that the catalytic activity of Au nanoparticles in Au/ZrO₂ for CO oxidation can be greatly improved by reducing the particle size of zirconia nanoparticles. In particular, nanocomposite Au/ZrO₂-AD-973 and Au/ZrO₂-AN-673 catalysts consisting of comparably sized Au-metal (4–5 nm) and ZrO₂ (5–15 nm) nanoparticles are found advantageous over those containing similarly sized Au-metal but larger ZrO₂ particles. This finding may have important implications in the designed preparation of advanced Au and other heterogeneous metal catalysts; it could also be informative for the improvements of many other related nanostructured chemical materials.

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