

New application of spray reaction technique to the preparation of supported gold catalysts for environmental catalysis

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Abstract

Taking the advantage of the characteristic preparation method of nanocomposites particles, spray reaction was applied for the preparation of supported gold catalysts, i.e., Au/TiO₂ and Au/Al₂O₃. The structure and the physical properties were characterized by means of powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), EXAFS and BET measurements. The exposed surface sites of metal were estimated by CO and/or NO adsorption. The marked catalytic activities for CO oxidation and NO–CO reaction were discussed in terms of the enhancement of synergistic effects due to the characteristic nanostructures. © 2002 Published by Elsevier Science B.V.

Keywords: Gold catalyst; Spray reaction; CO oxidation; NO–CO reaction; Environmental catalysis

1. Introduction

Catalytic activity of gold has become widely recognized for various reactions. Several investigations have been demonstrated that the catalytic properties of supported gold may change markedly depending on the particle size of gold, the nature of metal oxide supports, the interaction between gold and the supporting oxide as well as the nanostructure of the active sites [1–3]. The preparation method, therefore, is very important factor for us to obtain high-performance gold catalysts.

Various efforts have been focused on the preparation of gold catalysts by conventional methods such as impregnation, co-precipitation, sol–gel method and deposition–precipitation method [4,5]. Taking the advantage of spray technique, we have developed a new type of preparation method for multi-component fine particles and investigated various applications to the high-performance catalysts from multi-component oxides to metal-supported catalysts [6–9].

In this work, two kinds of supported gold catalysts, i.e., Au/TiO₂ and Au/Al₂O₃ were prepared by spray reaction (SPR) method and investigated their catalytic properties for CO oxidation over Au/TiO₂ and for NO–CO reaction over SPR-Au/Al₂O₃, respectively. Their catalytic properties were discussed in terms of the nanostructure and the surface characteristics.

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2. Experimental

2.1. Catalyst preparation

The titania-supported gold catalyst, Au/TiO₂, was prepared as follows: a mixture of aqueous solutions of HAuCl₄ and TiCl₄ (0.1 M as a total) was atomized by an ultrasonic device, and then heated in an air flow through a quartz tube reactor under the suction by an aspirator. The fine particles formed were collected on a glass filter at the exit. The alumina-supported gold catalyst, Au/Al₂O₃, was prepared in a similar manner using a mixed aqueous solution of HAuCl₄ and Al(NO₃)₃. The loading concentration of Au on the supports was 1 mol% if not otherwise noted. The SPR catalysts are hereafter symbolized, i.e., SPR-Au/TiO₂673 or SPR-Au/Al₂O₃673, indicating the SPR temperature.

2.2. Characterization

The physical properties of SPR catalysts were characterized by powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), EXAFS and BET measurements. XRD patterns were recorded on an X-ray diffractometer (MacScience MXP3) using Cu K α radiation. The crystallite sizes of Au and TiO₂ were calculated by Sherrer's equation from the half-widths of Au (200) and TiO₂ (101) peaks, respectively. BET surface areas of catalysts were obtained by N₂ adsorption at 77 K. XPS measurements were carried out with a Shimadzu ESCA-850 spectrophotometer with Mg K α radiation. The binding energy was corrected by referencing to the energy of C 1s (285.0 eV). The surface composition of the catalyst was determined from the peak areas of the corresponding lines using a Shirley-type background.

2.3. CO and NO adsorption

The CO and NO chemisorption were measured at 373 K in a static system over the catalyst pretreated with H₂ for 1 h at 573 K, followed by evacuation for 30 min at the same temperature.

2.4. Catalytic reaction

CO oxidation was studied with a closed circulation reaction system. A reaction mixture of CO (20 Torr)

and O₂ (10 Torr) was introduced into the circulatory line and the reaction products were analyzed by a gas chromatograph. The initial rate of CO₂ formation was used to stand for the catalytic activity. All of the catalysts used for CO oxidation were pretreated under the same conditions for CO chemisorption. NO–CO reaction was carried out with a 1:1 mixture gas (80 Torr) after pretreatment with a corresponding gas.

3. Results and discussion

3.1. SPR-Au/TiO₂ for CO oxidation

XRD patterns of SPR-Au/TiO₂ (as-sprayed) catalysts are shown in Fig. 1. In all XRD patterns for SPR-Au/TiO₂ the peaks ascribable to metallic Au and TiO₂ (anatase phase/unlabeled) were clearly observed. The TiO₂ peaks became stronger and the Au peaks showed slightly sharper with the increase of the SPR temperature. The crystallite sizes calculated from Au (200) and TiO₂ (101) diffractions are given in Table 1. For the crystallite size and BET surface area of SPR-Au/TiO₂673 and SPR-Au/TiO₂873 showed only slight difference. For SPR-Au/TiO₂1073, the sintering of Au and TiO₂ particles took place to give the particle sizes 24.3 nm (Au) and 12.8 nm (TiO₂), respectively. The great decrease in the BET surface area was also observed for SPR-Au/TiO₂1073. Thus the typical image of SPR-Au/TiO₂ is spherical

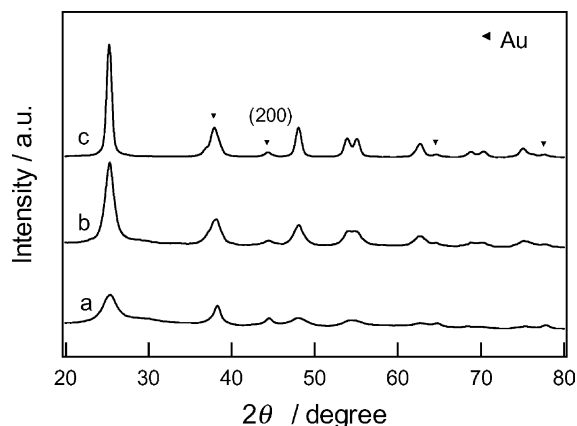


Fig. 1. XRD patterns of: (a) SPR-Au/TiO₂673; (b) SPR-Au/TiO₂873; (c) SPR-Au/TiO₂1073.

Table 1
Crystallite size of Au (200) and TiO₂ (101) and BET surface areas of SPR-Au/TiO₂

Catalysts	Crystallite size		BET surface area (m ² g _{cat.} ⁻¹)
	Au (nm)	TiO ₂ (nm)	
SPR-Au/TiO ₂ 673	9.1	4.2	82.3
SPR-Au/TiO ₂ 873	8.4	6.4	79.5
SPR-Au/TiO ₂ 1073	24.3	12.8	13.7

sub-micron composite that consist of a large number of TiO₂ with small number of Au clusters.

Fig. 2 shows XPS spectra of Au 4f region. In all spectra for SPR-Au/TiO₂ catalysts, Au 4f_{5/2} and Au 4f_{7/2} peaks were centered at 87.8 and 84.1 eV, respectively, and no appreciable shift in binding energy from that of the bulk gold. Thus most of the gold particles are in the metallic state. The Au 4f signal for SPR-Au/TiO₂1073 was much weaker compared with those for SPR-Au/TiO₂673 and SPR-Au/TiO₂873. Moreover, the surface composition of SPR-Au/TiO₂ determined by the relative peak areas is listed in Table 2. The surface concentration of Au in SPR-Au/TiO₂1073 was greatly decreased from those of SPR-Au/TiO₂673 and SPR-Au/TiO₂873. Therefore, it may be speculated that some of the gold particles in SPR-Au/TiO₂1073 are located under the surface of the composites. A similar result was also

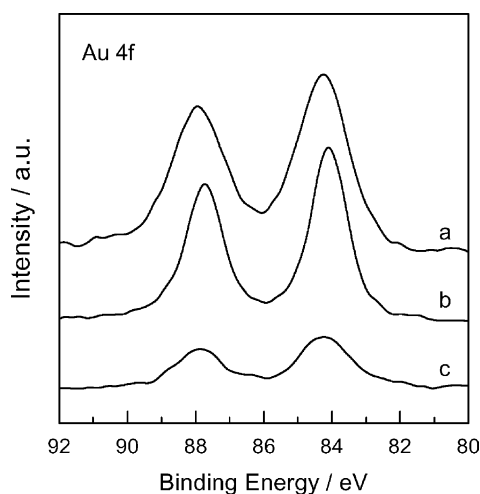


Fig. 2. XPS of Au 4f region for: (a) SPR-Au/TiO₂673; (b) SPR-Au/TiO₂873; (c) SPR-Au/TiO₂1073.

Table 2
Surface composition of SPR-Au/TiO₂ determined by the relative peak areas of XPS

Catalysts	Au (at.%)	Ti (at.%)	O (at.%)
SPR-Au/TiO ₂ 673	0.9	30.0	69.1
SPR-Au/TiO ₂ 873	0.5	28.8	70.7
SPR-Au/TiO ₂ 1073	0.2	26.9	72.9

reported where the decrease in the Au 4f signals of Au/Ti(OH)₄ was explained by the transfer of Au phosphine species from the surface to the bulk and/or inside of the composites [10].

The amount of CO chemisorption over SPR-Au/TiO₂ (Fig. 3) decreased with the SPR temperature raised. The CO chemisorption amount of SPR-Au/TiO₂1073 was about a half of that of SPR-Au/TiO₂673 and SPR-Au/TiO₂873, but the TOF value of SPR-Au/TiO₂1073 increased dramatically by one order of magnitude. The result cannot be explained simply by the sintering of Au. The surface concentration of Au estimated by XPS peak areas showed a similar tendency and in consistent with the change of CO chemisorption amount. It is suggested that only limited number and surface region of Au particles are exposed on the outer surface of the composites, especially as the catalyst prepared at the highest temperature, i.e., 1073 K.

These results can be interpreted further in terms of the difference of the decomposition temperature

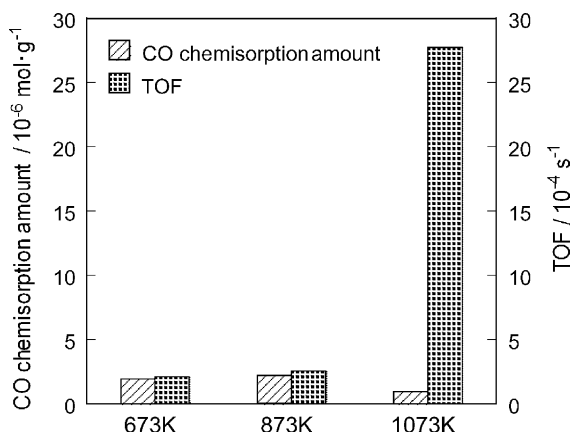


Fig. 3. CO chemisorption amount and TOF for CO oxidation over SPR-Au/TiO₂ at 373 K.

between HAuCl_4 (ca. 473 K) and TiCl_4 (ca. 673 K). At a high SPR temperature, Au clusters may be formed instantaneously, and then were covered by the surrounding TiCl_4 droplets. Consequently, most of the Au particles were partly buried and stabilized effectively during the formation and coagulation of the composite with the fine particles of TiO_2 support [11].

The catalytic activity (TOF) for CO oxidation over SPR-Au/ TiO_2 depended strongly on the SPR temperature (Fig. 3). The SPR-Au/ TiO_2 1073 gave the highest TOF value and very low activation energy irrespective of the limited number of active sites. The effects of high-temperature SPR on the activation energy drop were very dramatic, viz., from, 58 kJ mol^{-1} (673 K) to 48 kJ mol^{-1} (873 K) and finally to 18 kJ mol^{-1} (1073 K). Such change of activation energy suggests that the modification of the chemical property or the electronic states of Au particles due to the strong interaction at the interface of Au nanoparticles and the support [1].

Similar drops of activation energy were also found for the methanation of CH_4 over SPR-Ru/ TiO_2 in the previous work where the higher binding energy shifts of Ru was clearly observed by 0.2–0.3 eV [8]. The change can be interpreted in terms of a model where the synergistic effects between Ru and TiO_2 were enhanced at the region of perimeter interface which facilitates the high catalytic activity of SPR-Au/ TiO_2 1073 covering the decrease in the number the adsorption sites over Au clusters buried in the support.

3.2. SPR-Au/ Al_2O_3 for NO–CO reaction

The XRD patterns for SPR-Au/ Al_2O_3 (Fig. 4) indicate some different feature of the catalyst. For as-sprayed Au/ Al_2O_3 , Au particles supported on amorphous alumina show almost same in size (22–23 nm) (Table 3). While after the H_2 pretreatment, crystal growth of Au was observed. It should be noted that the effects of H_2 pretreatment on crystal growth decreased with the increase of SPR temperature, Au crystallite size calculated from XRD was in the order: SPR-Au/ Al_2O_3 1073 < SPR-Au/ Al_2O_3 873 < SPR-Au/ Al_2O_3 673, suggesting that the higher SPR temperature is effective to stabilize the Au clusters to prevent the sintering. The BET surface area ($20\text{--}29 \text{ m}^2 \text{ g}^{-1}$) of as-sprayed SPR-Au/ Al_2O_3 was little affected by further H_2 treatment as expected.

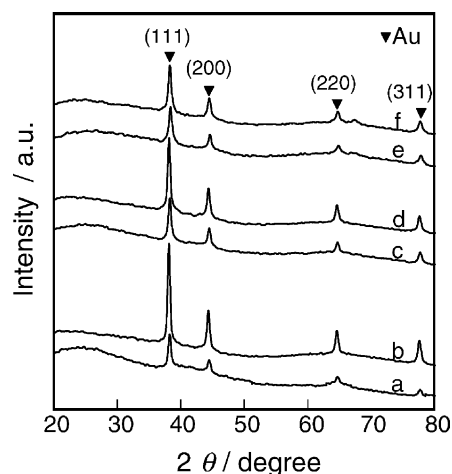


Fig. 4. XRD patterns of SPR-Au/ Al_2O_3 before and after H_2 pretreatment: (a) 673 K; (b) 673 K (pretreated); (c) 873 K; (d) 873 K (pretreated); (e) 1073 K; (f) 1073 K (pretreated).

The nanostructure of SPR-Au/ Al_2O_3 was suggested by XANES and EXAFS study. In the white X-ray region, the XANES spectra for Au on SPR-Au/ Al_2O_3 indicated the co-presence of Au_2O_3 with Au metal which can be partly reduced by the H_2 pretreatment. The coordination number (CN) of Au and bond distance parameters is listed in Table 4. The CN for

Table 3
Crystallite size of Au (1 1 1) before and after H_2 pretreatment and BET surface areas of SPR-Au/ Al_2O_3

Catalysts	Crystallite size of Au (1 1 1) (nm)		BET surface area ($\text{m}^2 \text{ g}_{\text{cat}}^{-1}$)
	As-sprayed	After H_2 pretreatment	
SPR-Au/ Al_2O_3 673	22	22	20
SPR-Au/ Al_2O_3 873	24	27	28
SPR-Au/ Al_2O_3 1073	22	33	29

Table 4
EXAFS parameters for SPR-Au/ Al_2O_3

Catalysts	Coordination	CN	Bond distance (nm)
Au foil	Au–Au	12	0.29
SPR-Au/ Al_2O_3 873 (H_2)	Au–Au	8.4	0.28
SPR-Au/ Al_2O_3 1073 (H_2)	Au–Au	7.8	0.29
SPR-Au/ Al_2O_3 873 ($\text{O}_2\text{--H}_2$)	Au–Au	13	0.28
SPR-Au/ Al_2O_3 1073 ($\text{O}_2\text{--H}_2$)	Au–Au	8.1	0.29

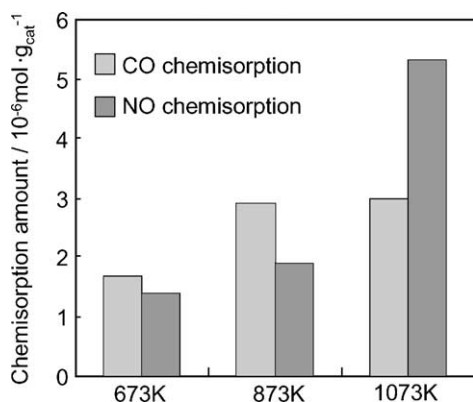


Fig. 5. NO and CO chemisorption over SPR-Au/Al₂O₃ at 298 K.

the as-sprayed catalyst was 8 which is less than that of Au foil (CN = 12) suggesting that Au particles are nanosize fine particles. Moreover, after successive pretreatment with O₂ and then H₂, the CN for SPR-Au/Al₂O₃873 increased up to 12 or more, indicating the crystal growth to bulky Au metal. In contrast, for SPR-Al₂O₃1073, it maintains the low CN value due to the stability of the composite prepared at high temperature. Furthermore, no change in the atomic distances was detected.

The amounts of CO and NO adsorption on SPR-Au/Al₂O₃ (Fig. 5) increased rather monotonously with SPR temperature up to 873 K. But the effect of high temperature at 1073 K was different from those for the others. The formation of adsorption sites for NO needs higher temperatures compared with those for CO adsorption.

The catalytic behavior for NO–CO reaction is shown in Fig. 6. The major product from the 1:1 starting mixture gas was CO₂ for all of the three catalysts. While final product of N₂ was effectively produced over the catalysts of SPR-Au/Al₂O₃873 and SPR-Au/Al₂O₃1073. For SPR-Au/Al₂O₃1073, the formation of N₂ was compensated with the intermediate product of N₂O. The non-stoichiometric formation of CO₂ may be due to the direct formation from CO reaction with the adsorbed oxygen on surface.

The effects of pretreatment on the catalytic activity are summarized in Fig. 7; the initial rates over SPR-Au/Al₂O₃1073 are in the order of the treatment: H₂ < H₂–O₂ < O₂ < O₂–H₂. The pretreatment with O₂ followed by H₂ turned out to be most effective for

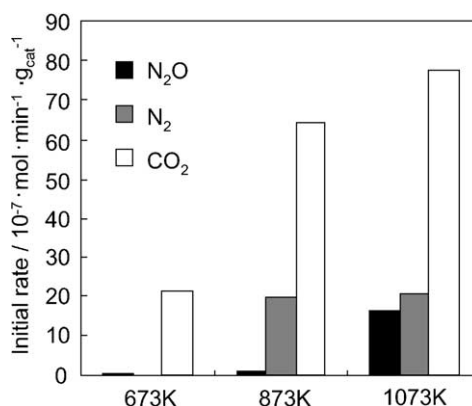


Fig. 6. Initial rates of NO–CO reaction at 673 K over SPR-Au/Al₂O₃ after H₂ pretreatment.

SPR-Au/Al₂O₃1073. The effects of SPR temperature were also confirmed by the results for the activation energy as given in Fig. 8. The catalyst prepared at a higher temperature of 1073 K gave the activation energy (ca. 52 kJ mol⁻¹), which is about a half of the value for SPR-Au/Al₂O₃873 (ca. 116 kJ mol⁻¹). The drastic effect of the SPR temperature is in consistent with the results for SPR-Au/TiO₂ and also observed for the similar Au/Al₂O₃ catalysts prepared by another technique of suspension SPR method [9].

Tsubota et al. [12] have suggested that the mechanism for CO oxidation showing the role of perimeter of Au nanoparticles and the support over the catalyst by precipitation–deposition method, i.e., the adsorbed CO on Au fine particles migrates toward the perimeter

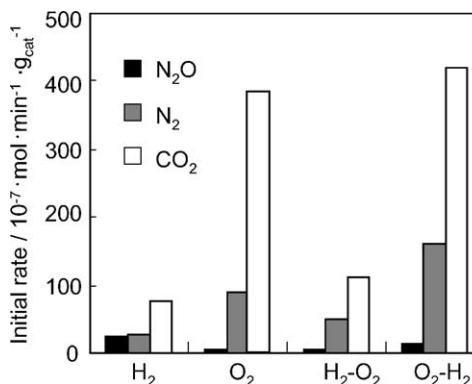


Fig. 7. Initial rates of NO–CO reaction at 673 K over SPR-Au/Al₂O₃1073 after different pretreatment.

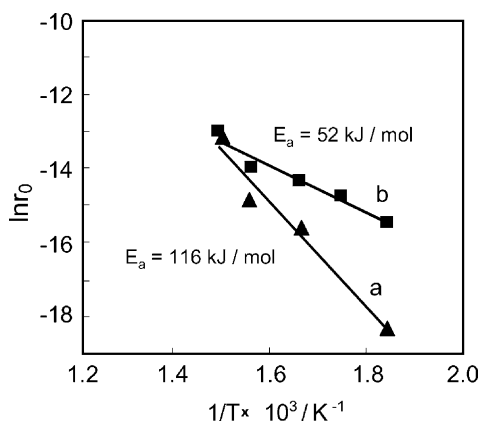


Fig. 8. Arrhenius plots for NO–CO reaction over: (a) SPR-Au/Al₂O₃873 and (b) SPR-Au/Al₂O₃1073.

where it reacts with adsorbed oxygen to form bidentate carbonates as the intermediate which finally decompose to form CO₂.

Therefore, the high catalytic activity of SPR-Au/TiO₂1073 and SPR-Au/Al₂O₃1073 can be explained by the effective formation of the extensive perimeter interface between Au and TiO₂ or Au and Al₂O₃. Such effective perimeter can be produced more effectively in the rapid process of high-temperature SPR where most of the gold particles are partially buried in the composites with both the supports Al₂O₃ and TiO₂. Such nanostructure on SPR catalysts also facilitates to enhance strong synergistic effects as suggested by the change in the activation energy, and binding energy shift observed for SPR-Ru/TiO₂ [8].

4. Conclusion

A solution SPR method using a homogeneous mixture of components was applied to prepare supported gold catalysts, i.e., SPR-Au/TiO₂ and

SPR-Au/Al₂O₃. The catalytic properties for CO oxidation over SPR-Au/TiO₂ and for NO–CO reaction over SPR-Au/Al₂O₃ were investigated, respectively. The ultrafine Au particles were stabilized by the high-temperature SPR for both SPR-Au/TiO₂ and SPR-Au/Al₂O₃, and O₂–H₂ pretreatment leading to stronger interaction between Au and the oxide supports for SPR-Au/Al₂O₃1073.

The dramatic increase of the catalytic activity (TOF) was obtained by the high-temperature SPR (1073 K) for both catalyst systems covering the loss of exposed active sites. Such effects can be attributed to the formation of extensive perimeter interface between Au and the support particles in the characteristic nanocomposites by the SPR method. These structures facilitate to the effective enhancement of synergistic effects for higher catalytic activities.

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