

Enhanced activity of Au catalysts from extra-high surface area CeO₂ for CO oxidation

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A series of Au/CeO₂ catalysts has been prepared with CeO₂ of varying surface areas and tested for low-temperature CO oxidation. With a higher surface area support, the Au/CeO₂ catalysts show a higher catalytic activity for CO oxidation (0.175 mol_{CO} g_{Au}⁻¹ h⁻¹ at 0 °C). Higher oxygen vacancies provided by the formation of solid solution of Au_xCe_{1-x}O_{2-δ} and higher CO chemisorption sites related to Au species are responsible for the enhanced activity.

Keywords: Catalysts, Solid catalysts, Oxidation, CO oxidation, Solid solutions, Oxygen vacancies, Gold, Ceria

Gold catalysts have generated tremendous interest in the past two decades due to their high activity for CO oxidation and various other reactions¹⁻³. For supported Au catalysts, factors such as Au particle size, preparation method, pretreatment conditions and choice of the support affect their catalytic behavior for CO oxidation⁴. Gold supported on reducible CeO₂ has been used as catalyst for CO oxidation⁵, water gas shift⁶ and selective oxidation⁷. However, when the conventional CeO₂ is used, the supported gold catalyst is not as active as those supported on other metal oxides such as TiO₂ and Fe₂O₃ for low temperature CO oxidation⁸. CeO₂ with high surface area as a support has several advantages. It can improve the stability and steady-state activity, and increase the dispersion of active components and the selectivity⁹⁻¹¹. Furthermore, nano-scale CeO₂ crystallite can provide more active oxygen and promote oxidation reaction¹². Carrettin *et al.*⁸ found remarkable enhancement in activity for CO oxidation by two orders of magnitude over an Au catalyst supported on a nano-sized CeO₂ ($S_{\text{BET}} = 180 \text{ m}^2 \text{ g}^{-1}$) compared with Au supported on conventional CeO₂ ($S_{\text{BET}} = 70 \text{ m}^2 \text{ g}^{-1}$). The gold catalyst supported on nano-sized CeO₂ has a higher specific rate than that supported on TiO₂ or Fe₂O₃. They attributed the enhanced activity to the

nanocrystallite CeO₂ particles. Based on these findings, a series of Au/CeO₂ catalyst were prepared using CeO₂ with varying surface areas and tested for low-temperature CO oxidation. The reasons for enhanced activity obtained on the high surface area Au/CeO₂ catalyst were studied.

Experimental

CeO₂ was synthesized by a surfactant-templated method, where CeCl₃·7H₂O, 99.5 % was used as a precursor and CH₃(CH₂)₁₁SO₄Na (99.0 %) as a template. With the different calcination temperatures (400, 600, 650 and 700 °C), CeO₂ with different surface areas (303, 200, 120 and 59 m² g⁻¹ respectively) were obtained. The detailed experimental procedure has been described in our previous work¹².

Au/CeO₂ catalysts were prepared by depositing gold on CeO₂ support by a deposition-precipitation method (DP). An aqueous solution of HAuCl₄ (100 ml, 1 mg ml⁻¹) was heated to 70 °C and pH was adjusted by the addition of 1 M NaOH solution, followed by addition of 2.0 g CeO₂. When pH 7±0.1 was attained, the suspension was vigorously stirred at 70 °C for 1 h. The solid was then isolated by centrifugation and washed until free of chloride and dried at 70 °C for 3 h. The actual Au content was analyzed by inductively coupled plasma (ICP) spectrometry. Au-1.86/CeO₂-303 catalyst indicates that the gold loading is 1.86 wt% and the surface area of the CeO₂ support is 303 m² g⁻¹.

Raman measurements were performed on a Renishaw RM1000 with a confocal microprobe Raman system using a 514 nm (Ar⁺ laser) laser as the excitation source with a resolution of 1 cm⁻¹.

Transmission electron microscopy (TEM) images of the catalysts were obtained on a JEM2010 microscope operated at 200 kV.

In situ diffuse reflectance infrared Fourier transform (DRIFT) spectra of CO adsorption for the samples were recorded using a Nicolet NEXUS 670 spectrometer equipped with an MCT detector and a DRIFTS cell (Harrick) with a resolution of 4 cm⁻¹. The ground catalyst (30 mg) was placed in the cell and pretreated at 100 °C for 0.5 h in He atmosphere to remove water and carbonate. Subsequently, the system was cooled to 20 °C, and a background

spectrum was recorded. After introduction of the gas mixture (1 % CO in N₂, 30 ml min⁻¹) for 15 min, the catalyst was purged with He to remove the physisorbed CO, before recording the spectra.

X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 high performance electron spectrometer using monochromatized Al-K_α excitation source ($h\nu = 1486.6$ eV). Binding energies were calibrated by using the contaminant carbon (C 1s = 284.6 eV).

The catalytic activity of CO oxidation was evaluated in a fixed-bed reactor (6 mm i.d.), using 300 mg of catalyst (80-100 mesh) without any pretreatment, as given in our earlier study¹². The total flow rate of the feed gas (1 % CO and 1 % O₂ in N₂) was 40 ml min⁻¹ with a space velocity (SV) of 8000 ml g⁻¹ h⁻¹. The reaction temperature was kept at 0 °C by immersing the reactor in a mixture of water and ice.

Results and discussion

Figure 1 shows the representative high resolution TEM images of the Au catalysts supported on CeO₂ of varying surface areas. It can be seen that the particle size of the deposited Au is similar (*ca.* 3-5 nm), despite the varying surface area of the support. This is due to the deposition-precipitation method for catalysts preparation, which leads to almost identical Au loading on per unit surface area of CeO₂. The inter-planar distance of 0.23 nm (Fig. 1c) indicates *d*(111) plane of gold crystallite¹³. XRD experiments were conducted; however, due to lower loading and smaller crystallites size, the diffraction peaks of Au were not observed.

Raman spectra of Au/CeO₂ catalysts and CeO₂ are shown in Fig. 2. The bands for Au/CeO₂ show features similar to those of CeO₂ samples, with the bands at 460 and 600 cm⁻¹ assigned to the *F*_{2g}

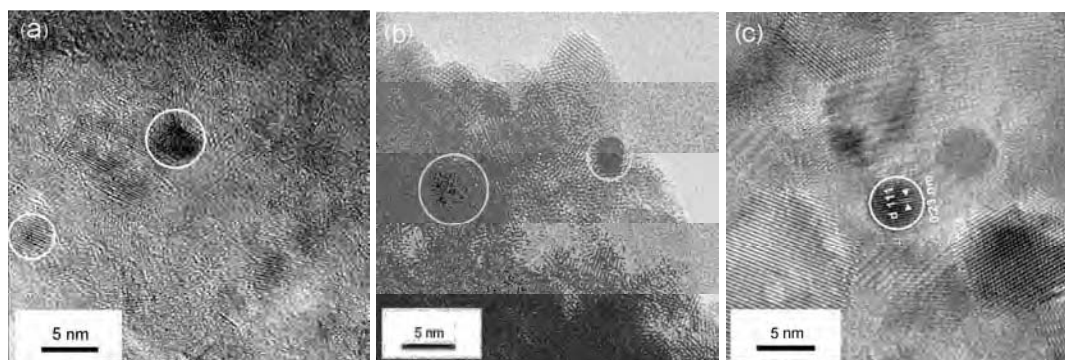


Fig. 1—High resolution TEM images of (a) Au-1.86/CeO₂-303, (b) Au-2.04/CeO₂-200, and, (c) Au-0.56/CeO₂-59 catalysts.

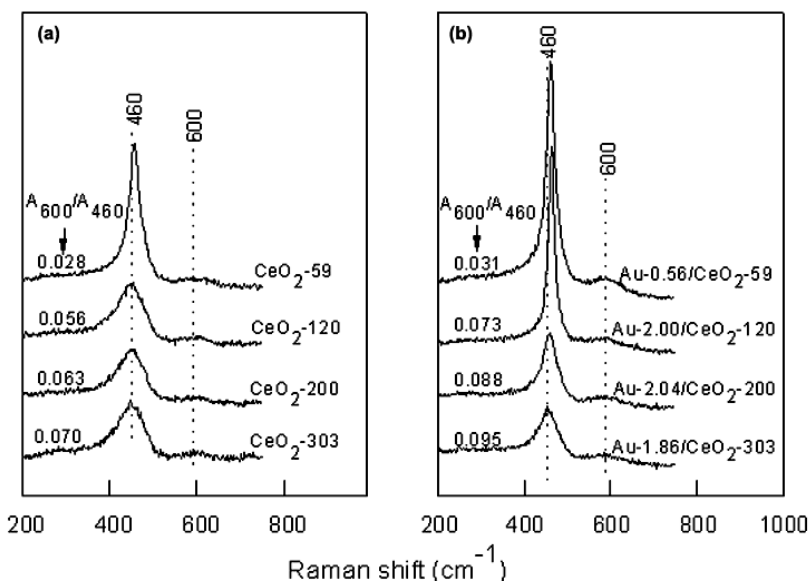


Fig. 2—Raman spectra of (a) CeO₂ and, (b) Au/CeO₂ catalysts with varying surface areas.

vibration mode of fluorite structure of pure CeO_2 and the oxygen vacancies^{14,15}, respectively. A_{600}/A_{460} values were calculated based on Fig. 2. It is found that the values for all Au/CeO_2 catalysts are higher than that of the corresponding CeO_2 support, indicating that the doping of Au on the CeO_2 support brings more oxygen vacancies, probably due to the formation of $\text{Au}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ solid solution. Also, the value increases with increasing surface area of CeO_2 , implying that more $\text{Au}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ solid solution forms in the catalyst with higher surface area support. Bera¹⁶ and Venezia¹⁷ have reported that the $\text{Au}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ solid solution could be easily formed when Au is supported on CeO_2 . Moreover, noble metals such as Pd and Pt may also result in the formation of $\text{Pd}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ and $\text{Pt}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ solid solutions¹⁸. The solid solution not only makes $\text{Au}^{\delta+}$ stable but also promotes the generation of oxygen vacancies, which is in accordance with the Raman results (Fig. 2b).

Figure 3 shows Ce 3d and Au 4f XPS spectra of the Au-1.86/ CeO_2 -303 and Au-0.56/ CeO_2 -59 catalysts. The Ce 3d XPS spectra show multiple states arising from different Ce 4f level occupancies in the final state¹⁹. Peak-fitting of the Ce 3d XPS spectra (Fig. 3a) was performed. For Au-1.86/ CeO_2 -303, binding energies at 883.6, 889.7 and 899.4 eV are the features of Ce(IV), while that at 886.0 eV is the feature of Ce(III). Likewise, for Au-0.56/ CeO_2 -59, binding energies at 884.0, 890.0 and 899.9 eV are the features of Ce(IV), and that at 886.2 eV is of Ce(III)^{20,21}. The Ce(III)/Ce(IV) atomic ratios i.e. the concentration of surface oxygen vacancies calculated by the peak area of Ce(III)/the total area of Ce(IV) peaks are 0.14 and 0.08 for Au-1.86/ CeO_2 -303 and Au-0.56/ CeO_2 -59, respectively. The ratio increases with increasing surface area of CeO_2 , implying that high surface area is beneficial for the formation of surface oxygen vacancies in CeO_2 . This is also in agreement with the Raman results (Fig. 2b).

The Au 4f XPS spectra of Au-0.56/ CeO_2 -59 (Fig. 3b) could be fitted with two components, with Au 4f binding energies at 84.6 and 86.8 eV, and in Au-1.86/ CeO_2 -303, at 85.1 and 86.9 eV. The low and high binding energies could be assigned to Au(I) and Au(III) species, respectively²². For Au-1.86/ CeO_2 -303, the surface compositions of Au(I) and Au(III) are 61.3 % and 38.7 %, respectively; while for Au-0.56/ CeO_2 -59, these are 76.0 % and 24.0 %, respectively. This indicates that in Au-1.86/ CeO_2 -303 the percentage of Au(III) species is higher than that in

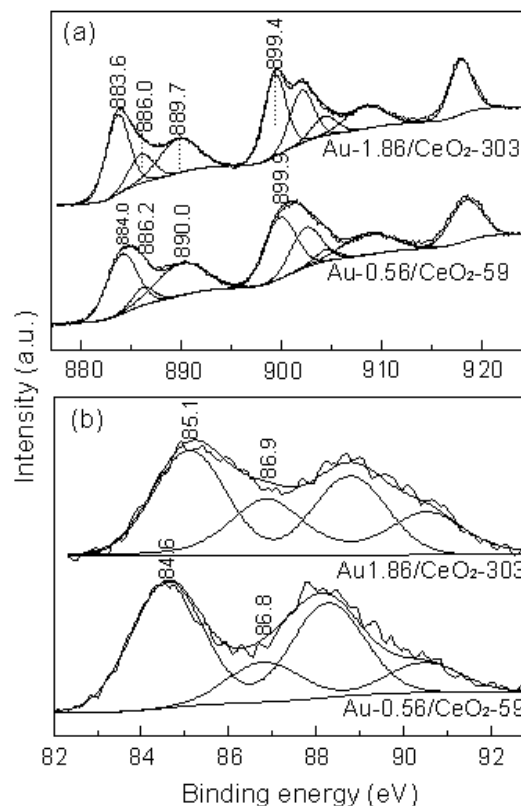


Fig. 3—(a) Ce 3d, and, (b) Au 4f XPS spectra of Au-1.86/ CeO_2 -303 and Au-0.56/ CeO_2 -59 catalysts.

Au-0.56/ CeO_2 -59. Furthermore, the average valence of surface gold species in these two catalysts was calculated as:

$$V_{\text{average-Au}} = \frac{A_{\text{Au(I)}}}{A_{\text{Au(I)}} + A_{\text{Au(III)}}} \times 1 + \frac{A_{\text{Au(III)}}}{A_{\text{Au(I)}} + A_{\text{Au(III)}}} \times 3$$

where $A_{\text{Au(I)}}$ and $A_{\text{Au(III)}}$ refer to the peak area of Au(I) and Au(III) species in the XPS spectra, respectively.

The average valence of the surface Au species in Au-1.86/ CeO_2 -303 and Au-0.56/ CeO_2 -59 catalysts are 1.77 and 1.48, respectively, indicating that the oxidation state of Au in high surface area CeO_2 is higher than that in low surface area CeO_2 . This is probably due to the formation of $\text{Au}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ solid solution in the high surface area catalyst, in which more Au cations are present as Au^{3+} .

The catalytic activities of CO oxidation at 0 °C over the Au/ CeO_2 catalysts and A_{600}/A_{460} values are listed in Table 1. It can be seen that the catalytic activity increases with increasing surface area of CeO_2 . Since bare CeO_2 is not active at 0 °C, we normalized the

Table 1—Catalytic activity of CO oxidation at 0 °C over Au/CeO₂ catalysts and A_{600}/A_{460} ratio

Catalyst	CO conversion (%)	Specific rate (mol _{CO} g _{Au} ⁻¹ h ⁻¹)	A_{600}/A_{460}
Au-1.86/CeO ₂ -303	90.4	0.175	0.095
Au-2.04/CeO ₂ -200	69.8	0.123	0.088
Au-2.00/CeO ₂ -120	48.8	0.088	0.073
Au-0.56/CeO ₂ -59	4.82	0.031	0.031

specific reaction rate based on the gold loading. The highest activity of 0.175 mol_{CO} g_{Au}⁻¹ h⁻¹ at 0 °C is obtained with the Au-1.86/CeO₂-303 catalyst. Table 2 shows the activity of the present Au-1.86/CeO₂-303 and other Au/CeO₂ catalysts for CO oxidation. Carretin⁸ and Huang²³ have reported that the specific rates of Au/CeO₂ catalysts are 0.37 and 0.15 mol_{CO} g_{Au}⁻¹ h⁻¹ at 5 °C, respectively.

For Au/CeO₂ catalysts, it is generally believed that the reaction takes place at the interface between Au and the support. The reaction obeys the Mars-van Krevelen mechanism²⁴. CO was mainly adsorbed on metallic Au or Au^{δ+} species²⁵⁻²⁷ and the active oxygen species was generated by chemisorption and activation of oxygen molecules on CeO₂ or Au_xCe_{1-x}O_{2-δ} solid solutions²⁸.

To evidence the CO chemisorption on Au/CeO₂ catalysts, DRIFT spectroscopy was performed (Fig. 4). The spectra were collected after the catalysts were exposed to the gas mixture (1 % CO in He) for 15 min and purged with He for 7-15 min subsequently at 20 °C. For Au/CeO₂ catalysts, besides the peaks at 1393, 1508 and 1681 cm⁻¹ assigned to the carbonate species²⁹, a new peak at 2105 cm⁻¹ and two peaks at 2360 and 2339 cm⁻¹ were also detected. The former may be assigned to the CO chemisorbed⁸ on metallic Au(0) and the latter two³⁰ to the gaseous CO₂. This implies that CO molecules adsorbed on the catalyst surface easily react with oxygen species and form CO₂. Moreover, on comparing Au-1.86/CeO₂-303 and Au-0.56/CeO₂-59 catalysts, it is found that after He purging for 15 min, the intensity of CO chemisorbed on Au-1.86/CeO₂-303 is stronger than that on Au-0.56/CeO₂-59, and the feature bands of gaseous CO₂ and carbonate species are much more intense on Au-1.86/CeO₂-303. This suggests that Au-1.86/CeO₂-303 is more active for CO oxidation than Au-0.56/CeO₂-59, and the reaction may go through a carbonate decomposition pathway³¹. Meanwhile, for Au-1.86/CeO₂-303 catalyst, the intensity of chemisorbed CO declines with increasing purging time, indicating that the CO is consumed by the surface oxygen of the support.

Table 2—Catalytic activity of Au-1.86/CeO₂-303 and other Au/CeO₂ catalysts for CO oxidation

Catalyst	Reaction gas	Reaction temp. (°C)	Specific rate (mol _{CO} g _{Au} ⁻¹ h ⁻¹)	Ref.
Au-1.86/CeO ₂ -303	CO/O ₂ /N ₂ 1/1/98	0	0.175	This work
Au/CeO ₂	CO/air/He 0.2/19.8/80	5	0.37	8
Au/CeO ₂	CO/O ₂ /He 1/20/79	5	0.15	23

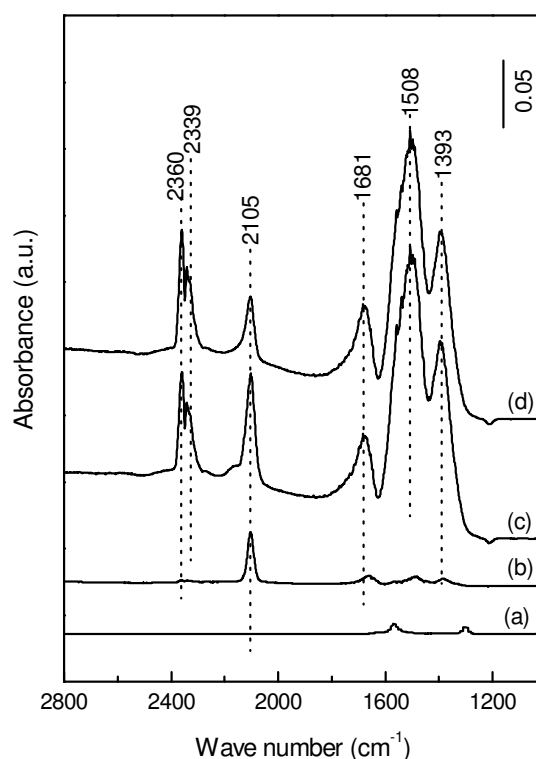


Fig. 4—DRIFT spectra of CeO₂ and Au/CeO₂ catalysts by He purge after CO adsorption.

Also, it is worth noting that the characteristic band at 2105 cm⁻¹ is usually assigned to the CO chemisorbed on metallic Au(0), which is inconsistent with the XPS results (Fig. 3) which show that the surface Au species are cationic (Au(I)+Au(III)). This is probably due to the reduction of cationic Au species during the CO chemisorption (Au^{δ+} + CO → Au + CO₂), since the reduction is easy and fast for Au supported on reducible oxides^{32,33}.

Moreover, as seen in Table 1, the activity of the Au/CeO₂ catalyst increases with increasing A_{600}/A_{460} ratio, suggesting that the higher concentration of oxygen vacancies may be responsible for the enhanced activity. This kind of doped catalyst system may enhance the activity for CO oxidation, as

reported by Shapovalov and Metiu, using a DFT calculation³⁴. Thus, the higher concentration of oxygen vacancies in the Au/CeO₂ catalyst may be a reason for the higher activity of CO oxidation.

Therefore, the enhanced activity obtained on the Au catalyst supported on high surface area CeO₂ may be attributed to two facts: (i) Au particles formed on the high surface area CeO₂ are favorable for CO adsorption (Fig. 4)^{10,11} and (ii) the high surface area CeO₂ provides more oxygen vacancies by the formation of Au_xCe_{1-x}O_{2-δ} solid solution, on which oxygen molecules could be transformed to active species (such as superoxide species) for the reaction²⁸.

The above study shows that gold catalysts supported on high surface area CeO₂ are very active for low temperature CO oxidation. The Raman spectroscopy results reveal that by the formation of Au_xCe_{1-x}O_{2-δ} solid solution, oxygen vacancies are formed, on which active oxygen could be subsequently generated. DRIFT spectra of CO adsorption suggest that the gold catalyst supported on high surface area CeO₂ provides more chemisorption sites compared to that supported on low surface area CeO₂. These two factors may be responsible for the high activity for low-temperature CO oxidation.

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References

- Beck A, Horváth A, Stefler G, Katona R, Geszti O, Tolnai G, Liotta L F & Guczi L, *Catal Today*, 139 (2008) 180.
- Pina C D, Falletta E & Rossi M, *J Catal*, 260 (2008) 384.
- Rebrov E V, Berenguer-Murcia A, Johnson B F G & Schouten J C, *Catal Today*, 138 (2008) 210.
- Bond G C & Thompson D T, *Catal Rev Sci Eng*, 41 (1999) 319.
- Manzoli M, Boccuzzi F, Chiorino A, Vindigni F, Deng W & Flytzani-Stephanopoulos M, *J Catal*, 245 (2007) 306.
- Karpenko A, Leppelt R, Plzak V & Behm R J, *J Catal*, 252 (2007) 231.
- Luengnaruemitchai A, Osuwan S & Gulari E, *Int J Hydrogen Energy*, 29 (2004) 429.
- Carrettin S, Concepción P, Corma A, Nieto J M L & Puentes V F, *Angew Chem Int Ed.*, 43 (2004) 2538-2540.
- Bickford E S, Velu S & Song C S, *Catal Today*, 99 (2005) 347.
- Lai S Y, Qiu Y F & Wang S J, *J Catal*, 237 (2006) 303.
- Campo B, Volpe M, Ivanova S & Touroude R, *J Catal*, 242 (2006) 162.
- Guo M N, Guo C X, Jin L Y, Wang Y J, Lu J Q & Luo M F, *Mater Lett*, 64 (2010) 1638.
- Ogi T, Saitoh N, Nomura T & Konishi Y, *J Nanopart Res*, 12 (2010) 2531.
- McBride J R, Hass K C, Poindexter B D & Weber W H, *J Appl Phys*, 76 (1994) 2435.
- Lin X M, Li L P, Li G S & Su W H, *Mater Chem Phys*, 69 (2001) 236.
- Bera P & Hegde M S, *Catal Lett*, 79 (2002) 75.
- Venezia A M, Pantaleo G, Longo A, Di Carlo G, Casaletto M P, Liotta F L & Deganello G, *J Phys Chem B*, 109 (2005) 2821.
- Hegde M S, Madras G & Patil K C, *Acc Chem Res*, 42 (2009) 704.
- Kotani A, Jo T & Parlebas J C, *Adv Phys*, 37 (1988) 37.
- Burroughs P, Hamnett A, Orchard A F & Thornton G, *J Chem Soc Dalton Trans*, 17 (1976) 1686.
- Fang J, Bi X Z, Si D J, Jiang Z Q & Huang W X, *Appl Surf Sci*, 253 (2007) 8952.
- Fu Q, Saltsburg H & Flytzani-Stephanopoulos M, *Science*, 301 (2003) 935.
- Huang X S, Sun H, Wang L C, Liu Y M, Fan K N & Cao Y, *Appl Catal B*, 90 (2009) 224.
- Bond G C, Louis C & Thompson D T, *Catalysis by Gold*, (Imperial College Press, London) 2006.
- Leppelt R, Schumacher B, Plzak V, Kinnea M & Behma R J, *J Catal*, 244 (2006) 137.
- Chen Y, Cheng J, Hu P & Wang H F, *Surf Sci*, 602 (2008) 2828.
- Weststrate C J, Resta A, Westerström R, Lundgren E, Mikkelsen A & Andersen J N, *J Phys Chem C*, 112 (2008) 690.
- Guzman J, Carrettin S, Fierro-Gonzalez J C, Hao Y, Gates B C & Corma A, *Angew Chem Int Ed*, 44 (2005) 4778.
- Terribile D, Trovarelli A, Llorca J, Leitenburg C de & Dolcetti G, *Catal Today*, 43 (1998) 79.
- Kantcheva M, Samarskaya O, Ilieva L, Pantaleo G, Venezia A M & Andreeva D, *Appl Catal B*, 88 (2009) 113.
- Daniells S T, Overweg A R, Makkee M & Moulijn J A, *J Catal*, 230 (2005) 52.
- Wu Z, Zhou S, Zhu H, Dai S & Overbury S H, *Chem Commun*, 28 (2008) 3308.
- Dekkers M A P, Lippits M J & Nieuwenhuys B E, *Catal Lett*, 56 (1998) 195.
- Shapovalov V & Metiu H, *J Catal*, 245 (2007) 205.