



The promoted effect of UV irradiation on preferential oxidation of CO in an H₂-rich stream over Au/TiO₂

Wenxin Dai, Xiangping Zheng, Haiyan Yang, Xun Chen, Xuxu Wang, Ping Liu, Xianzhi Fu*

Research Institute of Photocatalysis, State Key Laboratory Breeding Base of Photocatalysis, Fuzhou University, Fuzhou 350002, China

ARTICLE INFO

Article history:

Received 17 November 2008
Received in revised form 6 December 2008
Accepted 8 December 2008
Available online 13 December 2008

Keywords:

Preferential CO oxidation
Chemisorption
Hydrogen
UV irradiation

ABSTRACT

The catalytic oxidation of CO over Au/TiO₂ in an H₂-rich stream was performed under UV irradiation. It is found that UV irradiation over Au/TiO₂ promotes the preferential oxidation of CO in the H₂-rich stream. The respective chemisorption of CO, H₂ and O₂ at Au/TiO₂ can be described as a process of forming –OH or H₂O species. UV irradiation over Au/TiO₂ enhances the chemisorption of CO but suppresses the chemisorption of H₂ both at TiO₂ and Au surface. It is proposed that the photogenerated electrons from TiO₂ will cause the change of the chemisorption of CO, H₂ and O₂ at Au/TiO₂, which promotes the preferential oxidation of CO in an H₂-rich stream.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The selective oxidation of CO in an H₂-rich atmosphere has long been of considerable technical interest for purification of hydrogen feed gas in the fuel cell systems, e.g., proton exchange membrane fuel cell (PEMFC) [1,2]. Because the trace amount of CO in H₂ stream produced by reforming methanol and hydrocarbons will poison for the Pt-anode catalyst, a stringent removal of CO down to the ppm-level is necessary, and one promising method is the catalytic preferential oxidation of CO in an H₂-rich stream with air [3–5]. Supported noble metals, such as Pt [4–9], Pd and Rh [10,11] exhibit a good performance for catalytic preferential oxidation of CO. Since the highly dispersed Au nanoparticles on suitable metal oxides are highly active at a low temperature for CO oxidation [12–20], many studies of CO oxidation in the presence of H₂ over supported Au catalyst have also been attracted to a great extent [21–26,12,27–30]. Although the presence of H₂ promotes the activity and stability of CO oxidation, the selectivity of the oxidation of CO in an H₂-rich stream decreases due to the oxidation of H₂ itself [22,30].

With respective to a low temperature thermocatalytic oxidation of CO over Au nanoparticles deposited on metal oxides, it is generally proposed that there exist two active sites: one is CO adsorbed on Au nanoparticles, and another is O₂ (or its derivate species) adsorbed on the Au/oxide interface via surface oxygen vacancy sites (SOVs) at the oxide supports [31,32]. In addition, a higher electron density of Au nanoparticles can promote the adsorption of CO at

Au surface [33–36]. For example, as Au nanoparticles is dispersed on the surface of a reduced oxide support (e.g. TiO₂), the electron density on the surface of Au nanoparticles is increased due to the electrons transferring from the reduced oxides to Au nanoparticles, which further promotes the oxidation of CO [37].

Photocatalytic oxidation over TiO₂, as an alternative method to removing CO, has been early concerned in the last decade [38,39]. Recently, our preliminary work indicated that UV irradiation over a Au nanoparticles dispersed on TiO₂ (Au/TiO₂) could promote the oxidation of CO in the presence of H₂ with a low content (about 1.0 vol% H₂), while the oxidation of H₂ was entirely suppressed at a low temperature [40]. However, this case was little concern on the oxidation of CO in an H₂-rich stream, and the Au/TiO₂ presented a low thermocatalytic activity.

Considering that UV irradiation over TiO₂ can be somewhat regarded as the process of producing electrons, in this present study UV irradiation was introduced into the reaction system of CO oxidation over Au/TiO₂ with a high thermocatalytic activity in an H₂-rich stream. The chemisorption of reactants at the surface of Au/TiO₂ was analyzed with the testing result of temperature program desorption (TPD). It was expected that the photoexcited electrons could give rise to a change of the chemisorption of reactants at the surface of Au/TiO₂ via changing surface electron density of Au and TiO₂, and then promote the oxidization of CO.

2. Experimental

2.1. Preparation of Au/TiO₂

The preparation of TiO₂ powder: firstly, a TiO₂ sol was prepared by a method that involved the controlled hydrolysis of titanium

* Corresponding author. Tel.: +86 591 83738608; fax: +86 591 83738608.
E-mail address: xzfu@fzu.edu.cn (X. Fu).

tetraisopropoxide followed by dialysis to pH 3.0 [41]. Then, this obtained TiO₂ sols was dried at 80 °C and calcined at 400 °C in air at a ramping rate of 2 °C min⁻¹ for 2 h, and a porous TiO₂ powder was obtained.

Au/TiO₂ was prepared by deposition–precipitation method: HAuCl₄ (1 mL of 0.01 mg mL⁻¹) was added into 150 mL of H₂O under vigorous stirring. After adjusting this HAuCl₄ solution at pH 9.0 via NaOH (1 mol L⁻¹), a 1.0-g prepared TiO₂ powder was added to obtain a suspension. This obtained suspension was stirred for 2 h at 70 °C and pH 9.0, then aged at room temperature for 2 h, finally percolated to obtain a TiO₂ powder loaded with Au ions. This obtained powder was immersed into an aqueous solution of NaBH₄ (1.0 mol L⁻¹) to reduce the ionized Au for 2 h, then rinsed with deionized H₂O to remove Cl⁻, Na⁺ and other excess ions. After dried at 80 °C, a Au/TiO₂ catalyst containing ca. 2.0 wt% Au was obtained.

2.2. Characteristic of Au/TiO₂

Transmission electron microscopy (TEM) investigation was carried out on a JEOL JEM-2010 EX with field emission gun at 200 kV. X-ray diffraction (XRD) pattern was recorded on a Bruker D8 Advance powder X-ray diffractometer using Cu K α radiation ($\lambda = 0.15418$ nm) operated at 40 kV and 40 mA. The textural data of samples was measured by N₂ adsorption at liquid N₂ temperature with a micromeritics ASAP 2020 BET analyzer. Before the analysis the sample was outgassed at 250 °C under vacuum for 4 h.

2.3. Catalytic performance

Catalytic oxidation of CO was conducted in a fixed-bed flow reaction system at atmospheric pressure using 200 mg of catalyst at a total flow rate of 100 mL min⁻¹. The catalysts with a grain size of 0.2–0.3 mm were loaded in the quartz-glass tube, which was surrounded by three ultraviolet lamps (4w, a broad-band UV light with the main wavelength at 365 nm). The feed stream contained 0.5 vol% CO, 0.5 vol% O₂, 85 vol% H₂ and a balance He. The effluent stream was analyzed using an online gas chromatograph (GC) system equipped with a thermal conductivity detector (Agilent 4890D, TDX-01). This reaction system of CO oxidation in the H₂-rich stream was denoted as CO/H₂/O₂. The activity was evaluated by the turnover frequency (TOF) of CO oxidation to CO₂, which could be calculated on the basis of the content change of CO in the feed and effluent stream. The selectivity of CO oxidation is defined as the ratio of O₂ consumption for the CO oxidation to the total O₂ consumption. As a reference, the activity test of CO oxidation in the absence of H₂ (denoted as CO/O₂) was performed. Here the feed stream contained 0.5 vol% CO, 0.5 vol% O₂, and a balance He. As another reference, the oxidation of H₂ in the absence of CO (denoted as H₂/O₂) was also tested. Here the content of H₂ in inlet could be changed, while the content of O₂ was kept at 0.5 vol% with the balance He. During the testing process, the reaction temperature was kept at 50 °C. During the process of testing the pure thermocatalytic activity, the quartz tube was enclosed with Al foils to shut down UV light. However, no other product in outlet was observed except that H₂O and CO₂ in all reaction systems.

2.4. Temperature program desorption (TPD)

Temperature program desorption (TPD) of Au/TiO₂ was tested in Micromeritics Autochem 2910 instrument. Prior to the introduction of the adsorbed gas, about 100 mg of powder sample was firstly degassed in a high purity He stream (20 mL min⁻¹) at 200 °C for 30 min. After cooled down to room temperature, a specific process for the sample proceeded as follows: (1) introducing the gas to be adsorbed for 30 min at room temperature. Here, the O₂, CO,

H₂ and the mixed gas of H₂ and CO (H₂/CO) were introduced to the sample at a flow rate of 20 mL min⁻¹ in a stream of 5 vol% O₂–He, 10 vol% CO–He, pure H₂ and 10.0 vol% CO–H₂, respectively. (2) Switching He stream for 30 min. (3) Heating to 500 °C in a He stream at a ramping rate of 10 °C min⁻¹, and recording of a signal of TCD. Meanwhile, mass spectrometry signals with *m/z* of 18, 28, 32 and 44 were recorded to detect the masses of H₂O, CO, O₂, and CO₂ molecules, respectively. For testing TPD under UV irradiation, a UV light at 365 nm (high pressure mercury lamp) was introduced into the surface of sample during the process of adsorbing gas.

3. Results and discussion

3.1. Characteristic of Au/TiO₂

The TEM image of Au/TiO₂ in Fig. 1(a) shows that single Au particles with sizes of 3–5 nm are deposited on the surface of 10–20 nm TiO₂ particles. Here, Au particles present a (1 1 1) surface plane (the width of the surface unit cell is 0.24 nm), and the TiO₂ particles present a typical (1 0 1) surface plane (the width of the surface unit cell is 0.34 nm) (Fig. 1(b)). Fig. 2 indicates that TiO₂ can be almost described as the anatase phase in both TiO₂ and Au/TiO₂, although two samples contain a small amount of rutile and brookite impurity. However, no Au peaks is observed in the XRD pattern of Au/TiO₂, indicating that the loading Au nanoparticles are dispersed on the surface of TiO₂. Moreover, Au/TiO₂ exhibits a textural property (pore radius, pore volume and specific surface area) similar to that of pure TiO₂ powder (Table 1).

3.2. Catalytic performance in CO/O₂, CO/H₂/O₂ and H₂/O₂ systems

Table 2 shows the catalytic activities of Au/TiO₂ in CO/O₂ and CO/H₂/O₂ reaction systems under UV irradiation or not. In the CO/O₂ system, the turnover frequency (TOF) of CO to CO₂ is increased from 5.170 to 6.100 mmol g⁻¹ h⁻¹ with the introduction of UV irradiation. In CO/H₂/O₂ system, although the presence of H₂ decreases the TOF of CO to CO₂ from 5.170 to 4.776 mmol g⁻¹ h⁻¹ due to the oxidation of H₂, the introduction of UV irradiation over Au/TiO₂ increases the TOF of CO to CO₂ (from 4.776 to 5.043 mmol g⁻¹ h⁻¹) and decreases the TOF of H₂ to H₂O (from 8.651 to 8.423 mmol g⁻¹ h⁻¹). This result shows that UV irradiation over Au/TiO₂ can not only promote the oxidation of CO, but also increase the selectivity of CO oxidation (from 35.6% to 37.5%) in the H₂-rich stream. However, UV irradiation over Au/TiO₂ does promote the oxidation of H₂ in the absence of CO (H₂/O₂ system) (seen in Table 3).

Note that the introduction of H₂ not only suppress the oxidation of CO over Au/TiO₂ without UV irradiation, but also decreases the promoting effect of UV irradiation on the oxidation of CO (Table 2). This means that the H₂O formed by the oxidation of H₂ seems not to benefit the oxidation of CO in an H₂-rich stream over Au/TiO₂ under UV irradiation. That is to say, OH• radicals may be not mainly responsible for the oxidation of CO over Au/TiO₂ in this case, because the presence of H₂O can facilitate the formation of OH• radical under UV irradiation over TiO₂. Of course, the competitive oxidation of H₂ may also decreases the oxidation of CO especially in this case with a high content of H₂.

Table 1
Textural data of TiO₂ and Au/TiO₂.

Samples	Pore radius (nm)	Pore volume (mL g ⁻¹)	Specific surface area (m ² g ⁻¹)
TiO ₂	5.89	0.20	95.77
Au/TiO ₂	6.18	0.20	97.39

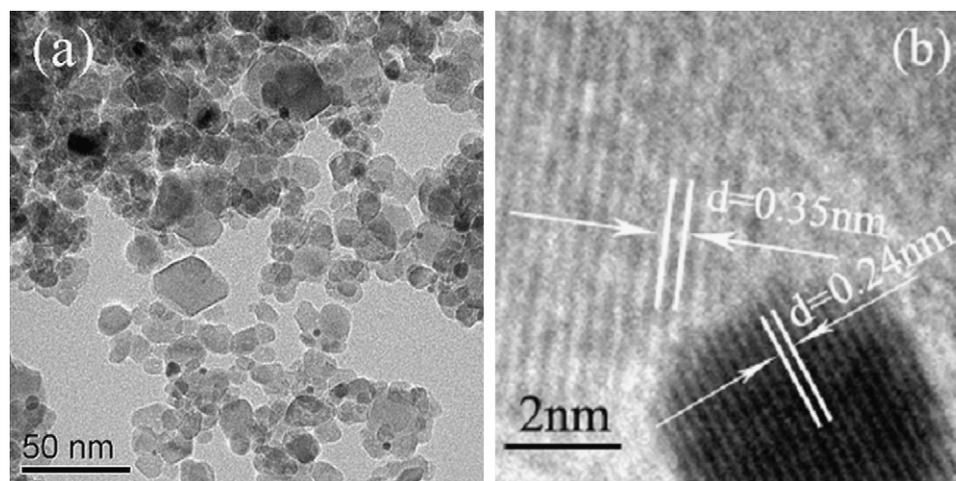


Fig. 1. TEM images of Au/TiO₂ with (a) low-magnification and (b) high-magnification.

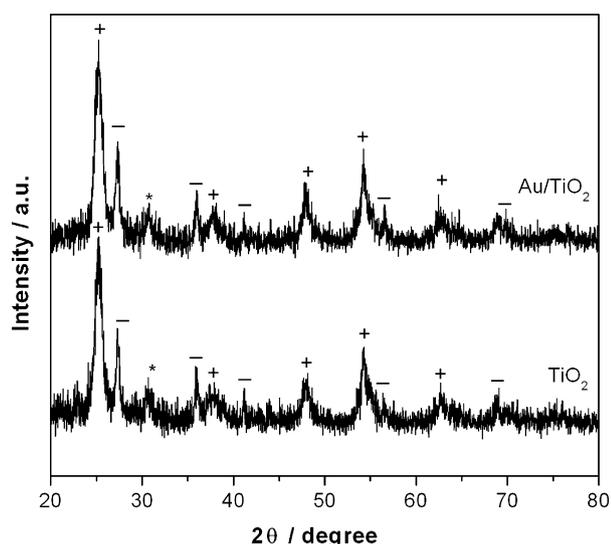


Fig. 2. XRD patterns of TiO₂ and Au/TiO₂. Symbols (+), (-), and (*) denote anatase, rutile, and brookite, respectively.

In fact, no apparent conversion of CO over pure TiO₂ is observed under UV irradiation in this fixed-bed flow reactor. This shows that the promoting effect of UV irradiation on the oxidation of CO over Au/TiO₂ cannot be attributed to the photocatalytic effect of pure TiO₂. This may be one reason that oxidation of CO over Au/TiO₂ under UV irradiation is not highly dependent on the OH• radicals. Considered that the thermocatalytic oxidation of CO over the supported Au catalyst is dependent on both the CO adsorbed at Au nanoparticles and the O₂ (or its derivate species) adsorbed at the Au/oxide interface [31,32], the chemisorption behaviors of CO, O₂ and H₂ at Au/TiO₂ surface under UV

Table 3

Turnover frequencies (TOFs) of H₂ oxidation over Au/TiO₂ in H₂/O₂ system at 50 °C under UV irradiation or not.

Content ratio of H ₂ to O ₂ ^a	TOF of H ₂ oxidation (mmol g ⁻¹ h ⁻¹)	
	No UV irradiation	UV irradiation
1	0.576	0.609
2	1.540	1.808
4	3.000	3.160
170 ^b	13.432	13.432

^a In the cases, the content of O₂ is kept at 0.5 vol%.

^b As the content ratio of H₂ to O₂ is 170 times (i.e. 85.0 vol% of H₂ vs. 0.5 vol% of O₂), O₂ has been totally consumed without UV irradiation. Here the introduction of UV irradiation cannot further increase the TOF of H₂ due to the absence of O₂.

irradiation are investigated via TPD testing in the following section.

3.3. TPD results of CO, H₂ and O₂ adsorbed at Au/TiO₂

3.3.1. TPD results under no UV irradiation

Fig. 3 shows the thermal conductivity detector (TCD) signals for the TPD of Au/TiO₂ adsorbing CO, H₂, O₂ and H₂/CO, respectively. During the thermodesorption process of Au/TiO₂ itself (curve He), two desorption peaks appear at 200 and 388 °C, respectively. With the introduction of O₂, CO, H₂ or H₂/CO, the peak temperature of the desorption at 200 °C falls to 185 °C, but that at 388 °C increases to 395 °C. In addition, a new desorption peak appears at 100 °C in the all curves of O₂, CO, H₂, and H₂/CO, and another appears at 340 °C in the two curves of H₂ and H₂/CO.

To assign the desorption peaks indicated by the TCD signals, the mass spectrometry signals with *m/z* values of 18, 28, 32, and 44 were recorded during the TPD processes, which correspond to the masses of H₂O, CO, O₂, and CO₂ molecules, respectively. However,

Table 2

Catalytic performances of Au/TiO₂ in CO/O₂ and CO/H₂/O₂ systems at 50 °C under UV irradiation or not.

Reaction systems	Reaction conditions	TOF ^a of CO oxidation (mmol g ⁻¹ h ⁻¹)	TOF ^a of H ₂ oxidation (mmol g ⁻¹ h ⁻¹)	Selectivity of CO oxidation (%)
CO/O ₂ ^b	No UV irradiation	5.170	–	–
	UV irradiation	6.100	–	–
CO/H ₂ /O ₂ ^c	No UV irradiation	4.776	8.651	35.60
	UV irradiation	5.043	8.423	37.50

^a TOF: turnover frequency of CO or H₂ oxidation to CO₂ or H₂O, and defined as the amount (mmol) of CO or H₂ oxidation over per gram catalyst per 1 h.

^b 0.5 vol% CO, 0.5 vol% O₂.

^c 0.5 vol% CO, 85 vol% H₂, 0.5 vol% O₂.

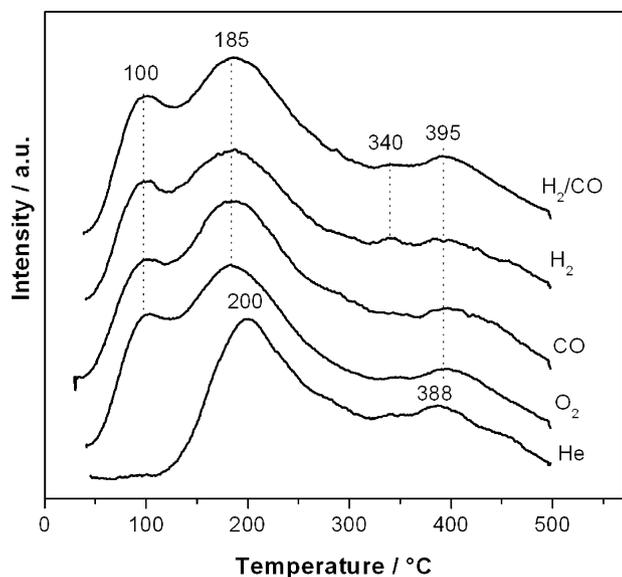


Fig. 3. TCD signals during TPD processes over Au/TiO₂ adsorbing different atmospheres under no UV irradiation. The baseline of each curve is in line with the corresponding smallest value of desorption intensity.

with the mass spectrometer employed, the signal of $m/z=2$ (H₂) could not be detected.

Fig. 4 shows the mass signals of CO, CO₂, O₂ and H₂O during the TPD process of Au/TiO₂ adsorbing He, CO, O₂, H₂ or H₂/CO. The species of CO, CO₂ and H₂O are observed in each case, which H₂O species exhibits the largest intensity (the intensity scale of H₂O in Fig. 4(b) was 10 times higher than that of O₂, CO and CO₂ in Fig. 4(a), 2(c) and (d), i.e. E-13 vs. E-14). Based on the TPD results with mass signals of pure TiO₂ in the same case (SI 3), the desorption behavior of Au/TiO₂ induced by the adsorption of He, CO, H₂, O₂ and H₂/CO can be explained as follows.

During the thermodesorption process of Au/TiO₂ itself (seen in curve He in Fig. 3), the desorption peak at 200 °C can be attributed to the formation of H₂O with a tiny concomitant CO and CO₂ (seen in curve He in Fig. 4(c and d)). Here the formation of H₂O can be ascribed to the desorption of surface OH species of TiO₂, while the formation of CO and CO₂ can be ascribed to the desorption of carboxylate-like (COO⁻) species at the surface of TiO₂. In addition, the desorption peak at 388 °C can be attributed to the formation of CO and CO₂ due to the desorption of COO⁻ species at Au surface (this desorption peak not observed over the pure TiO₂, seen in supporting information (SI)).

After Au/TiO₂ adsorbing O₂, three desorption peaks are observed at 100, 185 and 395 °C, respectively (curve O₂ in Fig. 3). The desorption peak at 100 °C is mainly attributed to the formation of H₂O, and that at 185 °C is attributed to the formation of H₂O with concomitant CO and CO₂ (seen in curve O₂ in Fig. 4). Compared with

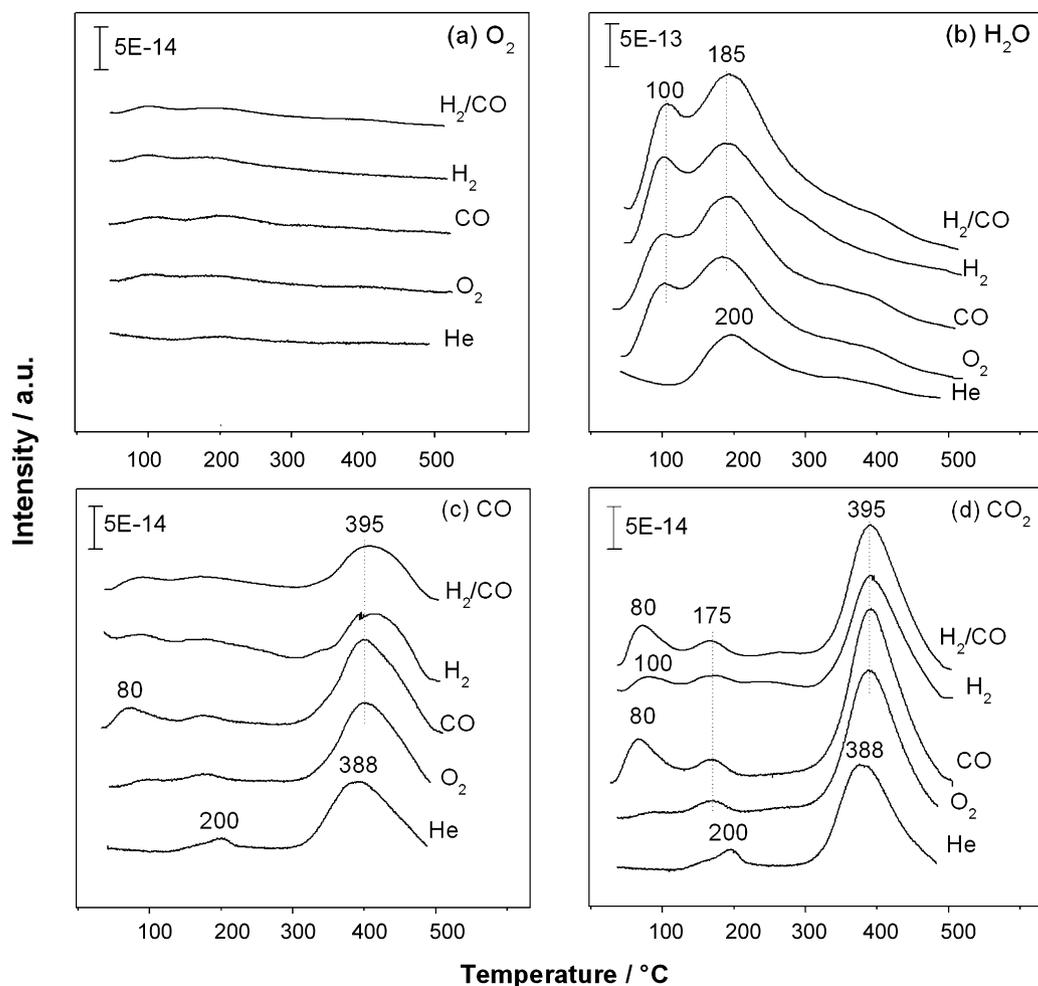


Fig. 4. Mass signals of (a) O₂, (b) H₂O, (c) CO, and (d) CO₂ during the TPD processes over Au/TiO₂ adsorbing different atmospheres under no UV irradiation. Here, the intensity of mass signals is expressed by a negative exponent $E-n$, a smaller number of n means a larger intensity.

the desorption peak at 388 °C in curve He, the desorption peak at 395 °C, assigned to the formation of CO and CO₂, shows a larger intensity. This finding indicates that the adsorption of O₂ promotes the desorption of COO⁻ species at Au surface.

Similarly to the case of adsorbing O₂, three different desorption peaks at 100, 185 and 395 °C are also observed after Au/TiO₂ adsorbing CO (curve CO in Fig. 3). However, the desorption peak at 395 °C (assigned to the formations of CO and CO₂) is larger than that in curve O₂. This shows that an extra CO can be adsorbed at Au surface. In addition, two new desorption peaks of CO and CO₂ at 80 °C appear (seen in curve CO in Fig. 4(c and d)), which can be ascribed to the desorption of CO adsorbed at TiO₂ surface.

After Au/TiO₂ adsorbing H₂, three desorption peaks at 100, 185 and 395 °C, similar to those in curve CO, are also observed (curve H₂ in Fig. 3). However, a new desorption peak at 340 °C appears in TCD signals. Because no desorption peak is observed at 340 °C in the all mass signals of O₂, H₂O, CO and CO₂ (Fig. 4), this desorption may be attributed to the formation of H₂ molecule due to the dissociative desorption of H atoms at Au surface.

After Au/TiO₂ adsorbing the mixed gas of H₂/CO, four desorption peaks similar to that in curve H₂ are also observed (curve H₂/CO in Fig. 3). However, the desorption peak of H₂ at 340 °C is smaller than that in curve H₂ due to the co-adsorption of H₂ and CO at Au surface. Moreover, two desorption peaks of CO and CO₂ at 80 °C are observed in this case (curve H₂/CO in Fig. 4(c and d)), similar to the case of Au/TiO₂ adsorbing CO (curve CO in Fig. 4(c and d)). Here the desorption peak of CO in curve H₂/CO is smaller than that in curve CO, while the desorption peak of CO₂ in the two curves are almost equal. This finding indicates that the presence of H₂ can promote the CO adsorbed at TiO₂ surface to be desorbed as CO₂ molecule.

Note that the introduction of O₂, H₂, CO and H₂/CO into Au/TiO₂ can bring about a new desorption peak at 100 °C (Figs. 3 and 4). This shows that all the adsorption of O₂, H₂, CO and H₂/CO at Au/TiO₂ can promote the formation of H₂O or OH species at TiO₂ surface. However, no desorption peak of O₂ is observed after Au/TiO₂ adsorbing these gases (seen in Fig. 4(a)), even if in the case of adsorbing O₂. This shows that O₂ at Au/TiO₂ can be adsorbed as new species (e.g. H₂O or OH) other than O₂ molecule.

With the viewpoint of Göpel and Rucker [42], the respective chemisorption of CO, H₂ and O₂ at TiO₂ surface can be described as follows: (1) the CO adsorbed at the surface oxygen vacancy sites (SOVs) of TiO₂ reacts with the adjacent lattice oxygen to form H₂O and CO₂ with new concomitant SOVs. (2) The dissociative adsorption hydrogen atoms at SOVs of TiO₂ reacts with the lattice oxygen of TiO₂ to form OH species with new concomitant SOVs. With the increase of temperature, the formed OH species will be further desorbed as H₂O molecules. (3) The O₂ adsorbed at the SOVs of TiO₂ reacts with SOVs to form new lattice oxygen with concomitant OH or H₂O species. According to the adsorption processes, the desorption peaks at 100 °C in curves of CO, H₂ and H₂/CO can not only represent the formation of related OH species, but also be described as a process of producing SOVs at TiO₂ surface. Here the corresponding intensity of this desorption peak represents the number of new SOVs. To contrast this, the chemisorption of O₂ at TiO₂ surface can be described as a process of reducing SOVs (but forming OH species). Here the intensity of desorption peak at 100 °C in curve O₂ represents the number of O₂ adsorbed at TiO₂ surface.

For the chemisorption of CO and H₂ at Au surface in Au/TiO₂, CO is usually adsorbed as CO molecule (Au-CO), while H₂ as the dissociative hydrogen atoms (Au-H). With the increase of temperature, these adsorbed CO molecules and hydrogen atoms can be desorbed as CO₂ and H₂ molecules, respectively, which correspond to the respective desorption peaks at 395 and 340 °C in Fig. 3.

Note that all the adsorption processes of CO, O₂ and H₂ at TiO₂ or Au surface proceeded at room temperature, while the TPD data just recorded the subsequent desorption behaviors originated from the

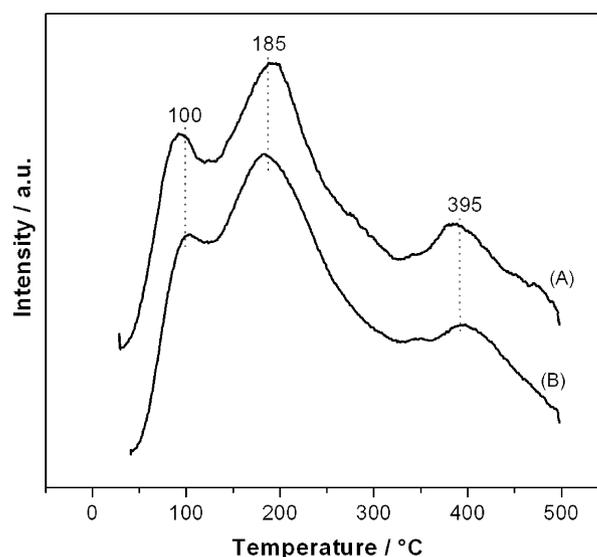


Fig. 5. TCD signals during TPD processes over Au/TiO₂ adsorbing O₂ under (a) UV irradiation and (b) no UV irradiation.

adsorption species during the process of increasing temperature. Therefore, this indirectly obtained conclusion from the TPD data can describe the adsorption behaviors of CO, O₂ and H₂ at Au/TiO₂ at room temperature, which is also available at reaction temperature (50 °C).

3.3.2. TPD results under UV irradiation

Fig. 5 shows the TPD results of O₂ adsorbed at Au/TiO₂ under UV irradiation. As can be seen, UV irradiation increases the intensity of the two desorption peaks at both 100 and 395 °C. This result shows that UV irradiation over Au/TiO₂ during the process of adsorbing O₂ increases both the formation of H₂O or OH species at TiO₂ surface and the desorption of COO⁻ species at Au surface. That is to say, UV irradiation promotes the adsorption of O₂ and its subsequent behaviors at TiO₂ or Au surface.

During the processes which H₂ is adsorbed at Au/TiO₂, UV irradiation over Au/TiO₂ decreases the intensity of the two desorption peaks at 100 and 340 °C (Fig. 6). This means that UV irradiation over Au/TiO₂ suppresses the chemisorption of H₂ at TiO₂ surface, that is,

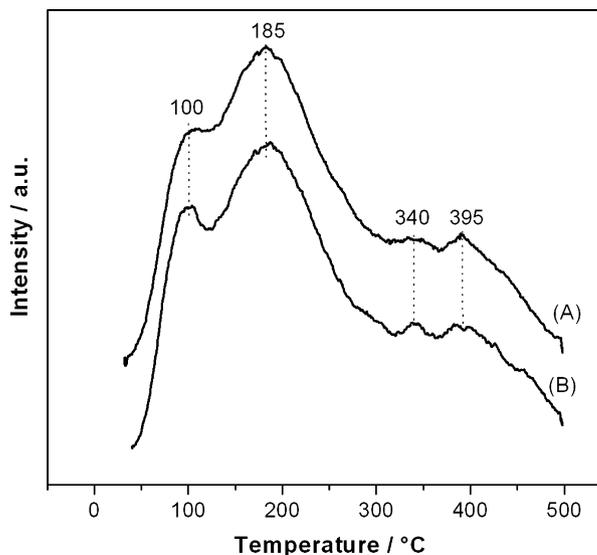


Fig. 6. TCD signals during TPD processes over Au/TiO₂ adsorbing H₂ under (a) UV irradiation and (b) no UV irradiation.

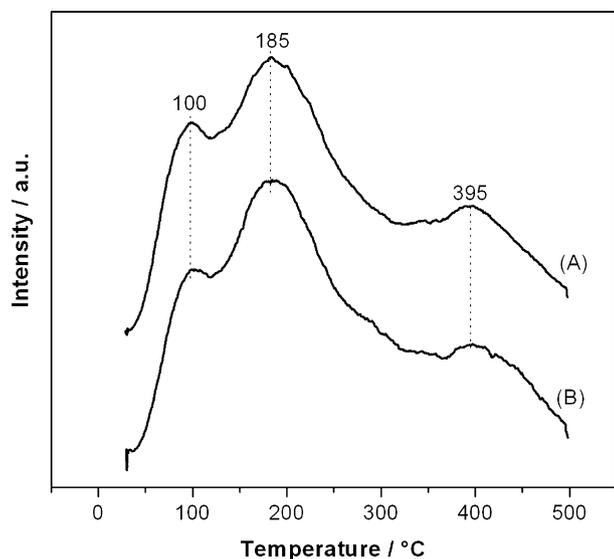


Fig. 7. TCD signals during TPD processes over Au/TiO₂ adsorbing CO under (a) UV irradiation and (b) no UV irradiation.

UV irradiation can suppress the process which H adatoms adsorbed at TiO₂ surface reacts with lattice oxygen to form SOVs. Moreover, UV irradiation also suppresses the dissociative adsorption of H₂ at Au surface.

The influence of UV irradiation on the adsorption of CO at Au/TiO₂ is shown in Fig. 7. UV irradiation over Au/TiO₂ increases the intensity of the desorption peak at 100 °C. This means that UV irradiation over Au/TiO₂ enhances the chemisorption of CO at TiO₂ surface. Here, the increased CO adsorbed at TiO₂ surface will react with lattice oxygen of TiO₂ to produce more SOVs. In addition, UV irradiation over Au/TiO₂ also promotes the desorption at 395 °C (the adsorption of CO at Au surface) to some extent.

During the process in which the mixed gas of H₂/CO is adsorbed at Au/TiO₂, the introduction of UV irradiation also causes the change of TPD results. As shown in Fig. 8, UV irradiation enhances the intensity of the desorption peak at 100 °C over Au/TiO₂. This shows that UV irradiation over Au/TiO₂ can promote the process in which the adsorbed H₂ or CO at TiO₂ surface reacts with lattice oxygen to form

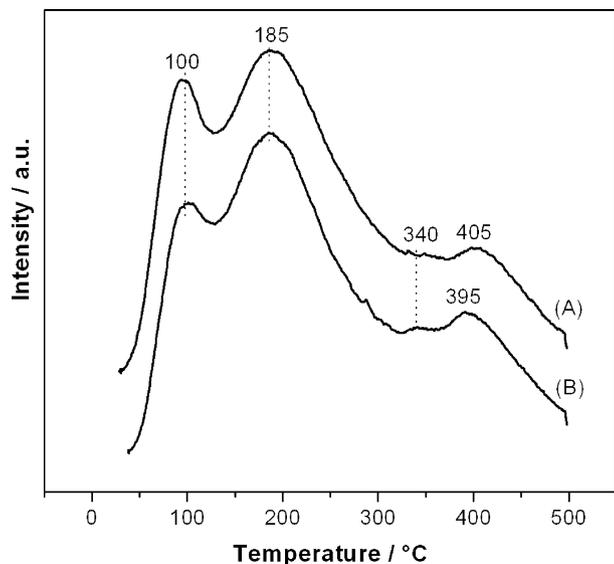


Fig. 8. TCD signals during TPD processes over Au/TiO₂ adsorbing the mixed gases of H₂/CO under (a) UV irradiation and (b) no UV irradiation.

Table 4

Influences of UV irradiation on the chemisorptions of different atmospheres on Au/TiO₂.

Chemisorptions of different atmospheres at TiO ₂ and Au surface	O ₂	H ₂	CO	H ₂ /CO	
				CO	H ₂
^a TiO ₂ surface	++	--	+	++	
^b Au surface	+	-	+	+	-

(+) promoting effect, (-) suppressing effect, (++) strong promoting effect, (--) strong suppressing effect.

^a The chemisorption means the subsequent reaction of adsorbed O₂, H₂ and CO with TiO₂. Here the intensity of the desorption peak at 100 °C represents the extent of chemisorptions of O₂, H₂ and CO.

^b This chemisorption means the chemisorption of CO and H₂ at Au surface.

new SOVs at TiO₂ surface. Moreover, UV irradiation over Au/TiO₂ increases the peak temperature of the desorption of CO and CO₂ at Au surface from 395 to 405 °C, but decreases the intensity of the desorption peak of H₂ at 340 °C. This finding indicates that UV irradiation over Au/TiO₂ promotes the adsorption of CO at Au surface, but suppresses the dissociative adsorption of H at Au surface.

This change of the chemisorption of O₂, H₂, CO and H₂/CO at Au/TiO₂ induced by UV irradiation is summarized in Table 4. On the one hand, UV irradiation promotes the chemisorption of O₂, CO and H₂/CO at TiO₂ surface, but suppresses the chemisorption of H₂ at TiO₂ surface. On the other hand, UV irradiation promotes the chemisorption of CO and O₂ at Au surface, but suppresses the chemisorption of H₂ at Au surface.

This above influence of UV irradiation on the chemisorption of CO and H₂ at Au surface may be attributed to the effect of electron transfer. For Au/TiO₂, the electron can transfer from TiO₂ to Au surface due to a higher work function of Au than that of TiO₂ [41]. With the introduction of UV irradiation over Au/TiO₂, the photo-generated electrons at the conduction band of TiO₂ can decrease the work function of TiO₂, resulting in the further electron transfer from TiO₂ to Au surface and then the increase of the electron density of Au surface. Finally, the higher electron density of Au surface promotes the chemisorption of CO at Au surface. However, two dissociative adsorption hydrogen atoms at Au surface (Au-H) can also accept the photogenerated electrons, and then recombine to H₂ molecule (2Au-H + 2e_{cb} → 2Au + H₂). Therefore, the chemisorption of H₂ at Au surface is suppressed under UV irradiation.

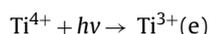
3.4. Relation between chemisorption of reactants and oxidation of CO

In the previous report, different mechanisms are proposed to describe the behavior of the adsorbed O₂ during the process of oxidizing CO over the supported Au nanoparticles. For example, Grunwaldt and Baiker [43] suggested that it was the adsorbed oxygen atoms (as the direct active species) to react with the adsorbed CO (Au-O + Au-CO → CO₂ + 2Au), but Costello et al. [27] suggested that it was the -OH species derived from the adsorbed oxygen to react with the adsorbed CO (Au-OH + Au-CO → CO₂ + Au + Au-H). In this work, the formation of H₂O instead of O₂ is observed during the TPD testing process of Au/TiO₂ adsorbing O₂ (curve O₂ in Fig. 3). This shows that O₂ can be adsorbed at TiO₂ or Au surface as OH species other than oxygen atoms. Therefore, the OH species may be acted as the direct active species during the process of oxidizing CO over Au/TiO₂. With this viewpoint, the peak intensity of desorption at 100 °C after Au/TiO₂ adsorbing O₂ (curve O₂ in Fig. 3) can be associated with the oxidation of CO to a great extent, the larger the intensity of this desorption peak, the more number of OH species and then the higher the activity of oxidizing CO over Au/TiO₂. For the chemisorption of H₂ and CO at Au/TiO₂, the desorption peak at 100 °C (seen in Fig. 3) can be described as the process of forming

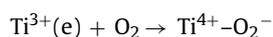
new SOVs (the adsorption sites) at TiO₂ surface. This new formation of SOVs can further promote the chemisorption of O₂ at TiO₂ surface. Therefore, the peak intensity of the desorption peak at 100 °C in curves of H₂, CO or H₂/CO in Fig. 3 can also represent the number of O₂ adsorbed at TiO₂ surface (i.e. the number of activated sites).

Based on the above explanation, the effect of UV irradiation on the catalytic activity of Au/TiO₂ may be due to the change of the respective chemisorption of O₂, H₂ and CO at TiO₂ and Au surface induced by UV irradiation. In the absence of H₂ (CO/O₂ system), owing to UV irradiation over Au/TiO₂ increasing both the chemisorption of O₂ at TiO₂ surface and that of CO at Au surface (Table 4), the oxidation of CO is promoted. The processes of catalytic oxidation of CO over Au/TiO₂ under UV irradiation may be proposed as follows:

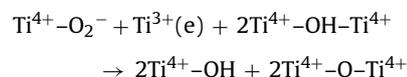
1. Formation of SOVs (Ti³⁺(e)) at TiO₂ surface under UV irradiation:



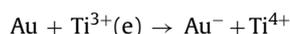
2. Adsorbed O₂ at SOVs of TiO₂ accepting photogenerated electrons to form the adsorbed O₂⁻:



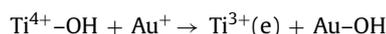
3. Adsorption oxygen reacting with OH species and SOVs to form new OH species:



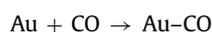
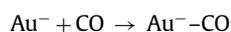
4. Au accepting photogenerated electrons from Ti³⁺:



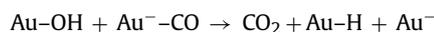
5. Spillover of the OH species located on Au/TiO₂ interfaces into Au⁺ surface:



6. Adsorption of CO at Au with rich-electron or Au atom:



7. OH species adsorbed at Au reacting with CO adsorbed at Au to form CO₂:



In the presence of H₂, H₂ can also be oxidized into H₂O over Au/TiO₂ (2Au–H + Au–OH → 3Au + H₂O) [44]. However, UV irradiation can exert two opposite effects on the oxidation of H₂ over Au/TiO₂. On the one hand, UV irradiation decreases the adsorption of H₂ at TiO₂ and Au surface (Table 4), which suppresses the oxidation of H₂. On the other hand, UV irradiation increases the chemisorption of O₂ at TiO₂ surface (Table 4), which promotes the oxidation of H₂. In the H₂/O₂ system, the latter promoting effect exceeds the former suppression effect, resulting in an apparent increase of H₂ conversion over Au/TiO₂ under UV irradiation. In the

CO/H₂/O₂ system, UV irradiation promotes the chemisorption of CO but suppresses the chemisorption of H₂ at Au surface. Here, the OH species (Au–OH) formed by the chemisorption of O₂ at TiO₂ surface may be inclined to react with Au–CO other than Au–H. Therefore, a promoting activity of preferential oxidation of CO in an H₂-rich stream is observed under UV irradiation. However, this promoting effect of UV irradiation on CO selective oxidation over Au/TiO₂ is rather small and that further research is needed if the technique is to acquire industrial relevance.

4. Conclusion

UV irradiation over Au/TiO₂ promotes the preferential oxidation of CO in an H₂-rich stream. The chemisorption of CO, H₂ and O₂ at TiO₂ surface can be described as a process of forming –OH or H₂O species. UV irradiation over Au/TiO₂ enhances the chemisorption of CO but suppresses the chemisorption of H₂ both at TiO₂ and Au surface. Moreover, UV irradiation also enhances the chemisorption of O₂ at TiO₂ surface. It suggests that the changes of the chemisorption of H₂, CO and O₂ at TiO₂ or Au sites may be responsible for the preferential oxidation of CO over Au/TiO₂ under UV irradiation.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (No. 20773025), National Basic Research Program of China (973 Program: 2007CB613306 and 2006CB708605), and the program for NCETFJ (No. HX2006-98).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jpowsour.2008.12.028.

References

- [1] J.C. Amphlett, R.F. Mann, B.A. Peppley, *Int. J. Hydrogen Eng.* 21 (1996) 673.
- [2] B. Hohlein, S. Von Andrian, T. Grube, R. Menzer, J. Power Sources 86 (2000) 243.
- [3] P. Landon, J. Ferguson, B.E. Solsona, T. Garcia, A.F. Carley, A.A. Herzing, C.J. Kiely, S.E. Golunski, G.J. Hutchings, *Chem. Commun.* (2005) 3385.
- [4] A. Manasilp, E. Gulari, *Appl. Catal. B* 37 (2002) 17.
- [5] H. Igarashi, H. Uchida, M. Suzuki, Y. Sasaki, M. Watanabe, *Appl. Catal. A* 159 (1997) 159.
- [6] I.H. Son, A.M. Lane, *Catal. Lett.* 76 (2001) 3.
- [7] O. Korotkikh, R. Farrauto, *Catal. Today* 62 (2000) 249.
- [8] X. Liu, O. Korotkikh, R. Farrauto, *Appl. Catal. A* 226 (2002) 293.
- [9] Y. Minemura, S. Ito, T. Miyao, S. Naito, K. Tomishige, K. Knimori, *Chem. Commun.* (2005) 1429.
- [10] S.H. Oh, R.M. Sinkevitch, *J. Catal.* 142 (1993) 254.
- [11] S. Ito, T. Fujimori, K. Nagashima, K. Yuzaki, K. Knimori, *Catal. Today* 57 (2000) 247.
- [12] R.J.H. Grisel, B.E. Nieuwenhuys, *J. Catal.* 199 (2001) 48.
- [13] M. Haruta, N. Yamada, T. Kobayashi, S. Iijima, *J. Catal.* 115 (1989) 301.
- [14] A. Knell, P. Barnickel, A. Baiker, A. Wokaun, *J. Catal.* 137 (1992) 306.
- [15] M.A. Bollinger, M.A. Vannice, *Appl. Catal. B* 8 (1996) 417.
- [16] J.D. Grunwaldt, C. Kiener, C. Wögerbauer, A. Baiker, *J. Catal.* 181 (1999) 223.
- [17] M. Haruta, M. Daté, *Appl. Catal. A: Gen.* 222 (2001) 427.
- [18] G. Avgouropoulos, T. Ioannides, Ch. Papadopolou, J. Batistac, *Catal. Today* 75 (2002) 157.
- [19] A.M. Venezia, L.F. Liotta, G. Pantaleo, V.L. Parola, G. Deganello, A. Beck, Zs. Koppány, K. Frey, D. Horváth, L. Guzzi, *Appl. Catal. A* 251 (2003) 359.
- [20] C.M. Yang, K. Martin, F. Schüth, K.J. Chao, *Appl. Catal. A* 254 (2003) 289.
- [21] M. Comotti, W.C. Li, B. Spliethoff, F. Schüth, *J. Am. Chem. Soc.* 128 (2006) 917.
- [22] D. Cameron, R. Holliday, D. Thompson, *J. Power Sources* 118 (2003) 298.
- [23] R.M.T. Sanchez, A. Ueda, K. Tanaka, M. Haruta, *J. Catal.* 168 (1997) 125.
- [24] M.J. Kahlich, H.A. Gasteiger, R.J. Behm, *J. Catal.* 182 (1999) 430.
- [25] B. Schumacher, V. Plzak, M. Kinne, R.J. Behm, *Catal. Lett.* 89 (2003) 109.
- [26] B. Schumacher, Y. Denkwitz, V. Plzak, M. Kinne, R.J. Behm, *J. Catal.* 224 (2004) 449.
- [27] C.K. Costello, M.C. Kung, H.S. Oh, Y. Wang, H.H. Kung, *Appl. Catal. A* 232 (2002) 159.
- [28] J.T. Calla, R.J. Davis, *Ind. Eng. Chem. Res.* 44 (2005) 5403.
- [29] C. Rossignol, S. Arrii, F. Morfin, L. Piccolo, V. Caps, J.L. Rousset, *J. Catal.* 230 (2005) 476.

- [30] M. Azar, V. Caps, F. Morfin, J.L. Rousset, A. Piednoir, J.C. Bertoline, L. Piccolo, J. Catal. 239 (2006) 307–312.
- [31] H. Liu, A.I. Kozlov, A.P. Kozlova, T. Shido, K. Asakura, Y. Iwasawa, Phys. Chem. Chem. Phys. 11 (1999) 2851.
- [32] H. Liu, A.I. Kozlov, A.P. Kozlova, T. Shido, K. Asakura, Y. Iwasawa, J. Catal. 185 (1999) 252.
- [33] L. Fan, N. Ichikuni, S. Shimazu, U. Takayoshi, Appl. Catal. A 246 (2003) 87.
- [34] H. Hakkinen, U. Landman, J. Am. Chem. Soc. 123 (2001) 9704.
- [35] M. Okumura, Y. Kitagawa, M. Haruta, K. Yamaguchi, Chem. Phys. Lett. 346 (2001) 163.
- [36] D.C. Meier, D.W. Goodman, J. Am. Chem. Soc. 126 (2004) 1892.
- [37] A. Sanchez, S. Abbet, U. Heiz, W.D. Schneider, H. Hakkinen, R.N. Barnett, U. Landman, J. Phys. Chem. A 103 (1999) 9573.
- [38] A. Linsebigler, G. Lu, J.T. Yates Jr., J. Phys. Chem. 100 (1996) 6631.
- [39] C.N. Rusu, J.T. Yates Jr., Langmuir 13 (1997) 4311.
- [40] W. Dai, X. Chen, X. Wang, P. Liu, D. Li, G. Li, X. Fu, Phys. Chem. Chem. Phys. 10 (2008) 3256.
- [41] W. Dai, X. Wang, P. Liu, Y. Xu, G. Li, X. Fu, J. Phys. Chem. B 110 (2006) 13470.
- [42] W. Göpel, G. Roker, Phys. Rev. B 28 (1983) 3427.
- [43] J.D. Grunwaldt, A. Baiker, J. Phys. Chem. B 103 (1999) 1002.
- [44] D.G. Barton, S.G. Podkolzin, J. Phys. Chem. B 109 (2005) 2262.