Efficient Elimination of Trace Ethylene over Nano-Gold Catalyst under Ambient Conditions

JINJUN LI,[†] CHUNYAN MA,[†] XIUYAN XU,[†] JUNJIE YU,[†] ZHENGPING HAO,^{*,†} AND SHIZHANG QIAO[‡]

Research Center for Eco-Environmental Science, Chinese Academy of Sciences, Beijing 100085, P. R. China, and ARC Centre for Functional Nanomaterials, School of Engineering and Australian Institute of Bioengineering and Nanotechnology, The University of Queensland, Brisbane, QLD 4072, Australia

Received May 26, 2008. Revised manuscript received August 24, 2008. Accepted September 22, 2008.

Nano-Au/Co₃O₄ catalyst with high gold loading was found to be a good catalytic material for the elimination of trace ethylene (ppb) at ambient conditions. The gold nanoparticles dispersed on the support nano-Co₃O₄ surface contribute to this high activity at room temperature. The relatively rapid deactivation trend was observed under high concentrations of ethylene (1000 ppm), because coke deposits were present on the catalyst surface during the reaction process. This type of nano-gold catalytic material shows great potential as a meaningfully environmental catalyst, particularly for indoor environmental control of trace ethylene (ppb) and keeping fruits fresh during warehouse storage.

Introduction

Ethylene, a low molecular weight volatile organic compound, is harmful, causing anesthetic illness and enhancing photochemical pollution. The allowable level for exposure in working environments is 100 mg/m (3). In some cases, its trace release into some special environments must be avoided. For example, in fruit storage areas (such as refrigerated warehouses), ethylene is released from fruits, which accelerates the maturing of the fruits and enhances their softening. In order to maintain freshness in this kind of controlled air quality system (CAQS), the removal of ethylene is necessary.

The elimination of ethylene is technologically important. In the warehouse, it is desirable to have ethylene levels reduced to a few ppb level. Although the oxidation of ethylene is a thermodynamically favored process, ethylene is thermally stable at room temperature, and catalysts are needed to oxidize it. In most cases, when air is treated for ventilation, the catalyst is required to operate at or below ambient temperature. For the refrigerated warehouse, this temperature range is from 0 to 20 °C.

Ethylene oxide is an important starting chemical in several petrochemical processes. The most widely used process for ethylene oxide is the ethylene epoxidation on supported Ag catalysts (1, 2). Most of the work on complete oxidation of

ethylene has been reported with some development of catalytic technology and catalyst materials.

It was reported that some photocatalysts were used for the oxidation reaction (3–6). A limited number of reports of solid catalysts are available, but their catalytic activities are not sufficient and their operating temperatures are too high (7, 8).

Through our investigations, the known catalysts for the complete oxidation of ethylene are found to have insufficient activity and stability, especially when used under severe conditions, such as low temperature near or lower than ambient temperature. It is necessary and desirable to seek and develop a new type of catalytic material to be used for the complete oxidation of ethylene at low temperature.

Gold's chemically inert character is due to its completely filled 5d shell and the relatively high value of its first ionization potential. Moreover, owing to its chemical inertia and difficulty to be dispersed, gold has been long regarded as a less active phase of catalyst than platinum group metals. However, the past decade has witnessed a rapid growth of interest in gold catalysis (9, 10). Lots of studies have focused on the unusual low-temperature activity and gold activation mechanism. The catalytic behavior of CO oxidation inspired scientists to investigate these nano-gold catalysts in other reactions. The recent studies have clearly shown that the nano-gold catalysts have good low-temperature catalytic performances, especially for CO oxidation, ozone decomposition, oxidation decomposition of (CH₃)₃N, oxidation of hydrogen, and the CO + NO reaction under ambient temperature (11–14). Both academia and industry have paid more attention to nano-gold catalysts and predicted more extensive and increasing application prospects (9, 10).

For efficient elimination of trace ethylene, our research was aimed at the development of suitable catalytic technology for ethylene oxidation to carbon dioxide and water with good catalytic performance under given environmental conditions. On the basis of our previous work on the active surface oxygen species, we understand that, even at room temperature, gold catalysts can easily produce active oxygen species such as O₂[−], which is crucial to complete oxidation (15). Through the research of ethylene epoxidation on Ag catalyst, we know that Ag can catalytically activate the ethylene molecule. Gold has some similar characteristics to Ag, such as chemisorption and catalytic properties, so our research focused on gold catalysis.

In this paper, we report our research results on efficient elimination of trace ethylene, specifically on the catalytic performances and deactivation characteristics, which are very important to develop the related technology and material for the efficient elimination of trace ethylene.

Experimental Section

Catalyst Preparation. Supports of Co₃O₄, Fe₂O₃, and ZnO were prepared by the same procedures as follows. An aqueous solution of nitrate was gradually added into Na₂CO₃ solution with continuous stirring. After 2 h, the resulting precipitate was filtered and washed with deionized water. The solids were dried at 70 °C and finally calcined at 500 °C for 3 h. Gold catalysts were prepared by the deposition–precipitation method by using urea as a precipitating agent and HAuCl₄·3H₂O as the gold precursor. For more details of the preparation procedure, refer to our previous work (16, 17). The gold loading amount of catalyst is expressed as weight percentage (wt %). The preparation of Ag/Co₃O₄ catalyst is similar to that of Au/Co₃O₄, except using AgNO₃ as the precursor chemical.

* Corresponding author phone: 86-10-62923564; fax: 86-10-62923564; e-mail: zpinghao@rcees.ac.cn.

[†] Chinese Academy of Sciences.

[‡] The University of Queensland.

Activity Measurement for Ethylene Oxidation. Catalytic tests were performed in a laboratory-scale fixed bed reactor. A 0.5 g catalyst (40–60 mesh) was tested, typically with a gas feed rate of $33.4 \text{ mL} \cdot \text{min}^{-1}$ of a certain concentration (1050, 50, and 5 ppm, respectively) of ethylene in synthetic air (O_2 , 22%; N_2 , balance). The outlet gas compositions (mainly ethylene and carbon dioxide) were detected by online gas chromatography (SP-2100, equipped with a hydrogen flame ionization detector and Ni catalytic translator connected with Porapak-R column) and monitored by the Bruker FT-IR (Tensor 27) with one gas cell. FT-IR spectra were obtained with a spectral resolution of 4 cm^{-1} by using this spectrometer equipped with a LN-MCT (liquid nitrogen–mercury cadmium telluride) detector. The ethylene conversion rate was calculated on the basis of the following formula: $[(C_{\text{C}_2\text{H}_4} \text{ inlet} - C_{\text{C}_2\text{H}_4} \text{ out}) / C_{\text{C}_2\text{H}_4} \text{ inlet}] \times 100\%$.

Structural Characterizations. *TPO Measurements.* Temperature-programmed oxidation (TPO) tests were carried out in a continuous flow quartz reactor, which was connected with a HQ200 M mass spectrometer. In each test, 0.45 g of catalyst was used, and the heating rate was 20 K/min .

TG–DSC Measurements. Thermogravimetric and differential scanning calorimetric analysis (TG–DSC) of the samples were carried out using a Setaram Labsys-16 thermal analyzer in the range of $15\text{--}800^\circ\text{C}$ in air. The heating rate was maintained at $10 \text{ K} \cdot \text{min}^{-1}$.

XPS Measurements. The surface element composition of used catalyst was measured by X-ray photoelectron spectroscopy (XPS). This data was accumulated on an Axis Ultra ESCA system with a monochromatic Al K α standard radiation source. The banding energies were calibrated by referencing the C1s at 284.8 eV .

TPR Measurements. Hydrogen temperature-programmed reduction (H_2 -TPR) of both $\text{Ag}/\text{Co}_3\text{O}_4$ and $\text{Au}/\text{Co}_3\text{O}_4$ catalysts was performed on a conventional TPR apparatus connected to a chromatograph (Varian 3700) equipped with a thermal conductivity detector (TCD). The catalyst samples (50 mg) were placed in a quartz reactor and sandwiched between two quartz wool plugs. Prior to each TPR run, the catalyst was heated up to 300°C under O_2 flow (40 mL/min). After 30 min pretreatment in the O_2 flow at 300°C , the reactor bed temperature was then lowered down to room temperature by keeping the same flow rate of oxygen. Then N_2 was fed to the reactor at 30 mL/min for 1 h at room temperature to purge any residual oxygen. The catalyst was then heated to 600°C at a constant heating rate of 10 K/min using 5% H_2/He under a flow rate of 50 mL/min . H_2 consumption was monitored by the TCD detector.

TEM Measurements. Transmission electron microscopy (TEM) images were taken on an H-7500 electron microscope (Hitachi Co.). All samples were crushed, dispersed in ethanol, and deposited on a microgrid prior to observation.

Results and Discussion

Through our previous comparative study, we realized that as the catalytic active component, among metal elements of the group IB (Cu, Ag, Au) of the periodic table, Au is similar to Cu and Ag, all these metals having a good catalytic active phase for some oxidations, such as CO oxidation (18–21). It was found that both Cu and Ag have no higher catalytic activities for the complete oxidation of ethylene (22), although Ag is regarded as the main component of catalyst successfully applied in the ethylene epoxidation.

Choice of Catalyst Support. Oxides such as Fe_2O_3 , Co_3O_4 , ZnO , and TiO_2 were chosen as supports of Au catalysts. All of these are common supports of nano-gold catalysts. Both ZnO and TiO_2 are semiconductor oxides (15, 23, 24), and Fe_2O_3 and Co_3O_4 are reducible oxides (25–28). The effect of supports was investigated, and the results are listed in Table 1. Compared with activities of various gold catalysts on

TABLE 1. Influence of Support on Catalyst Activity^a

Catalysts	C_2H_4 conversion at 20°C (%)	$T_{100\%}$ ($^\circ\text{C}$)
2% $\text{Au}/\text{Fe}_2\text{O}_3$	3.44	210
2% $\text{Au}/\text{Co}_3\text{O}_4$	7.40	160
2% Au/TiO_2	0	250
2% Au/ZnO	0	300

^a Concentration of ethylene is 1050 ppm.

TABLE 2. Influence of Gold Content on Catalyst Activity^a

Catalysts	C_2H_4 conversion at 20°C (%)	$T_{100\%}$ ($^\circ\text{C}$)
Co_3O_4	0	230
2% $\text{Au}/\text{Co}_3\text{O}_4$	7.40	160
4% $\text{Au}/\text{Co}_3\text{O}_4$	54.89	150

^a Concentration of ethylene is 1050 ppm.

FIGURE 1. Reaction tests for C_2H_4 conversion with time-on-stream over $\text{Au}/\text{Co}_3\text{O}_4$: (a) 5 ppm of C_2H_4 , 0°C ; (b) 50 ppm of C_2H_4 , 20°C ; and (c) 1050 ppm of C_2H_4 , 50°C .

different supports, it was found that support has a crucial influence on the catalytic activity. Among these supports, Co_3O_4 is the most suitable support for gold catalyst used for catalytic oxidation of C_2H_4 , which is similar to the Ahn HG's observation (8). In addition, cobalt oxide itself has been reported to be among the most active oxides in catalytic combustion (7).

Effect of Au Loading. Table 2 shows the activities of Co_3O_4 -supported gold catalysts with different gold contents. It was observed that the catalytic activity rises with increase of gold loading. When the gold loading is up to 4%, the gold catalyst can convert 54.89% of C_2H_4 at 20°C and can give complete 100% conversion at 150°C .

Effect of Ethylene Concentration in the Initial Gas. Reaction tests for C_2H_4 conversion with time-on-stream over 4% $\text{Au}/\text{Co}_3\text{O}_4$ under different concentrations are shown in Figure 1. With 1050 ppm of C_2H_4 in synthetic air admitted, the catalyst possesses 98% C_2H_4 conversion at 50°C , while when the C_2H_4 concentration was reduced to 50 ppm, the catalyst can completely eliminate ethylene gases at 20°C . Even at 0°C , 5 ppm ethylene gases can be nearly completely (98%) eliminated by 4% $\text{Au}/\text{Co}_3\text{O}_4$. However, it should be noticed that under condition of high C_2H_4 concentration, the catalyst exhibits a rapid deactivation trend with increasing time, in spite of its initially excellent activity. In contrast, at low concentrations of C_2H_4 , the deactivation rate of the catalyst was relatively slowed down. When the concentration of ethylene gas is only 5 ppm, the catalytic performance of 4% $\text{Au}/\text{Co}_3\text{O}_4$ was well-sustained within 60 min (98%

FIGURE 2. Ethylene reaction: FT-IR spectra of Au/Co₃O₄ (1050 ppm of C₂H₄, 50 °C).

FIGURE 3. TPR profiles of 4% Ag/Co₃O₄ (a) and 4% Au/Co₃O₄ (b) catalysts.

conversion), indicating the possibility that the gold catalyst could be applied to fruit warehouse for the elimination of trace ethylene. Generally, trace ethylene in a fruit warehouse is in the range of tens of ppb and for the removal of trace ethylene, this means to decrease tens of ppb to few ppb. However, it is difficult to simulate this low concentration of ethylene and investigate the catalytic performance at very low concentrations of ethylene. Therefore, the investigation centered around its catalytic behavior at the lowest possible concentration of 5 ppm ethylene in initial gas.

It should be stressed that there exists a serious imbalance of total carbon content under high concentration of ethylene conditions. During reaction tests, while a large amount of ethylene gases were oxidized over the catalyst, only a relatively small amount of CO₂ was detected. It is presumed that there is some correlation between deactivation of catalyst and imbalance of total carbon content. In order to explore the reasons for imbalance of total carbon content, pure Co₃O₄ support was also performed in the reaction test. Imbalance of the total carbon content cannot be observed on it, as the support Co₃O₄ possesses no activities below 80 °C. Subsequently, at elevated temperature, the activity rises, thus indicating that ethylene does not adsorb readily on Co₃O₄ surface, and the imbalance of total carbon content does not result from the adsorption of ethylene on the Co₃O₄ surface. In addition, no other substances than C₂H₄ and CO₂ were detected through FT-IR equipped with gas cell, as shown in Figure 2, thus presuming that coke deposits on the catalyst surface lead to an imbalance of total carbon content and rapid deactivation of the catalyst.

TPR Characterization. TPR experiments were carried out, and results of Ag/Co₃O₄ (a) and Au/Co₃O₄ (b) catalysts are shown in Figure 3. It can be observed that the curve of Ag/Co₃O₄ shows reduction peaks centered at 135 °C and around 200–440 and 440–600 °C that can be ascribed to the reduction of Co₃O₄ to CoO and CoO to Co, respectively. The peak at 135 °C could be assigned to the reduction of partially oxidized

FIGURE 4. TPO-MS (O₂ and CO₂) profiles for used 4% Au/Co₃O₄ catalyst.

FIGURE 5. (A and B) TG and DSC curves of fresh and used 4% Au/Co₃O₄ catalyst.

silver with very low amount. The curve of Au/Co₃O₄ shows reduction peaks centered at 90 °C and around 180–290 and 290–560 °C. Compared with TPR results of Ag/Co₃O₄ catalysts, it is clearly shown that the reduction peaks of Co₃O₄ to CoO and CoO to Co have been shifted to low-temperature range when Au is supported on Co₃O₄. The peak at 90 °C could be assigned to the reduction of partially oxidized gold with very low amount. For supported noble metal catalysts, generally speaking, the higher the oxidized state of active phase, the lower the corresponding reduction peak temperature of TPR and the higher the catalysis ability of oxidation reaction. The gold is remarkably active in ethylene

FIGURE 6. TEM images of 2% Au/Co₃O₄ (a) and 4% Au/Co₃O₄ (b) catalysts.

FIGURE 7. Reaction activities for C₂H₄ conversion (1050 ppm of C₂H₄, 50 °C) with time-on-stream over fresh catalyst (a) and regenerated catalyst (b).

oxidation at room temperature when supported in a partially oxidized state.

TPO, TG–DSC, and XPS Characterizations of Used Catalysts. In order to acquire evidence for the coke deposits, the spent catalyst (having suffered from reaction of high concentration ethylene for 60 min) was characterized by TPO, TG–DSC, and XPS techniques. Representative TPO–MS data illustrate the evolution of carbon dioxide and oxygen consumption during temperature-programmed burning off on a spent catalyst, as shown in Figure 4. An obvious peak relative to the production of CO₂ around 246 °C was observed, which is almost reflected by the oxygen consumption peak. According to the literature (29), the appearance of these peaks results from the total oxidation of the carbonaceous deposit on the catalyst.

Figure 5 shows the TG–DSC profiles of the fresh catalyst and the spent catalyst, which has undergone reaction test at 50 °C for 60 min. Both samples display the loss of mass in the temperature range of 50–600 °C, but the spent sample

loses much more mass than the fresh sample, with reference to the initial mass. It should be noted that the rate of mass lost around 214 °C for the spent sample is obviously faster than that for the fresh sample. Moreover, the spent sample shows the intense exothermic peak centered at this temperature, whereas the fresh sample remains unchanged in the DSC profile, further indicating the presence of the coke deposits on the surface of the spent catalyst.

Through XPS measurements and analysis, the O1s shoulder peak at high binding energy is attributed mainly to organic oxygen, barely detectable for the fresh catalyst. This indicates an accumulation of organic species on the used catalyst surface. Consistent with this finding, the C1s peak also indicates the presence of the surface carbon, which was calculated to be 10.5 atom % by composition. On all accounts, coke deposits readily came into being on the catalyst surface and thus block the active sites of the catalyst, leading to the fast decrease of the catalyst activity.

TEM Characterizations of Au/Co₃O₄ Samples. Figure 6 shows the TEM images of the Au/Co₃O₄ catalysts. Both the active phase and support are nanoscale; this kind of catalyst seems to be the so-called “nano combined catalyst”. The monodispersion gold particles of 2% and 4% Au/Co₃O₄ catalysts are less than 5 nm. Compared with 2% Au/Co₃O₄ catalyst, the gold nanoparticles do not grow in size in 4% Au/Co₃O₄ catalyst. The marked difference between 2% and 4% Au/Co₃O₄ catalyst is the amount of gold nanoparticles on the Co₃O₄ support surface.

Activities of fresh and regenerated catalysts are shown in Figure 7. The primary activity of fresh catalyst is 98.0%, and the initial activity of regenerated catalyst is 94.4%. It can be seen that the activity of used catalyst could be recovered by the oxidation in air at 300 °C for 3 h.

In summary, 4%Au/Co₃O₄ was found to be highly active toward eliminating trace ethylene (ppb) under ambient conditions, although it shows a rapid deactivation trend at high concentration of C₂H₄ (1000 ppm). The gold nanoparticles dispersed on the support surface also contribute to the high activity at room temperature. Nano-gold with partially oxidized state is remarkably active in ethylene oxidation at ambient temperature. Moreover, the reasons why coke deposits are readily produced on the catalyst surface and the method of sustaining or increasing catalyst stability are still under study.

Acknowledgments

The authors gratefully acknowledge support for this work from the National Science Foundation of China (20725723) and the National Basic Research Program of China (2004CB719500).

Literature Cited

- (1) Liu, Y.; Shen, S. K. Direct epoxidation of ethylene in a dilute reaction stream in oxidative coupling of methane. *Appl. Catal., A* **1995**, *121*, 57–68.
- (2) Ayame, A.; Eimaeda, S.; Feng, L.; Hayasaka, H. Oxygen adsorption on silver catalysts during the course of partial oxidation of ethylene. *Appl. Catal., A* **2006**, *304*, 93–108.
- (3) Park, D. R.; Zhang, J. L.; Ikeue, K.; Yamashita, H.; Anpo, M. Photocatalytic oxidation of ethylene to CO₂ and H₂O on ultrafine powdered TiO₂ photocatalysts in the presence of O₂ and H₂O. *J. Catal.* **1999**, *185*, 114–119.
- (4) Lin, L. Y.; Hu, C.; Wang, Z. Y.; Hao, Z. P. Photocatalytic degradation of ethylene over titania-based photocatalysts. *Chin. J. Environ. Sci.* **2004**, *25*, 105–108.
- (5) Chen, Y. L.; Li, D. Z.; Fu, X. Z.; Liu, P. Visible light induced photocatalytic oxidation of ethylene over Pt/Pt⁴⁺–TiO₂ catalyst. *Chem. J. Chin. Univ.* **2004**, *25*, 342–344.
- (6) Park, D. R.; Ahn, B. J.; Park, H. S.; Yamashita, H.; Anpo, M. Photocatalytic oxidation of ethylene to CO₂ and H₂O on ultrafine powdered TiO₂ photocatalysts: Effect of the presence of O₂ and H₂O and the addition of Pt. *Kor. J. Chem. Eng.* **2001**, *18*, 930–934.

- (7) Kim, S.; Watabe, Y.; Aida, T.; Niiyama, H. Complete oxidation of ethylene by co-modified mordenites under microwave irradiation. *J. Chem. Eng. Jpn.* **2005**, *38*, 828–834.
- (8) Ahn, H. G.; Choi, B. M.; Lee, D. J. Complete oxidation of ethylene over supported gold nanoparticle catalysts. *J. Nanosci. Nanotechnol.* **2006**, *6*, 3599–3603.
- (9) Bond, G. C.; Thompson, D. T. Gold-catalysed oxidation of carbon monoxide. *Gold Bull.* **2000**, *33*, 41–51.
- (10) Haruta, M. Gold as a novel catalyst in the 21st century: Preparation, working mechanism and applications. *Gold Bull.* **2004**, *37*, 27–36.
- (11) Haruta, M.; Tsbota, S.; Kobayashi, T.; Kageyama, H.; Genet, M. J.; Delmon, B. Low-temperature oxidation of CO over gold supported on TiO₂, alpha-Fe₂O₃, and Co₃O₄. *J. Catal.* **1993**, *144*, 175–192.
- (12) Hao, Z. P.; An, L. D.; Zhou, J. L.; Wang, H. L. A supported gold catalyst for the elimination of hydrogen from CO₂ feed gas in the production of urea. *React. Kinet. Catal. Lett.* **1996**, *59*, 295–300.
- (13) Hao, Z. P.; An, L. D.; Wang, H. L. Preparation, catalytic performance and application of supported gold catalysts. *J. Mol. Catal. (China)* **1996**, *10*, 235–240.
- (14) Hao, Z. P.; Cheng, D. Y.; Guo, Y.; Liang, Y. H. Supported gold catalysts used for ozone decomposition and simultaneous elimination of ozone and carbon monoxide at ambient temperature. *Appl. Catal., B* **2001**, *33*, 217–222.
- (15) Hao, Z. P.; Fen, L. P.; Lu, G. Q.; Liu, J. J.; An, L. D.; Wang, H. L. In situ electron paramagnetic resonance (EPR) study of surface oxygen species on Au/ZnO catalyst for low-temperature carbon monoxide oxidation. *Appl. Catal., A* **2001**, *213*, 173–177.
- (16) Xu, X. Y. Ph.D. Thesis; Research Center for Eco-Environmental Sciences, Chinese Academic Sciences, 2006.
- (17) Xu, X. Y.; Li, J. J.; Hao, Z. P.; Zhao, W.; Hu, C. Characterization and catalytic performance of Co/SBA-15 supported gold catalysts for CO oxidation. *Mater. Res. Bull.* **2006**, *41*, 406–413.
- (18) Pestryakov, A. N.; Bogdanchikova, N.; Simakov, A.; Tuzovskaya, I.; Jentoft, F.; Farias, M.; Díaz, A. Catalytically active gold clusters and nanoparticles for CO oxidation. *Surf. Sci.* **2007**, *601*, 3792–3795.
- (19) Ketchie, W. C.; Fang, Y.-L.; Wong, M. S.; Murayama, M.; Davis, R. J. Influence of gold particle size on the aqueous-phase oxidation of carbon monoxide and glycerol. *J. Catal.* **2007**, *250*, 94–101.
- (20) Jin, L.; Qian, K.; Jiang, Z.; Huang, W. Ag/SiO₂ catalysts prepared via γ -ray irradiation and their catalytic activities in CO oxidation. *J. Mol. Catal.* **2007**, *274*, 95–100.
- (21) Chen, C.-S.; You, J.-H.; Lin, J.-H.; Chen, Y.-Y. Effect of highly dispersed active sites of Cu/TiO₂ catalyst on CO oxidation. *Catal. Commun.* **2008**, *9*, 2381–2385.
- (22) Wang, D. H. Ph.D. thesis. Research Institute of Chemical Defense, P. R. China, 2003.
- (23) Rojluetchai, S.; Chavadej, S.; Schwank, J. W.; Meeyoo, V. Catalytic activity of ethylene oxidation over Au, Ag and Au-Ag catalysts: Support effect. *Catal. Commun.* **2007**, *8*, 57–64.
- (24) Greaves, J.; Al-Mazroai, L.; Nuhu, A.; Davies, P.; Bowker, M. Photocatalytic methanol reforming on Au/TiO₂ for hydrogen production. *Gold Bull.* **2006**, *39*, 216–219.
- (25) Hao, Z. P.; An, L. D.; Wang, H. L.; Lu, G. Q. Catalytic performance and structural characterization of ferric oxide and its composite oxides supported gold catalysts for low-temperature CO oxidation. *Sci. China Ser. B* **2001**, *44*, 596–605.
- (26) Hao, Z. P.; An, L. D.; Wang, H. L. The new catalyst for the elimination of hydrogen from CO₂ feed gas in the production of urea. *Chem. J. Chin. Univ.* **2000**, *21*, 1098–1110.
- (27) Hao, Z. P.; An, L. D.; Wang, H. L.; Hu, T. D. The gold activation mechanism of supported gold catalyst. *React. Kinet. Catal. Lett.* **2000**, *70*, 153–160.
- (28) Wang, D. H.; Hao, Z. P.; Chen, D. Y.; Si, X. C. Influence of pretreatment conditions on low-temperature CO oxidation over Au/MOx/Al₂O₃ catalysts. *J. Mol. Catal. A* **2003**, *200*, 229–235.
- (29) Hamoudi, S.; Larachi, F.; Adnot, A.; Sayari, A. Characterization of spent MnO₂/CeO₂ wet oxidation catalyst by TPO-MS, XPS, and S-SIMS. *J. Catal.* **1999**, *185*, 333–344.

ES801458V