



Room temperature O₂ plasma treatment of SiO₂ supported Au catalysts for selective hydrogenation of acetylene in the presence of large excess of ethylene

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ARTICLE INFO

Article history:

Received 6 June 2011

Revised 17 September 2011

Accepted 22 September 2011

Available online 28 October 2011

Keywords:

Gold

Silica

O₂ plasma

Acetylene hydrogenation

Selectivity

Excess ethylene

DRIFT

ABSTRACT

Supported gold nanoparticles have been proven to be active in the hydrogenation of the acetylene. In this work, we applied gold nanoparticles supported on silica for the selective hydrogenation of acetylene in excess ethylene that was close to current industrial practices. Amine group surface-functionalized silica was used to absorb the gold precursor AuCl₄⁻, and small size-controlled gold nanoparticles are formed after chemical reduction. For the first time, O₂ plasma was employed to remove the APTES grafted on the surface of silica for preparing the highly dispersed gold nanoparticles (~3 nm). The results of IR, TGA, XRD, and TEM showed that O₂ plasma working under mild conditions (room temperature and low pressure) can efficiently remove the organic compounds without causing the aggregation of the gold nanoparticles. The plasma-treated catalyst Au/SiO₂ gave excellent low-temperature selective catalytic activity in the hydrogenation of acetylene. The effects of the reduction temperatures on the catalytic performances of the Au/SiO₂ were investigated. The enhanced performance of gold nanoparticles supported on silica as pretreated by O₂ plasma was ascribed to two effects: (1) the small size of the gold nanoparticles supported on silica, (2) the nearly neutral charge on the Au nanoparticle, which is favorable to the activation of hydrogen.

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1. Introduction

Since the particle size of the metallic nanoparticles plays a key role in influencing the catalytic performances, controlling the size of metallic nanoparticles has been intensively studied in recent years. And a variety of efficient methods have been developed [1,2]. One of the important ones is the encapsulation–reduction method in colloidal state, by which one can obtain nanoparticles with precisely controlled particle size. And then, one obtains supported nanocatalyst by depositing the encapsulated nanoparticles on a support [3–5]. The removal of the capping agents or the functional organic ligands is often needed so as to gain enhanced catalytic activity. In order to circumvent this problem, one way is to not attach the capped nanoparticles on the support, instead deliberately designed ligands and reactions are selected [6–8]. Another way is to choose protecting agents that are volatilisable [9,10], aqueous soluble [11], or decomposable at low temperatures [12], so that they

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can be removed easily. However, in many other cases, the removal of the functional ligands is not so easy, for example, functionalizing the surface of the support with organic ligands (e.g., 3-aminopropyltriethoxysilane, H₂N(CH₂)₃Si(OC₂H₅)₃, etc.), which can anchor metallic nanoparticles [13–17]. At present, calcination is the standard procedure to remove organic groups for Au particles to be active for many catalytic oxidation reactions [3–5,12–18], for example, the selective oxidation of CO in H₂ [19–23]. However, the gold nanoparticles tend to agglomerate to bigger sizes after calcinations, which not only defeats the purpose of fine control of sizes, particularly on less adhering support such as silica, but also causes the decrease of catalytic activity [19–22,24]. Therefore, new methods should be developed to remove the organic encapsulating agents without causing the aggregation of nanoparticles.

Non-thermal plasma-based techniques for catalyst preparation have recently attracted significant attention for catalyst design and development [25–29]. RF plasma, known as conventional non-thermal plasma process at room temperature, is an effective way to modify catalysts to achieve high metal dispersion without the exposure of the material to high-temperature environment. It is also a unique way to induce metal–support interaction of supported metal catalysts. It has been observed that, with

non-thermal RF plasma treatments, Pd-based catalysts exhibited an enhanced low-temperature activity and stability in selective hydrogenation of acetylene as compared to the untreated counterpart [28,29]. Plasma pre-treatment of metallic nanocatalyst works under mild conditions is also attractive because it will not cause much sintering of the metal nanoparticles. It has been applied in a few recent catalysis studies. For example, Legrand et al. [30] applied microwave plasma of dihydrogen, instead of high-temperature reduction, to prepare zeolite-supported Au-based metallic catalysts at room temperature and found that the plasma was very efficient in avoiding the formation of big nanoparticles. Kim et al. [31] reported that non-thermal plasma was an efficient way in regenerating the Au/TiO₂ catalyst poisoned by C₃H₆ or toluene. Despite the above research findings, there is no report in the literature on applying plasma treatment to remove encapsulation agents till now. Therefore, in this study, we will develop an alternative way to activate Au catalysts without causing sintering of small Au particles by applying O₂ non-thermal plasma treatment.

The selective hydrogenation of acetylene is an important industrial process to remove traces of acetylene in the ethylene stream for polyethylene production [32,33]. It is well known that high selectivity is required in the hydrogenation of trace amounts of acetylene in ethylene to minimize the hydrogenation of ethylene to ethane. Supported Pd catalyst is used commercially to remove the acetylene contaminant in ethylene feedstock while minimizing ethylene hydrogenation. However, increasing acetylene conversion will accelerate the hydrogenation of ethylene to large amounts of undesired ethane and lead to poor selectivity for the acetylene removal process [34,35].

Supported gold nanocatalyst has been proven to be active in the hydrogenation of olefins and alkynes since the work of Bond and coworkers [36,37]. The catalytic activity of gold nanocatalysts was found to be lower than that of the group VIII metal catalysts, but they exhibit much higher selectivity due to the unique properties of gold, which adsorbs olefin molecules weakly compared to acetylene [37,38]. More recently, Au catalysts with small particles (3 nm or less) are reported to be active for selective hydrogenation reactions, including selective hydrogenation of acetylene [24,39]. Based on the literature, Au is close to 100% selective for hydrogenation of acetylene to ethylene at temperature up to 300 °C. Above 300 °C, the selectivity of Au catalysts decreases due to the formation of ethane [24,39]. Besides, gold and gold-based bimetallic nanoparticles (e.g., Au–Ni, Au–Pd, etc.) have attracted increasing attention in the selective hydrogenation of acetylene to ethylene with various supports (e.g., Al₂O₃, TiO₂, CeO₂, SiO₂, etc.) [40,41]. The catalytic performances of supported gold-based nanocatalysts have rarely been studied under high ethylene concentration conditions that are close to the industrial process. For promoting high selectivity at high ethylene concentration environment, one needs to promote the difference in adsorption abilities of acetylene and ethylene on gold nanoparticles, which would be more pronounced if the size of gold NP is smaller [42]. In this work, we focus on the investigation of O₂ non-thermal plasma treatment to activate Au catalysts with small Au particles for selective hydrogenation of acetylene in large excess of ethylene. Various characterizations including IR, TGA, XRD, TEM, and in situ DRIFT were applied to test the efficiency for removing the organic ligands and the particle size of gold nanoparticles. Furthermore, the intrinsic origin of the better catalytic activity over oxygen plasma-treated Au/SiO₂ is also discussed.

2. Experimental

2.1. Preparation of the catalyst

The catalyst was prepared by the method reported previously [13–17,19–23]. In brief, the silica gel (purchased from Qingdao

Ocean Chemical Plant, $S_{\text{BET}} = 467 \text{ m}^2/\text{g}$) was first modified by APTES. APTES-functionalized (1.0 g) silica gel (APTES-SiO₂) was dispersed into 15 mL of deionized water followed by the addition of 5 mL of HAuCl₄ solution (1.99 wt.%) under continuous stirring. After 30 min, the mixture was filtered and washed. The recovered precursor was redispersed in 20 mL of NaBH₄ solution (0.1 M) and stirred for another 20 min. The mixture was filtered and washed till there was no Cl⁻ detected by AgNO₃. The solid was dried at 110 °C and denoted as Au/APTES-SiO₂ catalyst.

2.2. Plasma treatment

Plasma treatments for the dried catalysts were carried out at room temperature in the custom-designed 360° rotating RF plasma system. The details of the system and the apparatus schematic are described in a previous publication [28,43]. A system pressure of 400 mTorr was used for plasma treatments in this study. Powder Au catalysts were pressed to pellets and broken down to smaller pieces before loading into the plasma chamber for oxygen plasma treatments. The duration of plasma treatment was set at 30 min with a continuous waveform of 130 W.

2.3. Catalyst characterization

The FT-IR spectra were collected at room temperature by using a commercial instrument (NICOLET 380, Thermo Electron Corporation). The powdered samples were mixed with certain amounts of KBr and compressed into thin disks of 3.0 mm in diameter. The background was collected before the sample was put into the cell.

The weight loss of the sample was performed on the thermogravimetric analyzer equipped with a temperature controller (TA Instrument 5100) under flowing air. The temperature was increased from room temperature to 800 °C with a rate of 10 °C/min.

X-ray diffraction (XRD) patterns were recorded on an X'Pert PRO (PANalytical) diffractometer equipped with a Cu K α radiation source ($\lambda = 0.15432 \text{ nm}$), operating at 45 kV and 40 mA. A continuous mode was used for collecting data in the 2θ range from 20° to 80° at a scanning speed of 10°/min.

TEM images were obtained on a transmission electron microscope operating at 200 kV (FEI Tecnai 20 G² S-Twin). Several drops of the suspension of the sample were put on micro-grid carbon polymer supported on copper grid and allowed to dry at room temperature for TEM observations. The particle size distribution was calculated by measuring more than 200 particles for different areas.

The diffuse reflectance infrared Fourier transform (DRIFT) spectra recorded with a Nicolet™ 6700 FT-IR spectrophotometer with a resolution of 4 cm⁻¹ equipped with a MCT detector. 20 mg of the sample were packed into the cell with a ZnSe window that can work under high temperature. Prior to CO adsorption, the sample was in situ pretreated in pure H₂ at 250 °C for 1 h and then cooled to room temperature. The gas flow was switched to pure He for collecting the background spectrum. Subsequently, the sample was exposed to a flowing mixture of 5 vol.% CO in Ar for 30 min. After purged with pure He for 2 min, the CO in the gas flow was flushed and the spectra were collected.

2.4. Reaction tests

All catalysts were tested for the selective hydrogenation of acetylene from 150 °C to 250 °C or 150 °C to 400 °C depending on the reduction procedure. A 1/4 in. quartz reactor (i.d., 4 mm) housed in a GC oven with temperature-programmed heating and cooling capabilities at low-temperature ranges was used. Catalysts (30 mg) were reduced in UHP hydrogen (Matheson, 99.999%) at 250 °C or 400 °C for 30 min and then underwent purging with

UHP nitrogen (Matheson, 99.999%) at starting reaction temperature before the reaction testing was carried out. Reaction temperature was kept constant for 30 min before being increased by 25 °C to the next temperature. A gaseous mixture containing about 0.80 vol.% C₂H₂ and 16.0 vol.% H₂ in balance C₂H₄ (mixture of 1.14 vol.% C₂H₂ in C₂H₄ with about 200 ppm C₂H₆ impurity from Scott Specialty Gases and UHP H₂ from Matheson) was fed into the reactor at a space velocity of 92,000 mL h⁻¹ g⁻¹. All flows were delivered by mass flow controllers. The analysis of the gas components from the microreactor was performed by an on-line Shimadzu GC 17A equipped with a 30 m × 0.32 mm (i.d.) × 1.50 μm GS-CARBONPLOT capillary column operating at 80 °C and a FID detector.

There was no signal of other C₂ products detected by GC/FID except C₂H₄ and C₂H₆. And the oligomerization is assumed to be negligible because of the short contact time and the relatively high H₂/C₂H₂ ratio. There is some impurity of C₂H₆ in the feed gas; therefore, the calculation of ethylene selectivity is based on the production of ethane from the reaction assuming ethylene and ethane are the only products for acetylene hydrogenation. The calculations of acetylene conversion and the selectivity to ethylene are defined as follows [44]:

$$\text{Conversion} = \frac{C_2H_2(\text{feed}) - C_2H_2}{C_2H_2(\text{feed})} \times 100\% \quad (1)$$

$$\text{Selectivity} = 1 - \frac{C_2H_6 - C_2H_6(\text{feed})}{C_2H_2(\text{feed}) - C_2H_2} \times 100\% \quad (2)$$

We note the definition of selectivity differs from most of previous research to take care the fact that we are using extremely high ethylene concentration in the feed. In many works [39], the definition of selectivity is

$$\text{Selectivity} = [C_2H_4]/([CH_4] + [C_2H_4] + [C_2H_6]) \times 100\% \quad (3)$$

If we used this conventional definition, our selectivity will always be very close to 100%. Because of the large excess of ethylene used (C₂H₄/C₂H₂ ~ 100), the selectivity as defined in our work could be negative. For example, a 80% selectivity according to our definition is considered a very good performance.

3. Results

3.1. Removal of APTES

We first show the RF plasma treatment effectively removes the surface functional groups on the gold nanoparticles. As was reported in our previous work [20], APTES played a key role in preparing highly dispersed gold nanoparticles by anchoring them on the surface of silica. However, the Au/SiO₂ exhibited very low catalytic activity if the APTES was not removed. Based on the previous results on similar catalyst materials, 500 °C is the lowest calcination temperature to ensure essential removal of APTES and proper catalytic activities. FT-IR is a very sensitive technique in characterizing the organic compounds. Therefore, we conducted IR experiment to determine whether the APTES can be removed by O₂ plasma treatment at room temperature. As shown in Fig. 1, the 2930 cm⁻¹ and 2865 cm⁻¹ bands, representing the -CH₂ stretching mode [45] on the dried Au/SiO₂ sample (Fig. 1a), decrease dramatically with increasing calcination temperature. After 30 min of O₂ plasma treatment at room temperature (Fig. 1e), there is no signal of -CH₂ stretching mode, similar to the effect of calcinations at temperatures higher than 300 °C for 6 h (Fig. 1b–d). This result showed that the O₂ plasma can remove the APTES efficiently under mild condition.

In order to obtain the quantitative data of the removal of the organic ligands, TGA analyses (as shown in Fig. 2) were carried

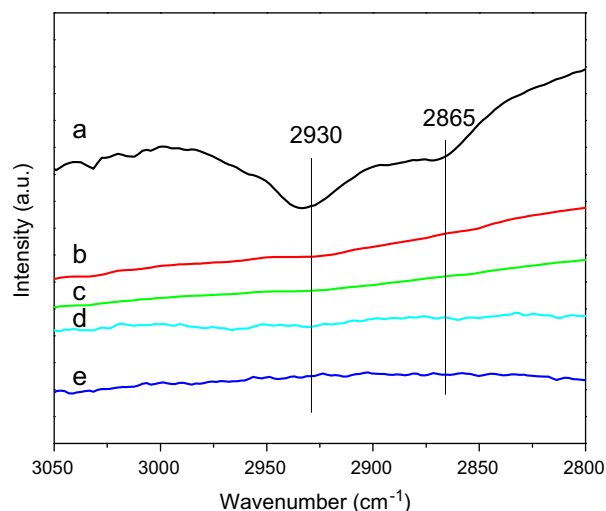


Fig. 1. FT-IR spectra of Au/SiO₂ catalysts pretreated under different conditions: (a) dried; calcined at (b) 300 °C, (c) 400 °C, (d) 500 °C; (e) O₂ plasma treated.

out over gold supported on SBA-15 that exhibits higher surface area and APTES loadings. With increasing temperature, the weight decreased and there is negligible weight loss after 650 °C. The sample calcined at 500 °C appears to be most “clean” in organics (Fig. 2a). The samples calcined at lower temperatures (400 and 300 °C) still show some organic residue above 500 °C (at about 5.5% and 4.1%, as shown in Fig. 2b and c, respectively). Therefore, in all our pre-treatments, we choose to calcine the catalysts at 500 °C. The weight loss curve of O₂ plasma-treated Au/SBA-15 (Fig. 2d) behaves differently from the dried (Fig. 2e) or calcined (Fig. 2a–c) samples: most of the weight loss happens at temperatures lower than 300 °C, indicating APTES have been decomposed to less stable compounds. But there is still a weight loss of about 5% between 300 °C and 500 °C. Gold nanoparticles might have helped by catalyzing the decomposition of APTES when pretreated by plasma according to the literature [46]. Therefore, under O₂ plasma treatment, the organic ligands on the surface of gold have been selectively removed from the surface of gold first.

3.2. XRD and TEM results

To test whether the gold nanoparticles were aggregated after O₂ plasma treatment, we tried to do further characterizations. We first determine the average particle sizes of gold by measuring the peak

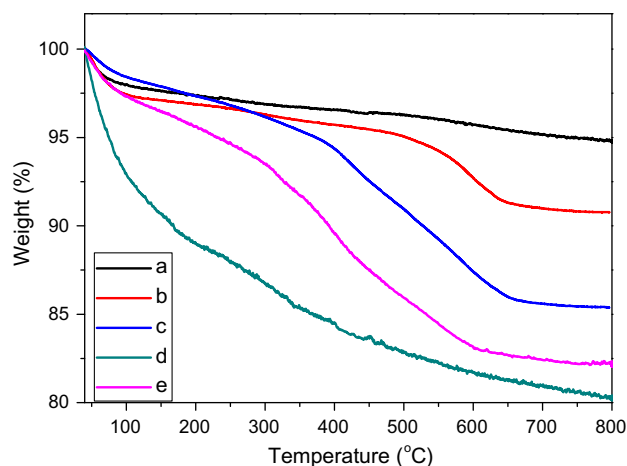


Fig. 2. TGA results of Au/SBA-15 catalysts pretreated under different conditions: calcined at (a) 500 °C, (b) 400 °C, (c) 300 °C; (d) O₂ plasma treated; (e) dried.

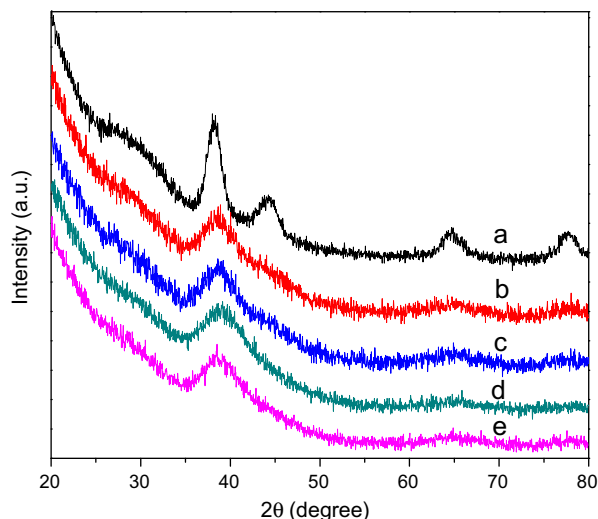


Fig. 3. XRD patterns of Au/SiO₂ catalysts pretreated under different conditions: calcined at (a) 500 °C, (b) 400 °C, (c) 300 °C; (d) dried; (e) O₂ plasma treated.

width of its XRD pattern. As shown in Fig. 3, the samples present diffraction peaks at 38.2°, which can be indexed as gold (111) reflections [14,19–23]. The average Au particle sizes estimated by Scherrer equation are 2.1 nm, 2.2 nm, 2.4 nm, 2.4 nm, and 4.0 nm for dried, O₂ plasma treated and calcined at 300, 400, and 500 °C Au/SiO₂, respectively. The TEM images and the size distribution diagrams also show that gold nanoparticles are highly dispersed on the surface of silica after being treated by O₂ plasma (Fig. 4b). It exhibited an average particles size of 3.1 nm, which is very close to that of the dried Au/SiO₂ (2.9 nm, Fig. 4a) and smaller than that of the calcined sample (3.5 nm, 4.0 nm, and 4.9 nm (Fig. 4c–e) calcined at 300, 400, and 500 °C, respectively). The XRD and TEM results demonstrate that O₂ plasma is effective in minimizing the aggregation of small Au particles while removing the grafted APTES.

3.3. Catalytic activity for selective hydrogenation of acetylene in excess ethylene

In order to test the efficiency of the removal of the organic ligands and to control the Au particle size, we choose the acetylene hydrogenation reaction as the probe reaction with a great industrial potential. The catalytic activities for catalysts calcined at 300 and 400 °C are much lower than those calcined at 500 °C (data not shown here). Thus, in the followings, the catalytic performances of Au/SiO₂ pretreated under different conditions: dried, oxygen plasma are compared after calcinations at 500 °C.

Fig. 5 lists the conversion of acetylene and the selectivity to ethylene of dried, oxygen plasma-treated, and calcined Au/SiO₂ catalysts after reduction at 250 °C for selective hydrogenation of acetylene at temperatures from 150 to 250 °C. As shown in Fig. 5a, the conversion of acetylene over dried Au/SiO₂ first increases then decreases with temperature. This is quite different from the result reported by Azizi et al. [39]: in the absence of ethylene under high H₂ to acetylene ratio that shows that the conversion continues to increase with increasing temperature at 150–400 °C. This may be because at high temperature, the high ethylene concentration leads to competitive adsorption of ethylene relative to acetylene. Throughout the temperature range tested, 30 min of oxygen plasma treatment increases the conversion of the dried Au/SiO₂ by ~20–30%. Calcination at 500 °C, on the other hand, decreases the acetylene conversion at lower temperatures but increases the conversion at higher temperatures. According to the TEM and XRD results, the

Au particle size in oxygen plasma-treated Au/SiO₂ is slightly bigger than the dried Au/SiO₂. However, the acetylene conversion of oxygen plasma-treated Au/SiO₂ is higher than the dried one. It is known that plasma treatment would tend to change the shape of metal particles or the metal–support interaction that could result in more active sites for acetylene hydrogenation [47]. Although, the large Au size of calcined Au/SiO₂ gave a lower conversion at lower temperatures (below 200 °C), it is not clear why it shows higher conversion than both the dried and oxygen plasma-treated Au/SiO₂ at the high-temperature range. It is likely that the decrease of conversion for both dried and oxygen plasma-treated Au/SiO₂ at higher temperatures is due to its significantly lower adsorption capacity of acetylene at high temperatures. On the other hand, the decrease of acetylene adsorption at high temperatures might not be a dominating factor for acetylene conversion over larger Au particles. Further study on acetylene, ethylene, and H₂ adsorption over small Au particles, especially after the plasma treatment, at various temperatures is needed to clarify the effect of particle size on conversion trend with temperature.

In our experiment, ethane was the only by-product that is consistent with that reported by Choudhary et al. [48] and Jia et al. [42] and different from Azizi et al.'s work [39] in which they reported that methane was also generated. Fig. 5b illustrates the selectivities of dried, oxygen plasma-treated, and calcined Au/SiO₂ catalysts at the same temperature range. The selectivity order is as follows: calcined Au/SiO₂ > OP-Au/SiO₂ > dried Au/SiO₂. The selectivity of the calcined Au/SiO₂ remains relatively constant with temperature. But, the selectivities of the dried Au/SiO₂ and OP-Au/SiO₂ do not seem to have any trend except with relatively lower values as compared to calcined Au/SiO₂. Again, this is different from the results reported by Azizi et al. [39] who claimed a selectivity close to 100% at temperatures below 300 °C. However, the high selectivity in the literature is mostly due to the fact that the reactions were carried out in the absence of ethylene. There is essentially no literature of Au catalyst for selective hydrogenation of acetylene in the large excess of ethylene, which is an industrial condition. The only Au literature of selective hydrogenation of acetylene in the presence of ethylene is reported by Gluhoi et al. [24]. However, the C₂H₄/C₂H₂ ratio used is only 1/1 that is much lower than the ratio of the feed gas used in this work. In fact, it severely underestimates the selectivity issue of Au catalysts.

As shown in Fig. 5b, oxygen plasma treatment increases the selectivity of dried Au/SiO₂ throughout the temperature range tested. On the other hand, the calcined catalyst shows the best selectivity at all temperatures. This phenomenon is also different from the traditional Pd catalyst for selective hydrogenation of acetylene where high ethylene selectivity is normally coupled with low acetylene conversion [25–27,35]. Both calcined and oxygen plasma-treated Au/SiO₂ show high conversion and relatively high selectivity at low temperatures.

High reduction temperature was normally used for calcined Au catalysts for conditioning [13–17,49]. All three Au catalysts were, additionally, reduced at 400 °C before acetylene hydrogenation reaction. Fig. 6 illustrates the conversion of acetylene and the selectivity to ethylene of dried, oxygen plasma-treated, and calcined Au/SiO₂ catalysts after reduction at 400 °C at reaction temperatures from 150 to 400 °C. As shown in Fig. 6a, the conversion activity of these catalysts reduced at 400 °C follows a similar trend as the catalysts reduced at 250 °C, first increases then decreases with temperature. The temperature of maximum acetylene conversion of the calcined Au/SiO₂ is higher than those of O₂ plasma-treated Au/SiO₂ and dried Au/SiO₂. Therefore, the conversion activity order at low temperature is O₂ plasma-treated Au/SiO₂ > dried Au/SiO₂ > calcined Au/SiO₂. The main difference of the catalysts reduced at 400 °C as compared to the catalysts reduced at 250 °C is that high reduction temperature at 400 °C

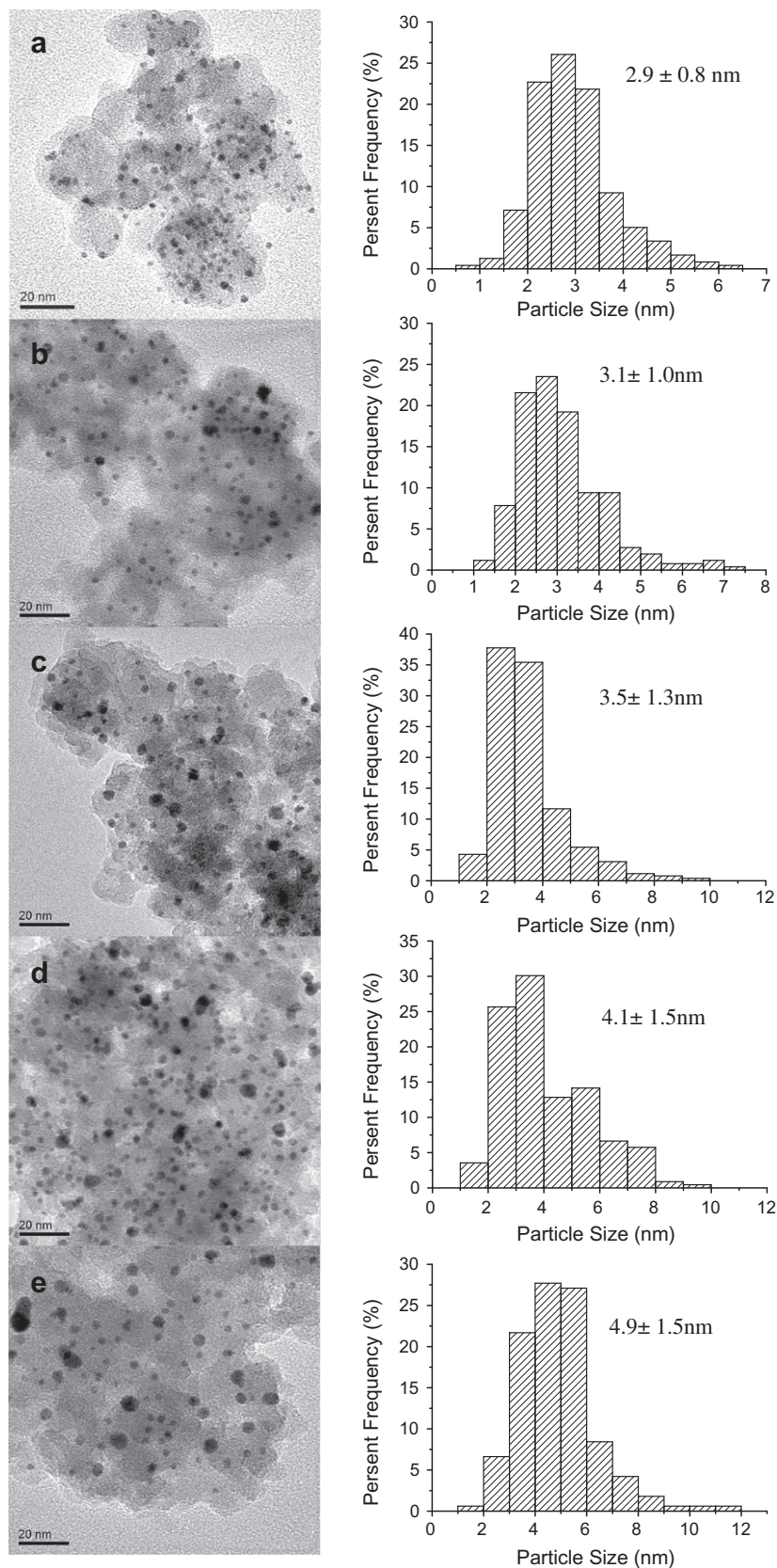


Fig. 4. TEM images of Au/SiO₂ catalysts pretreated under different conditions: (a) dried; (b) O₂ plasma treated; calcined at (c) 300 °C, (d) 400 °C, (e) 500 °C.

lowers the conversion at the whole temperature range. In contrast to the CO oxidation reaction [14–17,49], high reduction temperature is detrimental to the Au/SiO₂ catalysts under the conditions

tested. On the other hand, the selectivities of three catalysts reduced at 400 °C, as shown in Fig. 6b, are higher than the catalysts reduced at 250 °C. The results show that high reduction

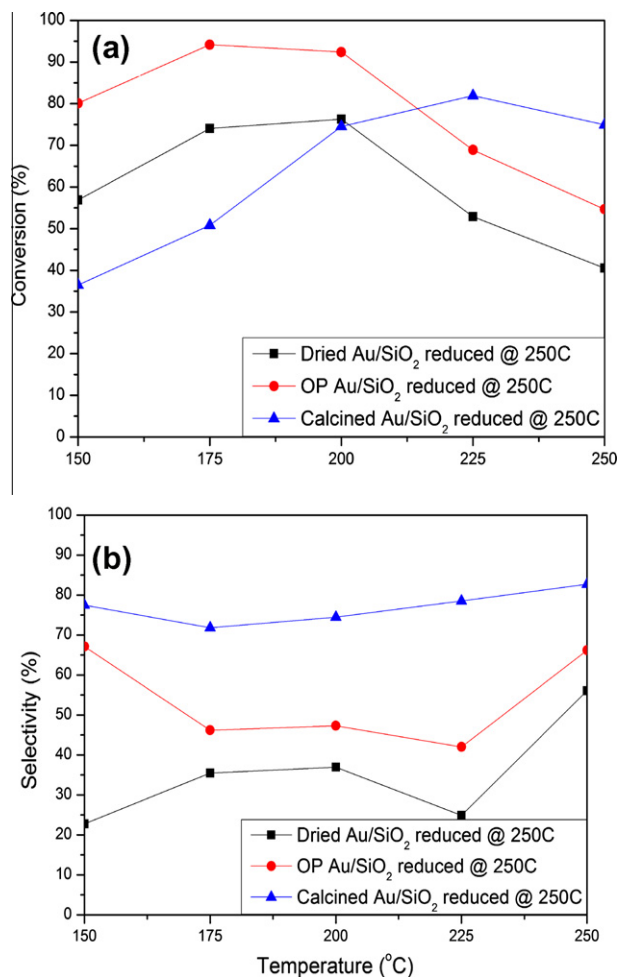


Fig. 5. Acetylene conversion (a) and ethylene selectivity (b) with increasing temperature in the selective hydrogenation of acetylene reaction over dried, O₂ plasma-treated and calcined Au/SiO₂ catalysts. Prior to the reaction, the catalysts reduced at 250 °C under pure H₂ for 30 min. The gaseous mixture containing about 0.80 vol.% C₂H₂ and 16.0 vol.% H₂ in balance C₂H₄.

temperature is beneficial to improve selectivity for selective hydrogenation of acetylene. With reduction at 400 °C, Au/SiO₂ catalysts behave similar to the Pd catalysts, i.e., high selectivity coupled with low conversion or low selectivity coupled with high conversion. However, the selectivity of Au/SiO₂ is always positive under large excess of ethylene, which is still a big advantage over industrial Pd catalysts where the selectivity could be a fairly large negative number, such as –100%, when the conversion is high [25–27,35].

4. Discussion

In this work, we applied non-thermal plasma of oxygen at low pressure and at room temperature to remove the APTES that was used for assisting the formation of small gold nanoparticles. Our results showed that O₂ plasma treatment at room temperature is demonstrated here to be an effective way to remove amine groups while controlling the Au particle size of dried Au/SiO₂ to ~3 nm. IR and previous TGA results showed that APTES had been removed by O₂ plasma treatment. And the XRD and TEM measurements indicated that the Au particles size of oxygen plasma-treated Au/SiO₂ remained at about 3 nm that is smaller than that of the calcined samples. The comparison is illustrated in Fig. 7. This demonstrated that non-thermal oxygen plasma is an efficient way to remove

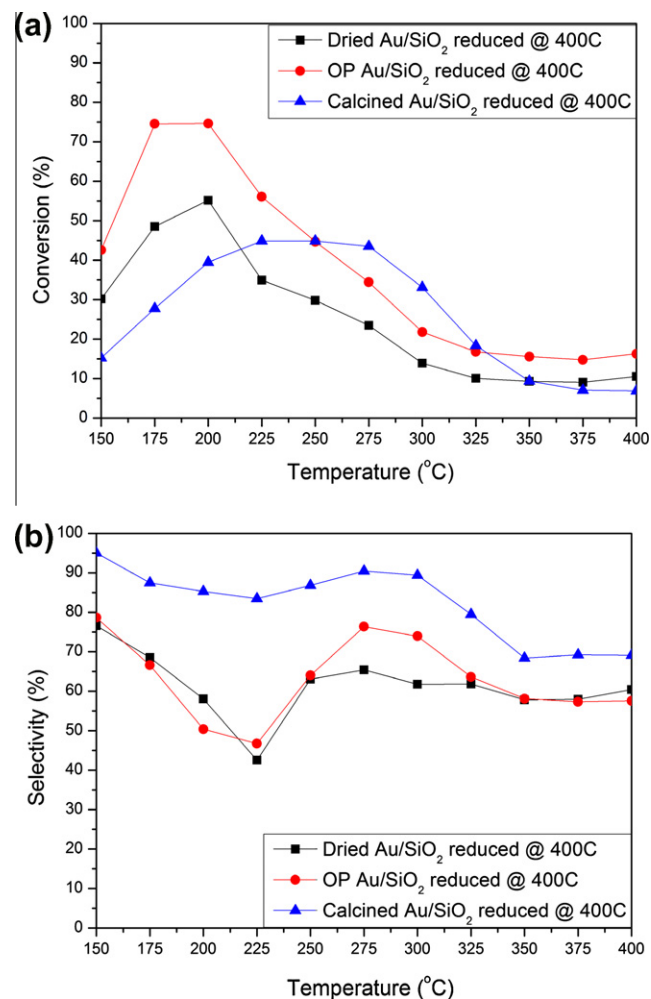
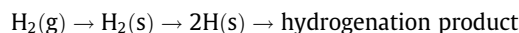


Fig. 6. Acetylene conversion (a) and ethylene selectivity (b) with increasing temperature in the selective hydrogenation of acetylene reaction over dried, O₂ plasma-treated and calcined Au/SiO₂ catalysts. Prior to the reaction, the catalysts reduced at 400 °C under pure H₂ for 30 min. The gaseous mixture containing about 0.80 vol.% C₂H₂ and 16.0 vol.% H₂ in balance C₂H₄.

organic molecules on metallic nanoparticles under mild condition. This is a potentially general method to be developed for preparing highly dispersed supported metallic nanoparticles to replace the severe pretreatment at high temperatures.

We would like now to discuss the origin of the good catalytic activity of the plasma-treated Au/SiO₂ nanocatalyst system. We noticed that the Au/SiO₂ pretreated by plasma exhibited similar or higher catalytic activity than that of the calcined catalyst especially at the ranges of lower temperature. In order to examine the role of hydrogen activation, we investigate the kinetics of hydrogenation by varying concentration of hydrogen. The reaction order of hydrogen was measured by varying the H₂/C₂H₂ ratios (20/1, 10/1, 5/1, and 2/1) at 175 °C (Fig. 8). For dried, calcined, and oxygen plasma-treated Au/SiO₂, they are 1.1, 1.3, and 1.1, respectively, which is close to that of Au/CeO₂ (1.0) [39] and larger than that of Au/Al₂O₃ (0.4) [42]. According to the adsorption–reaction scheme,



when the dissociation step is fast and in equilibrium, the reaction order of hydrogen would approach 1/2 [42]. However, in present work, the reaction order is near 1 indicating a fast hydrogenation step and a rate limiting step of hydrogen dissociation on the surface

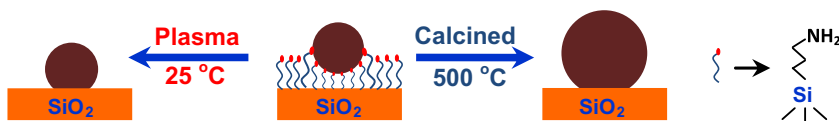


Fig. 7. Schematic illustration of the particle size changes of the dried Au/SiO₂ after O₂ plasma treatment and calcinations, respectively.

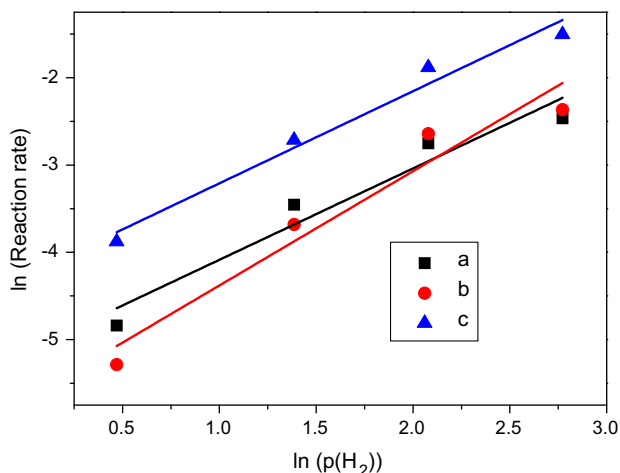


Fig. 8. Dependence of the catalytic rate on the partial pressure of H₂ over (a) dried, (b) calcined and (c) O₂ plasma-treated Au/SiO₂ catalysts at 175 °C. Symbols and lines represent measured and fitted results, respectively.

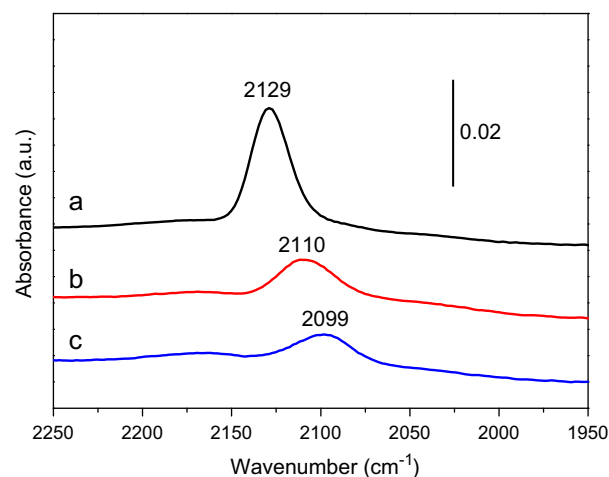


Fig. 9. In situ DRIFT spectra of (a) calcined, (b) O₂ plasma-treated and (c) dried Au/SiO₂ catalysts. Prior to the reaction, the catalysts reduced at 250 °C under pure H₂ for 1 h.

of gold. Therefore, metal–support interaction would influence strongly the reaction rate.

It has been reported that the vibrational frequency of adsorbed CO on the same support reflects the surface charges of the Au nanoparticle [50]. In order to explore the intrinsic cause of the non-thermal oxygen plasma promoting the catalytic activity in our Au/SiO₂ system, we conducted in situ DRIFT to determine the nature of the local electronic environment of the supported gold nanoparticles on silica. We thus studied the DRIFT spectra of adsorbed CO on our catalysts. Fig. 9 shows that DRIFT spectra for the CO adsorbed samples after helium flow over the catalyst for 2 min to remove physically adsorbed CO. The CO vibrational bands are positioned at 2099, 2110, 2129 cm⁻¹ on the dried, oxygen plasma-treated and calcined Au/SiO₂ catalyst, respectively. Despite the complex conditions that influencing the CO adsorption band positions of the supported gold nanoparticles [51–54], it is known that the vibrational stretching mode of CO on electron-rich and electron-deficient metallic gold particles shifts to lower and higher frequency, respectively [50,55]. Our DRIFT results, the order of CO vibration frequency: calcined Au/SiO₂ > O₂ plasma-treated Au/SiO₂ > dried Au/SiO₂, indicated that the gold nanoparticles of the calcined sample were more positively charged than those of the oxygen plasma treated and the dried ones. Corma et al. [50] showed by computation that the charges on the gold nanoparticles were linearly correlated with the vibrational frequency of adsorbed CO. They then show experimentally that neutral metallic gold could dissociate H₂ more efficiently than the positively charged gold or negatively charged gold [50,55]. Considering the trend in FT-IR frequency of our samples, this might explain why the oxygen plasma-treated Au/SiO₂ exhibited the best catalytic performance within the three samples at lower temperature range. The plasma-treated sample has a surface charge that is nearly zero. Thus, it activates the dissociative adsorption of hydrogen the most. The adsorption of acetylene and ethylene on the surface of Au/SiO₂ might also influence the catalytic activity. Further study on the catalytic mechanism is underway in our laboratory.

It is demonstrated for the first time that the Au nanocatalysts, with very small particle size, can be prepared with a surface functionalization method on silica surface, and the organic functional group can be removed in a mild low-temperature plasma treatment. The particle sizes remain relatively unchanged. The O₂ plasma-treated Au catalyst gave high selectivity at low temperatures for hydrogenation of acetylene even in the presence of large excess of ethylene. As Au nanocatalysts with very small particle size have been increasingly found to be active for many important oxidation or reduction reactions [18,56], new methods need to be developed for making sub 3 nm activated Au nanocatalyst. Besides, the activity and selectivity of supported gold nanoparticles also largely depend on the interface between gold and the support [57]. Therefore, the mild plasma treatment method would be potentially very useful to be combined with synthesis encapsulated gold nanoparticles and enhance the metal–support interaction. This would be also a highly desirable technique for making other new type of metallic nanoparticles including bimetallic nanoparticles for catalysis.

5. Conclusions

Selective hydrogenation of acetylene in the presence of large excess of ethylene has been demonstrated by the Au/SiO₂ nanocatalyst system with O₂ plasma treatments. The catalyst system was prepared with organic-functionalized silica to control its deposition and with mild plasma treatment to give activated gold for the catalytic reduction. Throughout the temperature range tested, 30 min of O₂ plasma treatment increases the conversion of the dried Au/SiO₂ by ~20–30%. Calcination at 500 °C, on the other hand, decreases the acetylene conversion at lower temperatures but increases the conversion at higher temperatures. The high activity for the plasma-treated catalyst was traced to (a) production of small sized Au nanoparticles of ~3 nm diameter supported on silica and (b) optimized neutral surface charge of the Au nanoparticle, which favors the dissociative adsorption of H₂.

The selectivity order of three catalysts in this study is as follows: calcined Au/SiO₂ > OP-Au/SiO₂ > dried Au/SiO₂. The selectivity remains relatively constant with temperature, but is less than 100%. The close to 100% selectivity claimed in the literature was due to the absence of ethylene or low ethylene to acetylene ratio. It demonstrates that previous studies severely underestimated the selectivity issue of Au catalysts under the condition with high C₂H₄/C₂H₂ ratios, which is the most critical issue of the industrial process of the acetylene removal from the ethylene stream. Although Au catalyst still shows the advantage in selectivity over Pd catalysts, its reaction kinetics remains too slow to compete with Pd catalysts. In the future, one may try to increase reaction rates by adding promoters or by changing reaction conditions. Further study on acetylene, ethylene, and H₂ adsorption over smaller Au particles, especially after the plasma treatment, is needed to clarify the effects of Au particle size and surface charge on selective hydrogenation of acetylene in the presence of large excess of ethylene.

Acknowledgments

This research was supported by a Grant from the National Science Council, Taiwan (NSC 98-2120-M-002-002), Welch Foundation (Grant No.: T-0014) and the NSF REU Grant (#0851966). We are very grateful to Mr. Chih-Yuan Tang from Instrumentation Center of National Taiwan University for the TEM characterization. We are very thankful to Prof. Shawn D. Lin and Dr. Hongkui Cheng from National Taiwan University of Science and Technology for their great help in the DRIFT experiment. We appreciate the great help given by Prof. Soofin Cheng (Chemistry Department, National Taiwan University) in the TGA experiment.

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