负载型 Pt 模型催化剂中 Pt 纳米粒子的形貌对 CO 氧化活性的影响

王家宁, 戴洪兴, 何 洪*

北京工业大学环境与能源工程学院化学化工系, 北京 100124

摘要: 采用简单的化学还原法制备了具有不同形貌特征的 Pt 纳米粒子, 并利用浸渍法将其负载到 SiO₂ 上, 得到了粒子分散均一的负载型 Pt 催化剂, 考察了其催化 CO 氧化反应性能。X 射线荧光分析、X 射线光电子能谱、红外光谱和透射电镜结果表明, Pt/SiO₂ 模型催化剂上 CO 氧化活性的不同来源于 Pt 纳米粒子不同晶面的贡献, 即 Pt 纳米粒子的晶型对 CO 在催化剂上的吸附和 Pt/SiO₂ 的 CO 氧化活性具有重要的影响。

关键词: 铂纳米粒子; 形貌效应; 结构敏感反应; 一氧化碳氧化

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*通讯联系人. 电话: (010)67396588; 传真: (010)67391983; 电子信箱: hehong@bjut.edu.cn

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Effect of the Morphology of Pt Nanoparticles of Supported Pt Model Catalysts on CO Oxidation

WANG Jianing, DAI Hongxing, HE Hong*

Chemistry and Chemical Engineering Department, College of Environmental and Energy Engineering,
Beijing University of Technology, Beijing 100124, China

Abstract: In order to investigate the influence of particle morphology on the catalytic activity of supported Pt model catalyst, platinum nanoparticles (NPs) with different morphologies were synthesized by a chemical method and loaded onto SiO₂ to give well-defined supported catalysts. CO oxidation was used as the probe to investigate the catalytic activities of these Pt/SiO₂ model catalysts. X-ray fluorescence, X-ray photoelectron spectroscopy, diffuse reflectance Fourier transform infrared spectroscopy, and transmission electron microscopy characterization demonstrated that the different activities of these Pt/SiO₂ catalysts were due to different crystal surfaces, which strongly influenced the adsorption and oxidation of CO on the Pt NPs.

Key words: platinum nanoparticle; morphology effect; structure sensitive reaction; carbon monoxide oxidation

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*Corresponding author. Tel: +86-10-67396588; Fax: +86-10-67391983; E-mail: hehong@bjut.edu.cn

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In the past few decades, many techniques have been developed to synthesize metal nanoparticles (NPs) with different morphologies. These include a photochemical process, radiating reduction, electrochemical reduction, and chemical reduction. Alcohol, hydrogen, and sodium borohydride were used as reductants and organic polymers were used as capping agents in the method of chemical reduction

[1–6]. In the field of nanocatalysis, shape control of the noble metal NPs, which cannot be achieved by classical impregnation and precipitation methods [6–8], has been of much interest since activity and/or selectivity can be regulated by the morphology of active phase. For example, only cyclohexane was produced over the Pt(100) surface, while both cyclohexane and cyclohexene were produced on the

Pt(111) surface, suggesting that benzene hydrogenation over Pt-based catalysts is structure sensitive [9]. Lee et al. [10–12] reported that the isomerization of the *trans* isomers of olefins to their *cis* counterparts was promoted by (111) facets of platinum. Even more interesting was that they also found a shape dependent effect in isomerization over supported catalysts [12]. Similarly, Christopher et al. [13,14] found a relationship between selectivity for ethylene epoxidation and the morphologies of Ag nanoparticles. Recently, more researches have further correlated the specific effect of morphology on the catalytic activities of nanocatalysts [15–19]. It was suggested that metal nanoparticles with controlled size and morphologies can provide an important platform with which to study heterogeneous catalytic processes [20,21].

In this work, Pt/SiO₂ model catalysts were prepared by supporting Pt NPs with different morphologies on SiO₂. CO oxidation was used as the probe to investigate these Pt supported catalysts. Significant differences in CO oxidation activity were observed over the three kinds of supported Pt model catalysts. Together with X-ray fluorescence, X-ray photoelectron spectroscopy (XPS), diffuse reflectance Fourier transform infrared (DRIFT), and high resolution transmission electron microscope (HRTEM) characterization, it was possible to conclude that the differences in CO oxidation activity should be attributed to the morphologies of the Pt NPs.

1 Experimental

1.1 Catalyst preparation

The Pt NPs were synthesized by a known polyol process [2]. Briefly, 2 ml of AgNO₃ of fixed concentration was added to a boiling ethylene glycol (EG) solution that was used as the solvent and reductant. 0.125 ml of a mixture of poly(vinylpyrrolidone) (PVP, $M_w = 30000$) and H₂PtCl₆ (PVP:Pt = 12:1) dissolved in EG was dropped into the above solution every 30 s over a 64-min period. The resulting mixture was refluxed for another 20 min, and then the acetone was added into the mixture to precipitate the Pt NPs. The Pt NPs were rinsed with a solution of ethanol and hexane and then centrifugated three times to remove the PVP and EG to give the cubic, cuboctahedral, and octahedral Pt NPs that were labeled as Pt-C, Pt-CU and Pt-O. The concentrations of AgNO₃ for fabricating cubic, cuboctahedral, and octahedral Pt NPs were 2, 20, and 60 mmol/L, respectively. After that, the Pt NPs were redispersed in an ethanol solution and loaded onto SiO₂ by impregnation followed by evaporation to get the highly dispersed Pt supported model catalysts. In order to eliminate the inhibiting effect of Ag⁺ on the catalytic activity due to physical site

blocking [22], the Pt/SiO₂ catalysts were etched by concentrated HNO₃, and then dried at 333 K for 24 h without any further calcination or reduction before use.

1.2 Catalyst characterization

The Pt and Ag contents of the catalysts were determined by X-ray fluorescence (PW2403). The surface composition was measured by XPS with an Axis Ultra spectrometer (Kratos, UK) using Mono Al K _{α} (1486.71 eV) radiation operated at 15 mA and 15 kV. HRTEM images were obtained on a JEM-2010 transmission electronic microscope (JEOL Ltd.) with accelerating voltage of 200 kV. The samples were dispersed in ethanol by ultrasonic treatment and deposited on a carbon coated copper grid for the examination.

DRIFT spectroscopy of CO adsorption was performed on a FTIR spectrometer (Tensor 27, Bruker) with a KBr window and a MCT detector working at liquid nitrogen temperature. A high temperature reaction chamber (Harrick) for in-situ pretreatment and reaction was coupled to the spectrometer. The catalyst powder was placed inside the chamber without packing or dilution. The spectra were collected at atmospheric pressure and temperatures from 303 to 493 K with a resolution of 4 cm⁻¹. In the experiments, the samples were pretreated in a flow of nitrogen at a flow rate of 50 ml/min at 303 K for 12 h. Before introducing CO to the cell, a series of background spectra were collected between 303 and 493 K under a stream of 50 ml/min nitrogen to calibrate the CO adsorption DRIFT spectra. After a decrease in temperature to 303 K, pure CO (99.99%) was introduced into the chamber cell at 303 K for 30 min. This was subsequently purged with pure nitrogen for 45 min to remove all the weakly adsorbed CO molecules on the catalysts. In the following step, the temperature was increased again to the desired temperature under a nitrogen atmosphere and CO adsorption spectra were repeatedly collected after the temperature had been stable for 0.5 h under two kinds of different atmospheres: a flow of pure nitrogen and a flow of gases containing 1% CO, 1% O₂, with a balance of N₂, respectively.

1.3 Catalyst activity evaluation

The CO oxidation activities over the three supported Pt model catalysts were evaluated in a quartz tube microreactor (i.d. = 6 mm) with a gas mixture of 1% CO + 1% O₂ + 98% N₂ in the temperature range of 400–900 K and a space velocity (SV) of 60000 h⁻¹. The mass of the catalyst sample was 50 mg that was well mixed with 1 g quartz sand with a thermocouple in the middle of the catalyst bed. The effluent gases were analyzed by an online gas chromatograph (GC)

system equipped with a TCD detector. CO conversion was calculated from the detected CO concentration by CO conversion = $[(\text{CO}_{\text{in}} - \text{CO}_{\text{out}})/\text{CO}_{\text{in}}] \times 100\%$, where CO_{in} and CO_{out} are the inlet and outlet CO concentrations.

2 Results and discussion

Pt NPs with different morphologies were synthesized successfully by the chemical reduction method with Ag^+ ions used as the agent to control the particle shape. The well-defined Pt NPs were loaded on SiO_2 to get supported Pt model catalysts with cubic, cuboctahedral, and octahedral Pt NPs, respectively. The TEM images of the Pt NPs and Pt/ SiO_2 catalysts are exhibited in Fig. 1. It can be seen that Pt NPs with the morphologies of cubic, cuboctahedral, and octahedral shapes were present with a narrow size distribution. After the Pt NPs were dispersed on the surface of SiO_2 , no significant change in the morphology of the Pt NPs could be observed. They also showed a uniform dispersion.

Fig. 1. TEM images of the Pt NPs and Pt supported model catalysts with Pt NPs morphologies of cubic (a, d), cuboctahedral (b, e), and octahedral (c, f) shapes.

The size dimensions of the three kinds of Pt NPs were calculated from the TEM images. The data for the Pt NPs size, metal dispersion, and Pt and Ag contents in the catalysts are summarized in Table 1. The average size of the Pt

Table 1 Properties of the Pt/ SiO_2 model catalysts

Catalyst	D^a/nm	MD ^b /%	Loading ^c (%)		Ratio of Ag surface/bulk
			Pt	Ag	
Pt-C/ SiO_2	8.9 ± 0.1	12.8	9.0	—	—
Pt-CU/ SiO_2	$16.2 \pm 0.2, 9.7 \pm 0.3$	10.9	8.6	0.2	0.05
Pt-O/ SiO_2	$18.4 \pm 1.2, 14.1 \pm 0.8$	9.8	9.1	0.89	0.034

^aAverage size for fifty particles based on the TEM images.

^bMetal dispersion calculated from the size given in this table according to the ideal shape.

^cPt and Ag contents were determined by XFS and the surface Ag content was determined by XPS.

NPs on the Pt-C/ SiO_2 catalyst was (8.9 ± 0.1) nm, which was the distance between two (100) facets. For the Pt-CU/ SiO_2 sample, the average vertex-to-vertex distance was (16.2 ± 0.2) nm and the face-to-face distance along the [001] zone axis was ca. (13.4 ± 0.2) nm. The lengths of the long and short axes of the octahedral Pt NPs for the Pt-O/ SiO_2 catalyst were (18.4 ± 1.2) and (14.1 ± 0.8) nm, respectively. The Pt metal dispersions were 12.8%, 10.9%, and 9.8% over the Pt-C/ SiO_2 , Pt-CU/ SiO_2 , and Pt-O/ SiO_2 catalysts, respectively. There was no significant difference in the metal dispersion for the three kinds of catalysts.

To investigate the catalytic properties of the synthesized supported Pt model catalysts, CO oxidation was chosen as the probe reaction. It is known to be structure sensitive and is very important in automobile emission control [23–25]. The CO oxidation catalytic activities over the Pt-C/ SiO_2 , Pt-CU/ SiO_2 , and Pt-O/ SiO_2 model catalysts are shown in Fig. 2. It can be seen from Fig. 2 that the Pt/ SiO_2 catalysts with different morphologies of the Pt NPs exhibited significant differences in CO oxidation activity. The CO complete oxidation temperatures were 483, 533, and 913 K for Pt-C/ SiO_2 , Pt-CU/ SiO_2 , and Pt-O/ SiO_2 , respectively. Taking into account the similar synthesis process and metal content and dispersion, we suggest that the differences in CO oxidation activity can be attributed to the different morphologies of the Pt NPs.

CO adsorption on the Pt surface is the first step for CO

Fig. 2. CO oxidation over Pt-C/ SiO_2 (1), Pt-CU/ SiO_2 (2), and Pt-O/ SiO_2 (3) catalysts.

oxidation in the widely accepted reaction mechanism of CO oxidation over Pt catalysts. In order to investigate CO adsorption and understand the catalytic properties of the supported Pt model catalysts with different morphologies of the Pt NPs, DRIFT spectra of CO adsorption were collected. CO adsorption is an excellent probe of the catalytic surface site since the stretching frequency of CO is sensitive to the strength of the Pt–CO bonding [26]. The CO DRIFT adsorption bands over SiO₂ and the Pt/SiO₂ catalysts are shown in Fig. 3. It can be seen that CO does not adsorb on the SiO₂ support. As time increased, CO gas was flushed out and the adsorption bands at 2174 and 2120 cm⁻¹, which can be assigned to free CO in the gas phase, became weaker and disappeared in the end.

Fig. 3. DRIFT spectra of CO adsorbed on the SiO₂ support at 303 K.

Figures 4 and 5 show the DRIFT spectra of CO adsorbed on Pt-C/SiO₂, Pt-CU/SiO₂, and Pt-O/SiO₂. It has been reported that the band in the range of 2000–2100 cm⁻¹ can be assigned to CO linearly (on top) adsorbed on Pt atoms [27,28]. Moreover, the position of this band depends on the dipole-dipole interaction and it

Fig. 4. DRIFT spectra of CO adsorbed on Pt-C/SiO₂ (a) and the disappearance of the adsorption band with time at 453 K (b).

Fig. 5. DRIFT spectra of CO adsorbed on the Pt-CU/SiO₂ (a) and Pt-O/SiO₂ (b) catalysts.

shifts with surface coverage [29] and coordination number of the Pt atoms [30]. Thus the CO adsorption bands in the DRIFT spectra at different temperatures can be attributed to linear CO adsorption on the surface of the Pt NPs and their differences originated from the morphologies of the Pt NPs. For the same temperature, the CO adsorption bands shifted to low frequency in the order of Pt-C/SiO₂ > Pt-CU/SiO₂ > Pt-O/SiO₂. It was reported that CO adsorption on step atoms appeared at a lower frequency as compared with those on terrace atoms [31]. The CO adsorption peaks on single crystal Pt(100) and (111) were located at 2100 [27] and 2090 cm⁻¹ [32], respectively. In the ideal model, the cubic NPs expose (100) facets and the octahedron NPs expose (111) surfaces. For the cuboctahedron, the surface is composed of six (100) and eight (111) planes in an area ratio of 1:0.578. Therefore, the differences in the CO adsorption bands on DRIFT spectra for the Pt-C/SiO₂, Pt-CU/SiO₂, and Pt-O/SiO₂ catalysts were due to the differences in CO adsorption on the (100) and (111) facets.

As the temperature increased, the CO adsorption bands shifted to lower frequencies and the intensity of the band decreased. This was attributed to surface roughness [33], which was correlated with the morphology of nanoparticles. From Fig. 6, it can be seen that there were significant differences in the stability of the CO adsorption band for the Pt-C/SiO₂ and Pt-CU/SiO₂ catalysts. For the Pt-C/SiO₂ sample, the intensity of the CO adsorption band at 2050 cm⁻¹ decreased and disappeared at 453 K under N₂ as the purging time increased. In the case of Pt-CU/SiO₂, the intensity of the CO adsorption band at 2012 cm⁻¹ remained

Fig. 6. DRIFT spectra of CO adsorbed over Pt-C/SiO₂ at 453 K (a) and Pt-CU/SiO₂ at 493 K (b).

unchanged at 493 K as the purging time was extended to 8 min. The same phenomenon was also observed over the Pt-O/SiO₂ catalysts (data not presented here), indicating that CO adsorption on the Pt-CU/SiO₂ and Pt-O/SiO₂ catalysts was more stable than on Pt-C/SiO₂.

The red shift with temperature was attributed to surface roughness, which was correlated with the morphology of the nanoparticles. Since CO oxidation was carried out under a gas mixture of 1% CO + 1% O₂ + 98% N₂, DRIFT spectra under the reaction condition were also collected to investigate the behavior of the CO adsorption under the CO oxidation condition. It can be seen that the CO adsorption bands at 373 and 423 K over Pt-C/SiO₂ (Fig. 7(a)) and Pt-CU/SiO₂ (Fig. 7(b)), respectively, disappeared gradually due to reaction with O₂. However, for the Pt-O/SiO₂ catalyst, no significant change in the CO adsorption band was observed (Fig. 7(c)) even at 493 K, suggesting that CO adsorption and reaction over the supported Pt model catalysts were highly dependent on the morphology of the Pt NPs. It has been reported that Pt(100) surfaces were easily roughened since the surface atoms that were arranged in a square

Fig. 7. DRIFT spectra of CO adsorption bands under a mixture of 1% CO + 1% O₂ + 98% N₂ over Pt-C/SiO₂ (a), Pt-CU/SiO₂ (b), and Pt-O/SiO₂ (c) at 373, 423, and 493 K, respectively.

symmetry were mobile [34]. Compared with Pt(100), the roughening of (111) facets required a higher temperature because of the low surface energy. Kung et al. [33] has reported that the Pt(111) surface can be roughened at 673 K. Surface roughness, which generates more low coordinated atoms, would benefit weak CO adsorption and desorption from the surface [35,36]. Strongly adsorbed CO would occupy the active sites on the Pt-O/SiO₂ catalyst and inhibit the adsorption of O₂, which is known as the CO

self-poisoning effect [37,38]. Therefore, the activities of Pt-C/SiO₂ and Pt-CU/SiO₂ for CO oxidation were much higher than that of Pt-O/SiO₂. On the one hand, more low coordinated atoms would be produced on Pt(100) than on the (111) facet, which are necessary for CO desorption and dissociation to form carbon species. The carbon species can be rapidly oxidized by O₂ [36]. On the other hand, unsaturated and low coordinated Pt atoms are also the active sites for O₂ activation, which will accelerate CO oxidation. In summary, Pt NPs with different morphologies undergo different roughening, and thus have different abilities for CO adsorption and activities for CO oxidation.

To further compare the catalytic properties of the supported Pt model catalysts with the different Pt NPs morphologies, the turnover frequencies (TOF) for CO oxidation were calculated [39] in the temperature ranges in which CO conversion varied from 1% to 10%. The starting temperatures were 423, 433, and 563 K for Pt-C/SiO₂, Pt-CU/SiO₂, and Pt-O/SiO₂, respectively. The Arrhenius plot (Fig. 8(a)) was constructed from the TOF data and the calculated activation energies were 98.1, 79.0, and 74.0 kJ/mol over the Pt-C/SiO₂, Pt-CU/SiO₂, and Pt-O/SiO₂ catalysts, respectively. It was reported [40] that the apparent activation energies with Pt(100) and (111) single crystal surfaces were 129 and 98 kJ/mol because the roughness of Pt(100) at low temperature led to an increase in the initial heat of adsorption of CO. The apparent activation energies over the sup-

ported Pt model catalysts can also be attributed to the morphologies of the Pt NPs with the different crystal facets. The TOF values as a function of reaction temperature were very different over the Pt-C/SiO₂, Pt-CU/SiO₂, and Pt-O/SiO₂ catalysts (Fig. 8(b)). The increase of the CO oxidation TOF over Pt-C/SiO₂ was much faster than those over Pt-CU/SiO₂ and Pt-O/SiO₂. In particular, in the case of the Pt-O/SiO₂ catalyst, no significant change in the TOF was observed, which was consistent with the CO adsorption behavior over the Pt-O/SiO₂ catalyst.

3 Conclusions

Well-defined supported Pt model catalysts with different morphologies of the Pt NPs were prepared by a chemical method. CO oxidation was used as a probe to investigate the catalytic properties of the Pt-C/SiO₂, Pt-CU/SiO₂, and Pt-O/SiO₂ catalysts. CO oxidation activity decreased in the order of Pt-C/SiO₂ > Pt-CU/SiO₂ > Pt-O/SiO₂. DRIFT experiments demonstrated that the CO adsorption band on Pt-O/SiO₂ was more stable than the bands over Pt-C/SiO₂ and Pt-CU/SiO₂. This is due to that it was more difficult to roughen the (111) surface. Pt-C/SiO₂ had the highest CO oxidation activity among the three supported Pt model catalysts because the cubic Pt NPs with (100) crystal surfaces were easily roughened and more low coordinated atoms could be generated. This is advantageous for CO oxidation.

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Fig. 8. Arrhenius plot (a) and TOF variety (b) of the Pt-C/SiO₂ (1), Pt-CU/SiO₂ (2), and Pt-O/SiO₂ (3) catalysts.

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