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Article (Dedicated to Professor Yi Chen on the occasion of his 80th birthday)

Nanosized FeO_x overlayers on Pt-skin surfaces for low temperature CO oxidation

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ABSTRACT

Pt-Cu/carbon black catalysts were prepared by an impregnation-reduction method followed by acid leaching. The structure and composition of Pt-Cu nanoparticles treated under different conditions were investigated by inductively coupled plasma atomic emission spectrometry, X-ray diffraction, and X-ray photoelectron spectroscopy. PtCu₃ alloy formed upon annealing Pt-Cu/carbon black catalysts in H₂. Acid leaching produced Pt-Cu nanoparticles consisting of Pt-skeleton surface structure and PtCu₃ alloy core. The Pt-skeleton could be transformed to well-defined Pt-skin structure through further annealing the leached Pt-Cu nanoparticles in H₂. Decorating the Pt-skin surfaces with Fe oxide nanopatches resulted in enhanced reactivity in the preferential oxidation of CO in excess H₂. The tri-component Pt-Cu-Fe catalysts exhibited comparable activity to the bi-component Pt-Fe catalysts but used much less Pt.

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1. Introduction

Many important catalytic processes currently make use of Pt-based catalysts. The high cost and low abundance of Pt means that such processes are being challenged to improve catalytic performance, so Pt usage can be reduced. One route to achieving this is the use of Pt-based multi-component catalysts, where Pt is mixed with other transition metals (TMs) such as Fe [1,2], Co [3–5], Ni [6,7], Sn [8], Mo [9], and Cu [10,11]. Pt-based multi-component catalysts have exhibited improved catalytic performance compared with pure Pt catalysts and use much less Pt.

Various configurations have been proposed for Pt-based multi-component catalysts, including core-shell, alloy, and side-by-side structures. Core-shell nanostructures (TM@Pt) with ultrathin Pt shells encapsulating TM or Pt-TM alloy cores have been widely investigated. For example, Pt skin structures are

commonly used as active structures for electrocatalytic oxygen reduction reactions [12–15]. TM@Pt (TM = Ru, Rh, Ir, or Pd) core-shell nanoparticles [16–18] also exhibit high activity in the low-temperature preferential oxidation of CO in excess H₂ (CO-PROX). Enhanced PROX reactivity has been attributed to an increased density of CO-free Pt surface sites available for O₂ activation, and also a H₂-mediated O₂ activation mechanism at Pt shell surfaces. Ko et al. [19] reported that PtCo alloy nanoparticles are highly active in low-temperature PROX. Komatsu et al. [20] suggested that the formation of Pt₃Co or PtCu intermetallic compounds is responsible for high PROX activity at low temperature.

We recently demonstrated an inverse catalytic system consisting of Pt surfaces decorated with TM (Fe, Co, Ni) oxide nanolayers (TMO-on-Pt), which exhibits high catalytic activity in low-temperature oxidations [21–25]. An interface confinement effect between the TMO and Pt stabilizes coordinatively

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unsaturated (CUS) cations at oxide-Pt boundaries, which are highly active for O₂ activation. The supported inverse nanocatalysts were constructed by decorating Pt nanoparticles with TMO nanopatches, and have been used in CO oxidation reactions. To minimize Pt usage, Cu@Pt core-shell nanoparticles were synthesized by a colloid chemistry method [26,27]. FeO nanopatches supported on Cu@Pt core-shell nanoparticles have been reported to exhibit similar CO conversion efficiency to FeO-on-Pt catalysts, but only use 0.9% Pt rather than 4% Pt in the latter [28]. Ultrathin Pt skin structure can confine active ferrous centers, similar to bulk Pt.

Acid leaching of Pt-based alloy nanostructures can produce Pt-rich surface structures through the preferential removal of less-precious TM atoms from alloy particle surfaces [14,29–34]. Acid leaching is a simple process for obtaining Pt skin surfaces, which can then support highly active TMO nanostructures. Herein, PtCu alloy nanoparticles are leached by acid solutions to produce Pt skin structure, which is used as supports for nanostructured iron oxide. The tri-component catalysts consisting of surface FeO_x nanopatches and surface Pt-rich Pt-Cu nanoparticles exhibit higher PROX activity than pure Pt catalysts. Activity is comparable to that of FeO-on-Pt catalysts, with the tri-component catalyst using much less Pt.

2. Experimental

2.1. Preparation

PtCu/carbon black (CB) samples were prepared by co-impregnation using H₂PtCl₆·6H₂O (Shenyang Nonferrous Metal Research Institute, China) and Cu(NO₃)₂·3H₂O (Tianjin Kemiou Chemical Reagent Co., Ltd., China) precursors. The Pt loading was 1% (mass fraction), and the Pt:Cu molar ratio varied from 1:2 to 1:12. Samples were dried overnight at 60 °C (denoted as-prepared PtCu/CB) and then reduced in pure H₂ at 750 °C for 2 h (donated PtCu/CB@750H₂). For acid leaching, 25 mg of reduced sample was immersed in 25 mL of dilute HNO₃ at room temperature. After filtering and thoroughly washing with deionized water, leached PtCu/CB was obtained. The leached samples were further annealed in H₂ at various temperatures for 2 h. Fe oxide was impregnated into the leached PtCu/CB samples from Fe(NO₃)₃, to produce FeO-on-PtCu/CB.

2.2. Characterization

The as-prepared PtCu/CB or PtCu/CB@750H₂ (25 mg) was washed in 25 mL of HNO₃ solution (29 mmol/L). Pt and Cu concentrations of leached solutions were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES, ICPS-8100, Shimadzu, Japan). Leached PtCu/CB was annealed in air at 550 °C to remove the CB support, and then dissolved in aqua regia. Pt and Cu concentrations of leached solutions were measured by ICP. X-ray diffraction (XRD) patterns were collected on a Rigaku D/Max 2500 diffractometer using Cu K α (λ = 0.15406 nm) radiation. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Scientific ESCALAB 250Xi instrument. Spectra were obtained using

an Al K α X-ray source, with the C 1s peak at 284.6 eV used as a reference for binding energy. In-situ CO chemisorption was carried out at 40 °C on a Quantachrome AUTOSORB-1-MS Chemisorb apparatus.

2.3. Catalytic activity

CO-PROX was carried out in a purpose-built microreactor using gas chromatography (GC, Agilent GC 6890) to analyze the gas composition. The reaction gas composition was CO:O₂:H₂ = 1:0.5:98.5. The gas hourly space velocity (GHSV) was 30000 mL/(g·h). Catalysts were reduced in flowing H₂ at 250 °C for 2 h before reaction. Catalytic performance was investigated from room temperature to 200 °C at a heating rate of 1 °C/min.

3. Results and discussion

Pt nanoparticles initially form upon reducing Pt-TM catalysts. This is because Pt precursors (e.g. H₂PtCl₆) can be reduced at low temperature, and reducing TM-containing precursors needs facilitating by H spillover from the Pt nanoparticles [35,36]. Reducing Pt-TM catalysts at elevated temperatures results in an inward diffusion of 3d-TM atoms toward subsurface regions and the surface segregation of Pt [37–39]. TM atoms at particle surfaces can be dissolved in acid solutions, while those encapsulated by the Pt skin surface structure are unaffected. The Cu distribution at PtCu nanoparticle surfaces and in nanoparticle cores can be studied by acid leaching combined with ICP measurements.

Table 1 shows Cu and Pt ion concentrations leached from PtCu/CB (1% Pt, 1.2% Cu) in various acid solutions. Dilute HNO₃ was first used to wash as-prepared PtCu/CB and PtCu/CB@750H₂. The former contains unreduced Pt and Cu precursor salts, so all Cu and Pt ions are expected to dissolve. The measured Cu and Pt concentrations in Table 1 are in agreement with the Pt and Cu loadings. The amount of Cu leached from PtCu/CB@750H₂ is 86% of that from as-prepared PtCu/CB. Leached PtCu/CB was further treated in 25 mL of aqua regia, which can dissolve all Pt and Cu. The measured Cu amount is 19% of that of as-prepared PtCu/CB, which remains inside nanoparticles after leaching with HNO₃. ICP data from leaching with HNO₃ and aqua regia are consistent with each other, demonstrating that significant Cu remains within nanoparticles after H₂ reduction and HNO₃ leaching. The Pt:Cu molar ratio of leached PtCu/CB is 1:0.9.

The measured Pt:Cu molar ratio of leached PtCu/CB is 1:1 for 1% Pt-0.6% Cu/CB subjected to the same reduction and leaching treatment. However, Pt:Cu ratios for 1% Pt-2.4% Cu/CB and 1% Pt-3.6% Cu/CB samples are much lower. The amount of Cu diffusing within nanoparticles does not continu-

Table 1
ICP-AES measurements of Cu and Pt leached from 1% Pt-1.2% Cu/CB by HNO₃ and aqua regia.

Sample	Acid solution	Cu (10 ⁻⁶)	Pt (10 ⁻⁶)
As-prepared PtCu/CB	HNO ₃	13.4	9.1
PtCu/CB@750H ₂	HNO ₃	11.6	—
Leached PtCu/CB	aqua regia	2.6	9.5

ously increase with increasing Cu loading. Thus, 1% Pt-1.2% Cu/CB is used in all subsequent experiments.

XRD measurements were used to investigate structural changes of PtCu/SiO₂ catalysts treated under different conditions (Fig. 1(a)). Diffraction by CB interferes with that by PtCu, so SiO₂ support was used in XRD measurements. PtCu alloys have face-centered cubic (fcc) structure, with the (111) reflection shifted to higher 2θ compared with that of pure Pt ($2\theta = 39.8^\circ$). The predominant diffraction peak of reduced PtCu/SiO₂ occurs at 42.5° , arising from the PtCu₃ alloy structure. The pattern of the leached sample exhibits a similar diffraction peak position. Thus, only surface Cu is removed during leaching, and particle cores retain the PtCu₃ alloy structure. Leached PtCu nanoparticles are expected to contain a Pt-skeleton surface [40,41], Pt-rich subsurface region, and Cu-rich PtCu₃ alloy core (Scheme 1). After annealing the leached sample in H₂ at elevated temperature, the weak diffraction peak of the PtCu alloy ($2\theta = 41^\circ$) is observed next to that of the PtCu₃ alloy. Deconvolution of the diffraction peak of the leached sample annealed in H₂ at 250 °C shows two distinct alloy phases of PtCu and PtCu₃. This indicates Cu rearrangement in leached PtCu nanoparticles during annealing in H₂. As leaching removes Cu from particle surfaces, a Cu concentration gradient forms between the particle surface and core. Reduction at elevated temperature is

thought to result in a slight outward diffusion of Cu from the Cu-rich core to Pt-rich subsurface, thus forming the PtCu alloy structure. The signal-to-noise ratio of the 1% Pt-1.2% Cu/SiO₂ XRD pattern is low because of the low metal loading and small particle size. XRD measurements of 4% Pt-4.8% Cu/SiO₂ are shown for comparison. A Cu(111) diffraction peak ($2\theta = 43.2^\circ$) of PtCu/SiO₂@750H₂ is observed next to that of the PtCu₃ alloy phase, and the patterns of all other leached samples exhibit only the PtCu₃ peak (Fig. 1(b)). The selective leaching of Cu from near surface regions of Pt-Cu nanoparticles does not result in a PtCu phase at high Pt loading. This is because of the larger nanoparticle size and PtCu₃ phase being predominant within the core.

Samples were further investigated by XPS. Figure 2 shows that all sample spectra contained a Pt 4f peak at 71.3 eV corresponding to Pt⁰, and its intensity did not show any obvious change. All Cu 2p_{3/2} binding energy positions were located at 932.4 eV, which probably arises from the presence of Cu⁰. The presence of surface Cu₂O cannot be excluded because Cu and Cu₂O exhibit similar Cu 2p binding energy [42,43]. Cu 2p peak intensity changes significantly with treatment. The Pt:Cu ratio changes from 1:1.6 in PtCu/CB@750H₂ to 1:0.6 in leached PtCu/CB and to 1:0.8 in leached PtCu/CB reduced at 250 °C. This indicates the selective leaching of surface Cu and slight outward diffusion of Cu upon annealing the leached nanoparti-

Fig. 1. XRD patterns of 1% Pt-1.2% Cu/SiO₂ (a) and 4% Pt-4.8% Cu/SiO₂ (b) subjected to different treatments. (1) PtCu/SiO₂@750H₂; (2) Leached PtCu/SiO₂; (3) Leached PtCu/SiO₂ reduced at 150 °C; (4) Leached PtCu/SiO₂ reduced at 250 °C.

Fig. 2. XPS spectra of the Pt 4f (a) and Cu 2p (b) spectral regions of PtCu/CB@750H₂ (1), leached PtCu/CB (2), and leached PtCu/CB reduced at 250 °C (3). Spectra are normalized to the C 1s peak intensity.

cles.

CO chemisorption was carried out to investigate catalyst surface structure. The CO monolayer uptake of 1% Pt/CB reduced at 750 °C is 13.2 $\mu\text{mol/g}$, and that of PtCu/CB@750H₂ is only 1.7 $\mu\text{mol/g}$. The effect of the Cu alloy weakens CO adsorption at the Pt surface [44,45], and surface Cu also decreases the density of surface Pt sites. The CO monolayer uptake of leached PtCu/CB is 7.3 $\mu\text{mol/g}$. In-situ annealing of this sample at 250 °C in H₂ decreases the CO uptake to 4.4 $\mu\text{mol/g}$. The leaching of PtCu alloy nanoparticles removes surface Cu sites, thus effectively increasing surface Pt sites available for adsorption. As leached nanoparticles have a rough surface Pt skeleton [40,41], which is restructured to well-defined facets upon annealing [29,46]. This change in surface structure may account for the slight decrease in CO uptake after annealing leached PtCu/CB in H₂.

PROX reactions were carried out in the presence of these catalysts. CO conversion, O₂ conversion, and CO selectivity data are shown in Fig. 3. The Pt/CB catalyst with 1% Pt loading was first tested as a comparison. The CO and O₂ conversions are 3% and 4% at room temperature, respectively, and reach 70% and 85% at 200 °C, respectively. PtCu/CB@750H₂ and leached PtCu/CB also exhibit low PROX activity. The CO selectivity data

of these catalysts suggest that a fraction of O₂ reacts with H₂. In summary, the PtCu alloy surface structure and Pt-skin surface structure exhibit PROX activity similar to that of a pure Pt surface.

Various Fe contents were loaded into leached PtCu/CB annealed in H₂ at 250 °C. PROX activity is shown in Fig. 4. The catalyst with 0.075% Fe loading exhibits CO and O₂ conversions of 64% and 67% at room temperature, respectively. When Fe loading increases to 0.15% and 0.3%, catalysts exhibit higher activity, in which CO conversion reaches 90% at room temperature and O₂ conversion is nearly 100% across the entire temperature range. Although catalytic activity varies with Fe loading, CO selectivity is maintained at 90% at room temperature. FeO_x addition significantly increases the reaction activity and selectivity, compared with PtCu/CB@750H₂ and leached PtCu/CB in Fig. 3. For comparison, 1% Pt/CB was annealed in H₂ at 750 °C and loaded with 0.075% Fe to produce FeO-on-Pt. This catalyst exhibited 40% CO conversion and 45% O₂ conversion at room temperature. The catalytic performance of FeO-on-Pt with low Pt loading is similar to our previous findings [28].

The above structural investigation suggests that annealing leached samples decreases their surface area and leads to re-

Fig. 3. PROX CO conversion (a), O₂ conversion (b), and CO selectivity (c) in the presence of Pt/CB@750H₂ (1), PtCu/CB@750H₂ (2), and leached PtCu/CB (3).

Fig. 4. PROX CO conversion (a), O₂ conversion (b), and CO selectivity (c) in the presence of leached PtCu/CB annealed at 250 °C and loaded with 0.075% Fe (1), 0.15% Fe (2), and 0.3% Fe (3), and Pt/CB@750H₂ loaded with 0.075% Fe (4).

construction of their rough surfaces. The effect of annealing temperature on PROX activity of FeO-on-PtCu/CB was therefore investigated. Figure 5 shows PROX activity of the leached PtCu/CB samples, which have been annealed in H_2 at various temperatures and then loaded with 0.15% Fe. For leached PtCu/CB not annealed and annealed at 150 °C, the resulting FeO-on-PtCu/CB catalysts exhibit similar activity with CO and O_2 conversions of ~80% and ~85% at room temperature, respectively. For leached PtCu/CB annealed at 250 °C, the resulting FeO-on-PtCu/CB catalyst exhibits CO and O_2 conversions of 90% and 100% at room temperature, respectively.

From the above characterization, several structural configurations of Pt-Cu nanoparticles are identified and are shown in Scheme 1. Annealing Pt-Cu in H_2 at elevated temperature forms an alloy between Pt and Cu, probably with additional Cu nanopatches at particle surfaces. Acid leaching selectively removes Cu species outside of and at nanoparticle surfaces. Leaching produces Pt-Cu nanoparticles with Pt-skeleton surfaces, which may also influence subsurface regions to a depth of a few monolayers, as suggested previously [29,47]. Following leaching, nanoparticles have Pt-skeleton surfaces and Cu-rich alloy cores (Scheme 1). Restructuring of particle surfaces subsequently occurs upon annealing leached nanoparticles in H_2 , in which

Scheme 1. Schematic showing Pt-Cu nanoparticle structure after various treatments.

the rough Pt-skeleton surface transforms to a well-defined “Pt-skin” structure. A slight outward diffusion of Cu occurs from the PtCu₃ alloy core to Pt-rich near-surface regions.

Leaching and annealing cause a Pt-skin structure formed on a Cu-rich core. This surface structure is not PROX active and exhibits performance similar to that of the pure Pt catalyst (Fig. 3). This differs from the reported high PROX activity of Ru@Pt catalysts [16,17]. Pt-skin surfaces decorated with FeO_x nanopatches exhibit higher PROX activity than FeO-Pt catalysts with similar Pt contents. This further confirms the PROX activity of the oxide-on-Pt structure [25]. Leaching and annealing are a simpler method of preparing Pt-skin structure, compared with sequential polyol processes used to prepare Cu@Pt core-shell nanoparticles [28].

4. Conclusions

A tri-component catalyst consisting of surface FeO_x nanopatches, Pt-skin surface, and Cu-rich PtCu₃ alloy core was prepared. It exhibited high PROX activity and used less Pt than Pt-Fe catalysts. The Pt-skin was prepared by alloying Pt and Cu via annealing in H_2 and subsequent leaching of the PtCu alloy in acid solution. PtCu nanoparticles with Pt-skins exhibit PROX activity similar to that of pure Pt catalysts. Decorating Pt-skin surfaces with FeO_x nanopatches enhances PROX reactivity. Thus, a highly active tri-component catalyst was easily obtained and used much less Pt than conventional analogs.

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Fig. 5. PROX CO conversion (a), O_2 conversion (b), and CO selectivity (c) in the presence of leached PtCu/CB annealed at room temperature (1), 150 °C (2), and 250 °C (3), and then loaded with 0.15% Fe.

Graphical Abstract

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Nanosized FeO_x overlayers on Pt-skin surfaces for low temperature CO oxidation

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The structural transformation of Pt-Cu catalysts upon reduction-leaching treatment is reported. Pt skin surfaces decorated with surface FeO_x nanostructures exhibit enhanced reactivity in CO preferential oxidation and use less Pt than Pt-Fe catalysts.

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Pt-表层限域的表面FeO_x结构用于低温CO氧化反应

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摘要: 通过简单的浸渍-还原并随后在酸性溶液中处理制备了Pt-Cu双金属催化剂. 利用电感耦合等离子体发射光谱、X射线衍射和X射线光电子能谱对不同处理条件下的Pt-Cu纳米粒子的结构和组成进行了表征. 研究发现, Pt-Cu催化剂在高温H₂中还原形成了PtCu₃合金结构, 酸洗处理后形成了包含Pt-骨架(Pt-skeleton)的表面结构和PtCu₃合金核的纳米粒子. 而Pt-骨架结构又可通过在H₂中退火转变为规整的Pt-表层(Pt-skin)结构. Pt-表层表面修饰Fe氧化物后在CO选择氧化反应中表现出较好的催化性能. 通过此方法制备的三金属Pt-Cu-Fe催化剂可达到与Pt-Fe相近的高活性, 并且催化剂中Pt的用量大大降低.

关键词: 一氧化碳氧化; 铂-表层; 铁氧化物; 界面催化

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