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Minireview

Recent progress in CO oxidation over Pt-group-metal catalysts at low temperatures

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ABSTRACT

CO oxidation is probably the most studied reaction in heterogeneous catalysis. This reaction has become a hot topic with the discovery of nanogold catalysts, which are active at low temperatures (at or below room temperature). Au catalysts are the benchmark for judging the activities of other metals in CO oxidation. Pt-group metals (PGMs) that give comparable performances are of particular interest. In this mini-review, we summarize the advances in various PGM (Pt, Pd, Ir, Rh, Ru) catalysts that have high catalytic activities in low-temperature CO oxidation arising from reducible supports or the presence of OH species. The effects of the size of the metal species and the importance of the interface between the metal and the reducible support are covered and discussed in terms of their promotional role in CO oxidation at low temperatures.

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1. Introduction

CO oxidation is a typical heterogeneous catalytic reaction. It is probably the most studied reaction in heterogeneous catalysis, which is not only useful as a model reaction for the fundamental study of reaction mechanisms and the surface properties and nature of catalysts, but also important in many practical applications such as air cleaning, automotive emission control, and removal of CO impurities from H₂ for polymer electrolyte membrane fuel cells (PEMFC) [1–3]. Hopcalite catalysts, which are the oldest commercially available catalysts for removal of CO from air, were discovered in the 1920s [4,5]. They are complex mixtures of CuO and MnO₂ and were developed at John Hopkins University and California University, USA for eliminating CO pollutants in the war. However, this type of cat-

alyst has low thermal stability at room temperature, undesirable behavior under transient cycling conditions, and is easily deactivated in the presence of sulfur and moisture [6,7].

In 1987, Haruta et al. [8,9] reported that an oxide-supported Au catalyst prepared using a wet chemistry method gave an unexpectedly high performance in CO oxidation at low temperatures. The nanoscale Au catalyst was highly dispersed, with good water resistance and stability. Au catalysts became the benchmark system for low-temperature CO oxidation. Interest in the CO oxidation reaction increased during the “gold rush” and as well as being used as from a model reaction to a chemical probe for studying the surface properties of catalysts [1,10,11]. Pt-group-metal (PGMs; Pt, Pd, Ir, Rh, Ru) catalysts have been studied for almost a century since Langmuir’s work [12]; however, they are generally one order of magnitude less

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Fig. 1. Conceptual description of performances of Au and Pt-group-metal catalysts for CO oxidation in terms of the temperature for 50% CO conversion and the magnitude of specific activities.

active than Au catalysts in low-temperature CO oxidation, as shown in Fig. 1. Although much effort has been made to improve their activities in CO oxidation, e.g., by adding promoters or using reducible oxides as supports, the use of PGM catalysts for room-temperature or cryogenic CO oxidation remains a challenge.

In CO oxidation over metal-based catalysts, O_2 adsorption and activation is often regarded as the rate-limiting step [13]. The use of traditional PGM catalysts with inert supports such as SiO_2 , Al_2O_3 , and zeolites is inefficient. On this type of catalyst, there is serious competition between adsorption and activation of CO and O_2 on the metal sites; CO is strongly adsorbed, which seriously hinders O_2 adsorption and activation. A high working temperature ($>100\text{ }^\circ\text{C}$) is therefore needed to weaken CO adsorption and facilitate adsorption of O_2 [14,15]. Effective strategies for weakening the adsorption of CO on PGMs at low temperatures and promoting adsorption and activation of O_2 are therefore needed. Various strategies for improving room-temperature and cryogenic catalytic activities in CO oxidation, such as reducing the PGM particle size from nano to sub-nano or to single atoms, and engineering metal-metal oxide (hydroxide) interfaces, have been used to develop new PGM catalysts (Fig. 1) with adsorption sites on the metal and the support and activation of oxygen in atomic or molecular form.

2. Advanced catalysts for low-temperature CO oxidation

In the past decade, it has been reported that CO conversion at or below room temperature can reach 100% over novel promoted PGM catalysts for CO oxidation or CO preferential oxidation (PROX) in an H_2 -rich stream. In the following sections, we summarize these advances, concentrating on the role of reducible oxide and OH species.

2.1. Reducible promoter or support

Reducible oxides as supports or promoters can supply the sites for O_2 adsorption, significantly improving the

low-temperature activities of PGM catalysts for CO oxidation. Iron oxide has been the most intensively studied metal oxide because of its outstanding promotional effect.

Deng's group focused on improving the CO oxidation performances below room temperature on Pd and Pt metals with FeO_x as a support. They prepared the first FeO_x -supported Pd catalyst with high activity and achieved complete oxidation of CO at $-15\text{ }^\circ\text{C}$ [16]. It was suggested that the partly reduced FeO_x support participated in CO oxidation, acting as an oxygen supply for reactions with CO on Pt and Pd with low-activation energy (30–34 kJ/mol). The presence of an oxygen reservoir on the FeO_x support has opened up new routes in the search for high activity in low-temperature CO oxidation [17,18].

FeO_x promoters can also improve the low-temperature activity in CO oxidation over inert oxide supported PGM catalysts. Shen's group prepared colloidal Pt-Fe bimetallic nanoparticles using a modified polyol method [19]. The prepared nanoparticles were deposited on an Al_2O_3 support. The $PtFe_3/Al_2O_3$ catalyst gave a CO conversion of 99% at $30\text{ }^\circ\text{C}$. Zhang et al. [20] designed a bifunctional catalyst, $IrFe/Al_2O_3$, for the reaction between CO adsorbed on Ir sites and O_2 adsorbed on FeO_x . A ^{57}Fe Mössbauer spectroscopic study suggested that the PROX activity increased with increasing amount of Fe^{2+} sites, and that Fe^{2+} species were the sites for oxygen adsorption [21]. Freund et al. [22] proposed that O adsorbed on FeO produced oxygen-rich FeO_x ($1 < x < 2$) species, which could react with CO over FeO/Pt catalysts. Bao's group suggested that interface-confined coordinatively unsaturated ferrous sites neighboring Pt acted as active centers for O_2 adsorption and activation. This enabled total CO oxidation at room temperature, as shown in Fig. 2 [23]. All these studies show that low-valence Fe sites are critical for low-temperature CO oxidation.

$Fe(OH)_x$, in which the Fe–O bond length is longer than that in traditional Fe_2O_3 , is easily reduced to form Fe^{2+} sites [24]. Zhang et al. [25–29] designed a series of PGM catalysts of Ir, Rh, Pd, Pt based on this property of $Fe(OH)_x$. It was found that $Fe(OH)_x$ generally promoted high dispersion of these metal species at the sub-nanoscale, i.e., around 1 nm, and gave complete CO conversion at room temperature. This versatile design strategy was based on the $Fe(OH)_x$ support promoting the adsorption and activation of O_2 , making the adsorbed oxygen species react with adsorbed CO at the metal-support interface through a noncompetitive Langmuir-Hinshelwood mechanism.

When the Pt loading was decreased to 0.17 wt%, all the Pt species were dispersed as single atoms, without the presence of any clusters or particles [30]. CO oxidation and CO preferential oxidation tests showed that the single-atom catalyst was two to three times more active than the cluster catalyst. However, because of the current limitations of low Pt loading of single-atom catalysts, total conversion of CO can only be achieved at a PEMFC working temperature of $80\text{ }^\circ\text{C}$. It is therefore still a challenge to achieve good performances with such low-loaded single-atom catalysts in certain catalytic reactions or to prepare high-loaded single-atom catalysts that improve the overall performance [31–33].

In addition to iron oxide, other reducible oxides are also effective for PGM-catalyzed CO oxidation. Zhu et al. [34] prepared

Fig. 2. Left: O₂ dissociative adsorption on coordinatively unsaturated ferrous (CUF) sites. Pt, Fe, and O atoms are indicated by blue, purple, and brown balls, respectively; Right: PROX reaction over Pt-Fe/SiO₂ catalysts under the conditions 1% CO, 0.5% O₂, and 98.5% H₂. Space velocity is 36000 mL/g·h reprinted from Ref. [23].

a Pd/CeO₂-TiO₂ catalyst using an incipient wet impregnation method; it gave complete CO conversion at room temperature despite significant deactivation after running for 100 min. It was suggested that the high activity of Pd/CeO₂-TiO₂ was the result of enhancement of CO activation by facilitation of the reduction of Pd²⁺ to Pd⁰, and O₂ activation through improvement of the surface oxygen supply and oxygen vacancy formation. CoO_x acts as a promoter in yttria-stabilized zirconia (YSZ)-supported Pt catalysts. This catalyst with 1 wt% Pt and Pt/Co=10 gave around 100% CO conversion and reduced the CO concentration to below 10 ppm at 60 °C [35]. Similarly, a Ru@Pt core-shell catalyst significantly increased CO conversion compared with that achieved using the monometal catalyst; it gave 100% CO conversion at 20 °C (0.1% CO and 0.5% O₂ in H₂) [36]. All these catalysts can work at room temperature or give good performances in the presence of H₂.

TiO₂ is a popular support on which oxygen atoms or molecular oxygen can participate in low-temperature oxidation of CO [13,37]. Okumura et al. [38] prepared a TiO₂-supported Ir catalyst using a deposition-precipitation method. The Ir species were present as a highly dispersed, 2 nm thick, positively charged layer. This catalyst gave 100% CO conversion at room temperature with 1% CO in air at a space velocity of 20000 mL g_{cat}⁻¹ h⁻¹. Yang et al. [39] found that a special wire-like RuO₂ on TiO₂ catalyst favored dissociative adsorption of O₂ and easy release of adsorbed oxygen, giving it a comparable activity to that of Au/TiO₂. Recently, Yates and co-workers [40] proposed a new reaction mechanism for CO oxidation on Au/TiO₂ in which the weakly adsorbed CO on TiO₂ sites diffused to react with O₂ activated at the interface between Au and TiO₂; CO oxidation at cryogenic temperatures was achieved (Fig. 3). The sequential delivery and reaction of CO first at TiO₂ sites and then at Au sites indicate that the catalytic reaction occurs at the Au nanoparticle perimeters. The role of TiO₂ in the adsorption and activation of CO shows that the reaction mechanism using this new catalyst differs from that at room temperature. The titanate sites, which have neighboring metal nanoparticles, appear to be responsible for opening up this new reaction channel [41]. The feasibility of such a mechanism for PGM-catalyzed CO oxidation at cryogenic temperatures has recently been verified. Guan et al. [42] prepared a novel Rh/TiO₂ catalyst with highly dispersed sub-nano Rh species

(0.4–0.8 nm). Fig. 4 shows that O₂ was easily activated as Rh–O–O–Ti (molecular superoxide species) at the Rh–Ti perimeter sites when Rh was present as sub-nano species. The superoxide reacted with the weakly adsorbed CO on TiO₂ sites, resulting in high activity at cryogenic temperatures, with total CO conversion at –50 °C. This confirms that the performances of PGM catalysts can rival that of the standard Au catalyst in the oxidation of CO far below room temperature.

2.2. Promotional role of OH species

The OH species that come from humidity or are generated as intermediates from H₂ reduction or during the PROX process are unavoidable in low-temperature CO oxidation in practical applications [43]. Usually, a moderate amount of OH species can promote low-temperature CO oxidation over Au catalysts. Daté et al. [44] suggested that water facilitated the activation of oxygen or decomposition of carbonates on Au catalysts. Saavedra et al. [45] recently provided direct evidence of a water-mediated reaction mechanism for room-temperature CO oxidation over an Au/TiO₂ catalyst. They found that the cover-

Fig. 3. Schematic of CO oxidation mechanism on Au/TiO₂, which showed that the CO adsorbed on TiO₂ sites, rather than that on Au sites, readily reacted with the O₂ activated at the interface between Au and TiO₂ at cryogenic temperature reprinted from Ref. [40].

Fig. 4. (a) typical HAADF-STEM image and size distribution of Rh/TiO₂ catalyst; (b) reaction model of CO adsorbed on TiO₂ with O₂ activated at the interface of Rh-TiO₂, which favored the total CO conversion at $-50\text{ }^{\circ}\text{C}$ over this Rh/TiO₂ catalyst reprinted from Ref. [42].

age of TiO₂ with weakly adsorbed water greatly changed the number of active sites and facilitated O₂ binding and activation. The resulting Au-OOH species readily reacted with adsorbed Au-CO, yielding Au-COOH and favoring the production of CO₂.

The effect of OH species is more dominant and important in promotion of CO oxidation over PGM catalysts at low temperatures than in the case of Au catalysts [46]. Smit et al. [47] reported the crucial role of surface OH groups on iron oxides, with which CO reacted to form highly active adsorbed formates, HCOO_(ads). Golunski et al. [48] found that the activity of iron oxide-supported Pd catalysts in CO oxidation was significantly enhanced by short exposure to H₂, without any subsequent thermal treatment. This was mainly related to the large amount of OH derived from the H₂ treatment. Tomita et al. [49] treated alumina-supported Pt/Fe catalysts with water and found that these catalysts could catalyze CO oxidation at temperatures below $0\text{ }^{\circ}\text{C}$, with a low apparent activation energy (9.2 kJ/mol). The OH species even played an important role in inert SiO₂ supported Pt catalysts. Fukuoka et al. [50] synthesized a catalyst consisting of Pt nanoparticles in mesoporous silica, and achieved complete CO conversion at $40\text{ }^{\circ}\text{C}$. The surface OH groups on SiO₂ attacked the adsorbed CO on Pt to form CO₂. The

presence of H₂ significantly enhanced low-temperature CO oxidation involving the formation of OH species. This effect was more pronounced when a reducible oxide or an alkali promoter was present. Xu et al. [51] directly proved that the interfacial CO_{ads} + OH_{ads} reaction on a FeO(111)/Pt(111) inverse model catalyst was facile and produced CO₂ at the Pt-oxide interface at low temperatures; this provides deep insights into the reaction mechanism. Zhang et al. [26,27] found that the use of Fe(OH)_x promoted the formation of OH species during CO oxidation and PROX over Ir/Fe(OH)_x and Rh/Fe(OH)_x catalysts; this greatly lowered the temperature for 100% CO conversion to room temperature and improved the catalyst stability. Fig. 5 shows that these OH species could originate from the reaction between adsorbed O on Fe²⁺ sites and adsorbed H on Ir or Rh sites, or activated H₂O species. They can change the reaction route for CO oxidation so that it occurs through adsorbed CO and OH, with a lower activation energy, rather than through adsorbed CO and O. Flytzani-Stephanopoulos et al. [52] suggested that various alkali metals promoted Pt catalysts by stabilizing atomic Pt species in the form Pt-O(OH)_x. The OH species neighboring the Pt atoms easily react with CO to produce CO₂.

Fig. 5. CO conversion as a function of reaction time at $40\text{ }^{\circ}\text{C}$ over Ir/Fe(OH)_x catalyst for CO oxidation with or without the presence of H₂ or H₂O; the Inset shows the corresponding Arrhenius plot of Ln TOF vs. $1/T$ for CO oxidation reprinted from Ref. [26].

Recently, Chen et al. [53] have made great progress in the development of Pt-based catalysts for room-temperature oxidation of CO via OH species on the catalyst surface. They synthesized iron–nickel hydroxide–platinum (transition metal–OH–Pt) nanoparticles of size less than 5 nm, which can fully remove CO from humid air without activity decay for 1 month. The composition and structure of the Fe–OH–Pt interface showed that the Ni played a key role in stabilizing this interface against dehydration. The OH groups at the Fe³⁺–OH–Pt interface readily reacted with the nearby adsorbed CO to directly yield CO₂ and simultaneously form coordinatively unsaturated Fe sites for O₂ activation. The creation of sub-monolayer hydroxides on noble metal clusters is expected to provide an effective method for preparing efficient PGM catalysts for CO oxidation.

3. Fundamental factors in low-temperature CO oxidation

3.1. Effect of metal species size

The development of characterization techniques for use in heterogeneous catalysis has enabled improved catalyst preparation and design to achieve better catalytic performances. A typical example is the discovery of Au catalysts for CO oxidation. Bulk Au is chemically inert and generally regarded as a poor catalyst. However, highly dispersed nanoscale Au is active in low-temperature CO oxidation. Haruta et al. [54] found that the turnover frequency in CO oxidation at 0 °C increased by one order of magnitude with decreasing Au size from 4 to 2 nm, as shown in Fig. 6. This discovery has caused much excitement in nanocatalysis. In particular, the great advances in high-resolution transmission electron microscopy have enabled the critical role played by the particle size to be observed experimentally. Herzing et al. [55] used aberration-corrected scanning transmission electron microscopy to identify bilayer Au clusters of size ~0.5 nm as the active centers for CO oxidation over an Au/Fe₂O₃ catalyst. Qiao et al. [56] prepared an Au₁/Co₃O₄ single-atom catalyst with an Au loading of only 0.05 wt%, which gave almost 100% CO conversion at room temper-

ature. They found that the Au₁/CeO₂ single-atom catalyst was highly active, selective, and extremely stable in preferential CO oxidation in a H₂-rich stream, giving >99.5% CO conversion over a wide temperature window, 50–100 °C. This suggests that Au single-atom catalysts have potential applications [57].

Based on the significant effect of the Au particle size, the effect of changing the PGM particle size on the catalytic activity in CO oxidation was investigated. Initially, it was believed that the Pt particle size had little effect on the CO oxidation activity [54]. Fig. 6 shows that the turnover frequency decreased or remained constant for PGMs with particle sizes lower than 5 nm. However, one crucial point ignored in those studies was that the particles investigated were mostly larger than 2 nm. PGMs with sub-nanoclusters or single atoms were not considered in CO oxidation. A comparison of PGMs and Au shows that CO adsorption is much stronger on PGMs, and this is a crucial cause of their lower activities. Electronic structures and properties can be greatly modified by reducing the particle size to sub-nanometer (~1 nm) [58–61]. For Pd metal, when the particle size decreased from nano- to sub-nano-clusters, CO adsorption was much weakened because the fraction of linear CO adsorption, which is more weakly bonded than bridged and multi-bonded species, increased with decreasing particle size [29,62,63]. This favors CO desorption and prevents CO poisoning of Pd in low-temperature oxidation of CO. However, for Pt, Ir, and Rh, it was found that the metal species on sub-nano catalysts were more positively charged than those on nanosized ones [25–28]. CO adsorption microcalorimetry and Fourier-transform infrared spectroscopy provided direct and quantitative evidence of the decreased strength of CO adsorption from nano to sub-nano species; this can increase the activity in CO oxidation by two orders of magnitude. This is a versatile strategy for PGM catalyst design, enabling total conversion of CO to CO₂ at room temperature. On further decreasing the size to single atoms, the PGM can be stabilized in the form of positive, high-valent atoms with the oxide support connected through oxygen bridges. This helps to reduce the CO adsorption energy and the activation barriers to CO oxidation. PGM single-atom catalysts on active or inert oxide supports are therefore expected to give good performances in CO oxidation [30,64,65].

3.2. Importance of interface

In modern catalyst design strategies, consideration of the indispensable role of the support is important for achieving higher performance [66–68]. The properties of heterogeneous catalysts are often determined by the synergy between the support and metal species, and the active sites are located at the metal–support interface. Bao et al. [23] used a specific preparation method to ensure that the Pt metal species on Pt/SiO₂ and PtFe/SiO₂ were all of size around 2 nm. The Fe species were present mainly on the outer layers of the Pt–Fe nanoparticles as small patches for the construction of a FeO-on-Pt inverse catalyst. The preferential adsorption and activation of O₂ over these coordinatively unsaturated ferrous sites on the interface prevented poisoning by CO, and the

Fig. 6. Turnover frequency of CO oxidation over Au and Pt catalysts as a function of particle size above 1 nm reprinted from Ref. [54].

strength of CO adsorption on the Pt metal was much decreased. A catalyst consisting of FeO on an ultrathin Pt layer with Cu as an alternative core can impose the same constraint; the Pt interface is decorated with FeO patches but much less Pt is used [69]. This type of catalyst gave total CO conversion at room temperature, similar to the case of Pt nanoparticles covered with surface FeO patches, indicating that the oxide–Pt interface plays a crucial role in CO oxidation. These “oxide-on-metal” catalysts provide a new architecture with enhanced catalytic performance.

The length of the metal–support interface can be tailored exactly by ensuring that the metal species size is monodispersed. Cargnello et al. [70] prepared monodisperse Pd and Pt nanoparticles by thermally decomposing metal (II) acetylacetonates; quantitative control of the metal size can be achieved by varying the surfactant concentration and reaction temperature. Metal–support interfaces of various sizes were obtained by depositing these particles on an active CeO₂ support, as shown in Fig. 7. The CeO₂-based metal catalysts showed strongly size-dependent activity. The CO oxidation rate decreased with increasing nanoparticle size in all cases. Model analysis results showed that the metal atoms at the nexus of the metal, support, and atmosphere were the active sites for CO oxidation, and smaller particles led to an increased boundary length and higher activity. Size-selected nanoparticles can be used to identify the role of interfacial sites in CO oxidation. Control of the contact dimension of the metal–support interface is another crucial factor in improving the length of interface sites. A study of the role of the Pt–Fe interface in maximizing the quantity of OH species provided direct evidence of this aspect, i.e., that the active species is an Fe³⁺–OH–Pt ensemble [53]. As shown in Fig. 8, to maximize the Pt–Fe interface, an alloy-assisted strategy was developed instead of a core-shell one which was not an ideal solution because most Pt atoms

Fig. 7. (a) Schematic illustration of the length of metal–support interface by controlling the size of metal species; (b) A model analysis of number of sites and TOF for CO oxidation at 80 °C with a particular geometry (surface and perimeter or corner atoms in contact with the support) reprinted from Ref. [70].

Fig. 8. Schematic illustration of the length of metal–support interface by changing contact dimension between metal and support reprinted from Ref. [53].

were not located on the surface. High-temperature-air-aged PtFeNi nanoparticles formed particles with interwoven, highly irregular structures on their surfaces. The number of Pt–OH–M sites on the PtFeNi catalysts can be increased by high Pt dispersion, and coordination of a high number of O species with Pt. If the Pt–Fe contact length is greater, a higher amount of OH species remain at the interface. Catalysts with such structures are highly stable, both in the reaction stream and during prolonged storage. The metal–support interactions can be changed by varying the metal size or the contact dimension; this enables clear and fundamental recognition of the interface sites between the metal and support in the low-temperature oxidation of CO.

4. Summary and remarks

The pioneering work by Haruta et al. which showed that CO could be oxidized over Au catalysts at low temperatures, initiated the research hot topic of nanocatalysis, and led to in-depth investigation of whether this goal can be achieved by tailoring PGM-based catalysts to have properties similar to those of Au catalysts. In this mini-review, we summarized recent advances in high-performance PGM catalysts for CO oxidation at or below room temperature. Weakening CO adsorption or providing alternative sites for O₂ adsorption/activation (or both) provides the basic strategy for enhancing the low-temperature activities of PGMs. Some excellent contributions have been made and fundamental recognition of active sites or species for designing highly effective catalysts has been achieved.

The fast development of nanotechnology has enabled the development of strategies for accurately controlling catalyst structures by decreasing the metal species size from nano to sub-nano, or even to single atoms, and engineering metal–metal oxide (hydroxide) interfaces. The PGM particle size can be changed in parallel with a change in the valence state from zero-valent to positive. In particular, maximum dispersion of PGMs in the form of single atoms gives positively charged, high-valent states. These factors help to reduce both the CO adsorption strength and activation barriers to CO oxidation. The metal–support interfaces can be engineered to favor CO oxidation with direct participation at the perimeter. Maximizing the length of the metal–support interface enables the active metal species or OH species to be tailored, which can change the CO oxidation route from a reaction of CO with oxygen species to one with OH species.

Advances in characterization techniques have enabled new catalysts or reaction routes for CO oxidation at or even far below room temperature to be identified. Adsorbed CO is supplied not only from metal sites but also from the support. CO adsorption on a TiO₂ support is much weaker than that on Rh sites, which acts as active species; this enables Rh/TiO₂ to catalyze CO oxidation at low temperatures. Furthermore, it is clear that O₂ activation is generally a key step in CO oxidation; however, O₂ is easily dissociated to atomic oxygen species on PGMs, and these can only react with CO above room temperature. Charge transfer from the support, probably from the metal-support interface sites, to the adsorbed O₂ species favors the formation of negatively charged molecular O₂ species such as superoxides or peroxides. These oxygen species are active and favor CO oxidation even at cryogenic temperatures. We therefore believe that a wide range of PGM catalysts with excellent performances, even comparable to those of Au catalysts, in CO oxidation at room temperature and cryogenic temperatures, will be developed.

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Graphical Abstract

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Recent progress in CO oxidation over Pt-group-metal catalysts at low temperatures

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This mini-review summarized the advances of various PGM (Pt, Pd, Ir, Rh, Ru) catalysts for CO oxidation at low temperatures in the past decade, especially those exhibiting comparable performance with the standard gold catalyst.

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铂族金属催化剂低温 CO 氧化研究近期进展

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摘要: CO 氧化可能是多相催化领域最常见的反应, 它不仅能作为探针反应研究催化剂结构、反应活性位等, 而且在诸多实际过程如空气净化、汽车尾气污染物控制、燃料电池所用氢源净化等扮演重要角色。最早的 CO 氧化催化剂为霍加拉特剂, 其组分主要为 CuO 与 MnO₂ 混合氧化物, 然而在实际应用过程中存在低温活性低、吸湿易失活等缺点。1987 年, Haruta 等发现湿化学法制备的氧化物负载 Au 催化剂表现出非常高的低温 CO 氧化活性及耐水稳定性, 其 Au 粒子以纳米尺度分散, 进而引发了催化研究领域的“淘金热”及纳米催化研究热潮。而 CO 氧化通常作为考察 Au 催化剂结构性质的探针反应, 也成为考核其它金属催化剂是否具有高活性的判据之一。

Pt 族金属上 CO 氧化反应从 Langmuir 等研究开始至今已有 100 多年, 然而低温下该金属催化剂活性与 Au 催化剂相比要低一个数量级。本质原因为 Pt 族金属上 CO 吸附较强, O₂ 吸附与活化受到抑制, 而该步骤被认为是 CO 氧化的速控步, 因而表现出较低的催化活性。通常 Pt 族金属催化剂需要 100 °C 以上 CO 才能脱附, O₂ 进而得以吸附。目前研究人员采取多种策略, 其基本原则为削弱 Pt 族金属上 CO 吸附强度或者提供其它活性位供 O₂ 吸附与活化。本综述将概括近十年来

Pt 族金属催化剂 CO 氧化研究进展, 主要总结室温甚至超低温条件下的研究成果.

高活性 CO 氧化催化剂主要是通过采用可还原氧化物为载体或助剂, 或者改变催化剂表面性质如使表面富 OH 基物种来形成. Au 催化剂的研究发现, 改变金属粒子尺寸极有可能获得不同寻常的催化性能, 而常规的 Pt 族金属催化剂研究主要是在纳米尺度. 近期人们发现逐渐减小 Pt 族金属粒子尺寸, 从纳米到亚纳米甚至单原子时, 其电荷状态逐渐呈正价形式, 这有利于削弱其 CO 吸附强度. 此外, 可通过增强金属载体间的相互作用, 改变金属载体接触方式, 如从核壳到交叉联结结构, 构筑出更多的金属载体界面, 使得 O₂ 更容易吸附与活化或稳定更多的 OH 基物种进而在此界面与吸附的 CO 反应.

伴随着表征技术的发展, CO 氧化机理的认识也更加深入, 这给催化剂的设计带来更多新的思路. (1) 改变 CO 吸附活化位, 将 CO 吸附活化位从金属转移到载体上, 从而大大降低 CO 吸附强度, 活化的 CO 物种在反应过程中容易溢流到金属载体界面处, 这甚至有利于超低温下 (–100 °C 左右) CO 氧化. (2) 改变 O₂ 活化形式. O₂ 通常在 Pt 族金属上容易以解离氧原子形式存在, 通过改变载体、金属载体界面性质使得 O₂ 以分子氧形式活化, 如形成超氧或过氧物种, 这有利于降低 CO 氧化的活化能垒, 进而提高其低温甚至超低温下 CO 氧化活性. 今后, 设计并合成出在超低温下能够氧化 CO 的 Pt 族金属催化剂将成为 CO 氧化催化剂研究的重要方向之一.

关键词: 一氧化碳氧化; 金; 铂族金属; 低温; 尺寸效应; 界面

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