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Dynamic structural changes of perovskite-supported metal catalysts during cyclic redox treatments and effect on catalytic CO oxidation

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ABSTRACT

CaTiO₃- and BaTiO₃-supported Ag and Pt catalysts were subjected to cyclic oxidation and reduction treatments and their surface structures were investigated using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The CO oxidation reactions over the Ag and Pt catalysts showed that the oxidized Ag/oxide catalysts performed better in CO oxidation than the reduced ones did, whereas the reduced Pt/oxide catalysts had higher CO oxidation activity than that after oxidation treatment. The XRD and XPS measurements revealed that the oxidation treatment helped to improve the dispersion of Ag nanoparticles, but their metallic state was retained, which enhanced CO oxidation. In contrast, the surfaces of the Pt nanoparticles were dominated by PtO₂ after the oxidation treatment, which lowered the CO oxidation activity compared with that of the reduced Pt catalyst.

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1. Introduction

Perovskite oxides (ABO₃) have important applications in heterogeneous catalysis because of their unique crystal structures and chemical properties. Perovskite oxides can be directly used to catalyze many reactions, e.g., BaMO₃ (M = Pb, Bi, Sn) for catalytic combustion of methane [1], LaMO₃ (M = Cr, Mn, Fe, Co, Ni) for oxidation of propylene [2], and LaCoO₃ for CO oxidation [3]. The A and B sites in the ABO₃ structure can both be partially substituted by other cations to form A_{1-x}A'_xB_{1-y}B'_yO_{3-δ} (A' = noble metal, B' = transition metal) composite oxides, which show excellent performances in many catalytic reactions. For instance, LaFe_{0.57}Co_{0.38}Pd_{0.05}O₃ [4] and LaFe_{0.95}Pd_{0.05}O₃ [5] catalysts are used in automotive emissions

control, and LaMO₃ (M = Mn, Fe, Co, and Ni) [6] and La_{0.6}Sr_{0.4}CoO_{3-δ} [7] catalysts give high performances in solid-oxide fuel-cells. Making use of their high chemical and thermal stabilities, these oxides can be used as supports for high-temperature catalytic reactions, e.g., Pt/La_{0.7}Sr_{0.2}Ce_{0.1}FeO₃ [8] and Pt/La_{0.5}Ce_{0.5}MnO₃ [9] catalysts in lean-deNO_x reaction, and Ag/LaMnO₃ [10] and Pd/LaMnO₃ [11,12] catalysts in the total oxidation of methane.

In perovskite-based catalysts, the surface structure of the catalyst depends sensitively on the pretreatment conditions. The chemical composition, atomic structure, and chemical state of the catalyst surface often exhibit dynamic changes in various gaseous environments. Among many pretreatment conditions, reduction and oxidation are the most frequently used process-

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es. The redox pretreatments affect the surface structure and, thus, the activity of the catalyst. Changes in the catalyst structure in response to various redox pretreatments may help in understanding the mechanisms of catalyst activation and deactivation [13,14]. For example, Nishihata et al. [4,5] have proposed “intelligent” catalysts, in which perovskite $\text{LaFe}_{0.57}\text{Co}_{0.38}\text{Pd}_{0.05}\text{O}_3$ and $\text{LaFe}_{0.95}\text{Pd}_{0.05}\text{O}_3$ catalysts were successfully used in automotive emissions control. When the catalysts were subjected to oxidizing conditions, noble metal atoms were incorporated into the perovskite lattice, and the activity decreased significantly. In contrast, the noble metal ions segregated on the oxide surfaces to form metal nanoparticles under reducing conditions, accompanied by an increase in the activity. During the reaction, the catalysts were subjected to alternating oxidation and reduction conditions, and the noble metal underwent reversible structural changes between metal cations in the oxide lattice and metal nanoparticles on the oxide surface, which prevented the sintering of metal particles and achieved self-regeneration of the catalysts. Scott group studied the treatment-structure-reactivity relationships of $\text{BaCe}_{0.95}\text{Pd}_{0.05}\text{O}_3$ catalysts [15,16]. They found that Pd atoms were doped in BaCeO_3 lattice after oxidation treatments, which produced a large number of oxygen vacancies in the oxide and enhanced CO oxidation activity. Under reducing conditions, Pd segregated on the surface to form nanoparticles, which caused a decrease in the CO oxidation activity. The Nishihata's group and Susannah's group have demonstrated opposite dependences of reactivity on redox treatments in perovskite-based catalysts, and the difference has not been explained very well. Here, we studied the structure and CO oxidation activity of Pt and Ag catalysts supported on perovskite oxides. Opposite dependences of the catalytic performance on the redox treatment was observed for the perovskite-supported Pt and Ag catalysts. Based on structural investigations, the different structural changes in the supported Pt and Ag catalysts in response to the redox treatments were used to explain their different catalytic behaviors.

2. Experimental

2.1. Catalyst preparation

BaTiO_3 (BTO)-supported Pt and Ag catalysts were prepared using a sol-gel method [17]. Typically, 2.0 g of BaCO_3 were dissolved in glacial acetic acid in a molar ratio of 1:10. In parallel, appropriate amounts of titanium(IV) butoxide, acetylacetone, and butanol in molar ratios of 1:2:5 were mixed to form a uniform solution. The BaCO_3 solution was added dropwise to this solution, and the mixture was stirred vigorously for 1 h. Then, 1 ml of 0.5 mol/L AgNO_3 or 1 ml of 0.5 mol/L $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ solution was added to the obtained solution and stirred at 50 °C. The resulting gel was dried at 100 °C for 10 h in an oven, and then calcined in air at 800 °C for 2 h. The obtained samples were designated as oxidized samples (M/BTO-Oxidized). The reduced samples (denoted by M/BTO-Reduced) were obtained by heating the oxidized samples in H_2 at 800 °C for 2 h. The reduced samples were calcined in air at 800 °C for 2 h, produc-

ing the reoxidized samples (M/BTO-Reoxidized).

CaTiO_3 (CTO)-supported metal catalysts were prepared using a similar sol-gel method [18]. Tetrabutyl titanate, $\text{Ca}(\text{NO}_3)_2$, and citric acid were dissolved in anhydrous ethanol and dispersed ultrasonically. Then 1 ml of AgNO_3 solution (0.5 mol/L) or $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ solution (0.5 mol/L) was added to the mixture. Using the same drying and calcining processes, the oxidized samples were obtained (M/CTO-Oxidized). Reduced (M/CTO-Reduced) and reoxidized samples (M/CTO-Reoxidized) were obtained using the same processes as for the M/BTO samples. In all the catalysts, the molar ratio of Ag or Pt to the oxide support was set at 0.05.

2.2. Catalyst characterization

X-ray diffraction (XRD) measurements were performed using a Rigaku D/MAX-RB X-ray diffractometer with $\text{Cu } K_\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$), operated at 40 kV and 200 mA at room temperature, with a scanning rate of 5°/min. X-ray photoelectron spectroscopy (XPS) studies were carried out using a VG ESCALAB MK2 instrument with an Al K_α excitation source ($h\nu = 1486.6 \text{ eV}$). The analyzer mode was set at a constant pass energy of 20 eV.

2.3. Catalyst activity

CO oxidation was carried out in a laboratory-built four-channel microreactor, in which four samples can be evaluated in parallel. The products were analyzed using an online six-channel mass spectrometer (Omnistar GSD 301 O2&GSS 300). The reaction gas consisted of 1% CO, 20% O_2 , and 79% He. The gas hourly space velocity was calculated to be 12000 ml/(g·h). The catalytic performance was evaluated using a temperature-programmed reaction process, with the reaction temperature ramped from room temperature to 300 °C at a ramping rate of 1 °C/min. For quantitative analysis of the CO conversion, one of the four channels was kept empty to have reference signals from the input reactants [19]. The bed temperature when the CO conversion reached 90% is denoted by T_{90} .

3. Results and discussion

3.1. Structural change of Ag/ ABO_3 catalysts with redox treatments

The structural changes in the BTO- and CTO-supported Ag catalysts with cyclic oxidation and reduction treatments were investigated using XRD (Fig. 1). The XRD patterns for the BTO and Ag/BTO samples are shown in Figure 1A. Diffraction peaks from the cubic BTO structure are clearly visible in each pattern (JCPDS 86-1570), suggesting that a well-crystallized perovskite structure was obtained using the sol-gel method. After the oxidation and reduction treatments, the patterns of all Ag/BTO samples show obvious peaks of metallic Ag ($2\theta = 38.2^\circ, 44.5^\circ, 64.5^\circ$; JCPDS 01-1167), and no diffraction peaks from Ag_2O are observed. In addition, the main BTO peaks have not shifted in

Fig. 1. XRD patterns of Ag catalysts supported on BTO (a) and CTO (b), and treated in oxidizing and reducing atmospheres. (1) Pure perovskite oxides; (2) Oxidized samples; (3) Reduced samples; (4) Reoxidized samples. The insets show the Ag(111) diffraction peaks.

the Ag/BTO samples compared with the pure BTO sample, indicating that the Ag species are present in the sample in the form of supported nanoparticles, not as a dopant. Figure 1(b) shows similar results for the Ag/CTO system, in which metallic Ag also remains as particles on the oxide surface.

Quantitative analysis of the Ag(111) diffraction peaks shows that the full-width at half-maximum (FWHM) of the peak becomes smaller when the oxidized sample is reduced in H_2 for 2 h at 800 °C. After the second oxidation treatment, the FWHM of the Ag(111) peak increases again. These changes suggest that the crystallite size of the Ag nanoparticles varies with the oxidation-reduction treatments. For the Ag/BTO-Oxidized sample, the crystallite size of Ag is calculated to be 33 nm, using the Scherrer equation; this increases to 47 nm after the subsequent reduction process. Finally, it decreases again to 32 nm after the second oxidation. The BTO-supported Ag nanoparticles therefore undergo a dispersion-aggregation-redispersion process in the oxidation-reduction-reoxidation treatments. For the Ag/CTO sample, the calculated particle size changes from 34 to 56 to 33 nm during the oxidation-reduction-reoxidation process, which indicates that the Ag nanoparticles supported on CTO surfaces are subject to similar dispersion-aggregation-redispersion changes.

Our previous studies have shown that high-temperature oxidation treatments of Ag catalysts result in dispersion of Ag nanoparticles on SiO_2 supports, whereas reduction treatments in H_2 at high temperatures induce aggregation of Ag nanoparticles [20]. The present results are similar to those observed in

our other work. We suggest that Ag nanoparticles are oxidized to form highly dispersed Ag oxide structures in the initial oxidation stage. At higher oxidation temperatures, the surface Ag oxides decompose and produce metallic Ag nanoparticles. The oxidation-decomposition process occurring in the oxidation treatment therefore helps to improve the dispersion of Ag nanoparticles. In contrast, Ag nanoparticles continue to aggregate during the reduction process, which results in a continuous increase in the Ag particle size.

Figure 2 shows the Ag 3d XPS spectra of Ag catalysts supported on BTO and CTO, treated under different conditions. After the oxidation and reduction treatments, the Ag $3d_{5/2}$ binding energies of all the Ag/BTO samples remain at 368.3 eV, which is from metallic Ag [21,22]. In contrast, the Ag 3d peak intensity changes significantly with the treatment. The reduced sample has a much lower intensity than the oxidized samples. Quantitative analysis shows that the ratio of Ag 3d and Ti 2p peak areas (Ag 3d/Ti 2p) changes from 17.32% for the oxidized sample to 7.29% for the reduced sample. After further oxidation, the Ag 3d/Ti 2p value increases to 10.12%. The XPS results show that the high-temperature reduction leads to aggregation of Ag particles, so the Ag 3d intensity becomes lower. This result is consistent with the above XRD data (Fig. 1(a)). For the Ag/CTO samples, similar XPS results were observed in the redox treatment process (Fig. 2(b)).

The XRD and XPS measurements both demonstrate that Ag species were well dispersed on the surfaces of BTO and CTO under oxidizing conditions. After reduction at high temperatures, the dispersed Ag nanoparticles aggregated significantly. Further oxidation treatment caused redispersion of the Ag nanoparticles.

Fig. 2. Ag 3d XPS spectra of Ag catalysts supported on BTO (a) and CTO (b), treated in oxidizing and reducing atmospheres.

3.2. Structural changes in Pt/ ABO_3 catalysts with redox treatments

Figure 3 shows the XRD patterns of Pt catalysts supported on BTO and CTO, and treated under various conditions. Peaks from the cubic BTO structure are clearly visible in each pattern (Fig. 3(a)). The lattice parameters and cell volume of the perovskite oxides are the same as those of the pure BTO sample. The patterns for the Pt/BTO samples show obvious diffraction peaks of metallic Pt ($2\theta = 39.8^\circ, 46.2^\circ, 67.4^\circ$; JCPDS 04-0802). No diffraction peaks from PtO_x crystallites are observed. The FWHM of the Pt(111) diffraction peaks of all the samples do not show any significant changes. The Pt crystallite sizes, calculated using the Scherrer equation, are all around 35 nm for the oxidized, reduced, and reoxidized samples.

Figure 4 displays the Pt 4f XPS spectra of Pt catalysts supported on BTO and CTO, and treated under various conditions. The Pt 4f_{7/2} peak acquired from the Pt/BTO-Oxidized sample can be deconvoluted into two component peaks at 71.8 eV and 75.4 eV, which are assigned to metallic Pt and PtO_2 , respectively [23,24]. In this spectrum, the component at 75.4 eV is dominant, indicating that the surface of the Pt nanoparticles is mainly composed of Pt oxide. After the subsequent reduction, the Pt 4f_{7/2} binding energy appears at 71.8 eV, which suggests that the particle surface has been reduced to metallic Pt. Upon reoxidation, the Pt 4f_{7/2} spectrum is again dominated by the PtO_2 signal. Quantitative analysis of the peak intensity shows that the peak area ratios of Pt 4f and Ti 2p are 10.4%, 10.8%, and 8.3% for the Pt/BTO-Oxidized, Pt/BTO-Reduced, and

Pt/BTO-Reoxidized samples, respectively. The dispersion of Pt nanoparticles is therefore almost the same after the different treatments. These results are consistent with the XRD analysis (Fig. 3). Accordingly, it can be concluded that for the Pt/BTO and Pt/CTO catalysts, PtO_2 is the major surface Pt species under oxidation conditions, and the surface Pt remains metallic after reduction. In all the treatments, the size of the Pt nanoparticles did not obviously change.

3.3. CO oxidation activity

Figure 5 shows the catalytic activities of Ag catalysts supported on BTO and CTO in CO oxidation. Pure perovskite oxides are almost inert in the reaction. Ag loading substantially increases the CO oxidation activity. For the Ag/BTO-Oxidized catalyst, T_{90} is observed at 245°C . After reduction, the activity shows an apparent decrease, with T_{90} at 295°C . Reoxidation results in full recovery of the activity. For the Ag/CTO catalysts, the CO oxidation behavior shows similar changes in activity with the treatment conditions. Forni et al. reported that metallic Ag and Ag^+ species in $Sr_{0.9}Ag_{0.1}TiO_{3\pm\delta}$ catalysts played an important role in the combustion of methane [25]. Rossetti et al. found that the activity in the catalytic combustion of methane of a $LaCoO_3$ -supported Ag catalyst increased with decreasing Ag nanoparticle size [26]. Metallic Ag nanoparticles therefore play a key role in catalytic oxidation reactions for perovskite-supported Ag catalysts. Based on the XRD and XPS characterization results, we have shown that the redox treatment can change the dispersion of perovskite-supported Ag nanoparticles. Accordingly, the observed higher activity over the oxidized and reoxidized Ag catalysts can be attributed to

Fig. 3. XRD patterns of Pt catalysts supported on BTO (a) and CTO (b), and treated in oxidizing and reducing atmospheres. (1) Pure perovskite oxides; (2) Oxidized samples; (3) Reduced samples; (4) Reoxidized samples. The insets show the Pt(111) diffraction peaks.

Fig. 4. Pt 4f XPS spectra of Pt catalysts supported on BTO (a) and CTO (b), and treated in oxidizing and reducing atmospheres.

Fig. 5. CO conversions in CO oxidation reaction (1% CO, 20% O₂, and He balance) over Ag catalysts supported on BTO (a) and CTO (b).

Fig. 6. CO conversions in CO oxidation reactions (1% CO, 20% O₂, and He balance) over Pt catalysts supported on BTO (a) and CTO (b).

improved dispersion of the Ag catalysts.

Figure 6 shows the catalytic activity of Pt catalysts supported on BTO and CTO. For the Pt/BTO-Oxidized sample, T_{90} is 240 °C. After reduction, the CO oxidation activity apparently increases, and T_{90} is lowered by 60 °C; the second oxidation decreases the activity again (T_{90} = 237 °C). CO oxidation over the Pt/CTO catalysts exhibit similar results to those with the Pt/BTO catalysts (Fig. 6(b)). It has been well documented that metallic Pt is the active species in CO oxidation reactions. The reduction treatment produces metallic Pt, as shown by XRD and XPS measurements, and thus it can be expected that the performances of reduced Pt/ABO₃ samples will be better than those of the oxidized ones.

4. Conclusions

Perovskite-supported Ag and Pt catalysts showed reversible structural changes and oxidation catalysis performances during cyclic oxidation and reduction treatments. For perovskite-supported Ag catalysts, the high-temperature oxidation treatment induced dispersion of Ag nanoparticles, which enhanced the CO oxidation activity compared with that of the catalyst after high-temperature reduction treatment. For perovskite-supported Pt catalysts, the size of the Pt nanoparticles was almost unchanged in the redox treatments. The active metallic Pt structure dominated the Pt particle surface under reduction conditions, whereas oxidation produced surface Pt oxide structure, lowering the CO oxidation activity.

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Graphical Abstract

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Dynamic structural changes of perovskite-supported metal catalysts during cyclic redox treatments and effect on catalytic CO oxidation

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Perovskite-supported Ag and Pt catalysts show reversible structural changes and oxidation catalysis performance during cyclic oxidation and reduction treatments. Supported Ag catalysts show better performance after oxidation treatment, whereas supported Pt catalysts have enhanced activity after reduction treatment.

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钙钛矿型氧化物负载纳米金属催化剂结构的动态调变及其催化氧化CO反应性能

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摘要: 研究了钛酸钡和钛酸钙负载的Ag和Pt纳米催化剂的表面结构随氧化-还原处理过程的动态变化及其对CO完全氧化反应性能的影响。发现氧化物负载的Ag催化剂在氧化处理后其催化活性较还原处理的高; X射线衍射(XRD)和X射线光电子能谱(XPS)表征结果表明, 氧化处理能够提高载体表面Ag颗粒的分散度, 而还原处理导致Ag颗粒的聚集, 从而降低了催化氧化CO反应的活性。氧化-还原处理改变了负载Ag纳米粒子的尺寸并影响其CO氧化反应活性。与此相反, 氧化物负载的Pt催化剂在还原处理后所表现出的CO氧化反应活性较氧化处理的高; 对比研究发现, 氧化和还原处理后Pt纳米粒子的尺寸基本相同, 但是氧化处理的样品中Pt表面物种以氧化态为主, 而还原处理后Pt表面物种主要为金属态。Pt纳米粒子表面化学状态随氧化-还原处理的调变是导致表面催化活性差异的主要原因。

关键词: 钙钛矿氧化物; 银; 铂; 氧化-还原; 结构调变; 一氧化碳氧化

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1. 前言

钙钛矿氧化物是一类具有 ABO_3 结构的无机材料, A通常为碱金属或稀土金属与氧形成十二配位结构, B通常为过渡金属与氧形成六配位结构. 由于该类氧化物所具有的独特晶体结构和化学性质, 其在多相催化中有着重要应用. 首先, 钙钛矿氧化物可直接作为催化剂催化相关反应, 例如 $BaMO_3$ ($M = Pb, Bi, Sn$)用于甲烷的部分氧化^[1], $LaMO_3$ ($M = Cr, Mn, Fe, Co, Ni$)用于丙烯氧化^[2], $LaCoO_3$ 用于CO氧化等^[3]. 此外, 钙钛矿结构中A和B位离子可以实现部分替代, 形成 $A_{1-x}A'_x B_{1-y}B'_y O_{3-\delta}$ 复合氧化物, 这种金属掺杂的钙钛矿氧化物在许多催化反应中表现出优异的性能. 例如 $LaFe_{0.57}Co_{0.38}Pd_{0.05}O_3$ ^[4]和 $LaFe_{0.95}Pd_{0.05}O_3$ ^[5]催化剂用于汽车尾气的净化, $LaMO_3$ ^[6] ($M = Mn, Fe, Co, \text{ and } Ni$)和 $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ ^[7]催化剂在固体氧化物燃料电池中应用于电催化反应. 最后, 由于钙钛矿氧化物具有高的化学和结构稳定性, 这些材料还可以作为金属催化剂的载体用于高温催化反应. 例如 $Pt/La_{0.7}Sr_{0.2}Ce_{0.1}FeO_3$ ^[8]和 $Pt/La_{0.5}Ce_{0.5}MnO_3$ ^[9]催化剂用于 $NO/H_2/O_2$ 反应, $Ag/LaMnO_3$ ^[10]和 $Pd/LaMnO_3$ ^[11,12]催化剂应用于甲烷氧化反应.

在基于钙钛矿氧化物的催化体系中, 催化剂的表面结构与催化剂所处的气体环境密切相关. 催化剂的表面组分和结构经常随着气氛条件的不同而发生动态变化, 而氧化和还原气氛是催化剂处理和催化反应中最常见的条件. 一方面, 可以通过氧化-还原处理有效控制催化剂的表面结构以及反应性能; 另一方面, 需要研究催化剂结构对气体环境的响应来理解催化剂活化或失活的机制^[13,14]. 例如, Nishihata等^[4,5]提出智能催化剂的概念, 利用 $LaFe_{0.57}Co_{0.38}Pd_{0.05}O_3$ 和 $LaFe_{0.95}Pd_{0.05}O_3$ 等钙钛矿氧化物用于汽车尾气净化处理. 他们发现当催化剂处于氧化气氛中, 贵金属Pd以氧化态的形式进入氧化物晶格中, 同时伴随反应活性的降低; 当其处于还原气氛中, Pd离子从体相中偏析并以纳米粒子的形式分散到表面上, 从而表现出良好的反应活性. 通过氧化还原气氛的交替变换实现贵金属物种从氧化态到金属态的交替变化, 这抑制了贵金属粒子的烧结, 进而实现负载催化剂的再生. Scott课题组^[15,16]研究了 $BaCe_{0.95}Pd_{0.05}O_3$ 催化剂的动态结构变化及其对CO氧化反应活性的影响, 认为Pd在氧化气氛中以 Pd^{2+} 的形式进入 $BaCeO_3$ 晶格, 产生氧空穴, 提高了晶格氧的迁移率, 从而表现出良好的CO氧化活性; 而在还原气氛下Pd以金属Pd的形式晶格中析出并在表

面团聚, 因此晶格氧的迁移率降低, 导致活性降低. 在这些研究结果的基础上, 本文选择常见的钙钛矿氧化物 $CaTiO_3$ (CTO)和 $BaTiO_3$ (BTO)作为催化剂载体, 分别负载Ag和Pt催化剂, 研究该体系在不同氧化还原处理条件下的表面结构变化, 进一步理解氧化还原处理与CO氧化反应性能之间的关系.

2. 实验部分

2.1. 催化剂的制备

M/BTO ($M = Ag$ 或 Pt , 摩尔比 $M/BTO = 0.05$)催化剂是通过溶胶-凝胶法制备^[17]. 将2.0 g碳酸钡以摩尔比1:10溶解在冰醋酸中. 随后, 按照化学计量比将钛酸正丁酯、正丁醇、乙酰丙酮以摩尔比1:2:5混合均匀, 再将所得碳酸钡的醋酸溶液逐滴加入该混合溶液并剧烈搅拌1 h. 然后加入1 ml $AgNO_3$ 溶液 (0.5 mol/L) (或者 $H_2PtCl_6 \cdot 6H_2O$ 溶液), 置于50 °C油浴, 搅拌老化至形成凝胶. 将湿凝胶在100 °C下干燥10 h形成干凝胶, 研磨后置于马弗炉焙烧(800 °C/2 h). 冷却至室温得到氧化后的样品(记为 M/BTO -Oxidized). 将该样品在 H_2 中于800 °C还原2 h得到还原的样品(记为 M/BTO -Reduced). 将还原后的样品在马弗炉于800 °C下焙烧2 h得到再氧化的样品(记为 M/BTO -Reoxidized). M/CTO ($M = Ag$ 或 Pt , 摩尔比 $M/CTO = 0.05$)催化剂采用上述相似的溶胶-凝胶法制备过程^[18]. 将一定量的钛酸正丁酯、柠檬酸和 $Ca(NO_3)_2$ 分别超声溶解于乙醇溶液中, 按化学计量比混合并剧烈搅拌1 h, 之后加入1 ml 0.5 mol/L $AgNO_3$ 溶液 (或0.5 mol/L $H_2PtCl_6 \cdot 6H_2O$ 溶液), 搅拌老化、干燥、焙烧得到氧化后样品(M/CTO -Oxidized). 还原样品(M/CTO -Reduced)与再氧化样品(M/CTO -Re-oxidized)的处理条件与上述 M/BTO 催化体系的相同.

2.2. 催化剂的表征

X射线衍射(XRD)测量采用Rigaku D/MAX-RB型粉末X射线衍射仪. 测试条件: $Cu K_\alpha$ 射线($\lambda = 0.15418$ nm), 电压40 kV, 电流250 mA, 室温, 扫描速度5°/min. X射线光电子能谱(XPS)在VG ESCALAB MK2型能谱仪上进行, 采用 $Al K_\alpha$ ($h\nu = 1486.6$ eV)作为激发源, 通能设定为20 eV.

2.3. 催化剂的活性测试

CO完全氧化反应是在实验室自制的四通道固定床微反应器上进行, 该装置可同时对四个样品进行平行评价. 尾气采用在线六通道质谱仪(Omnistar GSD 301 O2 & GSS 300)进行分析. CO完全氧化气氛组成为1% CO,

20% O₂和79% He, 反应空速设定为12000 ml/(g·h). 通过程序升温反应过程评价催化剂活性, 升温速率为1 °C/min, 由室温升至300 °C. 为了定量分析CO转化率, 四通道反应管中的其中一个未放样品, 从而测得空白样的参考信号强度^[19]. T_{90} 记为CO转化率达到90%时催化剂床层的温度.

3. 结果与讨论

3.1. 钙钛矿氧化物负载Ag催化剂在氧化-还原处理气氛中的结构变化

利用XRD研究BTO和CTO负载的Ag催化剂分别经过氧化和还原处理后结构的变化(图1). 由图1(a)可以看出, 未负载Ag的BTO样品和负载Ag的Ag/BTO样品经过空气焙烧处理后均有明显的立方相BTO衍射峰(JCPDS 86-1570), 显示通过这一溶胶-凝胶过程能够得到结晶良好的钙钛矿氧化物结构. Ag/BTO样品经O₂和H₂气氛处理后还可看到明显的金属Ag的衍射峰($2\theta = 38.2^\circ, 44.5^\circ, 64.5^\circ$; JCPDS 01-1167), 同时未观察到明显的Ag₂O衍射峰. 仔细对比所有BTO的主衍射峰位置发现, 负载Ag之后BTO的衍射峰没有出现明显位移, 这说明Ag主要以负载到氧化物表面上的纳米粒子形式存在, 没有形成掺杂离子的状态. 图1(b)的结果也显示金属Ag主要负载在CTO表面上.

对比不同气氛处理后所得样品的Ag(111)衍射峰, 可以发现氧化的样品经过800 °C, H₂气氛还原后, Ag(111)半峰宽有所减小, 说明Ag晶粒尺寸变大; 经过再氧化过程, Ag(111)半峰宽相对还原样品又有所展宽, 说明Ag晶粒尺寸通过再氧化处理又有所减小. 根据Scherrer公式计算在Ag/BTO-Oxidized样品中金属Ag的晶粒尺寸为33 nm, 还原后的Ag/BTO-Reduced样品的Ag晶粒尺寸增加到48 nm, 而再氧化后的样品中Ag晶粒降低到32 nm. 以上结果表明, 在BTO表面负载的Ag纳米颗粒在氧化-还原-再氧化的高温处理过程中发生了金属颗粒的分散-团聚-再分散的结构变化. CTO负载的Ag样品也具有类似的现象(图1(b)), Ag/CTO样品经过氧化-还原-再氧化循环处理后其中Ag的晶粒尺寸从34 nm, 56 nm, 变化到33 nm, 也说明了Ag颗粒经历了分散-团聚-再分散的变化过程. 之前的研究中我们也发现Ag/SiO₂催化体系中通过氧气处理能够使得表面金属Ag纳米粒子的分散度增加, 而高温H₂还原会使Ag颗粒发生团聚, 分散度降低^[20]. 这与我们在本工作中发现的结果相一致. 我们推测在氧化过程中Ag纳米颗粒首先被氧化形成高

分散氧化银结构, 而在进一步高温处理中氧化银又分解形成金属Ag, 因此在氧化-分解的过程中表面Ag颗粒分散度得以提高. 与此相反, 还原处理过程中Ag纳米颗粒一直保持金属的状态并且发生烧结的现象, 导致颗粒尺寸持续增加.

图2显示的是BTO和CTO负载Ag催化剂经过O₂和H₂气氛处理后的Ag 3d XPS谱. Ag/BTO样品经过氧化或还原处理后Ag 3d_{5/2}的主峰结合能位置基本保持在368.3 eV, 没有发生明显的位移, 该峰可以归属为金属Ag^[21,22]. 但是, 该催化剂在还原处理后Ag 3d峰的强度显著降低. 通过计算Ag 3d/Ti 2p的峰面积比发现还原后Ag/Ti峰面积比由氧化样品的0.17减少至0.07; 经过再氧化处理后, Ag/Ti增加至0.10. XPS结果表明高温还原使得表面负载的Ag纳米颗粒发生团聚, 因而导致Ag 3d峰强度降低; 在氧化处理中Ag仍然保持金属的状态但是颗粒得以分散, 因此Ag 3d峰强度又有所增加. 该结果与XRD结果相一致(图1). 在CTO负载的Ag催化剂中, 不同气氛处理后也看到了类似的XPS结果(图2(b)).

结合XRD和XPS的表征结果, 我们认为在氧化气氛下Ag以30 nm左右金属颗粒的形式分布于BTO(CTO)表面; 经过高温还原, 分散的Ag颗粒发生团聚, 粒径增长到近50 nm; 经过再氧化处理, Ag颗粒重新分散在表面, 粒径变小到30 nm左右.

3.2. 钙钛矿氧化物负载Pt在氧化-还原气氛中的结构变化

图3为BTO和CTO负载Pt催化剂样品经O₂和H₂气氛处理后的XRD谱. 由图3(a)可以看出, 未负载Pt样品和负载Pt的样品均有明显的立方相BTO衍射峰. 氧化物的晶格常数和晶胞体积在负载Pt后以及经过不同预处理后都没有发生改变. 负载Pt后的样品经O₂和H₂气氛处理后可看到明显的金属Pt衍射峰($2\theta = 39.8^\circ, 46.2^\circ, 67.4^\circ$; JCPDS 04-0802), 但没有看到PtO_x衍射峰. 比较不同气氛处理后的样品的Pt(111)衍射峰可以发现, Pt(111)半峰宽没有变化. 根据Scherrer公式计算得到金属Pt物种的晶粒尺寸为35 nm, 说明高温H₂还原或者氧化没有改变Pt的粒径大小.

图4为BTO和CTO负载Pt催化剂经O₂和H₂气氛处理后的Pt 4f XPS谱. 对于氧化的Pt/BTO样品, 其Pt 4f_{7/2}谱可以去卷积为两个组分, 位于71.8和75.4 eV, 分别归属为金属Pt和氧化态的PtO₂^[23,24]. 主峰位于75.4 eV, 说明BTO负载的Pt纳米粒子表面结构以PtO₂为主. 经氢气还原处理后, Pt 4f_{7/2}结合能位于71.8 eV, 说明在氧化样品

中存在的表面 PtO_2 被全部还原成金属Pt; 经过再氧化处理, Pt 4f_{7/2}谱与氧化样品(Pt/BTO-Oxidized)相比没有发生显著变化, 说明经过再氧化后BTO负载Pt粒子的表面组成和初次氧化的样品类似, 主要为 PtO_2 . XPS半定量分析显示, Pt/BTO-Oxidized, Pt/BTO-Reduced 和 Pt/BTO-Reoxidized样品的Pt 4f/Ti 2p峰面积比分别为0.10, 0.10和0.08, 说明经过不同气氛处理后BTO表面上负载的Pt物种的分散度基本相同, 该结果也得到了XRD的验证(图3). 因此, 在Pt/BTO和Pt/CTO催化体系中, 氧化处理后Pt纳米粒子的表面以氧化态为主, 经过还原处理后表面主要为金属Pt; 在不同气氛处理后氧化物表面负载的Pt纳米粒子的尺寸没有发生大的变化.

3.3. CO完全氧化的反应活性

BTO和CTO负载Ag催化剂上CO完全氧化反应活性如图5所示. 由图可以看出, 纯相的氧化物对于这个反应都表现出很低的反应活性. 当BTO负载Ag后, 其CO氧化活性显著提高. Ag/BTO-Oxidized样品的CO氧化反应的 T_{90} 为245 °C; 该催化剂经800 °C还原后CO氧化活性显著降低, T_{90} 增加了50 °C; 随后, 再次经过800 °C氧化处理后催化剂的活性得到恢复, T_{90} 为245 °C. 对于Ag/CTO催化剂, 在经过相同的氧化-还原-再氧化的循环处理后其CO氧化反应的活性也表现出高-低-高的变化趋势. Forni课题组^[25]研究发现, $\text{Sr}_{0.9}\text{Ag}_{0.1}\text{TiO}_{3\pm\delta}$ 催化氧化甲烷反应中金属态Ag和 Ag^+ 在催化剂的活性和稳定性等性能上起到显著性的作用; Rossetti课题组^[26]也指出 LaCoO_3 负载的Ag样品上甲烷氧化活性随着金属Ag粒径的增加而降低. 因此, 对于钙钛矿氧化物负载的Ag催化体系, 小尺寸的Ag纳米颗粒在催化氧化反应中起到关键的作用. 基于以上的XRD和XPS表征结果, 我们证实了氧化还原处理能够改变钙钛矿氧化物负载的Ag纳米粒子的分散度: 氧化处理的样品中Ag以较高分散度的纳米粒子存在, 故CO完全氧化反应的活性较高; 还原处理

后Ag粒子发生团聚, 从而导致CO完全氧化反应活性降低.

图6显示的是BTO和CTO负载Pt催化剂的CO完全氧化反应活性. 由图6(a)可以看出, 当BTO负载Pt后其CO氧化活性显著提高. Pt/BTO-Oxidized样品的 T_{90} 为240 °C, Pt/BTO-Reduced样品的 T_{90} 降低了60 °C; 还原样品经过再次氧化处理后其活性与Pt/BTO-Oxidized样品相当, T_{90} 为237 °C. Pt/CTO样品的CO氧化反应活性随氧化-还原处理的变化也表现出相同的规律. 已有的研究结果表明金属Pt是催化氧化反应的活性相. 结合以上的XRD和XPS表征结果, 我们发现氧化处理后钙钛矿氧化物负载Pt粒子表面结构以 PtO_2 为主, 因此CO氧化活性较低; 在还原处理后表面主要为活性的金属Pt物种, 因此活性提高. 这种Pt纳米粒子表面结构的变化很好地解释了Pt/BTO和Pt/CTO样品在氧化-还原-再氧化的循环处理中CO氧化活性表现出的低-高-低变化规律.

4. 结论

本文研究了BTO和CTO负载的Ag和Pt催化剂结构随氧化和还原处理的变化, 并进一步与CO氧化反应活性进行了关联. 发现负载Ag催化剂经过氧化和再氧化处理后, 表面Ag物种主要以高分散的Ag纳米粒子负载在BTO(CTO)载体表面上, 在CO完全氧化反应中表现较高的活性; 而在 H_2 中高温还原导致Ag颗粒的团聚, CO完全氧化反应活性降低. 氧化-还原处理主要改变了Ag纳米粒子的尺寸从而调变了CO氧化反应活性. 对于BTO(CTO)负载Pt催化剂在经过氧化和还原处理后, Pt纳米粒子的尺寸基本保持不变; 在氧化和再氧化的样品中表面Pt物种大多为 PtO_2 , CO氧化反应活性较低; 在 H_2 中800 °C还原后 PtO_2 全部还原成金属Pt, 从而CO氧化活性得到增强. 氧化-还原处理主要通过改变Pt纳米粒子表面化学态实现对其CO氧化活性的调变.