

0.1%Pt-0.02%Pd/不锈钢整体催化剂上丙酮氧化性能及稳定性

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摘要: 制备了 0.1%Pt-0.02%Pd/不锈钢整体催化剂。选取不锈钢为该催化剂的载体, 可克服传统 γ - Al_2O_3 和堇青石蜂窝载体热稳定性差的缺点。采用阳极氧化技术在不锈钢上自生长了结构致密的多孔阳极氧化膜, 并在其上负载 Pt 和 Pd 制备得到挥发性有机物(VOCs)净化催化剂。结果表明, 经 500、800 和 1000 $^{\circ}\text{C}$ 不同温度焙烧后, 该催化剂完全氧化丙酮的温度分别为 160、160 和 200 $^{\circ}\text{C}$ 。该催化剂表现出以下优点: (a) 高温稳定性能好; (b) 低温催化活性高; (c) 贵金属负载量低。通过 SEM 和 EDX 等技术对该催化剂的结构及活性组分分散情况进行了表征。

关键词: 阳极氧化; 丙酮氧化; 不锈钢整体催化剂; 催化燃烧

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0.1%Pt-0.02%Pd/Stainless Steel Monolith Catalyst: Catalytic Oxidation of Acetone and Thermal Stability

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Abstract: Stainless steel monolith was chosen as catalyst support to overcome the drawbacks of poor thermal stability with catalysts using traditional γ - Al_2O_3 and cordierite honeycomb as the substrate. During the catalyst preparation process, anodic oxidation technique was used to produce a porous membrane over the support surface, leading to effective dispersion of platinum and palladium on stainless steel monolith. The results show that the temperature for the total oxidation of acetone is 160, 160 and 200 $^{\circ}\text{C}$, respectively, with the catalyst calcined at 500, 800 and 1000 $^{\circ}\text{C}$. The role of porous membrane over the stainless steel monolith surface is important for fixing active components of platinum and palladium particles, which leads to the enhanced catalytic activity for total acetone oxidation. This 0.1% Pt-0.02% Pd/stainless steel monolith catalyst exhibits the following advantages: a) high temperature stability in the whole temperature range investigated (500~1000 $^{\circ}\text{C}$), b) better catalytic activity than those platinum and palladium supported catalysts over γ - Al_2O_3 and cordierite honeycomb support previously reported, c) low metal loading of platinum and palladium components (0.1wt% Pt and 0.02wt% Pd). The microstructures, surface dispersion condition of platinum and palladium active components were studied by means of scanning electron microscopy(SEM) and energy-dispersive X-ray spectroscopy(EDX).

Key words: anodic oxidation technique; acetone oxidation; stainless steel monolith catalyst; catalytic combustion

Volatile organic compounds(VOCs) are considered as one of the major factors causing the atmospheric

pollution because of their toxicity to human health and their involvement in the formation of photochemical

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smog^[1-2]. Due to the more strict environmental regulations on many countries, much attention has been attracted to the controlling of VOCs emission. Catalytic combustion is one of the most attractive ways used for elimination of VOCs emission, as it converts the toxic compounds into relatively harmless compounds such as water and CO₂ at lower operating temperatures^[3-5].

Platinum and palladium supported catalysts have been found to be the most active catalysts in the oxidation of a variety of VOCs^[6-8]. And catalysts supported on γ -Al₂O₃ have been extensively studied^[9-10]. But the problems of easy fragmentation and low thermal stability for those catalysts using the alumina as support have hindered its further development. Fabbrini et al.^[11] reported that catalyst using γ -Al₂O₃ as support showed a relatively poor stability at high temperature and led to rapid catalyst decay. Consequently, there is a big challenge in seeking for supports with higher thermal stability and better corrosion resistance. The stainless steel monolith may be a promising catalyst support, as it can be easily machine processed into various structures and has the character of thermal resistance and high thermal conductivity^[12-13]. One problem concerning the using stainless steel monolith as support is its lower surface area, which restricts its application as catalyst support. A porous alumina membrane on stainless steel monolith produced by electrochemical method of anodic oxidation has attracted much attention in recent years^[14-16]. The anodic oxidation treatment is applied to design porous membrane over the stainless steel monolith surface for supporting platinum and palladium^[17]. Moreover, from an economical point of view, a highly active catalyst with low platinum and palladium component is also expected.

In this work, a simple anodic oxidation preparation technique was used for forming a porous oxide membrane on stainless steel monolith surface. This anodic oxidation membrane is beneficial to supporting platinum and palladium particles on stainless steel monolith. Here, we report a new bimetallic 0.1% Pt-0.02%Pd/stainless steel monolith catalyst, which shows not only good catalytic activity for total acetone oxidation at lower temperature, but also high thermal

stability at 1 000 °C.

1 Experimental

1.1 Preparation of catalysts

The preparation of stainless steel monolith via anodic oxidation procedure was as follows: The oil, primary oxides and other superficial impurities were removed in alkaline solution. And the stainless steel monolith was then rinsed with distilled water, followed by putting into an isolated electrochemical cell with 30wt% sulphuric acid aqueous solution as electrolyte. In the anodic oxidation process, the whole reaction was performed at room temperature under constant voltages of 3~5 V and electric current density at 1.0 A·dm⁻² until an anodic oxidation membrane appeared on stainless steel monolith surface. Finally, the as obtained support was dried at 100 °C for 1 h in air. Low loading for platinum and palladium was chosen. The active components of 0.1wt% platinum and 0.02wt% palladium were loaded onto this typical support by aqueous impregnation method, using palladium chloride and platinum chloride as the precursor. The impregnated sample was then reduced in N₂H₄·H₂O for 3 h. After dried, the sample was calcined in air at 500 °C for 2 h at a heating rate of 2 °C·min⁻¹. The catalyst was denoted as 0.1%Pt/SSM, 0.02%Pd/SSM and 0.1%Pt-0.02%Pd/SSM catalyst.

For evaluating the thermal stability of the catalyst, a test of the catalyst treated at different calcination temperatures was carried out in the temperature range of 500~1 000 °C.

1.2 Catalytic activity test

Catalytic activity measurements for oxidation of acetone were carried out in a tubular quartz glass, fixed-bed reactor(i.d.12 mm) under atmospheric pressure in the temperature range of 100~400 °C. A thermocouple was placed inside the reactor in the center of the catalyst bed to monitor the reaction temperature. The speed velocity was held constant at 10 000 h⁻¹ and the acetone concentration was controlled in the range of 4~6 g·m⁻³. The composition of the combustion products was analyzed by on-line gas chromatography (GC-8A, Japan) equipped with a FID detector. The GC column

was 3 mm×0.3 μm×3 m stainless steel tubing packed with OV101. The analysis conditions were as follows: the temperatures of FID detector, injector and column chamber were 180, 180 and 140 °C, respectively. The conversion values were calculated based on the concentration of acetone in the inlet and outlet gas.

1.3 Catalyst characterization

The morphologies of the support and catalysts were observed by JEM-T20 scanning electron microscope (SEM) at an accelerating voltage of 25 kV. Prior to measurement, the samples were treated to remove the impurities on the surface. The chemical composition of the samples was determined by using energy-dispersive X-ray spectroscopy (EDX) (GENESIS4000 (U.S.A.)).

2 Results and discussion

2.1 Catalytic oxidation of acetone

Fig.1 shows the acetone oxidation results of 0.1% Pt-0.02% Pd/SSM, 0.1% Pt/SSM, and 0.02% Pd/SSM catalysts (calcined at 500 °C for 2 h in air). It can be seen that the temperature for total acetone conversion is 260 and 300 °C on 0.1% Pt/SSM and 0.02% Pd/SSM catalysts, respectively, despite lower noble metal content. The results indicate that the anodic oxidation adoption technique on stainless steel monolith ensures effective loading of active components of Pt and Pd on the support. In the case of the bimetallic catalyst with the same metal loading, 0.1% Pt-0.02% Pd/SSM catalyst exhibits much better catalytic activity for acetone oxidation than the monometallic Pt and Pd catalyst. The

temperature for total oxidation of acetone could be as low as 160 °C. It indicates that the addition of a second metal, palladium, brings a considerable increase in the catalytic oxidation of acetone. Since 0.1% Pt-0.02% Pd/SSM catalyst shows a good catalytic activity, there is a synergistic interaction between the particles of Pt and Pd that is responsible for the increase activity of acetone oxidation at low temperature, as literature reported^[18-20].

The catalytic activity of 0.1% Pt-0.02% Pd/SSM catalyst was investigated by varying the calcination temperature from 500 to 800 °C. The catalysts were calcined for 2 h in air. Fig.2 presents the results of catalytic tests carried out with bimetallic catalysts obtained at various calcination temperatures. In the case of 0.1% Pt-0.02% Pd/SSM catalyst calcined at 500 °C, the temperature for total oxidation of acetone is 160 °C. Interestingly, it can be found that, after 800 °C calcination, the total oxidation temperature of acetone remains at 160 °C and the catalyst does not lose activity with the increase of temperature. Therefore, it clearly shows that using stainless steel monolith as support brings about the resistance to high temperature in the case of 0.1% Pt-0.02% Pd/SSM catalyst. Especially, after 1 000 °C high temperature calcination, 0.1% Pt-0.02% Pd/SSM catalyst still shows good activity for total acetone oxidation at 200 °C, which is about 80 °C lower than that of Pt/Al₂O₃/Al catalyst^[21]. Thus, we believe that it attributes not only to the use of the stainless steel monolith as support, but also to the porous oxide membrane formed in the anodic oxidation.

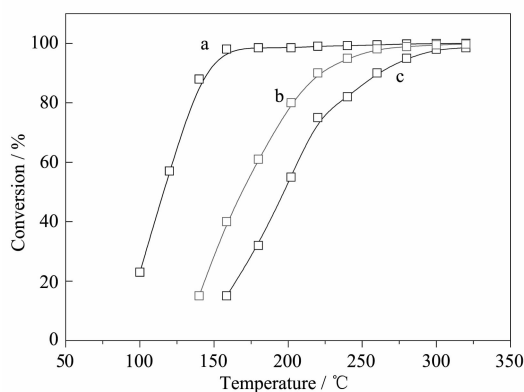


Fig.1 Catalytic oxidation for acetone on catalysts of 0.1%Pt-0.02%Pd/SSM (a); 0.1%Pt/SSM (b); 0.02%Pd/SSM (c)

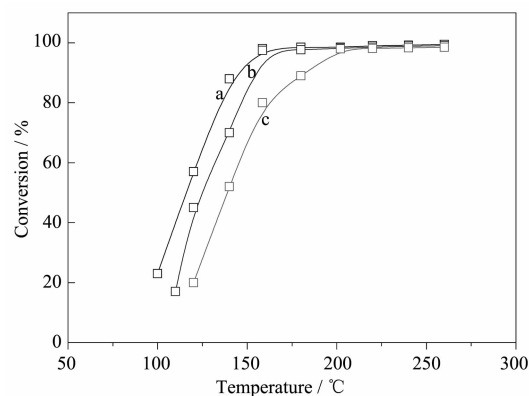


Fig.2 Catalytic activity for acetone conversion on 0.1%Pt-0.02%Pd/SSM catalyst calcined at different temperatures: 500 °C (a); 800 °C (b); 1 000 °C (c)

2.2 SEM and EDX results

Fig.3 shows the typical SEM photographs of the stainless steel monolith support before and after anodic oxidation procedure. As seen in Fig.3(a), the stainless steel monolith support is smooth, on which it is hard to load active components of Pt and Pd. After anodic oxidation procedure, it is observed that a thin oxide membrane obviously appears over the stainless steel monolith surface, which is characterized by pores and cracks. The surface area of the SSM has an increase from $13 \text{ m}^2 \cdot \text{g}^{-1}$ to $19 \text{ m}^2 \cdot \text{g}^{-1}$ after anodic oxidation procedure. The presence of these cracks and imperfections of the membrane is beneficial to increasing the surface area of the anodic oxidation membrane layer and favors for fixing active sites of Pt and Pd particles, leading to the enhanced catalytic performance and thermal stability for catalytic oxidation of acetone.

A cross-sectional view of 0.1%Pt-0.02%Pd/SSM catalyst at different calcination temperatures is shown in Fig.4. Clearly, it can be seen that the active components of Pt and Pd particles are dispersed on the anodic oxidation membrane layer of SSM support, and the size of Pt and Pd particles is 100~150 nm(Fig.4(a)). When the calcination temperature is increased from 500 to 800 °C, the dispersion of Pd particles changes greatly and the Pd particles grow up quickly in the form of sphere(Fig.4(b)). This phenomenon may be related to the decomposition of PdO into Pd accompanied by the change in crystal structure^[17]. When the temperature increases from 800 to 1 000 °C, the morphology of Pt and Pd particles are almost unchanged, which are in a steady state and are not affected by the high

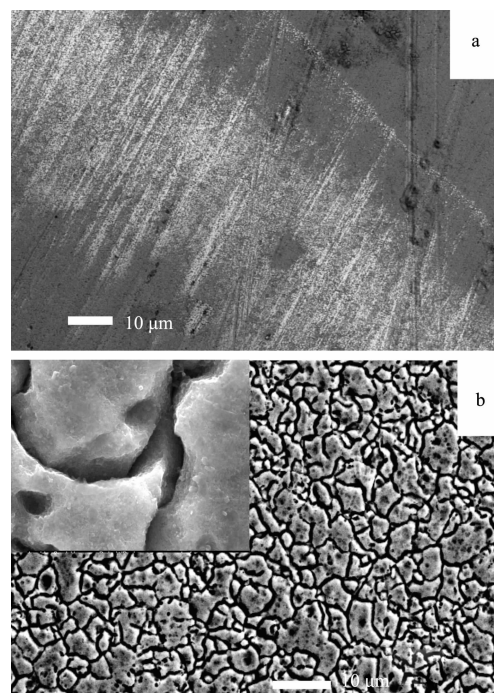
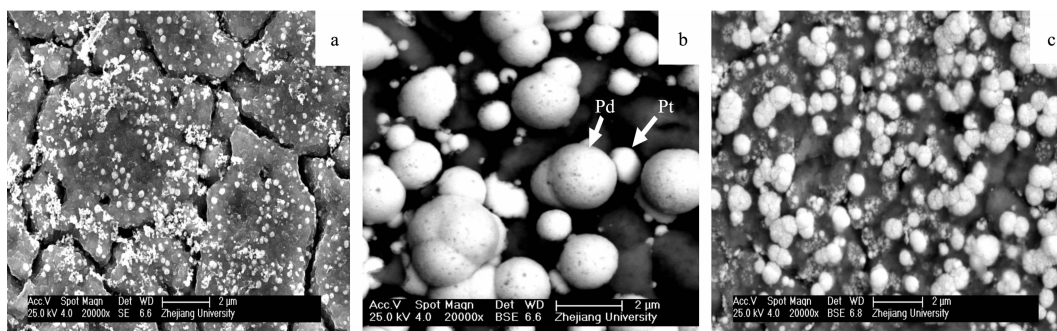


Fig.3 SEM images of SSM before (a) and after (b) anodic oxidation procedure

temperature, suggesting a strong interaction between the Pt and Pd particles.

The role of the anodic oxidation membrane in 0.1%Pt-0.02%Pd/SSM catalyst is to act as a stabilizer for Pt and Pd particles in a large temperature range. For this reason, we think that the existence of anodic oxidation membrane can improve the dispersion of Pt and Pd particles. On the other hand, the good thermal stability of 0.1%Pt-0.02%Pd/SSM catalyst may be attributed to a remarkable temperature-resistant capability of stainless steel monolith support.

The EDX analysis of the 0.1%Pt-0.02%Pd/SSM catalyst is shown in Fig.5. The elements of Si, Ti, Fe and Cr are found in the SSM support. In addition, the



(a) 500 °C; (b) 800 °C; (c) 1 000 °C

Fig.4 SEM images of 0.1%Pt-0.02%Pd/SSM catalyst calcined at different temperatures

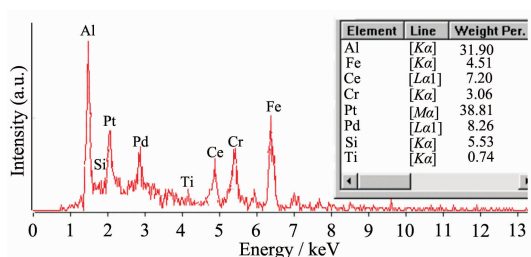


Fig.5 EDX pattern of 0.1%Pt-0.02%Pd/SSM catalyst

signal of Pt and Pd were visibly detected, which confirms the existence of the Pt and Pd particles on the membrane sub-surface.

3 Conclusions

0.1%Pt-0.02%Pd/SSM catalyst was prepared and applied for catalytic oxidation of acetone. The existence of anodic oxidation membrane can improve the dispersion of Pt and Pd particles and stabilize Pt and Pd in a high temperature range. Activity tests show that using SSM as support treated by anodic oxidation technique obviously improves the catalytic activity of 0.1% Pt-0.02% Pd/SSM catalyst for the acetone oxidation.

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