

[Article]

www.whxb.pku.edu.cn

甲苯、丙酮和乙酸乙酯在新型铂-钯/不锈钢丝网催化剂上的催化氧化

马莹 陈敏* 宋萃 郑小明

(浙江大学(西溪校区)催化研究所, 杭州 310028)

摘要: 采用阳极氧化法制备了一种用于催化氧化处理挥发性有机化合物(VOCs)的 0.1%Pt-0.5%Pd/不锈钢丝网(SSWM)催化剂. 活性测试结果表明, 0.1%Pt-0.5%Pd/不锈钢丝网催化剂具有较高的催化活性和热稳定性. 该催化剂上甲苯、丙酮和乙酸乙酯的完全氧化温度分别为 220、260 和 280 °C. 通过扫描电镜(SEM)、X 射线光电子能谱(XPS)和超声波等手段对催化剂和不锈钢丝网进行了表征. SEM 结果表明, 经阳极氧化工艺处理过的不锈钢金属丝网载体表面形成了一层沟壑形态的复合氧化膜. 该阳极氧化膜有利于活性组分 Pd、Pt 的分散.

关键词: 催化氧化; 不锈钢丝网; 阳极氧化; X 射线光电子能谱

中图分类号: O643

Catalytic Oxidation of Toluene, Acetone and Ethyl Acetate on a New Pt-Pd/Stainless Steel Wire Mesh Catalyst

MA Ying CHEN Min* SONG Cui ZHENG Xiao-Ming

(Institute of Catalysis, Zhejiang University (Xixi Campus), Hangzhou 310028, P. R. China)

Abstract: A new volatile organic compound (VOC) combustion catalyst of 0.1%Pt-0.5%Pd/stainless steel wire mesh (SSWM) was prepared *via* anodic oxidation treatment. The result of activity tests for complete oxidation of toluene, acetone, and ethyl acetate showed that 0.1%Pt-0.5%Pd/steel wire mesh catalyst had good catalytic activity and thermal stability. The total oxidation temperature for toluene, acetone, and ethyl acetate was at 220, 260, and 280 °C for the catalyst calcined at 500 °C, respectively. The catalyst and stainless steel wire mesh support were characterized by means of scanning electron microscopy (SEM), X-ray photoelectron spectrum (XPS), and ultrasonic vibration tests. The SEM results indicated that a typical donga structure layer appeared on the surface of stainless steel wire mesh support after anodic oxidation procedure. This typical anodic oxidation film was favorable for dispersing Pd and Pt components.

Key Words: Catalytic oxidation; Stainless steel wire mesh; Anodic oxidation; X-ray photoelectron spectra

Nowadays, the volatile organic compounds (VOCs), from chemical and petrochemical plants, have given rise to comprehensive attention as they are hazardous to the environment and human health^[1]. There are many different techniques used for the removal of VOCs, such as adsorption, absorption, biofiltration, thermal incineration, and catalyst combustion^[2–6]. Among them, catalytic deep oxidation that converts VOCs into carbon dioxide and water has been recognized as one of the most promising methods^[7–9].

Noble metal catalysts like Pt or Pd on a suitable support have generally been used as the most active catalysts for VOCs oxidation^[10,11]. As previously reported, Pt and Pd supported on alumina was the most active catalyst^[12–14]. However, it is frequently reported that alumina phase from γ to α transition would cause a drastic decrease in the surface area, and the sintering of the noble metals would also lead to the thermal deactivation of the catalysts. Therefore, to find a new series of catalysts, which are less expensive, higher temperature-resistance, and more efficient in

Received: January 7, 2008; Revised: March 19, 2008; Published on Web: May 7, 2008.

English edition available online at www.sciencedirect.com

*Corresponding author. Email: chenmin@zju.edu.cn, yingmy@yahoo.com.cn; Tel: +86571-88273495; Fax: +86571-88273283.

国家自然科学基金(20577042)及浙江省自然科学基金(Y505285)资助项目

low temperature for volatile organic compound combustion is needed.

The stainless steel wire mesh (SSWM) is regarded as an attractive replacement of conventional support in catalysts because of its high anticorrosion, high thermal conductivity, and ductile property. Our previous work^[15] reported that a 0.01%Pt-0.02% Pd/stainless steel catalyst showed high catalytic activity for toluene, acetone, and ethyl acetate oxidation. This work is a continuation of the previous work, in which 0.1% Pt-0.5% Pd supported on a new kind of stainless steel wire mesh was prepared and reported. The aim of this work is to investigate another kind of stainless steel used as support and extend its application.

1 Experimental

1.1 Preparation of catalyst

The stainless steel wire mesh (400 mm×40 mm×0.3 mm) was machined into a typical shape as needed. The anodic oxidation treatment was carried out in the subsequent process: the stainless steel wire mesh was put into an isolated electrochemical cell, in which 10% (*w*) sulphuric acid aqueous solution was used as electrolyte. Then at a constant stirring rate, keeping the constant voltages of 3–5 V and electric current density of 1 A·dm⁻², the anodized oxidation film appeared on the stainless steel wire mesh support surface. Finally, the stainless steel wire mesh support was dried at 110 °C for 1 h in the air atmosphere. The supported platinum and palladium catalyst was prepared by impregnation method. The aqueous solutions, H₂PtCl₆ and H₂PdCl₄, were used as precursors for Pt and Pd, respectively. Finally, the catalyst was dried at 110 °C for 1 h and then calcined at 500 °C for 1 h. The obtained catalyst was denoted as 0.1%Pt-0.5%Pd/SSWM in the following sections.

1.2 Measurement of activity

Catalytic activity tests were carried out at atmospheric pressure in a fixed bed flow-reactor system (length=600 mm, i.d.=28 mm). The typical VOCs substance of toluene, acetone, and ethyl acetate was introduced into the reactor by a carrying gas of air flow through a saturator maintained. The reactions were performed at temperature range of 180–400 °C, and the gas hourly space velocity (GHSV) is 10000 h⁻¹. The concentrations of toluene, acetone, and ethyl acetate in the feed were 0.10%–0.16%, 0.17%–0.25%, and 0.11%–0.17%, respectively. The catalyst was placed at the center of the reactor supported by quartz wool and a thermocouple was positioned to monitor the reaction temperature. The analysis of the concentration of VOCs in the inlet and outlet gas was performed on a GC-1690 chromatograph with a FID attachment. The GC column was 3 mm×0.3 μm×3 m stainless steel tubing packed with quartzite. The analysis conditions were as follows: the temperatures of injector, detector, and column chamber were 170, 140, and 150 °C, respectively. The flow rate of carrier gas (N₂) was 20 cm³·min⁻¹. The catalytic activities are characterized by parameter of T_{98} , which indicates the temperature at which acetone, ethyl acetate, toluene conversion

reaches 98%.

1.3 Catalyst characterization

The morphologies of the stainless steel wire mesh support and 0.1%Pt-0.5%Pd/SSWM were characterized by scanning electron microscopy (SEM, Instrument JEM-T20). X-ray photoelectron spectrum (XPS) experiment was carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg K_α radiation ($h\nu=1253.6$ eV). Binding energies were calibrated using the containment carbon (C 1s, 284.6 eV).

According to the method described in the published work^[16], the fastness of the obtained anodic oxidation film support was tested in an ultrasonic bath with water for 10–60 min to measure the mass loss of the sample.

2 Results and discussion

2.1 Activity measurement

Catalytic activities of acetone, toluene, and ethyl acetate complete oxidation over the sample of 0.1%Pt-0.5%Pd/SSWM calcined at 500 °C are shown in Fig.1. As seen from Fig.1, the total oxidation temperature (T_{98}) for toluene, acetone, and ethyl acetate is at 220, 260, and 280 °C, respectively. This indicates that the catalyst shows a higher catalytic activity compared with the catalyst of Pd/Al₂O₃/cordierite (the corresponding T_{98} is 230, 280, and 320 °C)^[17], and the T_{98} is 10, 20, and 40 °C lower for toluene, acetone, and ethyl acetate, respectively. Moreover, after the catalyst calcined at 700 °C, the total oxidation temperature for toluene, acetone, and ethyl acetate is 250, 300, and 320 °C, respectively. Compared with that of catalyst calcined at 500 °C, the T_{98} only increases by 30, 40, and 40 °C (not shown in Fig. 1), indicating that the catalyst has a better temperature-resistant property.

2.2 SEM results

The SEM images of stainless steel wire mesh before and after anodic oxidation treatment are shown in Fig.2, and obvious differences appear on the stainless steel wire mesh after anodic oxidation treatment (Fig.2(B)). Meanwhile, compared with the blank stainless steel wire mesh (Fig.2(A)), a film with domba structure layer visibly appears over the stainless steel wire mesh surface after anodizing oxidation procedure (Fig.2(C)). The enlargement

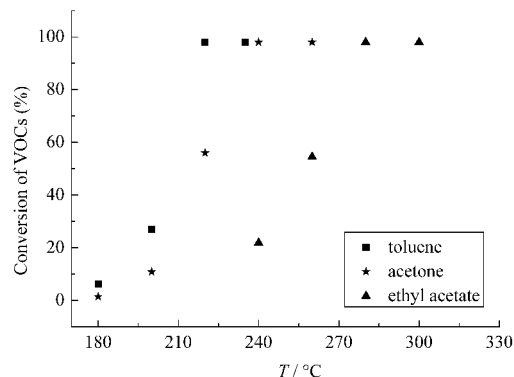


Fig.1 Light-off curves for toluene, acetone, and ethyl acetate combustion over 0.1%Pt-0.5%Pd/SSWM catalyst

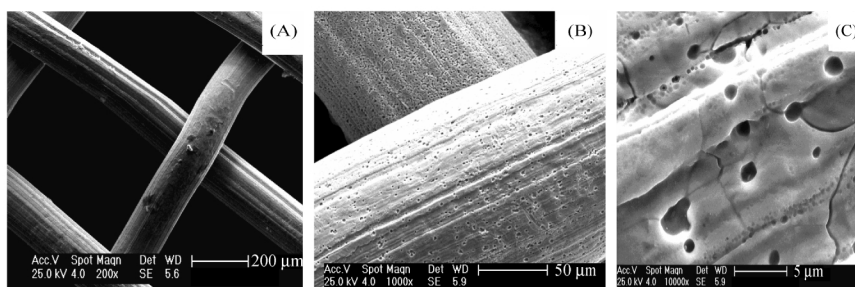


Fig.2 SEM images of SSWM before and after anodic oxidation procedure

(A) SSWM, (B) SSWM after anodizing oxidation treatment, (C) the enlargement of SSWM after anodizing oxidation treatment

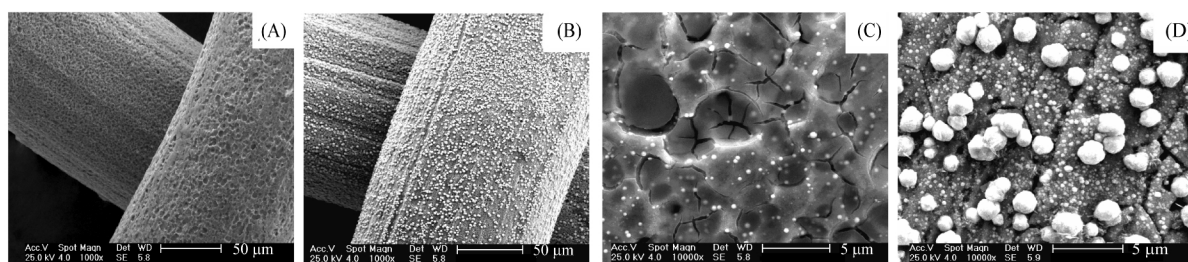


Fig.3 SEM images of different samples

(A) 0.1%Pt/SSWM, (B) 0.1%Pt-0.5%Pd/SSWM, (C) the enlargement of 0.1%Pt/SSWM, (D) the enlargement of 0.1%Pt-0.5%Pd/SSWM

of SSWM after anodizing oxidation treatment shown in Fig.2(C) suggests that this typical donga structure layer is favorable for dispersing platinum and palladium active phases. Thus, we think that the presence of anodizing oxidation film seems to be important to offer a synergistic interaction between the support and active composition; this is responsible for favoring the active phases of platinum and palladium that are easily dispersed on the surface of the stainless steel wire mesh support.

Fig.3(A) shows the representative SEM image of 0.1%Pt/SSWM catalyst, and an enlargement of this catalyst is displayed in Fig.3(C). Similarly, the SEM image of Fig.3(B) gives the microstructure of 0.1%Pt-0.5%Pd/SSWM catalyst and Fig.3(D) is an enlarged photograph of the catalyst. It is generally observed that the active phases, whether Pt or Pt-Pd, are well dispersed on the surface of stainless steel wire mesh support.

In contrast, Fig.4 gives the comparison of catalytic activity of 0.1%Pt/SSWM and 0.1%Pt-0.5%Pd/SSWM catalysts. It can be found that 0.1%Pt-0.5%Pd/SSWM catalyst shows better activity

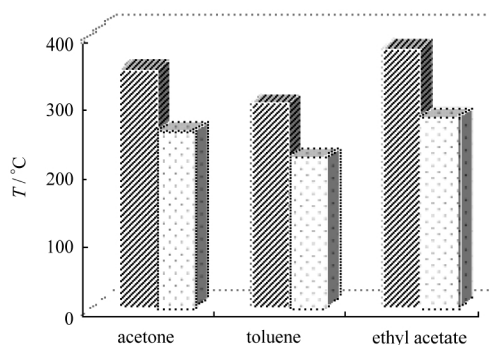


Fig.4 T_{98} of VOCs on different catalysts

▨ 0.1%Pt/SSWM, ▤ 0.1%Pt-0.5%Pd/SSWM

than 0.1%Pt/SSWM catalyst. As described in published works^[18,19], bimetallic catalysts can enhance catalytic stabilities and activities for their markedly different properties from either of the constituent metals. The result indicated in Fig.4 is consistent with this conclusion.

2.3 XPS results

Chemical states of surface atoms in the catalysts were investigated by XPS.

The spectra of the specific positions of Pd 3d peaks, Pt 4f peaks, and O 1s peaks of 0.1%Pt-0.5%Pd/SSWM catalyst before and after reaction are presented in Figs.5–7, respectively.

From Fig.5, it can be found that there is a shift from 337.1 eV to a lower position of 336.0 eV in the binding energy of Pd 3d_{5/2} in the sample after reaction. Here, Pd 3d_{5/2} of 336.0 eV can be assigned to the binding energies of PdO. However, Pd 3d_{5/2} of 337.1 eV can be ascribed to PdO₂ species^[20]. It indicates that a valence change of palladium onto the catalyst surface acts as an

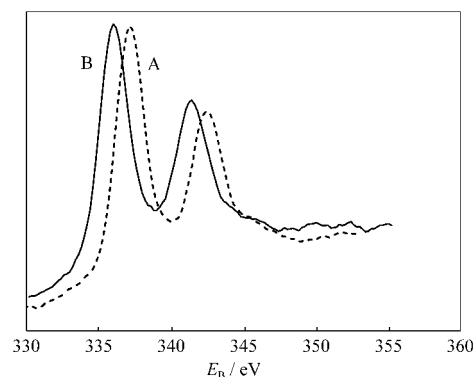


Fig.5 Pd 3d region of 0.1%Pt-0.5%Pd/SSWM catalyst before (A) and after (B) reaction

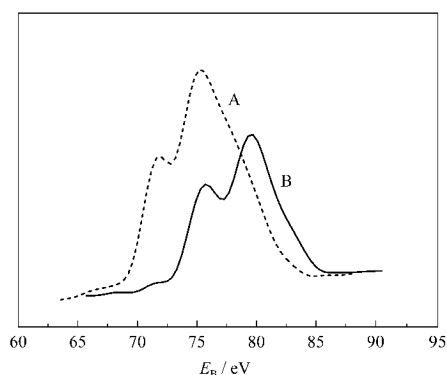


Fig.6 Pt 4f region of 0.1%Pt-0.5%Pd/SSWM catalyst before (A) and after (B) reaction

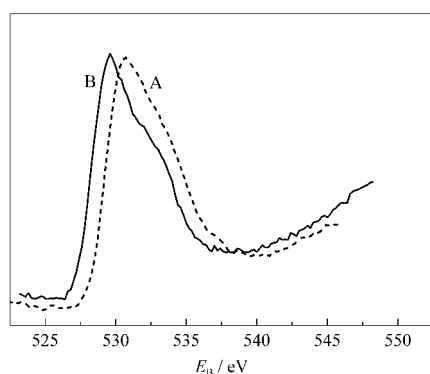


Fig.7 O 1s region of 0.1%Pt-0.5%Pd/SSWM catalyst before (A) and after (B) reaction

active redox site during the oxidation reaction. Additionally, some Pd^{4+} ions were formed during the sample calcination process and then the adsorbed oxygen species got into the PdO crystal lattice and resulted in the change of binding energy^[21].

XPS results of Fig.6 indicate that there are obvious changes in the positions of Pt 4f_{7/2} peaks on the spectra of 0.1%Pt-0.5%Pd/SSWM catalyst before and after reaction. It demonstrates that the environment around Pt 4f_{7/2} was changed.

As far as we know, the surface oxygen species of the catalyst is another important factor for catalytic activity. Fig.7 shows the XPS of O 1s analysis of the catalyst before and after reaction. Clearly, the O 1s peak located near 532.0 eV is attributed to adsorbed oxygen^[22] and it can be found that the binding energy of O 1s peak decreases in the sample after reaction. This can be explained as the amount of adsorbed oxygen species transformed into lattice oxygen during reaction. Therefore, we suppose that the adsorbed oxygen species has participated and played an important role in the oxidation reaction. The XPS result reveals that the adsorbed oxygen is the main contributor in this oxidation reaction, which is in agreement with the result reported by Titkov *et al.*^[23].

2.4 Adherence test of anodizing oxidation film

In order to investigate the fastness of anodizing oxidation film over SSWM, the ultrasonic vibrate test was carried out. As can be seen from Fig.8, a mass loss–time curve of the anodizing oxidation film over SSWM reveals some interesting facts. The mass

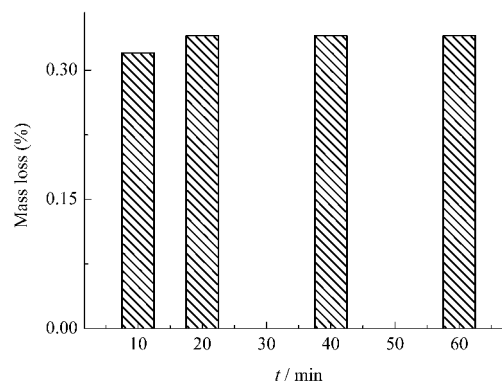


Fig.8 Mass loss–time curves of the anodized film on the SSWM by the ultrasonic vibration test

loss on SSWM by anodizing oxidation treatment is 0.32% (*w*) after 10 min ultrasonic treatment, then after testing for 60 min a mass loss of 0.34% (*w*) appeared, indicating that there are nearly no significant changes on the sample. Meanwhile, the mass loss tends to hold a fixed value after exposure to ultrasonic for 50 min. This suggested that the anodizing oxidation film on SSWM showed a good adherence state even at a long time breakage. This also indicated that a good synergistic interaction was in existence between SSWM support and anodizing oxidation film.

3 Conclusions

In this work, a new support and the 0.1%Pt-0.5%Pd/SSWM catalyst were prepared and characterized by SEM and XPS techniques. The research revealed that the new support of SSWM pretreated by an anodic oxidation process favored dispersing the palladium and platinum particles on the surface of SSWM support. From catalytic activity tests, it can be found that 0.1%Pt-0.5%Pd/SSWM catalyst shows optimum catalysis for toluene, acetone, and ethyl acetate. Using stainless steel wire mesh as catalyst support can overcome the shortcoming of $\gamma\text{-Al}_2\text{O}_3$ support. To sum up, the 0.1%Pt-0.5%Pd/SSWM catalyst is a promising catalyst for control of VOCs.

References

- 1 Pérez-Cadenas, A. F.; Kapteijn, F.; Moulijn, J. A.; Maldonado-Hódar, F. J.; Carrasco-Marín, F. C.; Moreno-Castilla, C. *Carbon*, **2006**, *44*: 2463
- 2 Pires, J.; Carvalho, A.; Carvalho, M. B. *Micropor. Mater.*, **2001**, *43*: 277
- 3 Ray, I. *J. Chem. Eng. Prog.*, **1993**, *89*: 37
- 4 Engleman, V. S. *Metal. Finishing*, **2000**, *98*: 433
- 5 Togna, A. P.; Singh, M. *J. Environ. Prog.*, **1994**, *13*: 94
- 6 Idakiev, V.; Tabakova, T.; Yuan, Z. Y.; Su, B. L. *Appl. Catal. A: Gen.*, **2004**, *270*: 135
- 7 Spivey, J. J. *Ind. Eng. Chem. Res.*, **1987**, *26*: 2165
- 8 Gandía, L. M.; Vicente, M. A.; Gil, A. *Appl. Catal. B: Environ.*, **2002**, *38*: 295
- 9 Centi, G.; Ciambelli, P.; Perathoner, S.; Russo, P. *Catal. Today*, **2002**, *75*: 3

- 10 Tsou, J.; Magnoux, P.; Guisnet, M.; Órfão, J. J. M.; Figueiredo, J. L. *Appl. Catal. B: Environ.*, **2005**, **57**: 117
- 11 Belver, C.; López-Muñoz, M. J.; Coronado, J. M.; Soria, J. *Appl. Catal. B: Environ.*, **2003**, **46**: 497
- 12 Avgouropoulos, G.; Oikonomopoulos, E.; Kanistras, D.; Ioannides, T. *Appl. Catal. B: Environ.*, **2006**, **65**: 62
- 13 Tidahy, H. L.; Siffert, S.; Lamonier, J. F.; Cousin, R.; Zhilinskaya, E. A.; Aboukais, A.; Su, B. L.; Canet, X.; de Weireld, G.; Frère, M.; Giraudon, J. M.; Leclercq, G. *Appl. Catal. B: Environ.*, **2007**, **70**: 377
- 14 Kapoor, M. P.; Ichihashi, Y.; Kuraoka, K.; Matsumura, Y. *Mol. Catal. A: Chem.*, **2003**, **198**: 303
- 15 Chen, M.; Ma, Y.; Li, G. F.; Zheng, X. M. *Catal. Commun.*, **2008**, **9**: 990
- 16 Hosseini, M.; Siffert, S.; Tidahy, H. L.; Cousin, R.; Lamonier, J. F.; Aboukais, A.; Vantomme, A.; Roussel, M.; Su, B. L. *Catal. Today*, **2007**, **122**: 391
- 17 Chen, M.; Shi, C. M.; Zheng, X. M. *Chin. J. Inorg. Chem.*, **2006**, **22**: 1828 [陈敏, 施春苗, 郑小明. 无机化学学报, **2006**, **22**: 1828]
- 18 Riahi, G.; Guillemot, D.; Polisset-Thfoin, M.; Khodadadi, A. A.; Fraissard, P. *Catal. Today*, **2002**, **72**: 115
- 19 Valentini, M.; Groppi, G.; Cristiani, C.; Levi, M.; Tronconi, E.; Forzatti, P. *Catal. Today*, **2001**, **69**: 307
- 20 Kim, D. H.; Woo, S. I.; Lee, J. M.; Yang, O. B. *Catal. Lett.*, **2000**, **70**: 35
- 21 Bi, Y. S.; Lu, G. X. *Appl. Catal. B: Environ.*, **2003**, **41**: 279
- 22 Flerro, J. L. G.; Tejuca, G. *Appl. Surf. Sci.*, **1987**, **27**: 453
- 23 Titkov, A. I.; Salanov, A. N.; Koscheev, S. V.; Boronin, A. I. *Surf. Sci.*, **2006**, **600**: 4119