Full Paper

Pd-Mn/Stainless Steel Wire Mesh Catalyst for Catalytic Oxidation of Toluene, Acetone and Ethyl Acetate

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A new 0.1%Pd-6%Mn/stainless steel wire mesh catalyst was prepared and used for volatile organic compounds (VOC) elimination. The supported palladium and manganese catalyst over the stainless steel wire mesh was prepared by using an impregnation method. When an anodic oxidation technology was employed, an anodic oxidation membrane appeared on the stainless steel wire mesh. On the 0.1%Pd-6%Mn/stainless steel wire mesh catalyst calcined at 500 ℃, the total oxidation of toluene, acetone and ethyl acetate was respectively at 260, 220 and 320 ℃. The activity could be stable for over 700 h for toluene oxidation. The scanning electron microscopy (SEM) investigation of the Pd-Mn/stainless steel wire mesh catalyst shows that the presence of anodic oxidation membrane on the support surface is important for better dispersion of active phases.

Keywords　Pd catalyst, anodic oxidation treatment, VOC oxidation

Introduction

Volatile organic compounds (VOC), emitted from many industrial processes, are considered as main contributors to the atmospheric pollution and to be dangerous to human health.[1,2] There are various techniques used for the removal of VOC, such as adsorption, absorption, biofiltration, thermal incineration, and catalytic combustion.[3-7] Among these techniques, catalytic oxidation is quite promising in the VOC elimination because of the lower operation temperature for the catalytic oxidation. It is helpful for reducing energy consumption and for avoiding the formation of toxic byproducts such as NO_x.[8,9] Many researchs have been concentrated on noble metal catalysts, and supported palladium catalysts were found to be fairly active for VOC elimination at relatively low temperature. But the high cost of the noble metal hindered its further development in the total oxidation of VOC. Therefore, the catalyst with low temperature catalytic combustion of VOC and good stability for a long reaction time is urgently required, especially for industrial application.

In addition, more and more researches concerned on the catalytic elimination of VOC by using supported transition metal oxides (Cu, Mn, V, Fe) as active compounds,[10-12] and the manganese oxide catalysts exhibited good activity. Alvarez-Galvan[12] found that the total combustion temperature of formaldehyde was 220 ℃ over 18.2% Mn/Al_2O_3 catalyst. On the other hand, the stainless steel wire mesh (denoted as SSWM) which has good stiffness and thermal stability, has attracted our attention.

In this paper, we reported a new supported palladium-manganese catalyst using SSWM as supporter for VOC elimination. The anodic oxidation treatment was applied to design a porous membrane over the stainless steel screen surface. For catalysts calcined at 500 ℃, the T_{98} of toluene, acetone and ethyl acetate was respectively at 260, 220 and 320 ℃. Notably, the significant temperature-resistant should be owed to the presence of anodic oxidation membrane.

Experimental

Preparation of catalysts

A stainless steel wire mesh (FeCrNi) (400 mm×40 mm×0.3 mm) was machined into a rippled shape as the requirement. After the pretreatment of SSWM, such as degreasing, the anodic oxidation treatment was carried out in the subsequent process: the stainless steel wire mesh was put into an isolated electrochemical cell for 30 min and 10 wt% sulphuric acid aqueous solution was used as electrolyte at a constant stirring rate. The whole reaction was performed at room temperature under constant voltages of 3—5 V and electric current density of 1.0 A/dm³. After it was dried, an SSWM-supported manganese oxide catalyst was prepared by an impregnation method, and the content of manganese was 6 wt%.

Then the aqueous solutions of H_2PdCl_6 were used as precursors for PdO. Finally, the catalyst was calcined at 500 ℃ for 1 h.[13] The catalyst was denoted as 0.1%Pd-6%Mn/SSWM in the following context.

Activity measurement

Activity measurement of the catalysts in the combustion of toluene, acetone and ethyl acetate was carried out in a flow-reactor bed (length＝600 mm, i.d.＝28 mm) at atmospheric pressure. The reactant was introduced to the reactor by a carrying gas of air flowing through a saturator. The reactions were performed in the temperature range of 220—340 ℃ at gas hourly space velocity (GHSV) of 10000 h^{-1}. The concentrations of toluene, acetone and ethyl acetate were in the range of 4—6 g•m^{-3}. The sample was placed at the center of the reactor and a thermocouple was positioned in the catalyst bed for accurate measurement of the reaction temperatures. The compositions of the feed stream and the products at the outlet of the reactor were evaluated on-line by gas-chromatography (GC-8A).

Characterization of catalysts

The morphologies of the stainless steel wire mesh support, 6%Mn/SSWM and 0.1%Pd-6%Mn/SSWM catalysts were characterized by a scanning electron microscope (SEM, JSM-5610Lv). Temperature programmed reduction (TPR) experiments by H_2 were carried out using 600 mg of catalysts under a gas flow (30 mL/min) of hydrogen (5%) and nitrogen (95%). The temperature of catalysts was linearly increased from 25 to 700 ℃ at a rate of 15 K/min, and the amount of hydrogen consumed was determined on-line by gas-chromatography (GC-1690) with a thermal conductivity detector (TCD). Moreover, the stability experiment was carried out on the 0.1%Pd-6%Mn/SSWM catalyst, with the atmosphere of toluene at 240 ℃ for 700 h. The gas hourly space velocity (GHSV) was also at 10000 h^{-1}, and the concentration of toluene was 4—6 g•m^{-3}.

Results and discussion

Externality of catalysts

SEM result The morphologies of SSWM before and after anodic oxidation treatment at room temperature were measured with scanning electron micrographs. It can be seen clearly from the SEM images of Figure 1 (A and B) that a membrane with donga structure layer is formed on the stainless steel wire mesh surface after anodic oxidation treatment. And the surface of the membrane layer is quite inhomogeneous with many pores the diameter of which was less than 1 μm. Therefore the anodic oxidation treatment significantly changes the surface morphology of SSWM. This structure of membrane layer was favorable for dispersing active phases, such as palladium or manganese. Thus, we think that the presence of anodic oxidation mem-
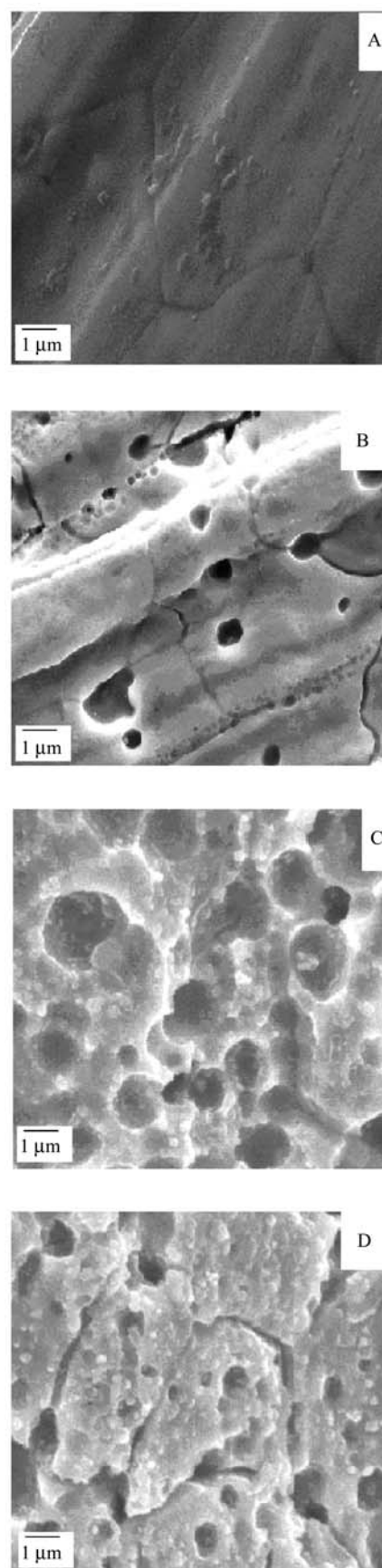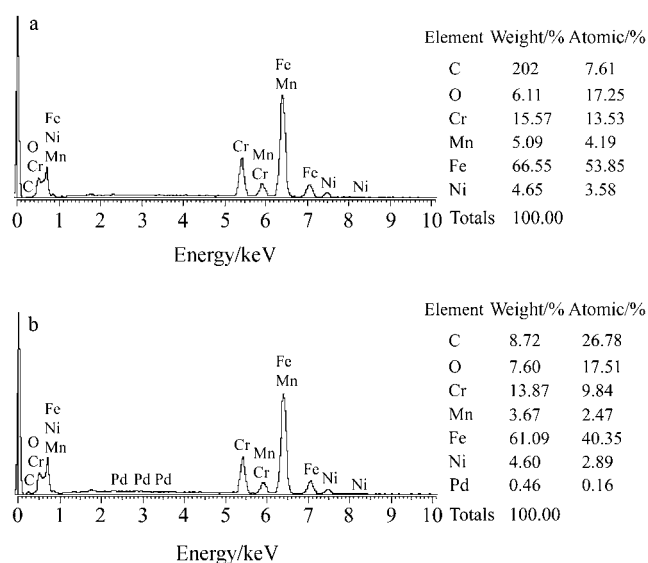

Figure 1 SEM images of different samples. (A) SSWM; (B) SSMW after anodic oxidation treatment; (C) Mn/SSWM; (D) Pd-Mn/SSWM.

brane seems to be important to offer a synergistic interaction between the support and active component[13].

The SEM images of the Mn/SSWM and Pd-Mn/SSWM catalysts were showed in Figure 1 (C and D). Compared with the pictures above (A and B), some alveolate-like hole appeared after the loading of active phases. After supporting Pd on the Mn/SSWM, the number of cavities seemed diminished. It may be related to an enhanced interaction between palladium and manganese particles, which resulted in the improvement in the catalytic performance. As literature described,[8,9] bimetallic catalysts have attracted extensive attention because of their markedly different properties from either of the constituent metals, and enhanced catalytic stabilities and activities. So later on, we found that the catalytic activities of Pd-Mn/SSWM catalyst were much better than that of the Mn/SSWM catalyst.

EDX results To further confirm the palladium and manganese compositions of the catalyst, energy-dispersive X-ray spectroscopy (EDX) was recorded in Figure 2. The result exhibits that besides some other metals, such as Cr and Ni, which are the makeup of SSWM, Mn and Pd can be detected on both of the two catalysts. It can be confirmed that the active components were loaded on the surface of catalyst.

Element	Weight/%	Atomic/%
C	202	7.61
O	6.11	17.25
Cr	15.57	13.53
Mn	5.09	4.19
Fe	66.55	53.85
Ni	4.65	3.58
Totals	100.00	

Element	Weight/%	Atomic/%
C	8.72	26.78
O	7.60	17.51
Cr	13.87	9.84
Mn	3.67	2.47
Fe	61.09	40.35
Ni	4.60	2.89
Pd	0.46	0.16
Totals	100.00	

Figure 2 EDX of the Mn/SSWM (a) and Pd-Mn/SSWM (b) catalysts.

Figure 3 showed the schematic of the formation of anodic oxidation process and the presence state of manganese and palladium over Pd-Mn/SSWM catalyst. Also, it is a sketch map to show that the active phases can be well loaded on the holes of the membrane on the SSWM. It can be seen that many special cavities that can offer more interface appeared on the membrane. Thus, the manganese oxide supported on SSWM, can be fastened onto the alveolate-like hole and offer more oxygen in the redox cycle during the reaction. Then,

after supporting palladium, a synergistic interaction between PdO and MnO_2 was formed.[12] In addition, the mechanism of toluene oxidation reactions over the Pd-Mn/SSWM catalyst is usually considered as Mars and van Krevelen's redox. The better performance of the supported palladium and manganese catalyst is related to the availability to release oxygen by the manganese and palladium oxides.
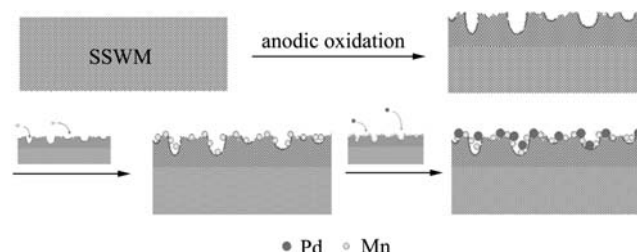
Figure 3 Schematic of the anodic oxidation process and the presence of manganese and palladium over Pd-Mn/SSWM catalyst.

TPR results

Figure 4 shows the TPR profiles of Mn/SSWM, Pd/SSWM and Pd-Mn/SSWM catalysts. For all samples investigated, there is a large peak around 500 ℃ corresponding to the reduction of SSWM. The peak at 90 ℃ on the supported Pd catalyst (A and B) can be attributed to the desorption of hydrogen adsorbed on the metallic palladium.[12,15] TPR curves (A and C) give an additional shoulder peak at 430 ℃, which can be attributed to the reduction of bulk phases of manganese oxide. To be noted, the reduction peak of SSWM was moved to lower temperature after PdO loaded on the support, which may be related to the interaction between the PdO activity phases and the support.
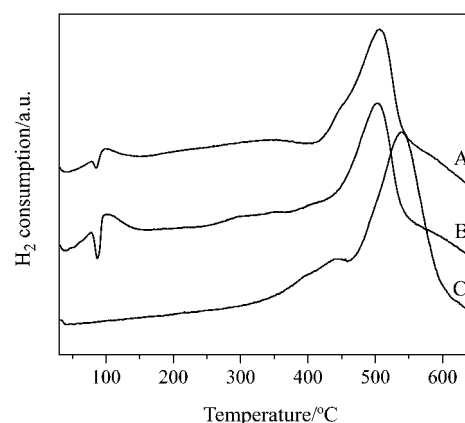

Figure 4 TPR profiles of Pd-Mn/SSWM (A), Pd/SSWM(B) and Mn/SSWM (C).

Activity measurement

Figure 5 shows the light-off curves of toluene, acetone and ethyl acetate oxidation over the series of the Mn/SSWM and Pd-Mn/SSWM catalysts calcined at 500 ℃. It can be seen clearly that 0.1%Pd-6%Mn/SSWM

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catalyst shows the highest activity. Taking toluene oxidation as a model, the light-off temperature is 260 ℃ for Mn/SSWM catalyst and decreases to 220 ℃ for 0.1%Pd-6%Mn/SSWM catalysts. The same trend can be found on the acetone and ethyl acetate oxidation processes. Simultaneously, it was found that the catalytic activity for the three VOC substances of toluene, acetone and ethyl acetate was enhanced by the addition of Pd. Compared with the previous work[13], 0.1%Pd-6%Mn/SSWM catalyst can obtain the same activity for toluene and acetone oxidation as the stainless steel supported Pt-Pd catalyst. The conversion of toluene and acetone oxidation reached 98% at 220 and 260 ℃. Apparently, it indicated that the 0.1%Pd-6%Mn/SSWM catalyst prepared using manganese element to replace some of platinum element showed an optimism application foreground.
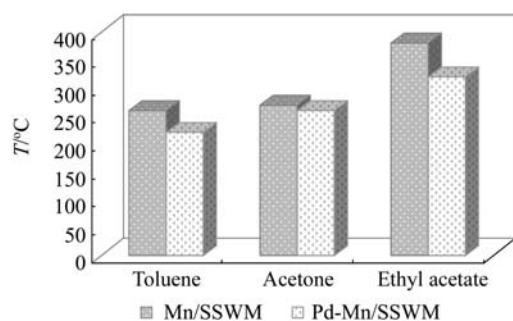

Figure 5 Light-off curves for toluene, acetone and ethyl acetate over different catalysts.

Stability test

The stability is one of crucial factors to evaluate the activity of catalysts. Furthermore, the carbon dioxide and water produced during the reaction, would cause changes of the catalyst surface and make the activity deteriorated. Similarly, it is clear that 0.1%Pd-6%Mn/SSWM catalyst shows high activity for toluene total oxidation. In order to examine its stability, the influence of reaction time on the toluene conversion was investigated. Controlling the reaction temperature of 240 ℃, gas hourly space velocity (GHSV) of 10000 h^{-1}, and the concentration of toluene in 4—6 g•m^{-3}, we found that the catalyst showed a novel stability even after 700 h long time test, as shown in Figure 6.

Conclusion

It is clear that 0.1%Pd-6%Mn/SSWM catalyst is a very active and suitable catalyst for the oxidation of toluene, acetone and ethyl acetate. Due to the new catalyst of palladium and manganese supported on SSWM, pretreated by an anodic oxidation, the palladium and
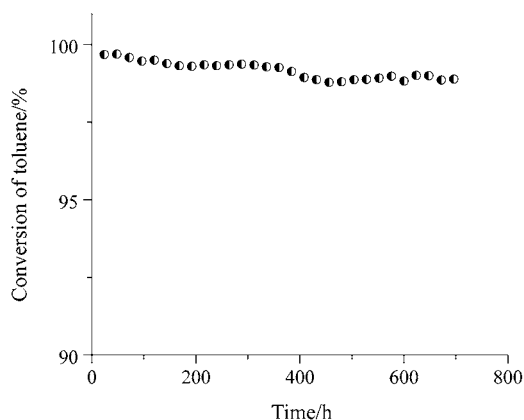
Figure 6 Conversion of toluene -time curve on Pd-Mn/SSWM.

manganese particles could well disperse on the surface of the support. Compared with Mn/SSWM catalyst, 0.1%Pd-6%Mn/SSWM shows much higher activity. Amazingly, the activity can be stable for over 700 h at 240 ℃ for toluene oxidation. SEM and TPR measurements demonstrated that the highly dispersed PdO and MnO_2 are active phases for these catalysts.

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