Noble metal catalysts growing on polyurethane foam monoliths by electroless plating deposition method for formaldehyde purification at room temperature

Zehua Xu, Jiawei Chen, Ying Feng, Jiankang Guan, Yongshen Dou, Sanmao Liu and Yongfeng Li

1School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, PR China
2Foshan Shunde Kinglei Environment & Technology Co., LTD, Foshan 528308, PR China

*Corresponding author e-mail: gdliyf@gdut.edu.cn

Abstract. A series of monolithic catalysts were prepared by growing noble metals of Pt and Pd on polyurethane foam (PUF) monoliths via electroless plating deposition method. The as-prepared Pt-Pd/PUF monolithic catalysts can preserve the same size, shape and macroporous network of the pristine PUF monoliths. And the noble metal active components of Pt and Pd nanoparticles were uniformly dispersed on the surface of PUF monoliths. Therefore, compared to the low formaldehyde conversion of 14% over pristine PUF monolith, the obtained Pt-Pd/PUF monolithic catalysts exhibited excellent formaldehyde purification activity at room temperature: the formaldehyde conversion can reach as high as 66%.

1. Introduction
Formaldehyde (HCHO) is currently the main indoor pollutant, usually from interior decoration materials. Because it seriously impact on human health [1], it is very meaningful to find a way to degrade formaldehyde at room temperature. To this end, people have developed a series of methods to purify formaldehyde: adsorption[2], plasma treatment[3], catalytic oxidation[4] and so on.

Nowadays, catalytic oxidation is a widely used method for treating polluted air[4]. The advantage of it is the ability to completely convert pollutants into carbon dioxide and water. Previously, He et al. have studied Pd/TiO$_2$ or Pt/TiO$_2$ catalyst, whose active component is Pt or Pd, and it has the ability to turn HCHO into CO$_2$ and H$_2$O at room temperature[5,6].In many studies, MnO$_2$ powder[3], Pd/TiO$_2$ powder[5] or Pt/TiO$_2$ powder[6] have been used as catalysts for purifying formaldehyde, but powdered catalysts are relatively easy to lose in practical and industrial applications. Thus, in practical applications, it is very urgent to find a method for loading Pt and Pd active components on monolithic support to prevent catalyst losing in application.

Polyurethane foam (PUF), as a common decorative material, has rich porous structures, which facilitates the diffusion of fluids so that PUF can be used as a kind of support for catalysis or adsorption [7]. It is meaningful to find a method to let platinum and palladium grow on the surface of PUF, and get PUF catalyst. Therefore, in this study, Pd-Pt/PUF monolithic catalysts was synthesized by electroless plating deposition (EPD), with formaldehyde purification capability at room temperature.
2. Experimental

2.1. PUF monolithic catalysts synthesis
The Pt-based catalysts supported on polyurethane foam (PUF) substrates were synthesized by the electroless plating deposition technique, as illustrated in Fig.1. The PUF substrates were cut into the cuboid shape, so that they could directly be used for formaldehyde purification activity test. In order to load Pd crystal nucleus on the surface of PUF, PUF must be immersed in 10.0 g/L SnCl₂ for 5min, and then put PUF into 0.05 g/L PdCl₂ for 5min. The sample obtained in the above steps is referred as actived PUF.

Subsequently, the pretreated samples were immersed in Palladium precursor solution (H₂PtCl₆: 0.25 g/L, NH₄Cl: 6.7g/L, NH₃•H₂O: 0.4 L/L). The PUF-loaded platinum precursor solution was placed in a hot water bath, heated to 40 °C for 30 minutes, held at 50 °C for 1 hour, and finally held at 60 °C for 30 minutes. At the same time, 10% hydrazine hydrate was used as a reducing agent for the reaction system. To ensure deposition of Pt particles on the PUF surface, 5 ml of 10% hydrazine hydrate was added to the PUF surface every 20 minutes during the reaction. The monolith catalyst is denoted as Pd-Pt/PUF.

2.2. Catalysts characterization
The samples were analyzed by scanning electron microscopy (SEM, Phenom pro) with energy dispersive spectrometer (EDS).

2.3. Catalytic test
The prepared PUF was placed on a small fan and placed in a simulation box (0.7 x 0.7 x 0.5 m, approximately 245 L) for formaldehyde purification test. According to GB / T 18204.2-2014, using the phenol reagent method, the TYQ-1000 atmospheric sampler was used to measure the HCHO concentration in the simulated box. The HCHO conversion was calculated and used to evaluate the activity of the catalyst to purify formaldehyde at room temperature.

3. Results and Discussion
Optical photographs of PUF samples obtained in different experimental stages are shown in Fig.2. The colour of PUF samples after load processing, has changed from the original yellow to a little grayish yellow. From the SEM images (Fig. 2. a’-c’), PUF, activated PUF and Pd-Pt/PUF have the same skeleton structures with rich pores of 100 to 300 μm diameter. It shows that electroless plating deposition method just make Pt and Pd active components on the PUF surface evenly without destroying the monolithic skeleton structures, so that reaction gases diffuse to the surface of Pd-Pt/PUF and conducive to catalytic reaction. Meanwhile, it reveals that As the reaction progresses, more and more active components are grown in-situ on the PUF, and the surface of the support becomes significantly rougher. As shown in higher magnification SEM images (Fig.2 a”- c”), activated PUF and Pd/Pt/PUF are significantly more white small spots on the skeleton walls than pure PUF, indicating that successful solid particles are deposited on the surface of the PUF.
EDS analysis of different PUF samples is shown in Tab. 1. Form the Tab. 1, C, N, and O elements are mainly composed of a monolithic PUF support. SEM images and EDS analysis of activated PUF reveal that Pd element successfully load on the surface of PUF. Moreover, through Fig. 2 c’’ and Tab. 1, Pd-Pt/PUF become rough, because Pd and Pt particles growing uniformly on the surface of PUF.

**Table 1. Main elements concentrations on the surface of different samples by EDS analysis.**

| Sample          | Elemental content (mass%) |
|-----------------|---------------------------|
|                 | O  | C   | N   | Pd  | Pt  |
| pure PUF        | 70.78 | 19.63 | 9.59 | —   | —   |
| activated PUF   | 69.67 | 22.51 | 7.08 | 0.75 | 0.00 |
| Pd-Pt/PUF       | 68.93 | 22.02 | 7.18 | 0.80 | 1.07 |

The room temperature formaldehyde purification of the prepared PUF samples is shown in Fig. 3. Pure PUF cause a little loss of formaldehyde concentration in simulation box, showing a certain formaldehyde conversion rate of 14.0%, because PUF has porous structures. And the porous structures of PUF are convenient for formaldehyde gas diffuse into the porous structures, and it can adsorb a small amount of formaldehyde gas. It is an obvious fact that formaldehyde purification activity of the activated PUF and Pd-Pt/PUF are better than that of the pure PUF. Under the same formaldehyde purification test condition, the HCHO conversion of Pd-Pt/PUF can be 66 %, when the HCHO conversion of activated PUF is 26%. The Pd and Pt particles on PUF synthesized by EPD are suitable for degrading formaldehyde at room temperature. When both Pd and Pt elements are present, the two elements can purify formaldehyde together, so that the Pd-Pt/PUF monolithic PUF catalyst has the best formaldehyde purification performance.
Figure 3. HCHO purification activity on different catalysts at room temperature.

4. Conclusion
The Pd-Pt/PUF catalysts are successfully prepared by electroless plating deposition without destroying the skeleton and original porous structures of the supports. Also, Electroless plating deposition method can make Pt and Pd dispersed on skeleton walls of PUF surface, so two active components can jointly purify formaldehyde gas on the same carrier surface. In first use, the HCHO conversion of Pd-Pt/PUF monolithic catalysts is obviously higher than Pd/PUF. Meanwhile, the formaldehyde conversion of Pd-Pt/PUF is able to reach to 66%.

Acknowledgments
This work was financially supported by National Natural Science Foundation of China (Grant No. 51678160), Guangdong Province Science and Technology Project (Grant No. 2016A020221033), Guangzhou Science and Technology Project (Grant No. 201704020202), and National Undergraduate Training Program for Innovation and Entrepreneurship (Design and development of a new multifunctional air purifier).

References
[1] J.J. Collins, R. Ness, R.W. Tyl, N. Krivanek, N.A. Esmen, T.A. Hall, A review of adverse pregnancy outcomes and formaldehyde exposure in human and animal studies, Regul Toxicol Pharmacol, 34 (2001) 17-34.
[2] S. Suresh, T.J. Bandosz, Removal of formaldehyde on carbon -based materials: A review of the recent approaches and findings, Carbon, 137 (2018) 207-221.
[3] T. Wang, S. Chen, H. Wang, Z. Liu, Z. Wu, In-plasma catalytic degradation of toluene over different MnO2 polymorphs and study of reaction mechanism, Chinese Journal of Catalysis, 38 (2017) 793-803.
[4] B. Bai, Q. Qiao, J. Li, J. Hao, Progress in research on catalysts for catalytic oxidation of formaldehyde, Chinese Journal of Catalysis, 37 (2016) 102-122.
[5] C. Zhang, Y. Li, Y. Wang, H. He, Sodium-promoted Pd/TiO2 for catalytic oxidation of formaldehyde at ambient temperature, Environ Sci Technol, 48 (2014) 5816-5822.
[6] C. Zhang, H. He, K.-i. Tanaka, Catalytic performance and mechanism of a Pt/TiO2 catalyst for the oxidation of formaldehyde at room temperature, Applied Catalysis B: Environmental, 65 (2006) 37-43.
[7] E.E. Baldez, N.F. Robaina, R.J. Cassella, Employment of polyurethane foam for the adsorption of Methylene Blue in aqueous medium, J Hazard Mater, 159 (2008) 580-586.