The influence of different thermal pretreatments on silica-supported Pt catalysts: particle formation and formaldehyde oxidation mechanism

Hung-Chi Wu,[a] Ching-Shiun Chen[a,b,*]

[a]*Center for General Education, Chang Gung University, 259, Wen-Hua 1st Rd., Guishan District, Taoyuan City 33302, Taiwan, Republic of China*

[b]*Department of Pathology, Chang Gung Memorial Hospital, Linkou, 5 Fusing St., Guishan District, Taoyuan City 33302, Taiwan, Republic of China*

**Corresponding author:* cschen@mail.cgu.edu.tw

Abstract: In this work, we synthesize Pt particles less than 1 nm in diameter that are uniformly dispersed on silica via thermal treatment of 0.2 wt.% Pt^{4+} deposited on SiO_2 through vacuum calcination and H_2 reduction (Pt/SiO_2-VH). The tiny Pt particles have an improved reaction rate and better catalytic stability for formaldehyde (HCHO) oxidation than traditional treatment catalyst, Pt/SiO_2-AH (air calcination/H_2 reduction on the same 0.2 wt.% Pt^{4+}/SiO_2). The CO decomposition product from HCHO could be the key intermediate in the course of HCHO oxidation, and the oxidative reaction pathway should be HCHO → CO → CO_2. Adsorbed HCHO may bond to the Pt surface in the η^2 configuration and form CO through a decomposition process.

Keywords: Platinum (Pt), catalyst, formaldehyde (HCHO) oxidation.

1. Introduction

Formaldehyde (HCHO) is a dominant indoor air pollutant, and long-term exposure to formaldehyde can cause several health problems.[1,2] Numerous methods have been investigated for reducing indoor HCHO pollution, and supported Pt catalysts have been used frequently and demonstrated to be effective for HCHO oxidation at low temperatures.[3-5] The synthesis of highly dispersed Pt catalysts with small particle size may be attributed to their potential for improving the efficiency of HCHO decomposition. Here, vacuum calcination of Pt particles deposited on SiO_2 was applied to significantly reduce their size to less than 1 nm. In this study, we characterize Pt/SiO_2 catalysts and probe the mechanism of particle formation to evaluate the catalytic mechanism leading to high activity.

2. Experimental

0.2 wt.% Pt/SiO_2 catalysts were prepared by impregnating SiO_2 with aqueous H_2PtCl_6 and calcined in vacuum or air environment, and then followed by reduction in H_2 at 400 ℃ for 5 h. We use XRD, TEM, H_2-TPR, TPD, FT-IR, and XAS methods to characterize the as-synthesized catalysts.

3. Results and discussion

HRTEM images of the Pt NPs from the reduced Pt/SiO_2-VH and Pt/SiO_2-AH catalysts are shown in Figure 1. The image of the reduced Pt/SiO_2-VH sample shows extremely tiny Pt particles that are uniformly dispersed on the SiO_2 surface. Conversely, the image of the Pt/SiO_2-AH sample reveals relatively large and inhomogeneous Pt NPs.

Figure 1 also shows the comparison of the temperature-dependent turnover frequencies (TOFs) for formaldehyde oxidation on the Pt/SiO_2-VH and Pt/SiO_2-AH catalysts. The reaction efficiency of Pt/SiO_2-VH was apparently higher than that of Pt/SiO_2-AH within the temperature range 25–100 ℃. Long-term tests for formaldehyde oxidation on both catalysts were further carried out at 100 ℃. Clearly, the Pt/SiO_2-VH catalyst provided high stability, as the initial TOF rate decreased slightly by ~10% over 60 h. Interestingly, the Pt/SiO_2-AH catalyst exhibited an initial TOF of 0.85 s^{-1} and then was strongly deactivated to 0.36 s^{-1}

within 60 h. Undoubtedly, the large difference in the reaction efficiency of formaldehyde oxidation between the two catalysts should be ascribed to the different calcination treatments.

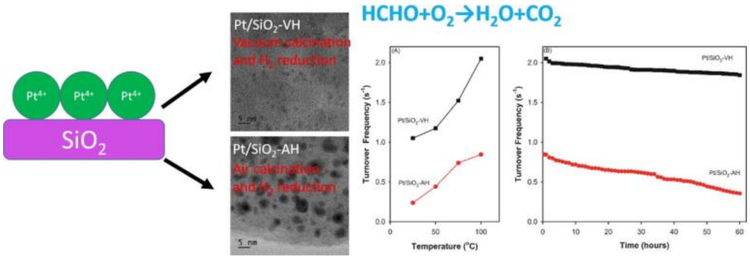

Figure 1. TEM images of Pt/SiO$_2$-VH and Pt/SiO$_2$-AH catalysts, and the comparisons for their formaldehyde oxidation behaviors.

A reaction pathway for the configuration of HCHO adsorption and catalytic oxidation was developed and is shown in Figure 2. Initially, η^2-HCHO was the major species for adsorption on the Pt surface. The η^2-HCHO could decompose to CO and atomic H, and then be oxidized by O_2, following pathway 1. The molecular η^2-HCHO could be converted to η^1-HCHO with O_2 adsorption on pathway 2, but contributed to the oxidation reaction with low efficiency. In this work, the η^2-HCHO adsorbed onto the Pt/SiO$_2$-VH catalyst might apparently tends to follow pathway 1, leading to high reactivity for catalytic oxidation.

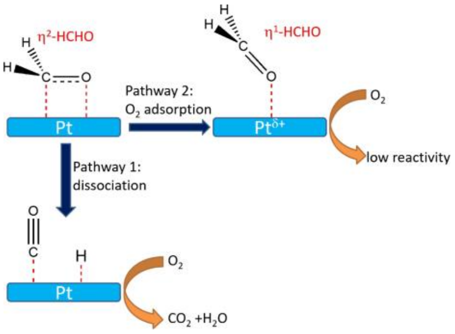

Figure 2. Proposed mechanism for the decomposition and catalytic oxidation of HCHO on the Pt surface.

4. Conclusions

Pt/SiO$_2$ catalysts prepared via vacuum calcination and H_2 reduction of a low Pt^{4+} concentration impregnated on SiO$_2$ have significantly better catalytic efficiency and catalytic stability for HCHO oxidation. The highly dispersed and tiny Pt NPs in Pt/SiO$_2$-VH are superior to induce HCHO decomposition. The adsorbed HCHO may bond to the Pt surface through the η^2 configuration, in which the carbonyl group is nearly parallel to the surface, and the decomposition of η^2-HCHO forms CO, and the reaction pathway would be HCHO → CO → CO_2. The high stability of the Pt/SiO$_2$-VH catalyst can be ascribed to the reducibility of Pt NPs not changing during HCHO oxidation, because the large amount of the CO intermediate resulting from HCHO dissociation can serve as a reductant and retard oxidation by air.

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