Complete oxidation of formaldehyde on Pd/TiO$_2$ catalyst at room temperature: the effect of temperature reduction

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Abstract: High temperature reduction generally induces the sintering of supported noble metals, therefore resulting in a negative effect on their performance. Here, we show that high temperature reduction was able to dramatically increase the activity of Pd/TiO$_2$ for ambient HCHO oxidation. We prepared a Pd/TiO$_2$ catalyst and pre-reduced it with H$_2$ at low temperature (300 ^oC) and high temperature (450 ^oC), respectively, and then tested the activity for HCHO oxidation at ambient temperature. The Pd/TiO$_2$-450R catalyst showed a much better performance than Pd/TiO$_2$-300R at room temperature, which can be attributed that high temperature reduction could induce the strong metal-support interaction (SMSI), decreasing the surface Pd particle size by partially encapsulating and trapping Pd clusters with TiO$_2$, and also could produce more oxygen vacancies, beneficial to the activation of O$_2$ and formation of surface OH groups.

Keywords: formaldehyde, catalytic oxidation, Pd/TiO$_2$

1. Introduction

Catalytic oxidation of Formaldehyde (HCHO) to CO$_2$ at ambient conditions is of great interest for indoor HCHO purification.[1] Most recently, it was found that Pd based catalysts exhibited the excellent activity for HCHO oxidation at room temperature and that their activities were closely related to the reduction treatment [2], alkali metal promoter [3] and morphology of support [4]. According to the previous works, it was reported that the reduction treatment, especially reduction temperature, have great effects on the activity of Pd based catalysts for some reactions. [5, 6] Therefore, it is worth to explore the influence of reduction temperature on Pd/TiO$_2$ catalyst for HCHO oxidation. In this study, Pd/TiO$_2$ catalyst was prepared and pre-reduced at low temperature (300 ^oC) and high temperature (450 ^oC) by H$_2$ before tested for HCHO oxidation at ambient temperature. Based on the results of Characterizations, the mechanism of promotion effect of high temperature reduction are discussed and elucidated.

2. Experimental

1 wt. % Pd/TiO$_2$ were prepared by co-impregnation. Before activity test and characterization, the samples were reduced with H$_2$ at 300 ^oC or 450 ^oC for 1 h. Specific surface area ($S_{BET)}$, CO pulsed chemisorption, X-ray photoelectron spectroscopy (XPS), High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and HCHO temperature program desorption (HCHO-TPD) were carried out to elucidate the influence of high temperature reduction.

3. Results and discussion

Figure 1 showed that compared to Pd/TiO$_2$-300R catalyst, the Pd/TiO$_2$-450R catalyst possessed an excellent performance of HCHO oxidation at room temperature. According to **Table 1**, Pd dispersion of Pd/TiO$_2$-450R decreased, compared to that of Pd/TiO$_2$-300R, which may be attributed to agglomeration of Pd particles. However, based on the result of HAADF/STEM (as showed in **Table 1**), the Pd particle size on Pd/TiO$_2$-450R catalyst reversely decreased. This kind of abnormal phenomenon should be ascribed to the encapsulation of Pd particle by the reduced TiO$_2$ (TiO$_{2-x}$) during the reduction treatment which facilitates the electron transfer from the TiO$_{2-x}$ to the metallic Pd and further can enhance O$_2$ adsorption. Meanwhile, the Pd/TiO$_2$-450R catalyst possessed more Ti-OH species than Pd/TiO$_2$-300R, which may be due to oxygen vacancies formed during high temperature reduction enhanced H_2O dissociation. The presence of abundant surface OH groups could facilitate O_2 activation and diffusion and also accelerate the partial oxidation of HCHO to formate and also could directly react with formate species to final CO_2 and H_2O at ambient temperature which can be demonstrated from the result of HCHO-TPD (in **Figure 2**). As shown in **Figure 2a**, abundant CO and CO_2 and a little of H_2 was desorbed on Pd/TiO_2-300R, while only the CO_2 desorption was observed on the Pd/TiO_2-450R catalyst, indicating that there may be a more effective pathway for the direct oxidation of surface formate on Pd/TiO_2-450R catalyst.

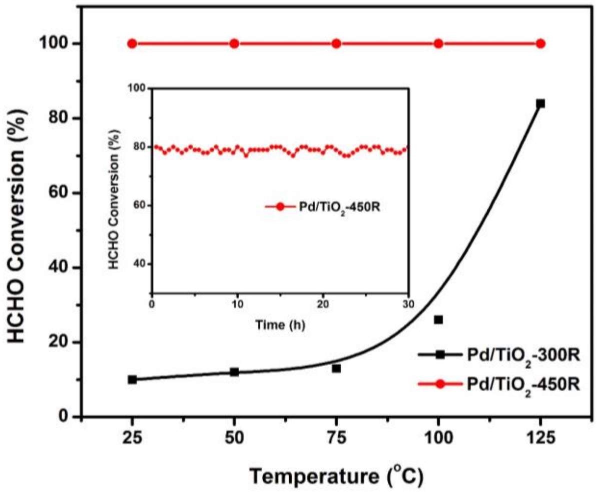

Figure 1. HCHO conversion over Pd/TiO_2 catalysts.

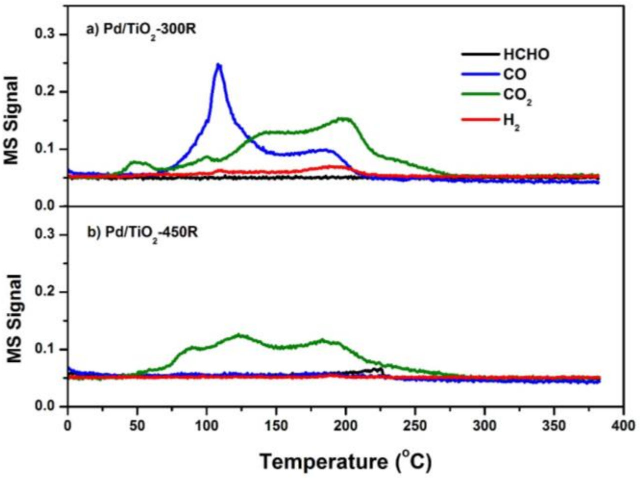

Figure 2. HCHO-TPD of Pd/TiO_2 catalysts

Table 1. Pd dispersion (DCO), Pd mean particle size (ds) and relative amount of surface OH groups (Ti-OH) of Pd/TiO_2 samples.

samples	D_{CO} [a] (%)	d_s [b] (nm)	Ti-OH [c] (%)
Pd/TiO_2-300R	21.4	4.9	14.9
Pd/TiO_2-450R	16.9	3.8	23.3

[a] Pd dispersion measured with CO pulse chemisorption; [b] Pd mean particle size from HAADF-STEM;
[c] Concentration of Ti-OH calculated from the XPS of O 1s.

4. Conclusions

The SMSI induced by high temperature reduction could partially encapsulate the Pd particles, resulting in a smaller particle size on the catalyst surface, and subsequently promoting the activation of O_2. In addition, the partial reduction of TiO_2 at high temperature resulted in more oxygen defects and further enhanced the dissociation of H_2O to form abundant surface OH groups. Therefore, the Pd/TiO_2-450R catalyst exhibits much higher activity than Pd/TiO_2-300R for HCHO oxidation at room temperature.

References

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