

Sodium-promoted Pd/TiO₂ for catalytic oxidation of formaldehyde at ambient temperature

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Introduction

Catalytic oxidation of Formaldehyde (HCHO) to CO₂ under ambient conditions is of great interest for indoor HCHO removal.[1] Compared with the transition metal oxides, the noble metal catalysts such as Pt-, Pd- and Au-based catalysts have exhibited excellent activity for catalytic oxidation of HCHO at around 25 °C and therefore are more suitable for indoor air HCHO removal. [2] Previously, we demonstrated that the addition of alkali ions (such as Li⁺, Na⁺ and K⁺) could dramatically promote the catalytic efficacy of Pt/TiO₂ catalyst by inducing and stabilizing an atomically dispersed Pt species. We also proposed that this promotion effect of alkali ions on Pt catalysts may apply to other noble-metal-based catalysts. [3] Considering the high cost of Pt-based catalysts, it is worth exploring whether the Na-promotion effect for Pt is also manifested for Pd catalysts. In this study, we prepared Pd/TiO₂ catalysts with and without sodium (Na) addition and tested their catalytic activity for HCHO oxidation at low temperature. Based on the characterization results, the mechanism of the Na-promotion effect on the Pd/TiO₂ catalyst was clearly elucidated.

Materials and Methods

The 1 wt.% Pd/TiO₂, 2 wt.% Na/TiO₂ and 2 wt.% Na-1 wt.% Pd/TiO₂ samples were prepared by co-impregnation of TiO₂ (Degussa P25) with aqueous NaNO₃ and Pd(NO₃)₂ (Aldrich) for 1 h. After impregnation, the excess water was removed in a rotary evaporator at 60 °C. The samples were dried at 110 °C for 12 h and then calcined at 400 °C for 2 h. The samples reduced with H₂ at 350 °C for 30 min were denoted as 2Na/TiO₂-R, Pd/TiO₂-R and 2Na-Pd/TiO₂-R. The experiments were conducted at a GHSV = 95,000 h⁻¹ and HCHO inlet concentration of 140 ppm. The mechanism of the Na-promotion effect was investigated by Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), CO chemisorption, Temperature-programmed reduction by H₂ (H₂-TPR), X-ray photoelectron spectroscopy (XPS) and Temperature-programmed desorption by O₂ (O₂-TPD) methods.

Results and Discussion

Figure 1 shows the HCHO conversion over TiO₂, 2Na/TiO₂, Pd/TiO₂ and 2Na-Pd/TiO₂ samples before (a) and after (b) reduction at different temperatures. Remarkably, Na addition demonstrated a dramatic promotion effect on Pd/TiO₂ after H₂ reduction. Table 1 summarizes the dispersion of Pd and XPS data for Pd/TiO₂ and 2Na-Pd/TiO₂ catalysts. Na addition to Pd/TiO₂ remarkably increased the Pd dispersion from 9.8% for Pd/TiO₂-R to 32.9% for 2Na-Pd/TiO₂-R, which induced a more dispersed Pd species on the 2Na-Pd/TiO₂-R catalyst that exposed more Pd sites for HCHO oxidation. Compared with Pd/TiO₂-R, the 2Na-Pd/TiO₂-R catalyst showed a Pd 3d_{5/2} peak at the low binding energy of 334.0 eV, indicating that the doped Na, as an electron donor, led to the formation of a negatively-charged Pd species by its

strong interaction with metallic Pd. The negatively-charged Pd species could enhance O₂ adsorption. In addition, a negative shift of Ti 2p occurred over the reduced sample, which indicated that the doped Na species may improve the reduction of TiO₂. The presence of oxygen vacancies could facilitate the activation of chemisorbed H₂O, which could be demonstrated by the O 1s XPS results, that is, there were more Ti-OH species (530.8 eV) for the 2Na-Pd/TiO₂-R sample than the other catalysts.

Figure 1 HCHO conversion over TiO₂, 2Na/TiO₂, Pd/TiO₂ and 2Na-Pd/TiO₂ samples before (a) and after (b) reduction at different temperatures.

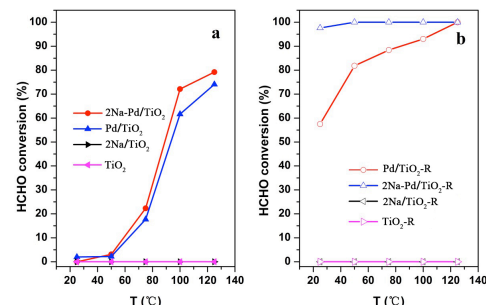


Table 1 XPS data and Pd dispersion for Pd/TiO₂ and 2Na-Pd/TiO₂ catalysts

Sample	XPS					D _{co} ^a /%
	Pd 3d _{5/2}		O 1s		Ti 2p	
	B.E.(eV)	Ratio/%	B.E.(eV)	Ratio/%	B.E.(eV)	
Pd/TiO ₂	336.4	100	529.7 531.4	91.1 8.9	458.8	--
Pd/TiO ₂ -R	335.1 336.4	66.0 34.0	529.1 531.4	90.5 9.5	458.5	9.8
2Na-Pd/TiO ₂	336.4	100	529.3 531.8	91.1 8.9	458.3	--
2Na-Pd/TiO ₂ -R	334.0 335.1 336.4	65.1 19.3 15.6	529.2 530.8	84.3 15.7	458.0	32.9

^a dispersion of Pd measured by CO chemisorption.

Significance

Herein, we discover that Na addition has a dramatic promotion effect on Pd/TiO₂ after H₂ reduction and demonstrate the mechanism of the Na-promotion effect.

References

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