



Significant enhancement in activity of Pd/TiO₂ catalyst for formaldehyde oxidation by Na addition



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ABSTRACT

Developing an effective material for indoor HCHO elimination at ambient temperature is of great significance. In this work, a series of Pd/TiO₂ catalysts with different Na loadings were prepared and tested for their activity in HCHO oxidation. The results indicated that Na addition had a remarkable promotion effect on Pd/TiO₂ catalysts for HCHO oxidation, and the optimal Na loading was 2 wt.%. Features of the catalysts including the reducibility, Pd dispersion and valence state of Pd and O were elucidated using a variety of characterization techniques. The results showed that 2.0Na-Pd/TiO₂ exhibited more exposure of active Pd sites and contained abundant surface OH groups, giving it the best HCHO catalytic oxidation performance of the studied catalysts. The 2.0Na-Pd/TiO₂ catalyst also had high resistance to effects of space velocity and relative humidity (RH), maintaining high HCHO conversion over a wide gas hourly space velocity range of 80,000–190,000 h⁻¹ and RH of 25%–65%.

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1. Introduction

With the advance of technology, people have gradually come to prefer an indoor lifestyle, resulting in that increasing numbers of people suffer from Sick Building Syndrome (SBS). Among indoor air pollutants, formaldehyde (HCHO), which is mainly emitted from consumer products and building/furnishing materials, is considered the most toxic [1]. It is well known that long-term exposure to indoor air containing HCHO, even at very low ppm level, may lead to serious health problems including nasal tumors, irritation of the mucous membranes of the eyes and respiratory tract, skin irritation, decreased concentration, and weakened immunity [2,3]. Therefore, to improve indoor air quality and reduce public health risk, effective materials and technologies for indoor air HCHO removal are urgently needed.

Over the past decades, researchers have focused their attention on four technologies including adsorption [4,5], photo-catalysis [6], plasma technology [7] and catalytic oxidation [8–15]. Among these methods, catalytic oxidation is regarded as the most promising

method for indoor HCHO elimination due to its characteristics of high efficiency and non-pollution [16,17]. Transition metal oxides, such as Co₃O₄ [12], MnO₂ [13,18] and Ag₂O [19], generally need relatively high temperatures to completely oxidize HCHO, while supported noble metal catalysts such as those with Pt [9–11], Au [20–22], Rh [23] or Pd [15,24,25] have proved to be effective for HCHO elimination at low or even room temperature, and therefore they are more suitable for indoor air HCHO purification.

Alkali metals can serve as electronic or textural promoters for catalysts in various catalytic processes [26] including oxidation of NO [27] and CO [28,29], CO hydrogenation [30] and the water-gas shift reaction [31–33]. Recently, we found that addition of alkali metals (Li, Na and K) to Pt/TiO₂ catalysts could lead to more atomically dispersed Pt species and effectively enhance the O₂ and H₂O activation, resulting in a remarkable promotion effect on the performance of alkali-Pt/TiO₂ catalysts in HCHO oxidation [10]. Moreover, it was further found that Na addition also had an obvious promotion effect on Pd/TiO₂ catalysts for HCHO oxidation, due to the negatively charged and well-dispersed Pd species induced and stabilized by Na addition [25].

Herein, a series of Pd/TiO₂ catalysts with various amounts of Na addition were prepared and tested to clarify the effect of the amount of doped Na on their performance in HCHO oxidation. It was found that the performance of the Pd/TiO₂ catalyst was enhanced by different degrees by 1.0–8.0 wt.% Na addition, that is, 2 wt.% Na

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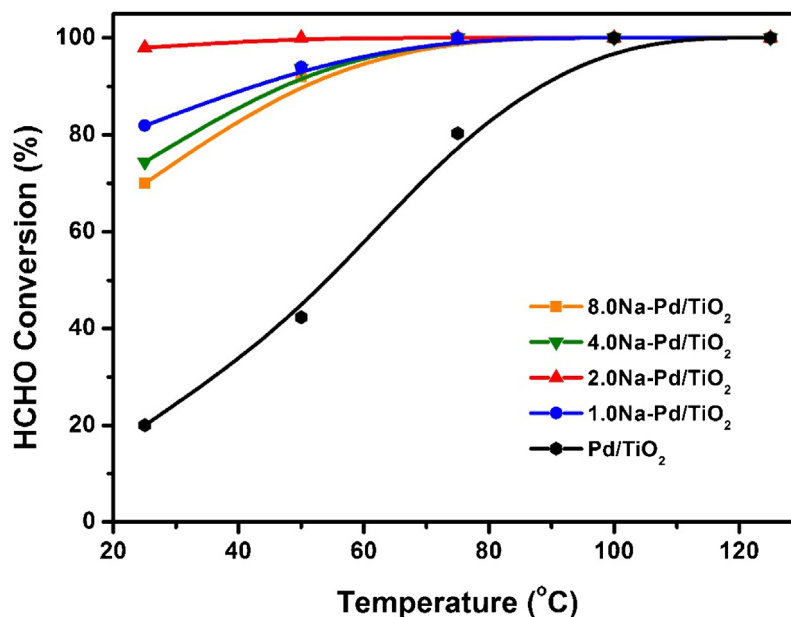


Fig. 1. HCHO conversion over Pd/TiO₂ catalysts. Reaction conditions: 140 ppm HCHO, 20% O₂, 25% RH, He balance, GHSV 95,000 h⁻¹.

addition exhibited the best performance in HCHO oxidation, with 100% conversion of 140 ppm HCHO at GHSV of 95,000 h⁻¹. Meanwhile, the activities of Na-Pd/TiO₂ catalysts were also affected by GHSV and relative humidity.

2. Materials and methods

2.1. Materials preparation

1 wt.% Pd/TiO₂ and Na-doped 1 wt.% Pd/TiO₂ catalysts with 1, 2, 4 and 8 wt.% Na addition were prepared by co-impregnation of TiO₂ (Degussa P25) with aqueous Pd(NO₃)₂ (Sigma-Aldrich) and NaNO₃ (Sinopharm Chemical Reagent Beijing Co., Ltd). After impregnation, the excess water was removed in a rotary evaporator at 60 °C. The samples were dried at 110 °C overnight and then calcined at 400 °C for 2 h. Before activity testing and characterization, the samples were reduced with H₂ at 350 °C for 30 min, and denoted as Pd/TiO₂, 1.0Na-, 2.0Na-, 4.0Na- and 8.0Na-Pd/TiO₂. The samples without pretreatment are denoted as TiO₂-fresh, Pd/TiO₂-fresh, 1.0Na-, 2.0Na-, 4.0Na- and 8.0Na-Pd/TiO₂-fresh.

2.2. Characterization of catalysts

Powder X-ray diffraction (XRD) was used to identify the crystalline phases present in the catalysts. Their XRD patterns were collected with an X'Pert PRO MPD X-ray powder diffractometer with Cu K α radiation operated at 40 kV and 40 mA. A Quantachrome Quadrasorb SI-MP analyzer was used to analyze the specific surface area and pore characterization of the catalysts, operated at -196 °C over the whole range of relative pressures. H₂ temperature-programmed reduction (H₂-TPR) experiments were performed in a Micromeritics AutoChem II 2920 apparatus, equipped with a computer-controlled CryoCooler and a thermal conductivity detector (TCD). The samples were placed in a U-type tube and pretreated in air (50 mL min⁻¹) at 400 °C for 30 min and then cooled down to 25 °C. After purging with Ar for 30 min, the reduction profiles were collected by passing a flow of 10% H₂/Ar through the sample at a rate of 50 mL min⁻¹. The temperature was increased from -50 to 600 °C at a rate of 10 °C min⁻¹, and the H₂ consumption was monitored by TCD after removal of the H₂O produced. The Pd dispersion of the

catalysts was measured by CO pulse chemisorption, which was also conducted on the Micromeritics AutoChem II 2920 apparatus. The samples (30 mg) were first pre-reduced at 350 °C for 30 min in 10% H₂/Ar, then purged with He for 30 min. Subsequently, the temperature was lowered to room temperature in He flow. Pulses of 5% CO/He were introduced to the catalyst until uptake saturation was obtained. The CO consumption was monitored by TCD. The dispersion of Pd was calculated assuming a CO/Pd stoichiometric ratio of 1 [15]. X-ray photo-emission (XPS) measurements were recorded on a Scanning X-ray Microprobe (AXIS Ultra, Kratos Analytical, Inc.). The C 1s peak (284.8 eV) was used to calibrate the binding energy (BE) values.

2.3. Catalytic activity testing

The activity tests of the catalysts (~60 mg) were conducted in a fixed-bed quartz flow reactor (i.d. = 6 mm) in an incubator kept at 25 °C. Gaseous HCHO generated by decomposition of paraformaldehyde was carried by helium. Water vapor was generated by flowing helium through a water bubbler at 25 °C. The feed gas was composed of 140 ppm HCHO, 20% O₂ and 25% RH balanced by helium. The total flow rate was 100 mL min⁻¹, corresponding to a gas hourly space velocity (GHSV) of 190,000 h⁻¹. The inlet and outlet gases were monitored by an FTIR spectrometer (Nicolet 380) equipped with a 2 m gas cell and DTGS detector; resolution: 0.5 cm⁻¹. More details about quantitative analysis have been described in our previous work [25].

3. Results and discussion

3.1. Catalytic performance

The performance of Pd/TiO₂ and 1.0Na-, 2.0Na-, 4.0Na- and 8.0Na-Pd/TiO₂ catalysts for HCHO oxidation was tested and the results are shown in Fig. 1. For Pd/TiO₂, 20% conversion of HCHO was achieved at 25 °C and 100% at 100 °C. Its performance was improved by Na addition, and 70%, 75% and 80% of HCHO could be converted to H₂O and CO₂ with no any by-products on 8.0Na-Pd/TiO₂, 4.0Na-Pd/TiO₂ and 1.0Na-Pd/TiO₂ respectively at room temperature, and 100% HCHO conversions could be

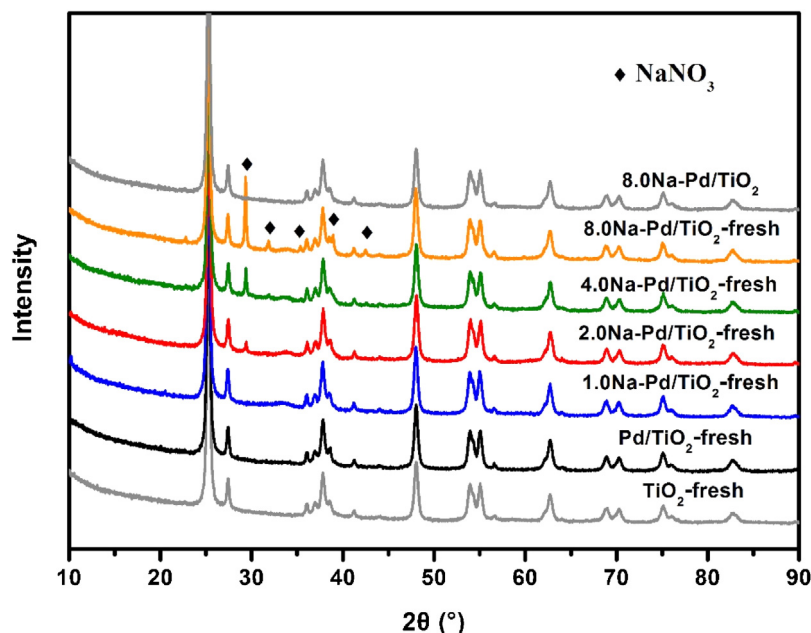


Fig. 2. XRD patterns of fresh Pd/TiO₂ and Na doped Pd/TiO₂ catalysts together with fresh TiO₂ samples and reduced 8.0Na-Pd/TiO₂.

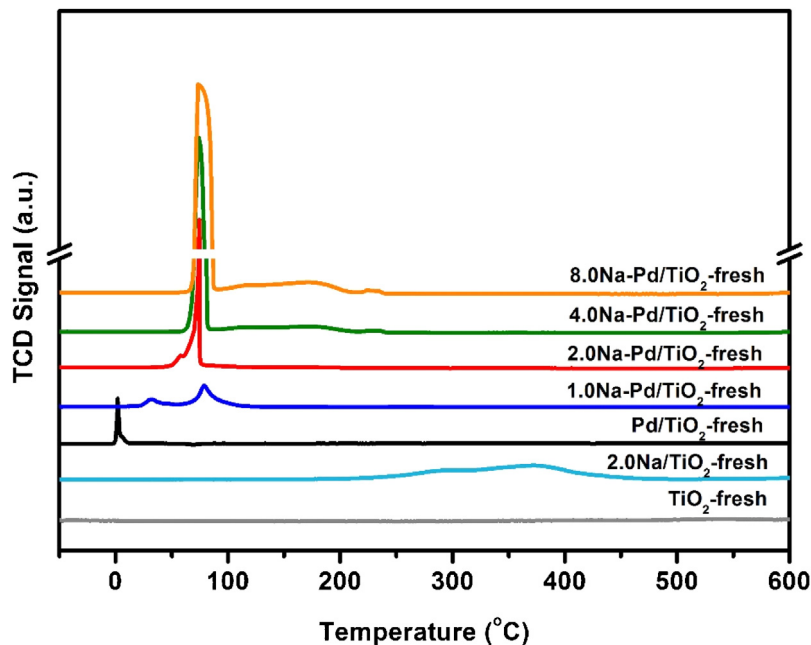


Fig. 3. H₂-TPR profiles of fresh samples including fresh Pd/TiO₂ and Na doped Pd/TiO₂ samples together with fresh TiO₂ and 2.0Na/TiO₂.

obtained on all three catalysts at about 80 °C. By comparison, almost 100% HCHO conversion was achieved on 2.0Na-Pd/TiO₂ at room temperature. The above results showed that the performance of Pd/TiO₂ catalysts for HCHO catalytic oxidation followed the order 2.0Na-Pd/TiO₂ > 1.0Na-Pd/TiO₂ > 4.0Na-Pd/TiO₂ > 8.0Na-Pd/TiO₂ > Pd/TiO₂. It was clear that Na addition had a promotion effect on Pd/TiO₂ catalysts for HCHO catalytic oxidation, and that the optimal Na loading was 2 wt.%.

3.2. Characterization of catalysts

3.2.1. Structural features of samples

Catalyst structures were characterized by XRD. As shown in Fig. 2, there were no Pd species (Pd and PdO) observed on the

Pd/TiO₂-fresh samples, indicating that Pd species had a very high dispersion degree on the samples. A peak at $2\theta = 29.9^\circ$ appeared when the amount of doped Na was higher than 2.0 wt.% and its intensity was gradually increased with further increase in the amount of Na addition. In addition, other peaks at $2\theta = 31.9, 38.9, 42.5$ and 56.5° were also observed on 8.0Na-Pd/TiO₂-fresh, which are all attributed to residual NaNO₃ (PDF #00-001-0840). After reduction, the peaks associated with residual NaNO₃ on the 8.0Na-Pd/TiO₂ catalyst disappeared, indicating that it was removed during H₂ reduction.

The specific surface areas (S_{BET}) of the catalysts were measured. As shown in Table 1, the S_{BET} of pure TiO₂ was 58.9 m²/g and the 1.0Na-Pd/TiO₂ and 2.0Na-Pd/TiO₂ catalysts exhibited S_{BET} of about 54.0 m² g⁻¹, which was similar with that of the Pd/TiO₂ catalyst.

Table 1The specific surface area (S_{BET}) and Pd dispersion of the catalysts.

| Sample | BET ($\text{m}^2 \text{g}^{-1}$) | D_{CO}^a (%) | TOF ($\times 10^{-2}, \text{s}^{-1}$) ^b |
|---------------------------|------------------------------------|-----------------------|------------------------------------------------------|
| TiO ₂ | 58.9 | – | – |
| Pd/TiO ₂ | 53.1 | 9.8 | 0.44 |
| 1.0Na-Pd/TiO ₂ | 54.0 | 25.8 | 0.88 |
| 2.0Na-Pd/TiO ₂ | 53.9 | 32.9 | 0.97 |
| 4.0Na-Pd/TiO ₂ | 43.8 | 20.5 | 1.00 |
| 8.0Na-Pd/TiO ₂ | 36.6 | 16.0 | 1.01 |

^a dispersion of Pd measured by CO chemisorption.^b TOF is calculated based on D_{CO} with the HCHO conversion kept below 30%.

However, it remarkably decreased when the amount of Na addition was more than 4 wt.%, that is, $43.8 \text{ m}^2 \text{ g}^{-1}$ for 4.0Na-Pd/TiO₂ and $36.6 \text{ m}^2 \text{ g}^{-1}$ for 8.0Na-Pd/TiO₂, which may be due to excess Na species depositing in and blocking the small pores, so that the reactants have difficulty diffusing to the active sites in the pores. This is possibly one of the reasons for the poorer performance of 4.0Na-Pd/TiO₂ and 8.0Na-Pd/TiO₂ catalysts, compared to the 2.0Na-Pd/TiO₂ catalyst.

3.2.2. Reducibility of catalysts

The reducibility of the catalysts was studied by H₂-TPR, and their profiles are shown in Fig. 3. No H₂ consumption was observed on pure TiO₂ in the temperature range since the reduction of TiO₂ normally occurs at $T > 600^\circ\text{C}$ [34]. With Na addition on pure TiO₂, a wide H₂ consumption peak at 200–450 °C appeared on fresh 2.0Na/TiO₂, which may be ascribed to the reduction of residual NaNO₃ on the fresh samples. With Pd loaded on pure TiO₂, a sharp PdO reduction peak appeared at around 0 °C on fresh Pd/TiO₂ catalyst [35]. With Na addition on Pd/TiO₂, two H₂ consumption peaks were obtained on the fresh 1.0Na-Pd/TiO₂ and 2.0Na-Pd/TiO₂. The peaks at low temperature (30 °C for fresh 1.0Na-Pd/TiO₂ and 57 °C for fresh 2.0Na-Pd/TiO₂) are associated with the reduction of PdO, and the ones at high temperature (79 °C for fresh 1.0Na-Pd/TiO₂ and 72 °C for fresh 2.0Na-Pd/TiO₂) may be attributed to the reduction of residual NaNO₃. With further increases in Na loading, the two peaks completely merged into one sharp and strong peak at 76 °C for both fresh 4.0Na-Pd/TiO₂ and 8.0Na-Pd/TiO₂. Based on the above results, there may be an interaction between Na and Pd species (promoter-metal interaction), which stabilizes the PdO for the fresh catalysts and facilitates the reduction of the residual alkali metal nitrates [31].

3.2.3. Pd dispersion

Pulse CO chemisorption was used to measure the Pd dispersion of the catalysts, and the results are listed in Table 1. Without Na addition, the Pd/TiO₂ catalyst showed a low Pd dispersion of 9.8%. With 1.0 wt.% Na addition, the Pd dispersion on 1.0Na-Pd/TiO₂ remarkably increased to 25.8%. It reached its maximum of 32.9% on the 2.0Na-Pd/TiO₂ catalyst. However, with more than 2.0 wt.% Na addition, it slightly decreased to 20.5% and 16.0% on 4.0Na-Pd/TiO₂ and 8.0Na-Pd/TiO₂ catalysts, which may be attributed to the coverage of Pd by the excess Na species. Based on the results of Pd dispersion, TOFs of Na-doped Pd/TiO₂ catalysts for HCHO oxidation were calculated at 25 °C and the results were added in Table 1. The value of TOF was $0.44 \times 10^{-2} \text{ s}^{-1}$ for the Pd/TiO₂ catalyst. After Na addition, it was improved to $0.88 \times 10^{-2} \text{ s}^{-1}$, $0.97 \times 10^{-2} \text{ s}^{-1}$, $1.00 \times 10^{-2} \text{ s}^{-1}$ and $1.01 \times 10^{-2} \text{ s}^{-1}$ for 1Na-, 2Na-, 4Na- and 8Na-Pd/TiO₂ catalysts, respectively. It is clear that the catalytic activities were not only related to the Pd dispersion, but also affected by some other factors, such as the concentration of surface hydroxyl. Moreover, it is clear that a proper amount of Na addition has a promoting effect on the Pd dispersion because of the promoter-metal interaction, while excess Na addition will result in a negative effect on the performance of Pd/TiO₂ catalysts for HCHO oxidation.

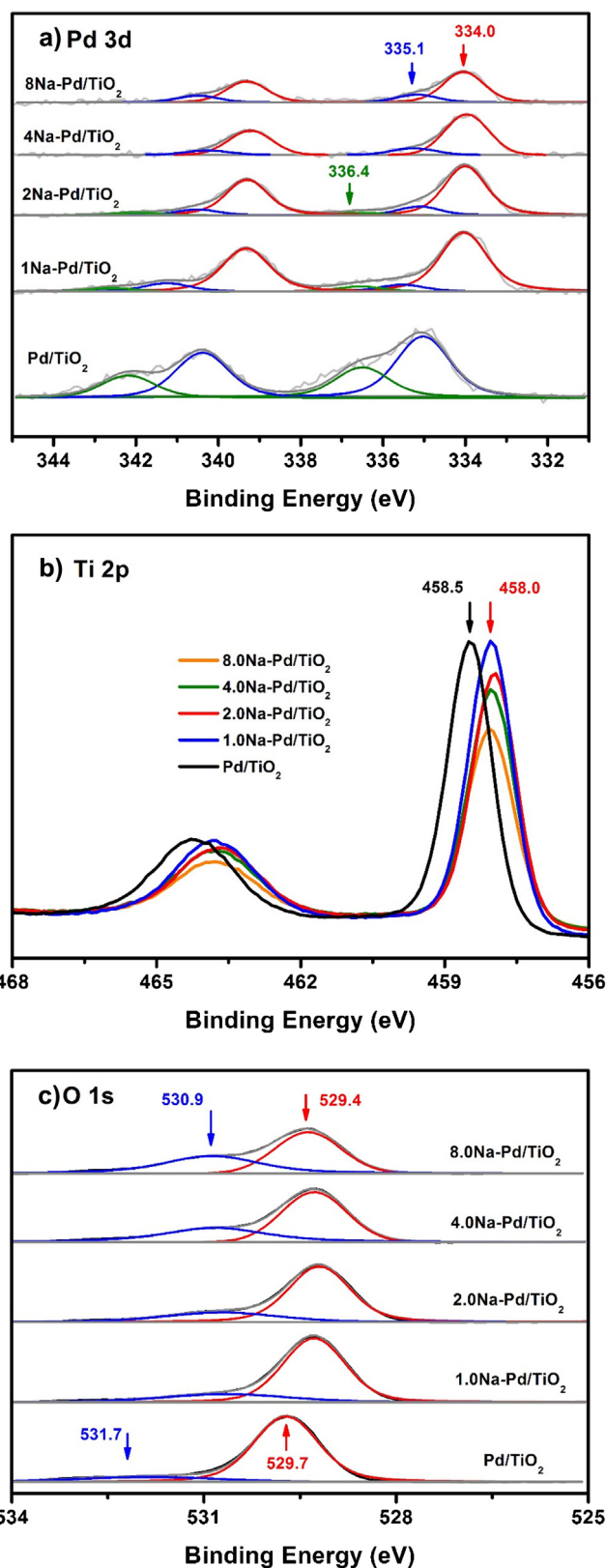


Fig. 4. XPS spectra of Pd/TiO₂ and Na doped Pd/TiO₂ catalysts: (a) Pd 3d, (b) Ti 2p and (c) O 1s.

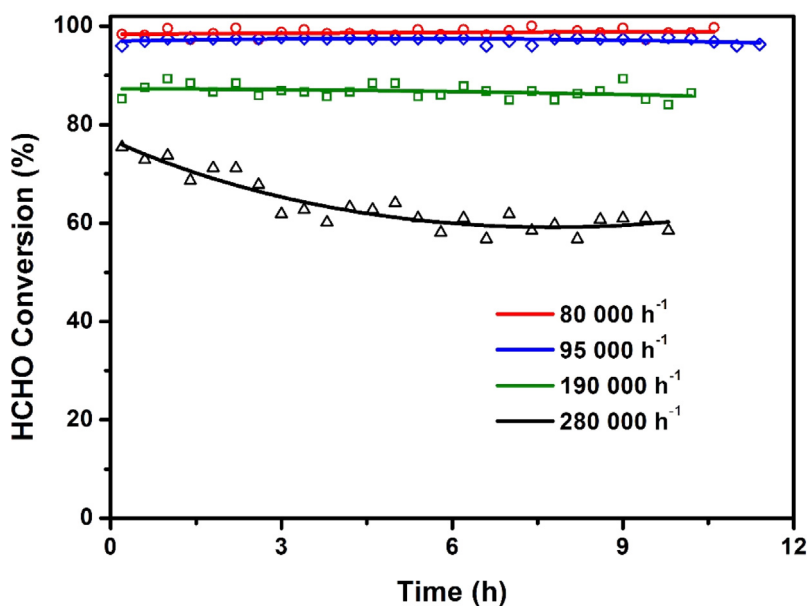


Fig. 5. Effect of gas hourly space velocity (GHSV) on HCHO conversion over the 2.0Na-Pd/TiO₂ catalyst (reaction conditions: HCHO 140 ppm, RH=25%).

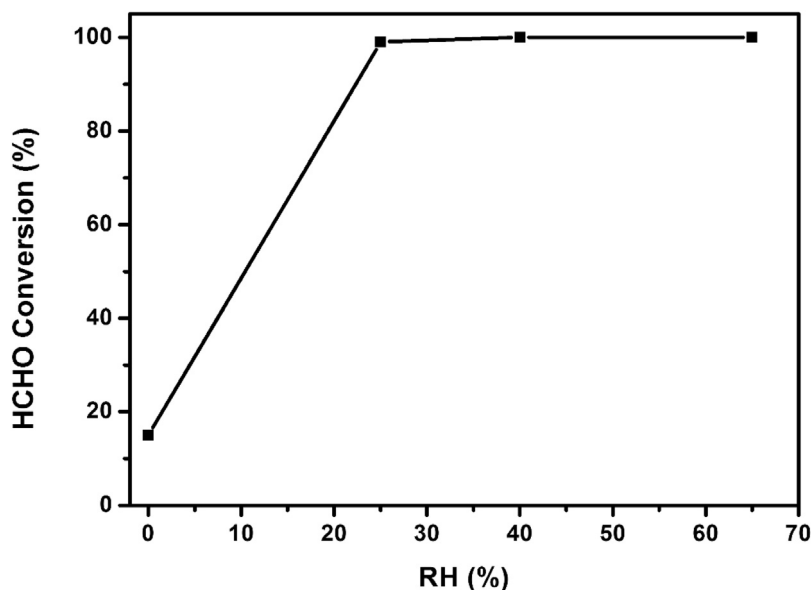


Fig. 6. Effect of relative humidity (RH) on HCHO conversion over the 2.0Na-Pd/TiO₂ catalyst (reaction conditions: HCHO 140 ppm, GHSV=95,000 h⁻¹).

3.2.4. XPS analysis

The states of Pd, Ti and O elements on the catalyst surface were identified by XPS measurements. As shown in Fig. 4a, two peaks were observed on the Pd/TiO₂ catalyst. Specifically, the main peak at 335.1 eV is attributed to metallic Pd [36,37] and the one at 336.4 eV is ascribed to PdO [38] formed by re-oxidation of metallic Pd by O₂ and/or H₂O before transfer of the samples to the XPS chamber. With Na addition, a third peak was obtained at lower binding energy, 334.0 eV, which can be attributed to negatively charged metallic Pd, formed by electron transfer from Na species to the metallic Pd because of the promoter-metal interaction [39]. The negatively charged metallic Pd species could facilitate oxygen chemisorption [15]. With increasing amounts of Na addition, the PdO species gradually decreased on the 1.0Na- and 2.0Na-Pd/TiO₂ catalysts and finally disappeared on the 4.0Na- and 8.0Na-Pd/TiO₂ catalysts, which together with the gradual decrease of Pd XPS intensity may due to the coverage of Pd species by excess Na

species. According to Fig. 4b, the binding energy of Ti 2p shifted from 458.5 eV (for Pd/TiO₂ catalyst) to 458.0 eV (for 1.0Na-, 2.0Na-, 4.0Na- and 8.0Na-Pd/TiO₂ catalysts) after Na addition, which may be attributed to Na addition facilitating the reduction of TiO₂ to form oxygen vacancies. It is well known that oxygen vacancies not only could facilitate oxygen adsorption [40] but also dissociation of adsorbed water to form surface OH groups [41]. O 1s XPS spectra of the catalysts are shown in Fig. 4c. Two oxygen species were observed on all the catalysts. The one at 529.7 eV for Pd/TiO₂ and 529.4 eV for the Na doped Pd/TiO₂ catalysts is ascribed to lattice oxygen of TiO₂ while the other one is attributed to surface OH groups [42]. It is clear that the Na addition increased the concentration of surface OH groups. Our recent work has clarified the important role of surface OH groups in HCHO catalytic oxidation on alkali metal doped Pt/TiO₂ catalysts, that is, the intermediate formate can be directly oxidized to H₂O and CO₂ by the surface OH groups, resulting in a more effective pathway for HCHO oxidation

[10]. Though both the 4.0Na- and 8.0Na-Pd/TiO₂ catalyst possessed abundant surface OH groups, the coverage of their active sites by the excess Na species resulted in a decrease in their performance. In contrast, abundant surface OH groups and the exposure of more active sites led to 2.0Na-Pd/TiO₂ having the best HCHO oxidation performance among the catalysts in the present work.

3.3. Effect of GHSV and RH

The performance of the 2.0Na-Pd/TiO₂ catalyst in HCHO oxidation at room temperature was evaluated at various gas hourly space velocities (GHSV) and relative humidity (RH).

3.3.1. Effect of GHSV

Fig. 5 shows the conversion of HCHO at room temperature as a function of reaction time over the 2.0Na-Pd/TiO₂ catalyst at GHSV of 80,000, 95,000, 190,000 and 280,000 h⁻¹. It is obvious that 2.0Na-Pd/TiO₂ exhibited excellent performance at both 80,000 and 95,000 h⁻¹, with almost 100% HCHO conversion at room temperature. Impressively, a high HCHO conversion of 90% was still obtained at the relatively high GHSV of 190,000 h⁻¹, although the conversion decreased to 60% at 280,000 h⁻¹ because of the reduced contact time.

3.3.2. Effect of RH

As we know, water is an important component in the air and the relative humidity changes with territory and climate; therefore, it is of significance to investigate the effect of RH on HCHO catalytic oxidation at room temperature. The HCHO conversion of 2.0Na-Pd/TiO₂ as a function of RH (0%, 25%, 40% and 65%) is shown in Fig. 6. Without water, only 15% HCHO conversion was obtained on the 2.0Na-Pd/TiO₂ catalyst. However, the conversion was improved to 99% at a RH of 25% and it reached 100% at RH of 40% and 65%. It is clear that the moisture has a remarkable promotion effect on the activity of the 2.0Na-Pd/TiO₂ catalyst at ambient temperature. The promotion effect of water may be attributed to the fact that the water adsorbed on the 2.0Na-Pd/TiO₂ can be activated to form active surface OH groups, leading to a more effective pathway for HCHO catalytic oxidation [10]. Based on the above results, the 2.0Na-Pd/TiO₂ catalyst exhibited excellent performance in a range of RH = 25–65%; therefore, it is a promising material for elimination of indoor HCHO.

4. Conclusions

Na addition had a dramatic promoting effect on Pd/TiO₂ catalysts for HCHO oxidation. The performance of Na-Pd/TiO₂ catalysts closely depended on the amount of Na addition, and the optimal Na loading was found to be 2 wt.%. The appropriate amount of Na addition could induce and stabilize a well-dispersed and negatively charged metallic Pd, which would facilitate oxygen adsorption and also increase the concentration of surface OH groups, therefore leading to the high performance of the 2.0Na-Pd/TiO₂ catalyst in HCHO catalytic oxidation. However, excess Na addition may cover some of active Pd sites and then result in the decrease of catalytic activity for 4.0Na-Pd/TiO₂ and 8.0Na-Pd/TiO₂ catalysts.

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