Acid-treated TiO₂ nanobelt supported platinum nanoparticles for the catalytic oxidation of formaldehyde at ambient conditions

Weiye Cui ^{a,b}, Dan Xue ^c, Xiaoling Yuan ^b, Bin Zheng ^b, Mingjun Jia ^{b,*}, and Wenxiang Zhang ^{b,*}

^a Key Laboratory of Chemical Cleaner Production Technology of Jilin Province, Jilin Institute of Chemical Technology, 132022 Jilin, China

^b Key Laboratory of Surface and Interface Chemistry of Jilin Province, College of Chemistry, Jilin University, 130021 Changchun, China

^c School of chemistry & chemical engineering, Xi'an Shiyou University, 710065 Xi'an, China

* Corresponding authors: Tel: (+86)431-85155390; Fax: (+86)431-85168420.

Email address: jiamj@jlu.edu.cn (M. Jia); zhwenx@jlu.edu.cn (W. Zhang)

ABSTRACT

In this work, two kinds of novel Pt/TiO₂ catalysts were prepared by impregnation method using hydrothermally synthesized TiO₂ nanobelt (TiNB) and sulfuric acid-treated TiO₂ nanobelt (TiNB-ac) as supports, and their catalytic properties were investigated in the oxidation of formaldehyde. It was found that Pt/TiNB-ac exhibits much higher catalytic activity, which can efficiently convert formaldehyde to CO₂ and H₂O at ambient temperature. The addition of water vapor into the feed stream can further promote the catalytic activity of Pt/TiNB-ac catalyst. A variety of characterization results showed that TiNB-ac possesses much rougher surface, and more defect sites (including abundant chemisorbed oxygen and surface hydroxyl species) due to the treatment by sulfuric acid. These features should be beneficial to achieve high dispersion of Pt nanoparticles on the rough-surface of TiNB-ac, to produce more interface active sites like Pt-O(OH)_x-Ti species through the interaction between the Pt nanoparticles and the surface hydroxyl species of TiNB-ac support, thus resulting in the formation of highly efficient Pt/TiNB-ac catalyst for the oxidation of formaldehyde under mild conditions.

Keywords: TiO₂ nanobelt, acid-treatment, Pt nanoparticles, catalytic oxidation, formaldehyde.

1 Introduction

As a major indoor air pollutant, formaldehyde (HCHO) has been classified as a human carcinogen Group 1 of hazardous substances by International Agency for Research on Cancer (IARC) [1-4]. For removing trace HCHO in air, different methods have been developed, including adsorption [5-6], plasma [7], degradation [8], photo-catalysis [9-10] and catalytic oxidation [11-36]. Among them, catalytic oxidation has been regarded as one of the most efficient and environmentally benign technologies. So far, a variety of supported noble metal catalysts (e.g., Au [11-12], Pt [13-31], Pd [32-33], Ag [34-35]) have typically been employed for the removal of HCHO through the catalytic oxidation process. By selecting suitable supports and optimizing preparation conditions, some highly active supported Pt nanoparticles catalysts such as Pt/TiO₂, Pt/Fe₂O₃, Pt/AlOOH, Pt/CeO₂-AlOOH, and PtNi(OH)_x/Al₂O₃ have been developed, and part of them could even achieve excellent catalytic property at ambient temperatures [13-31].

A few literature works have shown that the morphology, the microstructure and the surface properties of TiO₂ supports can significantly influence the catalytic performance of TiO₂ supported Pt catalysts for HCHO oxidation [18,20-23,30]. For instance, by using TiO₂ nanosheet with exposed (001) facet or using mat-like hierarchically porous TiO₂ nanofiber as support, Nie et al. [18,22] obtained two kinds of Pt/TiO₂ catalysts with high catalytic activity for room-temperature oxidation of HCHO. Chen et al. [20,21] reported that highly efficient Pt/TiO₂ catalyst could be prepared using ordered pore-through TiO₂ nanotube arrays as supports. Qi et al. [30]

found that mesoporous TiO_2 hollow chain supported Pt catalyst exhibits very high catalytic activity toward HCHO oxidation. These results suggested that changing the microstructure and the surface properties of TiO_2 supports can influence the dispersion of Pt nanoparticles, and adjust the interaction between Pt and TiO_2 , which may finally enhance the catalytic performance for HCHO oxidation. At present, it is still an interesting subject to explore how the surface chemistry and the structure factors of TiO_2 support could influence the nature of active sites of Pt/ TiO_2 catalysts, and what are the main features of a highly efficient Pt/ TiO_2 catalysts for the low-temperature oxidation of HCHO.

In this work, we tried to use TiO_2 nanobelt (TiNB) and sulfuric acid-treated TiO_2 nanobelt (TiNB-ac) as supports to prepare two kinds of Pt/ TiO_2 catalysts (Pt/TiNB and Pt/TiNB-ac) for the application in low-temperature oxidation of HCHO. Previous literatures have shown that TiO_2 nanobelt with high surface-to-volume ratio and defined crystalline orientation can be used as suitable support to prepare efficient noble metal supported catalysts for some significant catalytic processes [37-39]. More interesting, the surface chemistry of TiO_2 nanobelt could be further adjusted by acid-treatment, which may produce more rough and activated surface species for special application [37,40]. Here, we found that the Pt/TiNB-ac catalyst derived from the acid-treated TiO_2 nanobelt exhibits excellent catalytic activity toward HCHO oxidation at room temperature. The existence of abundant hydroxyl species on the surface of TiNB-ac can provide more anchor sites for achieving high dispersion of Pt nanoparticles, and can also produce more interface active sites like $\text{Pt-O(OH)}_x\text{-Pt}$

species through the metal-support interaction, which can finally resulting in the formation of highly efficient Pt/TiO₂ catalyst for the oxidation of HCHO at ambient conditions.

2 Experimental section

2.1 Catalyst preparation

TiO₂ nanobelt materials were synthesized through a simple hydrothermal procedure reported in literatures [37,39]. Typically, 0.6 g TiO₂ (Degussa P-25, composed of 80% anatase and 20% rutile crystallites of TiO₂) was mixed with 100 ml of 10 M NaOH aqueous solution, followed by hydrothermal treatment at 200 °C in a 150 ml Teflon-lined autoclave for 72 h. The product of Na₂Ti₃O₇ nanobelt was collected and washed thoroughly with deionized water until a pH value of about 7 is reached. The washed samples were immersed in 0.1 M HCl aqueous solution for 24 h and then washed thoroughly with deionized water to get H₂Ti₃O₇ nanobelt. After dried at 70°C for 10 h, H₂Ti₃O₇ nanobelt was thermally annealed at 600 °C for 3 h to produce TiO₂ nanobelts (TiNB). Sulfuric acid-treated TiNB (denoted as TiNB-ac) were prepared through an acid-assisted hydrothermal approach [37,40]. Typically, 0.6 g of TiNB samples were added in 100 ml of 0.02 M H₂SO₄ aqueous solution under vigorous stirring, and the mixture was transferred to Teflon-lined autoclave and kept at 100°C for 12 h. After filtrating, washing and drying, the resultant TiNB-ac materials were obtained via calcining the solid powder at 600 °C for 3 h.

Pt/TiNB and Pt/TiNB-ac catalysts were prepared by impregnation method. Typically, 0.6 g of TiNB or TiNB-ac sample was added into H₂PtCl₆ aqueous solution

under vigorous stirring. After impregnation for 1 h, 4.0 ml of a mixed aqueous solution containing NaOH (0.5 M) and NaBH₄ (0.1 M) were quickly added into the slurry and vigorously stirred for another 1 h. After that, the slurry was evaporated at 80 °C under stirring. Finally, the solid sample was dried at 80 °C for 12 h. For comparison, a Pt-supported P25 catalyst (Pt/P25) was also prepared under similar conditions by using the commercial Degussa P25 as support. The loading of Pt is approximately 1.0 wt% for each catalyst, which is calculated from the amount of H₂PtCl₆ used for catalyst preparation.

2.2 Catalyst characterization

The X-ray diffraction (XRD) analyses of the catalysts were carried out using a D/Max-rA X-ray diffractometer operated at 30 kV and 40 mA employing nickel-filtered Cu Ka radiation. Transmission electron microscopy (TEM) images and the high-angle annular darkeld STEM (HAADF-STEM) images were obtained using a FEI Tecnai F20 EM operated at 200 kV and equipped with an energy-dispersive spectroscopy analyzer. H₂-O₂ titration experiments were carried out on a Builder PCA-1200 Pulse Chemisorption System to determine the Pt dispersion of the catalysts. The X-ray photoelectron spectra (XPS) measurements were carried out on an ESCALAB250 X-ray photoelectron spectrometer with Al Ka radiation as excitation source. The XPS spectra were corrected by adjusting the C 1s peak to a position of 284.6 eV. Temperature programmed reduction by H₂ measurements (H₂-TPR) were carried out using an adsorption instrument equipped with a TCD. The samples were loaded and pretreated with Ar at 100 °C for 30 min. The H₂-TPR experiment was

performed under the mixture of 5% H₂ in N₂ flow (30 mL/min) over 0.1g of catalyst at a heating rate of 10 °C/min.

2.3 Catalytic test

For the HCHO oxidation tests, 0.1 g of solid catalyst (40 – 60 mesh) was loaded in a quartz tube reactor. The gas mixture consisted of 400 ppm HCHO, 20 vol% O₂, and a certain amount of water vapor (with relative humidity RH of 0 – 30%), and balanced by N₂. Gaseous HCHO was generated by flowing N₂ (coming from a mass flow controller) through aqueous formaldehyde in an incubator. Products and reactants were analyzed by Techcomp GC-7900 gas chromatograph equipped with TCD detector, and the catalytic activity of the catalysts was evaluated by the conversion of formaldehyde to CO₂.

3 Results and discussion

3.1 Characterization of the catalysts

XRD patterns of TiO₂ nanobelts and their precursors are presented in Fig.1. The samples of Na₂Ti₃O₇ nanobelt and H₂Ti₃O₇ nanobelt show some intense and sharp diffraction peaks, which are in good agreement with the characteristic signals of Na₂Ti₃O₇ (JCPDS No. 31-1329) and H₂Ti₃O₇ (JCPDS No. 47-0561) crystalline phase, respectively. For the TiNB and TiNB-ac, all the diffraction peaks match well with the standard peaks of anatase phase (JCPDS No. 21-1272), indicating that the samples of TiNB and TiNB-ac are mainly composed of anatase. As for the Pt supported catalysts (Pt/TiNB and Pt/TiNB-ac), no characteristic peaks corresponding to Pt species in the XRD patterns could be discernible (Fig.1b), which should be a sign that the Pt

particles are very small and highly dispersed on the surface of TiNB or TiNB-ac supports.

The SEM images of the TiO₂ nanobelts and their precursors were shown in Fig. 2. The as-synthesized Na₂Ti₃O₇ and H₂Ti₃O₇ samples are composed of long and straight belts with width between 50 to 100 nm, smooth surface and uniform morphology (Fig. 2a, b). The sample of TiNB, which is derived from calcining H₂Ti₃O₇ composite in air at 600 °C, shows similar belt-like morphology as its precursor (Fig. 2c). The SEM image of TiNB-ac shows relatively short nanobelts with much rougher surface, which is likely resulted from the sulfuric acid-treated process [37].

Fig. 3 shows the HRTEM and TEM images of various samples. Clearly, some lattice defects are present in the HRTEM images of TiNB and TiNB-ac, and relatively more defect sites appear in the sample of TiNB-ac (Fig. 3a, b). These results confirm further that the microstructure of TiNB-ac have been changed somewhat after suffering the acid-treated process. The TEM images of Pt/TiNB and Pt/TiNB-ac reveal that Pt nanoparticles are highly dispersed on the surface of the TiNB and TiNB-ac supports, with mean particle size of around 3.0 nm and 2.5 nm, respectively (Fig. 3c,d). In the HRTEM image of Pt/TiNB-ac (Fig. 3e), the lattice fringes with the d-spacing of 0.224 nm are consistent with the lattice spacing of (111) plane of metallic Pt, while the lattice fringes with d-spacing of 0.352 nm correspond to the (101) plane of anatase TiO₂.

Fig.4 shows the nitrogen adsorption/desorption isotherms and the corresponding pore-size distribution curves of the four as-prepared samples. The isotherms show

high absorption volume at high relative pressure range ($P/P_0 > 0.8$), indicating the presence of some macropores on account of packing of particles. The textual parameters of the TiO_2 nanobelts, P25 and the supported Pt catalysts are given in Table 1. Among them, TiNB-ac has relatively high specific surface area. After introducing Pt particles and reducing by $\text{NaBH}_4/\text{NaOH}$, obvious decrease in the specific surface area could be detected for the TiO_2 supported Pt catalysts.

The data of Pt dispersion, determined by pulse $\text{H}_2\text{-O}_2$ titration experiments, are also listed in Table 1. It was found that the Pt dispersions on Pt/TiNB-ac, Pt/TiNB and Pt/P25 are 37.1%, 31.8% and 27.9%, respectively. The relatively high dispersion of Pt/TiNB-ac should be related to the fact that TiNB-ac possesses much rougher surface and higher surface area than TiNB and P25.

The XPS analysis results of various supported Pt catalysts are shown in Fig. 4 and Table 2. The presence of Ti, O, Pt, Na, and C elements with photoelectron peaks appearing at binding energy (BE) of 458.35 (Ti 2p), 529.75 (O 1s), 70.60 (Pt 4f), 1071.85 (Na 1s) and 284.6 eV (C 1s) were observed respectively on the XPS survey spectra of Pt/TiNB-ac (Fig. 4a). The Na 1s peak at 1071.85 eV stems from the residual Na^+ on account of the introduced NaOH and NaBH_4 reactants in the catalyst preparation process. The Pt 4f spectra of Pt/P25, Pt/TiNB and Pt/TiNB-ac show two peaks at 70.4 and 74.2 eV, which can be assigned to Pt 4f_{7/2} and Pt 4f_{5/2} of metallic Pt, respectively (Fig. 4b). As shown in Table 2, the surface atomic ratio of Pt/Ti in Pt/TiNB-ac is 0.036, which is higher than that in Pt/TiNB (0.030) and in Pt/P25 (0.026), confirming further the relatively high dispersion of Pt/TiNB-ac. Notably, the

bind energy of Pt 4f_{7/2} in the three supported Pt catalysts shifts negatively in comparison with the standard binding energy of the bulk metallic Pt (approximately 71.2 eV) [17,19,41], which can be assigned to the partial electron transfer from TiO₂ supports to Pt nanoparticles on account of the stronger metal-support interactions.

Fig. 4c shows the Ti 2p XPS spectra of the three supported Pt catalysts. The binding energies of Ti 2p_{3/2} appear at 458.70, 458.45 and 458.35 eV for Pt/P25, Pt/TiNB and Pt/TiNB-ac, respectively, which are lower than that of common TiO₂ support (459.3 eV) reported in the related literature [17]. The decrease in the binding energy of Ti 2p_{3/2} should arise from the reduction of a part of Ti⁴⁺ to Ti³⁺ during the NaBH₄ reduction process, indicating that a part of lattice oxygen has been abstracted from the surface of TiO₂, resulting in the formation of some oxygen vacancies [30,42,43]. Relatively low Ti 2p_{3/2} binding energy of Pt/TiNB-ac should be also an indicative that more defect sites are present in this catalyst. The O 1s XPS results of various catalysts are shown in Fig. 4d and Table 2. The O 1s peak at around 530 eV (OI) is assigned to the lattice oxygen of TiO₂ (Ti-O-Ti), and the peak at about 532 eV (OII) can be attributed to the chemisorbed oxygen and the surface hydroxyl (Ti-(OH)_x) species, which might be originated from the adsorption of H₂O and O₂ on the surface defect sites (oxygen vacancies) of TiO₂ support upon exposure to air [43]. The fact that Pt/TiNB-ac shows relatively strong signal of OII species provides a further evidence that the acid-treated TiO₂ nanobelt has more surface defect sites, which can certainly resulting in formation of more chemisorbed oxygen species and Ti-(OH)_x species on the surface of catalyst. The presence of abundant defect sites in TiNB-ac,

including surface adsorbed oxygen and hydroxyl species, should play critical role in achieving high dispersion of Pt nanoparticles, building relatively strong interaction between the Pt nanoparticles and TiNB-ac, and forming Pt-O-Ti and Pt-O(OH)_x-Ti species at the interfaces of Pt/TiNB-ac catalyst.

3.2 Catalytic properties

The catalytic properties of the supported Pt catalysts are studied for the aerobic oxidation of HCHO at low temperatures. As shown in Figure 6, the supports of TiNB and TiNB-ac are inactive under the tested conditions. All the three supported Pt catalysts Pt/P25, Pt/TiNB and Pt/TiNB-ac are catalytically active for oxidizing HCHO to CO₂ and H₂O in the presence of water vapor (RH 30%). A 91% conversion of HCHO is obtained over Pt/TiNB-ac catalyst at the reaction temperature of 25°C, much better than that of Pt/TiNB (42% conversion) and Pt/P25 catalyst (39% conversion). The catalytic activity of the supported Pt catalysts increase with the increase of reaction temperatures, while complete conversion of HCHO could be achieved at 40 °C, 60 °C and 80 °C over Pt/TiNB-ac, Pt/TiNB and Pt/P25, respectively. These results suggest that the acid-treated TiO₂ nanobelt could be used as a suitable support to prepare highly active supported Pt catalyst for low-temperature oxidation of HCHO. Its superior catalytic performance is even comparable with the most active supported Pt catalysts reported in literatures, like Fe₂O₃, AlOOH, or MnO_x promoted TiO₂ nanotube supported Pt catalysts [14,21,27].

It should be mentioned here that the existence of water vapor in the reactants feed has quite positive effect on improving the catalytic activity of the TiO₂ nanobelt

supported Pt catalysts. As shown in Fig. 7, Pt/TiNB-ac catalysts exhibit relatively low catalytic activities under the dry condition (without addition of water vapor). At the reaction temperature of 25 °C, the conversion of HCHO decreases from 91% to 71% when water vapor is removed from the feed. This feature of the catalyst is quite significant concerning the fact that the presence of water vapor in the reactants feed is nearly inevitable under the practical operation environment of the catalytic oxidation process.

The durability of the catalysts is also investigated under both dry and moisture conditions. As shown in Fig. 8, the catalytic activity of Pt/TiNB-ac catalyst is nearly unchanged during the term of seven days-experiments, in which three hours-reaction is carried out on each day. Besides, Pt/TiNB-ac can still work well even after stored in a vial under ambient atmosphere for a few months, indicating the excellent stability of this catalyst.

3.3 Discussion

Previously, it has been proposed that the catalytic activity of the TiO₂ supported Pt-based catalysts could be significantly improved by adjusting the microstructure and surface properties of the TiO₂ supports [18,20-23,30]. The optimized structure and surface properties can usually increase the dispersion degree of Pt nanoparticles, and produce more interface active sites through a metal-support interaction between Pt nanoparticles and TiO₂ supports. The present work shows that TiO₂ nanobelt (TiNB) could also be used as a suitable support to develop active supported Pt catalyst for low-temperature oxidation of HCHO. More interesting, the acid-treated TiO₂ nanobelt

(TiNB-ac) shows great advantage in fabricating more efficient TiO_2 supported Pt catalyst.

By comparing the structure and surface property of TiNB and TiNB-ac, as well the catalytic property of Pt/TiNB and Pt/TiNB-ac, it can be concluded here that the excellent catalytic activity of Pt/TiNB-ac catalyst should be mainly related to the features of TiNB-ac support, such as larger surface area, rougher surface, and more defect sites (including surface adsorbed oxygen and hydroxyl species). These features could bring significant effects on the dispersion of Pt nanoparticles, and produce more efficient active sites for low-temperature oxidation of HCHO through the interaction between Pt nanoparticles and acid-treated TiO_2 nanobelts.

According to a few related literatures of supported Pt catalysts [17,31,44-47], it was known that the existence of large amount of hydroxyl species on the surface of support is a critical factor in forming highly active interface active sites for low-temperature oxidation of CO and HCHO. For instance, Jaroniec and coworkers [27] proposed that the superior performance of Pt/AlOOH (in compared with Pt/ Al_2O_3) for HCHO oxidation can be mainly attributed to the abundance of surface hydroxyls, high dispersion of Pt nanoparticles, and high specific surface area of AlOOH nanoflakes. He and coworkers [15] found that the addition of alkali-metal ions to Pt/ TiO_2 catalyst could significantly promote the activity for HCHO oxidation due mainly to the formation of highly active Pt-O(OH)_x alkali-metal species on the catalyst surface. They also proposed that the introduced Na^+ ions play critical role in producing and stabilizing large amount of the active hydroxyl species on the surface

of Pt/TiO₂ catalyst. Therefore, we may conclude here that the existence of relatively large number of hydroxyl species in TiNB-ac support should be one of the most important factors for the formation of more interface active hydroxyl species (like Pt–O(OH)_x–Ti) in Pt/TiNB-ac catalyst, while the introduced Na⁺ ions (during the NaBH₄ reduction process) should also play quite positive role in stabilizing these interface active hydroxyl species, thus resulting in the formation of highly active and stable TiO₂ nanobelt supported Pt catalyst for the oxidation of HCHO at mild conditions.

4 Conclusions

Acid-treated TiO₂ nanobelt could be used as suitable support to prepare highly active supported Pt catalyst for low temperature oxidation of HCHO. The existence of relatively abundant surface hydroxyl species Ti(OH)_x on the acid-treated TiO₂ nanobelt is a critical factor in achieving high dispersion of Pt nanoparticles on the surface of support, and in producing more interface active sites like Pt–O(OH)_x–Ti species, thus resulting in the formation of highly efficient supported Pt catalyst for the aerobic oxidation of formaldehyde under mild conditions.

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Table 1 Physical properties and Pt dispersion of the as-prepared samples.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{pore} ($\text{m}^3 \text{g}^{-1}$)	D_{pore} (nm)	Pt dispersion (%)
P25	51	0.18	16.4	
TiNB	33	0.12	13.5	
TiNB-ac	79	0.22	11.2	
Pt/P25	41	0.14	17.3	27.9
Pt/TiNB	24	0.10	14.1	31.8
Pt/TiNB-ac	56	0.16	12.0	37.1

Table 2 XPS analysis results for the catalysts of Pt/P25, Pt/TiNB and Pt/TiNB-ac.

Catalysts	BE (eV)			Surface atom ratio	
	Pt4f _{7/2} (Pt4f _{5/2})	OII (OI)	Ti 2p	OII/(OI+ OII) ^a	Pt/Ti
Pt/P25	70.65 (74.15)	532.15 (530.05)	458.70	0.43	0.026
Pt/TiNB	70.70 (74.00)	531.75 (529.70)	458.45	0.48	0.030
Pt/TiNB-ac	70.60 (74.00)	531.85 (529.75)	458.35	0.61	0.036

a Calculated from the corresponding areas of fitted peaks done by XPS PEAK 4.1 with Shirley background.

Fig.1 X-ray diffraction patterns for all samples.

Fig. 2. SEM images of the (a) Na₂Ti₃O₇, (b) H₂Ti₃O₇, (c) TiNB and (d) TiNB-ac samples.

Fig. 3. The HRTEM images of (a) TiNB, (b) TiNB-ac and (f) Pt/TiNB-ac, and the TEM images of the (c) Pt/TiNB and (d, e) Pt/TiNB-ac samples.

Fig. 4. Nitrogen adsorption/desorption isotherms and the corresponding pore-size distribution curves (inset) of various samples.

Fig. 5. (a) XPS survey spectra of Pt/TiNB-ac. (b) High-resolution XPS spectra of Pt 4f, (c) Ti 2p and (d) O 1s of Pt/P25, Pt/TiNB and Pt/TiNB-ac.

Fig.6. Catalytic activities for HCHO oxidation over various catalysts. Reaction conditions: HCHO 400 ppm, O₂ = 20 vol%, N₂ balance, RH = 30%, GHSV: 60000 cm³g⁻¹h⁻¹.

Fig.7. Catalytic activities of Pt/TiNB-ac catalysts with under moisture conditions .Reaction conditions: HCHO 400 ppm, O₂ = 20 vol%, N₂ balance, RH = 30%, GHSV: 60000 cm³ g⁻¹ h⁻¹, temperature: 25°C.

Fig.8. Stability test of Pt/TiNB-ac for HCHO oxidation at 25 °C under dry and moisture conditions.

GRAPHICAL ABSTRACT