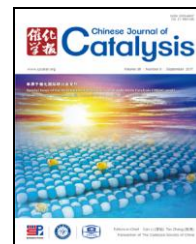




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# Photochemical route for preparing atomically dispersed Pd<sub>1</sub>/TiO<sub>2</sub> catalysts on (001)-exposed anatase nanocrystals and P25

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## ABSTRACT

Atomically dispersed catalysts have shown promising prospects in catalysis studies. Among all of the developed methods for synthesizing atomically dispersed catalysts, the photochemical approach has recently aroused much attention owing to its simple procedure and mild preparation conditions involved. In the present study, we demonstrate the application of the photochemical method to synthesize atomically dispersed Pd catalysts on (001)-exposed anatase nanocrystals and commercial TiO<sub>2</sub> (P25). The as-prepared catalysts exhibit both high activity and stability in the hydrogenation of styrene and catalytic oxidation of CO.

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## 1. Introduction

As a new frontier in catalysis, atomically dispersed catalysts [1,2] have attracted widespread interest in diverse research areas such as chemistry, material science and environmental science. By using atomically dispersed catalysts, several new catalytic mechanisms have been discovered, thereby enriching our understanding on the most basic subject in nature and chemical industry: catalysis [3–11]. Though conventional preparation methods (e.g., co-deposition, impregnation) have proven effective for preparing various atomically dispersed catalysts, many new methods are emerging for creating atomically dispersed catalysts that are difficult to synthesize by traditional methods. For instance, mass-selected and soft-landing techniques allow the preparation of catalysts based on single

metal atoms or clusters of fixed metal atoms [12,13]. Atomic layer deposition was successfully used in anchoring Pd and Pt on graphene [14,15]. UV-based deposition followed by sodium cyanide leaching was successfully employed to prepare atomically dispersed Au on TiO<sub>2</sub> [10,16]. Recently, an effective photochemical route has been developed to prepare highly active and stable Pd<sub>1</sub>/TiO<sub>2</sub> catalysts with a high Pd loading content [17]. The key point of the photochemical route is the UV-induced formation of ethyl glycol (EG) radicals that facilitate the removal of Cl<sup>-</sup> and ensure the stabilization of Pd atoms via the formation of more Pd–O bonds. However, it is yet to be determined whether the photochemical method is universal for different TiO<sub>2</sub> supports.

Atomically dispersed catalysts provide an ideal system for investigating complex interface phenomena in catalysis. For

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example, though the catalytic oxidation of CO is a widely studied model reaction, the reaction mechanism remains unresolved [18–22]. To investigate the mechanism, Pt<sub>1</sub> and Pd<sub>1</sub> catalysts synthesized through different methods have been studied. However, quite controversial results have been reported [2,11–13,23,24]. Some studies have claimed that Pt<sub>1</sub> and Pd<sub>1</sub> catalysts are highly active even at 303 K [2,24], whereas others have shown that the atomically dispersed catalysts only show decent catalytic activity at high temperatures e.g., above 500 K [11,12,23]. The different performance of the catalysts could be caused by the different coordination environments around the single-atom metal centers [25], similarly to the so-called “support effect” in traditional heterogeneous catalysis. Hence, it is important to evaluate the effectiveness of different methods in preparing atomically dispersed catalysts on various supports or even similar supports of different surface properties.

In the present study, we report the application of the photochemical method to prepare atomically dispersed Pd catalysts on two different TiO<sub>2</sub> supports, (001)-exposed anatase nanocrystals (NCs) and commercial TiO<sub>2</sub> (P25). The 0.1% Pd<sub>1</sub>/TiO<sub>2</sub> catalysts, which are prepared on both TiO<sub>2</sub> supports, show higher activity and stability in the hydrogenation of styrene when compared with catalysts prepared by other methods. Moreover, the catalysts show a low-temperature activity in the catalytic oxidation of CO that is the highest among the best Pd-based catalysts reported to date [24].

## 2. Experimental

### 2.1. Materials

Titanium(IV) fluoride (TiF<sub>4</sub>, 99%), 1-octadecene (1-ODE, 90%) and styrene were purchased from Acros Organics. Oleylamine (OLAM, 70%) and oleic acid (OLAC, 90%) were purchased from Sigma-Aldrich. P25 was purchased from Degussa. Palladium chloride (PdCl<sub>2</sub>, 59.8%) was purchased from Kunming Institute of Precious Metals. Pd/C was purchased from Alfa Aesar. Hydrochloric acid (HCl, ~35%), ethanol, toluene, hexanes, acetone, methanol, *N,N*-dimethylformamide (DMF) and 2-propanol were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). H<sub>2</sub> (99.999%) was purchased from Linde Gas (Xiamen Corporation Ltd, China). The water used in all experiments was ultrapure (18.2 MΩ). All chemicals were used as received without further purification.

### 2.2. Preparation of TiF<sub>4</sub> stock solutions

Preparation of the TiF<sub>4</sub> stock solutions was achieved by following the procedure reported therein [26]. The synthesis was undertaken in a glovebox under a nitrogen atmosphere. After mixing 0.2 mol/L TiF<sub>4</sub> and 1.0 mol/L OLAC in 1-ODE, the mixture was stirred in a water bath at 353 K to promote dissolution of TiF<sub>4</sub>. Once dissolved, the TiF<sub>4</sub> stock solution was orange-brown.

### 2.3. Synthesis of TiO<sub>2</sub> NCs

The synthesis was performed using standard Schlenk line techniques under a nitrogen atmosphere. In a 125-mL flask, 30 mmol OLAM, 10.2 mL 1-ODE, and 0.48 mL (1.5 mmol) OLAC were combined, and the reaction mixture was degassed at 393 K for 1 h and cooled to 333 K under N<sub>2</sub> atmosphere. Then, 1.5 mL TiF<sub>4</sub> stock solution was added, and the resulting mixture was promptly heated to 563 K and held for 10 min to allow the formation of seeds. Then, 8 mL TiF<sub>4</sub> stock solution was injected into the flask at 0.3 mL/min with a syringe pump. The heating mantle was then removed to allow the flask to cool naturally to room temperature. Then, the reaction contents were diluted with 5 mL toluene and centrifuged at 6000 r/min for 5 min to separate the NCs. The NCs were then redispersed in toluene via sonication, precipitated by 2-propanol and methanol and recovered by centrifugation. This washing procedure was repeated twice.

Prior to using the NCs as a support for the catalyst preparation, they were treated with NaOH solution [27]. Briefly, 50 mg NCs was dispersed in 5 mL NaOH aqueous solution (H<sub>2</sub>O/ethanol = 1:1) and stirred in the dark for 8 h to remove surface fluoride.

### 2.4. Synthesis of Pd/TiO<sub>2</sub> catalysts

The general synthesis of the Pd/TiO<sub>2</sub> catalysts was performed by dispersing either TiO<sub>2</sub> NCs or P25 (100 mg) in 10 mL water. Then, 0.2 mL H<sub>2</sub>PdCl<sub>4</sub> solution (5 mmol/L) was added to the dispersion under stirring. The dispersion was then subjected to UV treatment at room temperature under stirring. The UV treatments were conducted on a xenon-lamp parallel light source system (CHF-XM35-500W, Beijing Trusttech Co. Ltd.) equipped with an optical filter that only allowed the transmission of 365 nm UV. All UV treatments were performed at an operating current of 10 A. The power density of the UV light was 1.94 mW/cm<sup>2</sup>, as measured by a radiometer (FZ-A, Beijing Normal University photoelectric instrument factory). After 10-min irradiation, the light grey 0.1% Pd/TiO<sub>2</sub> product was collected via centrifugation and subsequently washed with water. The reference sample 1% Pd/TiO<sub>2</sub> was prepared using the same procedure, however, using 2 mL H<sub>2</sub>PdCl<sub>4</sub> solution. Subsequently, 0.1% Pd/P25 was calcined at 623 K for 4 h.

### 2.5. Characterization

Transmission electron microscopy (TEM) studies were performed on a TECNAI F-30 transmission electron microscope operating at 300 kV. For the analysis, the samples were ultrasonically dispersed in ethanol, and droplets of the suspension were deposited on a copper grid coated with a holey carbon film, followed by drying under ambient conditions.

X-ray absorption spectroscopy (XAS) of the samples was performed by recording the X-ray absorption spectra at the Pd K-edge of the samples at the XAFS station (BL14W1) of the Shanghai Synchrotron Radiation Facility. The electron storage ring was operated at 3.5 GeV. Using Si (311) double-crystal monochromator, data collection was performed in transmission mode for Pd XAS. All spectra were collected in air at room

temperature. By using the third ionization chamber, standard compounds, including Pd foil, PdO standard were measured simultaneously for the respective edges and used for energy calibration. The beam size was limited by the horizontal and vertical slits, achieving a measurement area of  $1 \times 4 \text{ mm}^2$ . The XAS data were processed using WinXAS version 3.11.

X-ray absorption fine structure (XAFS) simulations were conducted using the *ab initio* self-consistent field code FEFF8.2 [28]. The model of bulk Pd was built with Diamond program for the FEFF input file, and the coordination number of Pd–Pd was fixed at 12 to determine the amplitude reduction factor ( $S_0^2$ ). All data were processed using a consistent methodology of background subtraction,  $k^2$ -weighting and a  $k$ -range of  $\sim 3.5\text{--}10.5 \text{ \AA}^{-1}$  for one-shell fits to FT  $R$ -space. Reliable parameter values, such as bond distances and coordination numbers, were determined via single-shell  $R$ -space fitting of Pd spectra.

## 2.6. Catalysis tests

For the catalysis studies, the catalysts were first dispersed in ethanol. For styrene hydrogenation,  $5 \times 10^{-3} \mu\text{mol}$  Pd was diluted in 10 mL ethanol in a glass pressure vessel to achieve a Pd/styrene mole ratio of 1:10000. The catalyst dispersion was then sonicated and mixed with 50  $\mu\text{mol}$  styrene by a magnetic stirring bar. The vessel was then charged with  $\text{H}_2$  to 0.1 MPa and maintained at 303 K in a water bath during stirring. The reaction was stopped after the desired time (every 10 min) to extract 100- $\mu\text{L}$  aliquots of the reaction mixture for gas chromatographic analysis and conversion determination.

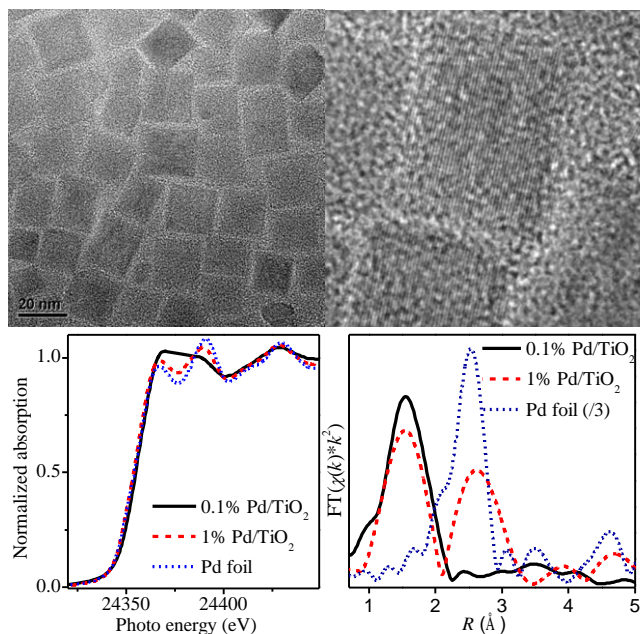
For CO oxidation, the performance of the catalysts was investigated using a fixed-bed glass reactor (internal diameter 10 mm). CO conversion was monitored by an online gas chromatograph. The gas mixture of air (40 mL/min) and CO (10 mL/min, 5 vol % in  $\text{N}_2$ ) was regulated by mass flow controllers at atmospheric pressure and passed through the catalysts with a space velocity of 3750 L/(g·h). The reactor was heated, and the temperature of the catalyst was measured with a K-type thermocouple. The temperature of the reactor was incrementally ramped from room temperature to 473 K. CO conversion ( $X_{\text{CO}}$ ) was calculated as follows:

$$X_{\text{CO}} \text{ conversion (\%)} = \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}} \times 100$$

## 3. Results and discussion

### 3.1. Structure characterization of $\text{TiO}_2$ NCs and Pd/ $\text{TiO}_2$ catalysts

The (001)-exposed  $\text{TiO}_2$  NCs were prepared through a seeded growth technique, following the synthetic method reported by Murray et al. [26]. Small  $\text{TiO}_2$  crystal seeds were formed by rapidly heating the 1-ODE solution of  $\text{TiF}_4$  with excess surfactants OLAC and OLAM. Then, the stock solution was slowly added via a syringe pump to prevent further nucleation. Preferential adsorption of  $\text{F}^-$  on anatase (001) facet allowed the formation of uniform anatase NCs with a high percentage of (001) facets [6], as shown in Fig. 1(a). Before photodeposition of Pd on  $\text{TiO}_2$  NCs, the surface  $\text{F}^-$  was substituted by  $\text{OH}^-$  by



**Fig. 1.** Structure characterization of  $\text{TiO}_2$  NCs and Pd/ $\text{TiO}_2$  catalysts. (a) Representative TEM image of  $\text{TiO}_2$  NCs, the inset is a schematic representation of a  $\text{TiO}_2$  NC; (b) HRTEM image of 0.1% Pd/ $\text{TiO}_2$  prepared by photochemical method; (c,d) XANES and FT-EXAFS  $R$ -space of 0.1% Pd/ $\text{TiO}_2$ , 1% Pd/ $\text{TiO}_2$  and Pd foil.

treating the surface with NaOH. The photochemical method was then applied to anchor the Pd atoms to the surface of  $\text{TiO}_2$  NCs. By treating the water dispersion of  $\text{TiO}_2$  NCs and  $\text{H}_2\text{PdCl}_4$  with UV light, two catalysts with Pd loading contents of 0.1% and 1% (weight ratio,  $m_{\text{Pd}}/m_{\text{catalysts}}$ ) were prepared for comparison. As observed in the high-resolution TEM (HRTEM) image in Fig. 1(b), Pd nanoparticles were not detected in 0.1% Pd/ $\text{TiO}_2$ .

To further demonstrate the atomic dispersion of Pd, XANES and EXAFS of 0.1% Pd/ $\text{TiO}_2$  were examined. The shape of the XANES spectrum of 0.1% Pd/ $\text{TiO}_2$  was identical to that of Pd oxide, but significantly different from that of Pd foil [29,30], thereby suggesting that all Pd species are positively charged. The Fourier transform (FT) of  $k^2$ -weighted EXAFS data of 0.1% Pd/ $\text{TiO}_2$  revealed the absence of peaks attributed to Pd–Pd bonds that in contrast were observed in the spectrum of Pd foil at  $\sim 2.5 \text{ \AA}$ . However, an apparent peak attributed to Pd–Pd bonds was observed in the FT-EXAFS profile of 1% Pd/ $\text{TiO}_2$ , thus indicating the formation of Pd clusters or nanoparticles.

To conduct fittings of the experimental data, simulations of EXAFS scattering paths were performed using the *ab initio* self-consistent field computational code FEFF8.2. As shown in Table 1, the coordination number for Pd–O was  $\sim 4$  for 0.1% Pd/ $\text{TiO}_2$  and 3 for 1% Pd/ $\text{TiO}_2$ . No Pd–Pd path was observed in the fitting result of 0.1% Pd/ $\text{TiO}_2$ , thereby confirming the sole presence of atomically dispersed Pd species in 0.1% Pd/ $\text{TiO}_2$ .

### 3.2. Formation mechanism of 0.1% Pd/ $\text{TiO}_2$

In our previous study, Pd atoms were photochemically deposited on EG-capped  $\text{TiO}_2$  nanosheets owing to the

**Table 1**  
EXAFS parameters of reference and Pd/TiO<sub>2</sub> catalysts.

Sample	Shell	CN	<i>R</i> (Å)	$\sigma^2$ (Å <sup>2</sup> )	$\Delta E_0$ (eV)
PdO	Pd–O	3.6	2.02	0.0008	2
	Pd–Pd	5.3	3.06	0.005	3
	Pd–Pd	5.8	3.44	0.003	3
Pd	Pd–Pd	12.0*	2.75	0.0053	0.5
	Pd–O	3.8	2.02	0.003	3.9
0.1% Pd/TiO <sub>2</sub>	Pd–O	3.1	2.01	0.004	–3
	Pd–Pd	4.3	2.75	0.008	–6.1
1% Pd/TiO <sub>2</sub>	Pd–O	2.0	2.02	0.002	3
	Pd–Cl	1.9	2.27	0.005	–5

CN, coordination number; *R*, bonding distance;  $\sigma^2$ , Debye-Waller factor;  $\Delta E_0$  shift in absorption edge energy.

\*This value was fixed during EXAFS fitting based on the known structure of Pd.

UV-induced formation of EG radicals that assisted the removal of Cl<sup>–</sup> from Pd atoms [17]. To investigate the formation mechanism of 0.1% single-atom Pd catalyst in the present study, a sample was prepared following the same procedure used for preparing 0.1% Pd/TiO<sub>2</sub>, however, in the absence of UV treatment. By simply impregnating TiO<sub>2</sub> NCs with H<sub>2</sub>PdCl<sub>4</sub>, the sample was collected through centrifugation and washed with water twice. The EXAFS data revealed that both Pd–O and Pd–Cl paths were detected in the first-shell coordination environment of the Pd atoms (Fig. 2). The coordination numbers for Pd–O and Pd–Cl were ~2.0 and ~1.9, which were quite similar to our previously reported result for the EG-capped TiO<sub>2</sub> nanosheets system. After UV treatment, Cl<sup>–</sup> atoms were completely removed from Pd. In the literature, it is well documented that the production of reactive oxygen species, such as hydroxyl radicals (·OH), on TiO<sub>2</sub> is enhanced by the presence of anatase (001) facets owing to the selective migration of photo-generated holes to the (001) facets [31–34]. We believe that the UV-assisted removal of Cl<sup>–</sup> is highly related to the photochemical reactions occurring on TiO<sub>2</sub> NCs. The developed photochemical route is applicable to prepare single-atom Pd catalysts on other TiO<sub>2</sub> systems.

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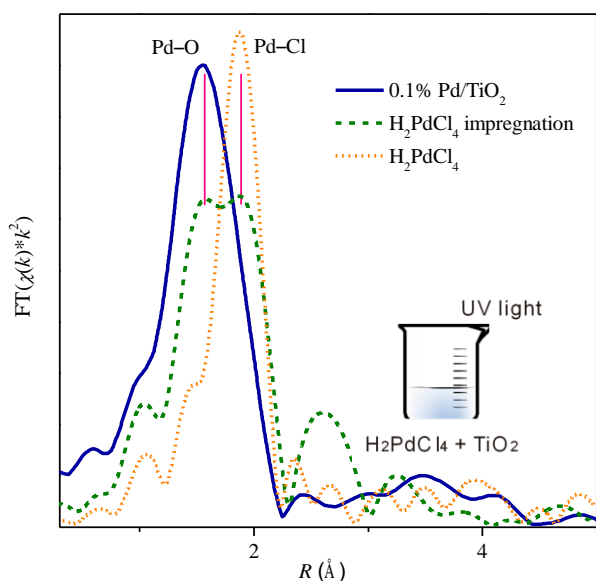
### 3.3. Catalytic studies

The as-prepared 0.1% Pd/TiO<sub>2</sub> on TiO<sub>2</sub> NCs was highly active in the hydrogenation of styrene. The turn-over frequency (TOF) was calculated to be 6000 h<sup>–1</sup>, which is considerably higher than that of commercial Pd/C catalyst (TOF = 970 h<sup>–1</sup>). More importantly, 0.1% Pd/TiO<sub>2</sub> prepared through photochemical method was notably more stable than catalysts prepared by chemical reduction methods. After impregnating TiO<sub>2</sub> NCs with H<sub>2</sub>PdCl<sub>4</sub>, either NaBH<sub>4</sub> or H<sub>2</sub> was used as a reducing agent to prepare reference samples. As shown in Fig. 3(b), the conversion-time curves of both reference samples were not straight lines during the entire reaction period, indicating activity loss during catalytic reaction. As styrene hydrogenation is a zero-order reaction with respect to styrene [35,36], the concentration of styrene has no effect on the reaction rate. Thus, the declines in the reaction rates of the reference samples can be attributed to changes in the state of the catalysts. Such changes might involve the aggregation of Pd atoms into small clusters or nanoparticles. For the catalyst 0.1% Pd/TiO<sub>2</sub> prepared through photochemical method, the UV-assisted removal of Cl<sup>–</sup>, previously adsorbed on Pd atoms, at room temperature and easy formation of four-oxygen-coordinated Pd atoms on TiO<sub>2</sub> might be the key for the high stability of the catalyst.

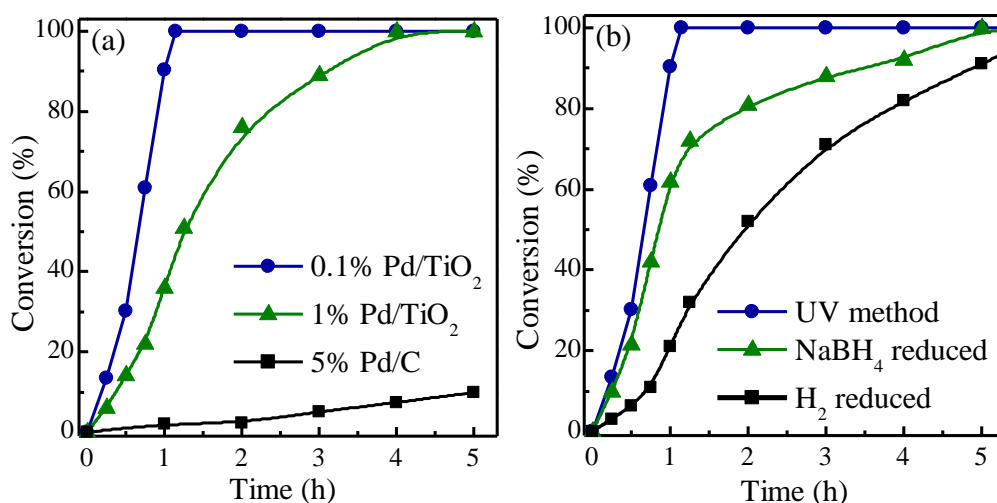
With the current understanding, we extended the use of the photochemical method to the synthesis of atomically dispersed Pd catalyst on commercial TiO<sub>2</sub> (P25). As shown in Fig. 4(a) and (b), the TEM image and FT-EXAFS *R*-space spectrum of 0.1% Pd/P25 clearly demonstrated the sole presence of Pd as single atoms. Neither the formation of Pd nanoparticles nor Pd–Pd scattering was observed in the TEM and XAS data, respectively.

Because CO oxidation is highly sensitive to the chemical environment around the metal centers, it was chosen as a model reaction to investigate the difference among catalysts prepared by the photochemical method. As shown in Fig. 4(c), the 0.1% Pd deposited on TiO<sub>2</sub> NCs and P25 catalysts showed high activities toward CO oxidation even at temperatures below 373 K. Various investigations on the catalytic performances of single-atom Pd catalysts toward CO oxidation have been conducted by several groups. Pd<sub>1</sub>/MgO prepared by mass-selected techniques could convert CO into CO<sub>2</sub> if the catalyst was pre-adsorbed by O<sub>2</sub> [37]. In contrast, Pd<sub>1</sub>/TiO<sub>2</sub> prepared using the same method showed no activity even at 500 K [12]. To date, the most active Pd-based catalyst for CO oxidation is Pd/La-doped alumina [24], which shows a low-temperature activity with an onset temperature of 313 K. The TOF of Pd/La-doped alumina at 343 K was reported to be 1.9 × 10<sup>–3</sup> s<sup>–1</sup>.

In the present work, the activity of 0.1% Pd/TiO<sub>2</sub> in CO oxidation was much higher than that of Pd/La-doped alumina. As shown in Fig. 4(a), both 0.1% Pd<sub>1</sub>/TiO<sub>2</sub> catalysts showed activity at room temperature with an onset temperature as low as 303 K. Over 96% conversion was achieved at 373 K. When compared with the highest TOF achieved by Pd catalysts



**Fig. 2.** FT-EXAFS *R*-space of 0.1% Pd/TiO<sub>2</sub>, H<sub>2</sub>PdCl<sub>4</sub> and reference sample prepared by impregnating TiO<sub>2</sub> NCs with H<sub>2</sub>PdCl<sub>4</sub>.



**Fig. 3.** (a) Comparison of the catalytic performances of 0.1% Pd/TiO<sub>2</sub>, 1% Pd/TiO<sub>2</sub>, 5% Pd/C in styrene hydrogenation; (b) Comparison of the catalytic performances of 0.1% Pd/TiO<sub>2</sub> (prepared by UV method) and reference samples (prepared by reduction method with NaBH<sub>4</sub> and H<sub>2</sub>) in styrene hydrogenation. Reaction conditions: 10 mL ethanol,  $5 \times 10^{-3}$  μmol Pd, 50 μmol styrene; 303 K, 0.1 MPa.

(Pd/La-doped alumina) reported in the literature, the measured TOF of 0.1% Pd/TiO<sub>2</sub> (NC) catalyst at 303 K was  $6.7 \times 10^{-3}$  s<sup>-1</sup>, which represents a 3.3-fold increase. Such an enhancement could be attributed to the support effect of TiO<sub>2</sub>. Moreover, though 0.1% Pd/P25 also showed a high activity at low temperature, the calculated apparent activation energy of 71.2 kJ/mol was much higher than that of 0.1% Pd/TiO<sub>2</sub>. It should be noted that the formation of Pd nanoparticles was not detected in either catalyst (0.1% Pd/P25 and 0.1% Pd/TiO<sub>2</sub>) after the catalytic reaction. This result reveals that the catalytic performance of single-atom catalysts is highly influenced by the surface state of support. Though the atomically dispersed spe-

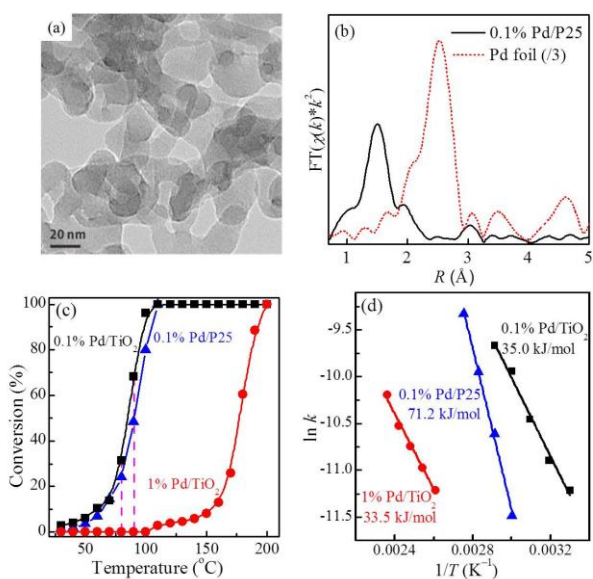
cies was the same in both 0.1% Pd/TiO<sub>2</sub> and 0.1% Pd/P25, the catalytic oxidation of CO on these two catalysts proceeded under different mechanisms, which needs further investigation. In contrast, through the pre-exponential factor for 0.1% Pd/TiO<sub>2</sub> was much higher, the activation energies for 0.1% and 1% Pd/TiO<sub>2</sub> were similar, thereby indicating that the reaction center of both catalysts might be similar.

#### 4. Conclusions

In the present study, we demonstrated that the photochemical method could be extended to the preparation of atomically dispersed Pd catalysts on various TiO<sub>2</sub> supports. Using (001) facets-exposed TiO<sub>2</sub> nanocrystals and commercial TiO<sub>2</sub> P25 as supports, 0.1% Pd/TiO<sub>2</sub> and 0.1% Pd/P25 atomically dispersed catalysts were prepared by simply mixing with H<sub>2</sub>PdCl<sub>4</sub>, followed by UV irradiation. UV irradiation was essential to remove Cl<sup>-</sup> adsorbed on Pd atoms to obtain the catalysts at room temperature. However, in the absence of surface passivation of organic ligands (e.g., ethylene glycolate) on TiO<sub>2</sub>, Pd loading was limited. Increasing the loading of Pd up to 1% led to the formation of small Pd clusters or nanoparticles. The as-prepared 0.1% Pd/TiO<sub>2</sub> catalysts exhibited excellent catalytic activities and stabilities in both the hydrogenation of styrene and oxidation of CO. A low-temperature activity in CO oxidation was observed for the 0.1% Pd/TiO<sub>2</sub> catalysts prepared using (001) facets-exposed TiO<sub>2</sub> nanocrystals and P25 as supports. Their TOFs were the highest among all Pd-based catalysts reported to date.

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**Fig. 4.** Structure characterization of 0.1% Pd/P25 and catalytic performances of the catalysts in the oxidation of CO. (a) Representative TEM image of 0.1% Pd/P25; (b) FT-EXAFS *R*-space of 0.1% Pd/P25 and Pd foil; (c) Conversion–temperature curves and (d) Calculated apparent activation energies of the catalysts.

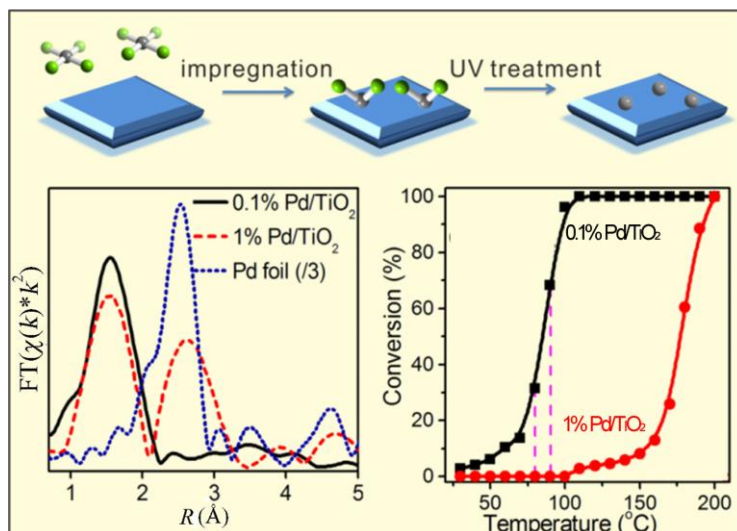
## Graphical Abstract

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Photochemical route for preparing atomically dispersed Pd<sub>1</sub>/TiO<sub>2</sub> catalysts on (001)-exposed anatase nanocrystals and P25

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Pd<sub>1</sub>/TiO<sub>2</sub> catalysts prepared via a photochemical route showed excellent catalytic activities and stabilities in both styrene hydrogenation and CO oxidation.

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## 光化学法制备基于(001)面暴露的锐钛矿和商用P25二氧化钛的单原子分散钯催化剂

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**摘要:** 单原子分散催化剂由于其独特的结构和性质, 在催化研究中已展现出巨大的潜力, 成为了催化研究的前沿领域. 传统的催化剂制备方法(例如共沉积, 浸渍法等)在单原子分散催化剂的制备中卓有成效, 但不断涌现的新方法能够制备出传统方法不能制备的新型单原子分散催化剂. 最近, 光化学方法由于其步骤简单和制备条件温和的优点而引起了广泛关注. 在之前的研究中我们揭示了光化学法制备单原子分散催化剂的分子机制. 我们发现, 紫外光照的作用在于将二氧化钛纳米片表面的乙二醇基激发生成乙二醇自由基, 后者不仅有利于氯钯酸根中氯离子的脱除, 还可通过Pd–O键将钯原子锚定在载体上, 形成了独特的“钯-乙二醇-二氧化钛”的界面. 根据对光化学法制备技术的理解, 本文将光化学法拓展到其他二氧化钛体系, 成功制备了基于(001)面暴露的锐钛矿纳米晶和商用二氧化钛P25的单原子分散钯催化剂. 通过吸附和紫外光照, 可以在室温下简单地制备单原子分散钯催化剂. 扩展X射线吸收精细结构实验表明, 紫外光照的作用是促进钯原子上氯离子的离去和更多Pd–O键的形成. 与通过其它方法制备的催化剂相比, 光化学法制备的两种Pd<sub>1</sub>/TiO<sub>2</sub>催化剂在苯乙烯的催化氢化反应中表现出更高的活性和稳定性. 转化频率TOF为商用Pd/C催化剂的6倍.

单原子分散催化剂为研究催化反应中复杂的界面效应提供了理想的模型体系. 由于CO的催化氧化反应性能对金属活性中心的化学配位环境高度敏感, 因此我们选择它作为模型反应以研究光化学法制备的单原子分散催化剂之间的差异. 结果发现, 两种载体制备的单原子分散钯催化剂都具有很好的催化CO氧化低温活性, 373 K时CO转化率均可高达96%. 其中, 负载在(001)面暴露的锐钛矿纳米晶的催化剂在343 K时TOF高达 $6.7 \times 10^{-3} \text{ s}^{-1}$ , 比有文献报道的活性最高的Pd/La-修饰Al<sub>2</sub>O<sub>3</sub>催化剂在相同条件下高3.3倍, 是目前Pd基催化剂在催化CO氧化反应中的活性最佳记录. 这可能是由于二氧化钛的载体效应引起的. 虽然两种催化剂的催化活性相当, 但Pd/P25的表现活化能比Pd/TiO<sub>2</sub>(NC)高一倍左右. 两种催化剂的金属都以单原子态分布, 催化CO氧化反应的机制却可能完全不同. 这说明单原子分散催化剂的性能与载体的表面性质密切相关. 本文为单原子催化中载体的选择和原子尺度的界面调控提供了新的研究思路.

**关键词:** 单原子分散催化剂; 光化学法制备; 紫外辅助制备; 苯乙烯氢化; 一氧化碳氧化

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