

Cite this: *Chem. Sci.*, 2019, 10, 10531

All publication charges for this article have been paid for by the Royal Society of Chemistry

Modulating the surface defects of titanium oxides and consequent reactivity of Pt catalysts†

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In heterogeneous catalysis, it is widely believed that the surface states of catalyst supports can strongly influence the catalytic performance, because active components are generally anchored on supports. This paper describes a detailed understanding of the influence of surface defects of TiO₂ supports on the catalytic properties of Pt catalysts. Pt was deposited on reduced (r-), hydroxylated (h-), and oxidized (o-) TiO₂ surfaces, respectively, and the different surface states of TiO₂ not only lead to differences in metal dispersion, but also distinct electronic interactions between the metal and the support. The highest reactivity for catalytic CO oxidation can be achieved over the Pt catalyst supported on reduced TiO₂ with surface oxygen vacancies. The turnover frequency (TOF) of this catalyst is determined to be ~11 times higher than that of Pt supported on oxidized TiO₂. More importantly, the reactivity is seen to increase in the sequence of Pt/o-TiO₂ < Pt/h-TiO₂ < Pt/r-TiO₂, which is well consistent with the trend of the calculated Bader charge of Pt.

Received 24th June 2019

Accepted 24th September 2019

DOI: 10.1039/c9sc03119g

rsc.li/chemical-science

Introduction

It has long been recognized that supports play an important role in heterogeneous catalysis, because supports can promote the catalytic performance and reduce the usage of noble metal catalysts.^{1–5} Understanding the interfacial interaction between metals and supports, studied here, is of critical importance as metal-support interactions help the dispersion of active components and sintering resistance. Additionally, a support has also been proposed as a promoter to cause changes in the electronic structure of active components and thereby alter their catalytic properties. As such, a detailed understanding of metal interactions with supports is of high importance. Previously, extensive studies showed that metal nanoparticles and single atom catalysts exhibit variable catalytic reactivity when they are deposited on different supports, such as SiO₂, Al₂O₃, CeO₂, TiO₂, FeO_x and many others.^{6–12} Surprisingly, the influence of different surface states of oxide supports on the structure and catalytic performance of metal catalysts has only been studied using model surface science systems while little is known about this factor in real supported catalysts.^{13–16}

Recently, several related studies on this issue have been published. Jia and Si *et al.* discovered that the surface states of iron oxide supports, hydroxylated or dehydrated, play an important role in the performance of Au/FeO_x in CO oxidation.¹⁷ Similarly, Wang *et al.* compared the performance of Au single atoms on perfect and defective TiO₂ nanosheet supports, in which the defective one shows a better performance in CO oxidation for a lower energy barrier and weaker competitive adsorption.¹⁸ Furthermore, the study of Christopher *et al.* provides a detailed understanding of the structure-performance relationship of atomically dispersed catalysts.^{19,20} They show that not only the intrinsic properties of metal atoms, but also the local coordination environment plays a pivotal role in the performance of catalysts.

Surface defects are ubiquitous in many materials and can affect their physical and chemical properties significantly. For example, Xie *et al.* showed that the Zn vacancies of ZnIn₂S₄ mediate the electron-hole separation efficiency and boost the reactivity of CO₂ reduction.²¹ Surface science studies have shown that the surface defects of supports will affect the binding strength of metal atoms on them. For example, Thornton *et al.* recently unraveled the binding sites of Au atoms on a reduced TiO₂ (110) substrate, and found that bridging oxygen vacancies are the preferential anchoring sites for Au atoms.²² Nevertheless, Buratto *et al.* discovered that the Au atoms on oxygen vacancies can be easily replaced by water molecules.²³ Besenbacher *et al.* demonstrated that oxygen adatoms bind metal atoms stronger than oxygen vacancies.^{13–15}

As one of the most frequently used supports in heterogeneous catalysis, reducible oxides show a diversity of point

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† Electronic supplementary information (ESI) available: Experimental and theoretical details, supporting figures and tables. See DOI: 10.1039/c9sc03119g

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defects at surfaces, such as oxygen vacancies, hydroxyls, oxygen adatoms, *etc.* It has been demonstrated that these defects are fragile, environmentally sensitive and facile to transform from one to another. For example, the oxygen vacancies at the surface of many oxides can interact with water molecules and easily break them into two hydroxyl groups.^{24–28} Upon annealing treatment in a vacuum or a reductive atmosphere, hydroxyls will recombine into water again, forming a reduced surface with oxygen vacancies.²⁹ Consequently, direct studies of the influence of a specific kind of surface defect on the catalytic reactivity remain a great challenge, in particular for catalysts supported on oxide nanoparticles.

This paper focuses on the influence of different surface defects of TiO₂ supports on the catalytic properties of Pt catalysts, because Pt/TiO₂ has been extensively used in heterogeneous catalysis, photocatalytic water splitting, and electrochemistry.^{30–34} By finely tuning the surface states of TiO₂, we prepare Pt catalysts deposited on reduced (r-), hydroxylated (h-) and oxidized (o-) surfaces, respectively. It is shown that the surface states of TiO₂ not only influence the degree of metal dispersion, but also change the electronic metal-support interactions which affect the catalytic properties of Pt directly.

Results and discussion

Modulating the surface states of TiO₂ supports

TiO₂ supports with different surface states were prepared in a specific atmosphere. The detailed preparation process is given in Fig. S1†. First, commercial rutile TiO₂ was calcined in Ar and O₂ to remove contaminants, such as carbonate and moisture. To prepare a reduced surface, TiO₂ was treated in an Ar atmosphere at 700 °C for 1 h.³⁵ Upon the exposure of r-TiO₂ to water vapor at 130 °C for 1 h, a hydroxylated surface can be obtained. At this temperature, the molecular water should be desorbed.³⁶ On the other hand, oxidized TiO₂ was prepared by exposing r-TiO₂ to O₂ at room temperature. X-ray diffraction (XRD) results (Fig. 1A and Table S1†) show the same peak position and peak shape over the different TiO₂ supports, indicating that their bulk structures are the same. Additionally, the E_g peak and full width at half maximum (FWHM) in visible Raman spectra (Fig. 1B and Table S2†) do not change after the hydroxylation

and oxidation of reduced TiO₂, which also indicates that the bulk states of the different TiO₂ samples should be the same.^{37,38}

To understand the surface states of TiO₂, X-ray photoelectron spectroscopy (XPS) was carried out (Fig. 1C). The binding energy (BE) of XPS Ti 2p_{3/2} on hydroxylated and oxidized surfaces is 459.3 eV, which can be assigned to Ti⁴⁺.^{39,40} Over reduced TiO₂, a small shoulder peak at a lower BE of 457.5 eV is observed, which indicates the presence of the Ti³⁺ state on the reduced surface.^{39,40} When r-TiO₂ was exposed to water vapor, a small shoulder peak at a higher BE of the O 1s peak appears (Fig. S2A†), suggesting the formation of surface hydroxyl groups *via* H₂O dissociation at oxygen vacancies.⁴¹ Upon the exposure of r-TiO₂ to O₂, the oxygen vacancies should be filled and oxygen adatoms will be generated on the top of regular Ti_{5c} sites (Fig. S2B†). The dissociation mechanism of O₂ on TiO₂ was clarified in previous investigations.^{42–44} The disappearance of the XPS Ti³⁺ peak on h-TiO₂ and o-TiO₂ further indicates that the dissociative adsorption of water and O₂ can occur at oxygen vacancies.

Preparation of Pt/TiO₂ catalysts

To prepare Pt catalysts on different supports, the pre-treated TiO₂ was transferred into a glove box filled with Ar, and thus the surface states of pre-treated TiO₂ will remain unchanged. In order to exclude the influence of O₂, water and other contaminants in air during the preparation process, Pt/TiO₂ catalysts were also synthesized in a glove box under the protection of an Ar atmosphere.

The influence of surface states of TiO₂ on the dispersion of Pt catalysts was determined by chemisorption, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and XPS measurements. The CO chemisorption and H₂-O₂ titration results suggest that the dispersion of Pt catalysts is highest on r-TiO₂, followed by Pt/h-TiO₂ and Pt/o-TiO₂ (Tables 1 and S3†). From HAADF-STEM studies (Fig. 2), it was found that the Pt nanoparticles on r-TiO₂ present uniform size distribution with an average diameter of 1.19 nm. In contrast, larger Pt nanoparticles are observed on h-TiO₂ (1.56 nm) and o-TiO₂ (1.61 nm). For the size distribution of catalysts after reaction (1.46 ± 0.36 nm, 1.46 ± 0.39 nm and 1.61 ± 0.43 nm for Pt/r-TiO₂, Pt/h-TiO₂ and Pt/o-TiO₂, respectively), only a small variation of particle size can be observed. From XPS investigations (Table

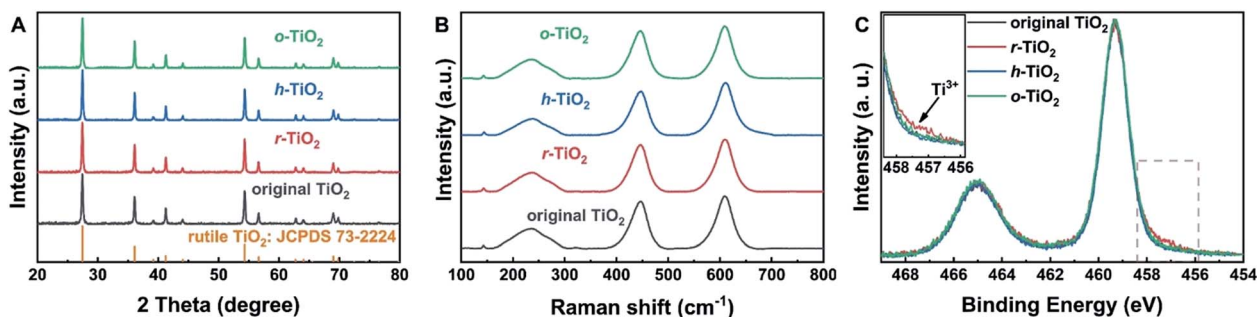


Fig. 1 Bulk and surface properties of TiO₂ supports. (A) XRD patterns of different TiO₂ supports; (B) Raman spectra of different TiO₂ supports; (C) XPS Ti 2p peaks of different TiO₂ supports. The inset in (C) shows the Ti³⁺ species on reduced TiO₂.



Table 1 Catalytic properties of different catalysts

Sample	Dispersion ^a	Specific rate $\times 100^b$ (mol CO/(g Pt $\cdot$ h))	TOF _a $\times 100^c$ (s ⁻¹)	TOF _b $\times 100^d$ (s ⁻¹)
Pt/r-TiO ₂	86%	226	14.2	200.2
Pt/h-TiO ₂	53%	81	8.2	187.0
Pt/o-TiO ₂	36%	8	1.3	42.6

^a The dispersion is tested by CO chemisorption. ^b The specific rate is derived from the CO conversion at 80 °C. ^c The TOF_a is calculated based on the dispersion of metal nanoparticles. ^d The TOF_b is calculated based on the length of the perimeter between Pt nanoparticles and TiO₂.

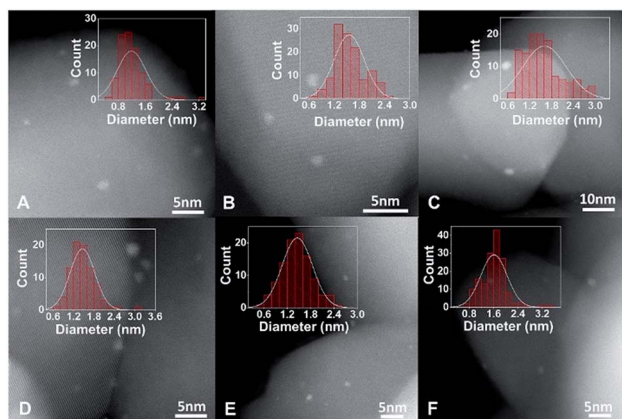


Fig. 2 HAADF-STEM and size distribution of Pt/TiO₂ catalysts. (A–C) and (D–F) are HAADF-STEM and size distribution of Pt/r-TiO₂, Pt/h-TiO₂ and Pt/o-TiO₂ before and after reaction, respectively.

S4†), it was found that the Pt/r-TiO₂ catalyst shows a stronger normalized peak area of Pt 4f/Ti 2p than Pt/h-TiO₂ and Pt/o-TiO₂, indicating that the Pt nanoparticles are more highly dispersed on r-TiO₂. The results from H₂-O₂ titration, CO chemisorption, HAADF-STEM and XPS are well consistent with each other, which illustrates that the dispersion of Pt catalysts increases in the sequence of Pt/o-TiO₂ < Pt/h-TiO₂ < Pt/r-TiO₂.

Catalytic performance

The reactivity to CO oxidation was comparatively studied over the different catalysts (Fig. 3A). Not surprisingly, the best reactivity is observed on Pt/r-TiO₂. With this catalyst, 50% CO conversion takes place at 87.6 °C. In contrast, the Pt/h-TiO₂ and Pt/o-TiO₂ catalysts exhibit worse performance, in which 50% CO conversion occurs at 102.3 and 126.3 °C, respectively. It is noteworthy that a similar trend of CO oxidation reactivity can be observed over the catalysts with different concentrations of surface defects, which are prepared through different treatment times (Fig. S3 and S4†).

The kinetic measurement of CO oxidation was further conducted. It can be found that the specific rate of Pt/r-TiO₂ to CO oxidation is ~ 2.8 and ~ 28 times higher than that of Pt/h-TiO₂ and Pt/o-TiO₂, respectively (Table 1). In addition, the turnover frequency (TOF) values based on the surface area (TOF_a) and the perimeter length of Pt nanoparticles (TOF_b) are shown in Tables 1 and S3.† The Pt/r-TiO₂ catalyst shows a TOF_a of 0.142 s⁻¹ and a TOF_b of 2.002 s⁻¹, while the Pt/h-TiO₂ and Pt/o-TiO₂ catalysts

exhibit much lower values. For the CO oxidation reaction occurring over noble metal catalysts, many previous studies suggested that the reaction obeys the Mars-van Krevelen (M-vK) mechanism on reducible catalysts or the Langmuir-Hinshelwood (L-H) mechanism on non-reducible catalysts.^{30,45–47} The reaction order test shows that the orders of CO and O₂ on different catalysts are almost the same, negative for CO and near to zero for O₂ (Fig. S5†), which is consistent with the M-vK mechanism. Furthermore, the comparable apparent activation energy (E_a) derived from the Arrhenius plot demonstrates that the CO oxidation on the different catalysts should follow the same reaction mechanism (Fig. 3B).

Electronic metal-support interactions

It has been generally agreed that supported Pt catalysts show low structure sensitivity for CO oxidation. For example, Iglesia and Lu *et al.* suggested that the catalytic properties of Pt/Al₂O₃ and Pt/TiO₂ catalysts for CO oxidation are independent of Pt cluster size.^{30,47} Although theoretical calculations and surface

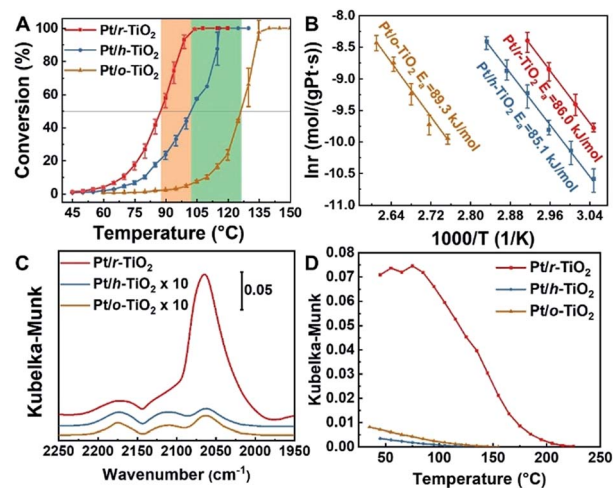


Fig. 3 Reactivity, kinetic properties and DRIFTS of CO adsorption on Pt/TiO₂ catalysts. (A) Light-off curves of CO conversion on different catalysts. The CO oxidation was conducted with a gas composition of 1% CO, 20% O₂ and He balanced, keeping GHSV at 18 000 ml g_{cat}⁻¹ h⁻¹. Each point is tested at a fixed temperature three times and then ramped to higher temperature. (B) Arrhenius plot of CO oxidation on different catalysts. (C) DRIFTS in CO oxidation (1% CO, 20% O₂ and He balanced) at 80 °C. The spectra were acquired after 5 minutes of reaction. (D) Plot of CO adsorption amount as a function of temperature in an Ar atmosphere. CO was pre-adsorbed at room temperature.



science experiments suggested that the reaction should be highly structure sensitive,^{48–50} Christopher *et al.* showed that CO-induced structure reconstruction of Pt nanoparticles mitigates the inherent structure sensitivity.⁵¹ Therefore, the observed reactivity difference of Pt/TiO₂ catalysts can be attributed to the different electronic metal-support interactions.

From XPS studies of nano-sized materials, it was found that the final state effect will make BE shift to a higher position for smaller metal nanoparticles.^{52–54} Although the size of Pt nanoparticles on r-TiO₂ is smaller than that on h-TiO₂ and o-TiO₂, the BE of XPS Pt 4f_{7/2} peaks from Pt/r-TiO₂ is even ~0.2 eV lower than that from Pt/h-TiO₂ (Fig. S6, S7 and Table S4†). This indicates that Pt may accept more electrons from r-TiO₂ or transfer fewer electrons to r-TiO₂ compared to Pt/h-TiO₂ and Pt/o-TiO₂ catalysts.

Diffuse reflection infrared Fourier transform spectroscopy (DRIFTS) of CO adsorption was also conducted to demonstrate the electronic metal-support interactions. It can be found that the better catalyst for CO oxidation shows a larger amount of CO adsorption in Kubelka–Munk units, which are assumed to be linearly related to the adsorbate coverage (Fig. 3C).^{4,55} Besides the larger CO adsorption amount, the Pt/r-TiO₂ catalyst also presents ~80 °C higher temperature for complete CO desorption compared to Pt/h-TiO₂ and Pt/o-TiO₂, which indicates that CO binds stronger with Pt/r-TiO₂ (Fig. 3D). The higher CO coverage induced by electronic interactions should be detrimental to the reactivity of Pt/r-TiO₂ in kinetic aspects due to the negative reaction order. However, Pt/r-TiO₂ shows better reactivity than Pt/h-TiO₂ and Pt/o-TiO₂. Therefore, it can be drawn that electronic interactions play a dominant role thermodynamically in reactivity modulation which is demonstrated by the DFT calculations.

Theoretical calculations

Density functional theory (DFT) calculations provide further insights into the electronic interactions between metals and supports, and their influence on catalytic reactivity. Bader charge analysis shows that the average charges of Pt on r-TiO₂, h-TiO₂ and o-TiO₂ are determined to be +0.04, +0.08 and +0.10, respectively (Fig. S8†), which agrees with XPS measurements.

The CO adsorbed at the interface of Pt/r-TiO₂ is found to have a binding energy of 2.08 eV, which is 0.29 and 0.21 eV higher than those for the CO adsorbed at the interface of Pt/h-TiO₂ and Pt/o-TiO₂, respectively. This result is well consistent with the DRIFTS results. Furthermore, the reaction barriers of adsorbed CO with the lattice oxygen of TiO₂ (CO + O) were also calculated. Fig. 4 shows the energy barriers and TS geometries for CO oxidation on the different catalysts. It can be found that the energy barriers for the CO reaction are 0.89 eV, 0.96 eV and 1.04 eV on Pt/r-TiO₂, Pt/h-TiO₂ and Pt/o-TiO₂, respectively. The barrier is consistent with E_a derived from the kinetic test (~0.95 eV). However, compared with the reaction path on Pt/h-TiO₂ and Pt/o-TiO₂, the route on Pt/r-TiO₂ is energetically more favorable which is downhill for further CO₂ desorption and the free energy barrier of the CO oxidation process is also slightly

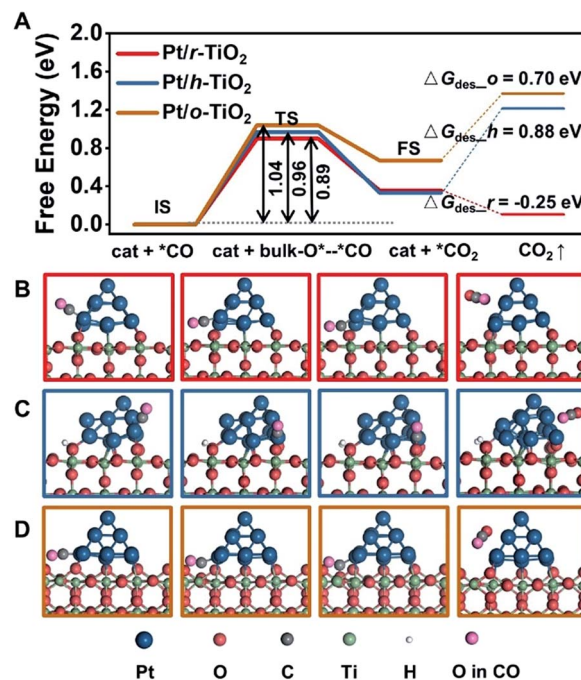


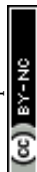
Fig. 4 Calculated CO oxidation over Pt/TiO₂ catalysts. (A) Free energy barriers for CO oxidation. (B–D) Models from left to right represent the initial state (IS), transition state (TS), final state (FS) and CO₂ desorption of CO oxidation on Pt/r-TiO₂, Pt/h-TiO₂ and Pt/o-TiO₂, respectively.

favorable. This indicates that Pt/r-TiO₂ should exhibit better reactivity for CO oxidation than Pt/h-TiO₂ and Pt/o-TiO₂. Subsequently, the reaction barriers for CO oxidation on different Pt/TiO₂ surfaces with oxygen vacancies (CO + O₂ + O_{vac}) were calculated (Fig. S9†). It can be seen that the reaction barriers for CO + O₂ + O_{vac} are much lower than those for CO + O over different catalysts.

Conclusions

Although it has been known that the surface states of supports should play an important role in the catalytic properties of catalysts, an understanding of the correlation between the surface states of supports and catalytic performance is still lacking, especially for real supported catalytic systems. Surface science investigations have shown that metal nanoparticles can be trapped at O adatoms and O vacancies on the TiO₂ (110) surface under ultra-high vacuum conditions.^{13–15,22} However, in practice, the influence of air atmosphere and the structural complexity has made direct studies of real supported catalysts very difficult. In the present study, the preparation of different catalysts was carried out under the protection of an Ar atmosphere, and thus the influence of active molecules (O₂, H₂O, etc.) in air can be excluded, but this was often ignored before.

In summary, we demonstrate how sensitively the catalytic performance of Pt catalysts depends on the surface states of TiO₂ supports. Before depositing Pt catalysts, different TiO₂ supports, including reduced, hydroxylated and oxidized types, were obtained *via* pre-treatments in different atmospheres. The



highest reactivity for CO oxidation was achieved using Pt catalysts supported on r-TiO₂, whereas worse performance was seen for the catalysts supported on h-TiO₂ and o-TiO₂. The established surface state–electronic structure–reactivity relationship clearly illustrates the important role of surface defects in catalytic performance and can be readily extended to many other metal/oxide catalytic systems.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was financially supported by the National Key Research and Development Program of China (No. 2016YFB0600901), the National Science Foundation of China (No. 21525626, 91645106, and 21603159) and the Program of Introducing Talents of Discipline to Universities (No. B06006). We thank Jie Xu and Prof. Jun Luo from Tianjin University of Technology for HADDF-STEM characterization and Chao Wang from Dalian Institute of Chemical Physics for XPS characterization. We also thank Hao Li from Tianjin University, and Dr Lijun Gao and Dr Jinhua Dong from Dalian Institute of Chemical Physics for fruitful discussions.

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