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Praseodymia–titania mixed oxide supported gold as efficient water gas shift catalyst: modulated by the mixing ratio of oxides†

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Modulating the active sites for controllable tuning of the catalytic activity has been the goal of much research, however, this remains challenging. The O vacancy is well known as an active site in reducible oxides. To modify the activity of O vacancies in praseodymia, we synthesized a series of praseodymia–titania mixed oxides. Varying the Pr : Ti mole ratio (2 : 1, 1 : 2, 1 : 1, 1 : 4) allows us to control the electronic interactions between Au, Pr and Ti cations and the local chemical environment of the O vacancies. These effects have been studied by X-ray photoelectron spectroscopy (XPS), CO diffuse reflectance Fourier transform infrared spectroscopy (CO-DRIFTS) and temperature-programmed reduction (CO-TPR, H₂-TPR). The water gas shift reaction (WGS) was used as a benchmark reaction to test the catalytic performance of different praseodymia–titania supported Au. Among them, Au/Pr₁Ti₂O_x was identified to exhibit the highest activity, with a CO conversion of 75% at 300 °C, which is about 3.7 times that of Au/TiO₂ and Au/PrO_x. The Au/Pr₁Ti₂O_x also exhibited excellent stability, with the conversion after 40 h time-on-stream at 300 °C still being 67%. An optimal ratio of Pr content (Pr : Ti 1 : 2) is necessary for improving the surface oxygen mobility and oxygen exchange capability, a higher Pr content leads to more O vacancies, however with lower activity. This study presents a new route for modulating the active defect sites in mixed oxides which could also be extended to other heterogeneous catalysis systems.

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1. Introduction

Metal oxides as one of the largest families of heterogeneous catalysts play a very important role in both industry application and academic research.^{1–6} The varieties in compositions,

electronic and geometrical structures lead to a broad spectrum of chemical properties. Among them, redox ability is considered as the key characteristic of metal oxides which determines the activities in heterogeneous catalysis.^{1,5,7} The reducible oxides are usually considered as more active for the redox reactions, such as the CO oxidation, water gas shift reactions (WGS) and reforming reactions.^{2,8} In most cases the reducible oxides follow a Mars–van Krevelen (MvK) mechanism in reaction.^{1,5,9} The key of the MvK mechanism is O from the oxide lattice can be removed and refilled.^{1,10} The fast O exchange ability is therefore considered as a prerequisite for high activity.

Praseodymium oxide similar to ceria contains a mixed-valence state (Pr⁴⁺/Pr³⁺), which is reported to have the highest O mobility among the rare earth oxides (REOs) holds great promise in catalysis.^{10–15} Our recent work on Au/PrO_x shows praseodymia is rich in O vacancies can facilitate H₂O dissociation in the WGS. However, the reactivity of Au/PrO_x is not as high as expected (several times higher than Au/CeO₂), although it has a relatively high O vacancy ratio (0.32).¹² Zhou *et al.* also find the catalytic performances of some catalysts are not always increase with the concentration of O defects.^{16,17} One possible reason is that not all the O vacancies are the active sites, only those can balance the easy adsorbing of reactant molecules and

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desorbing of product molecules are the active sites.¹⁷ In fact, both the STM and DFT studies already prove that the O vacancies can be divided into different types according to their arrangements.^{18,19} For example, in the CeO₂ single crystal, O vacancies are in the forms of an isolated single point, linear clusters and triangular trimers, which also correspond to different activities and stabilities.²⁰

One of the benchmark reactions that is usually used for testing the O vacancies activities is the WGS. Due to O vacancies on the oxide play a crucial role in facilitating H₂O dissociation (limiting step) for the WGS (Fig. 1).²¹ In addition, WGS is known as an essential process for hydrogen generation and CO removal in various energy-related chemical operations.^{21–26} Recently, its potential application in proton-exchange membrane fuel cells (PEMFCs) for eliminating CO and simultaneously producing hydrogen has aroused great interest, especially after the discovery of gold/oxide system shows high performance for the low temperature (200–300 °C) WGS by Flytzani-Stephanopoulos and co-workers. They proposed that the atomically dispersed nonmetallic Au or Pt is the active site for the WGS. Inspired by this study, recently the single-site catalysts have become a very active frontier of heterogeneous catalysis.^{22,24–29}

In order to further improve the efficiencies of supported catalyst, many attentions have been paid to synthesize single active site or modify the chemical environment of O vacancies on an oxide support.^{26,30–34} One effective way to modulate the local environment of the O vacancy is by doping heteroatoms.^{1,3,5,6} The substitution of a metal cation with another dopant will result in a direct change in the chemical environment and electronic structure of oxide.⁸ According to Stacchiola *et al.*, the Ti⁴⁺ cations dopant can decrease the O vacancy formation energy in ceria, therefore leads to easier reduction of ceria–titania mixed oxides.⁶ The theoretical study indicates the incorporation of Ti into ceria induces half of the oxygen ions moving toward Ti⁴⁺ and the other half away from Ti⁴⁺ in Ce_{0.8}Ti_{0.2}O₂ and high degrees of strain are introduced to the bulk lattices.⁶ The recent study on Pr–TiO_x/nanoporous gold (npAu) shows Pr–TiO_x mixed oxides functionalized npAu exhibits higher catalytic activity than PrO_x/npAu and TiO_x/npAu for the WGS.¹¹ Inspired by the inverse design catalyst, we are questioning if the Pr–TiO_x mixed oxides supported Au can also show better catalytic activities in the WGS in Fig. 1.^{15,35} As

praseodymium oxide is rich in O vacancies, the praseodymia–titania mixed oxides are a good system to study these relationships between O vacancies chemical environment and catalytic activities, to the best of our knowledge, this has been rarely studied.

In this work, we employed a sol–gel method for preparing praseodymia–titania mixed oxides. Gold was then loaded using a modified deposition–precipitation method. The catalytic activity of Au/Pr_aTi_bO_x for the WGS was studied in a plug-flow reactor. The structure of the catalysts was investigated with high-resolution transmission electron microscopy (HRTEM), high-angle annular dark-field imaging (HAADF) and energy-dispersive X-ray fluorescence (EDX) elemental mapping. The interactions of metal and support, as well as the metal cations inside the mixed oxides were examined by X-ray photoelectron (XPS) and CO diffuse reflectance Fourier transform infrared spectroscopy (CO-DRIFTS), which also gives information on changes in the chemical environment. The temperature-programmed desorption/reduction (CO-TPR, H₂-TPR) were used to evaluate the surface oxygen exchange capability and reducibility of catalysts which was closely related to the reactivity of the surface O vacancy site. Altogether, this enabled us to explain the origin of the doping ratio's effect of mixed oxides on catalytic performance and to illustrate the importance of the special chemical environment of O vacancies in promoting the limiting step of H₂O dissociation.

2. Experimental

2.1 Catalyst preparation

2.1.1 Synthesis of Pr_aTi_bO_x. Praseodymia–titania mixed oxides (denote as Pr_aTi_bO_x) were prepared *via* a sol–gel method reported previously. Typically, 1.5 mL TBOT (tetrabutyl-orthotitanate, Sinopharm Chemical Reagent Co., purity 98%) was added to absolute ethanol (200 mL, Sinopharm Chemical Reagent Co., purity 99.5%) under stirring for 15 min at room temperature. The desired amount of Pr(NO₃)₃ precursor solution (1 mol L^{−1}, Meryer Chemical Technology Co., purity 99.5%) was added drop-wise to above solution and stirred for 15 min. After adding 0.6 mL concentrated ammonia solution (Tianjin Kermel Chemical Reagent Co., concentration 28 vol%) a stack solution was formed and leaving it stirred for 24 h. Praseodymia–titania mixed hydroxides were obtained after drying for 12 h at 80 °C. Finally, the mixed hydroxides were calcined at 400 °C (heating rate: 3 °C min^{−1}) for 4 h in a muffle furnace to get the praseodymia–titania mixed oxides (Pr₁Ti₂O_x). The other mole ratios of Pr/Ti (*a/b* = 0, 1/4, 1/1, 2/1) mixed oxides were prepared following the same procedure.

2.1.2 Synthesis of Au/Pr_aTi_bO_x catalysts. Au was loaded on Pr_aTi_bO_x through a modified deposition–precipitation (MDP) method. In brief, 0.3 g of Pr₁Ti₂O_x powder was added to a HAuCl₄ (0.313 mL, Sinopharm Chemical Reagent Co., 9.56 g L^{−1}) and KOH mixed aqueous solution (Sinopharm Chemical Reagent Co., 85%, 1 mol L^{−1}) in a beaker. The pH was maintained at around 9 by KOH solution (yielding a nominal Au

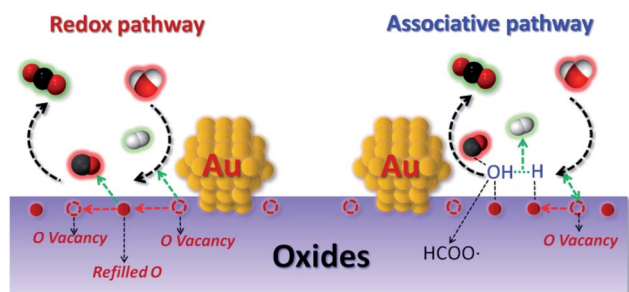


Fig. 1 Schematic illustration of the redox and associative pathway with redox regeneration for the WGS at metal/oxide interface sites.

loading of 1 wt%). The above solution was aged for 3 h then adding 20 mL ammonia solution ($\text{pH} = 9$) to remove Cl^- . Subsequently, the suspended solution was filtered, washed, and dried at 60°C overnight. The resulting sample was denoted as $\text{Au/Pr}_x\text{Ti}_y\text{O}_z$. The other samples Au/TiO_2 , Au/PrO_x were synthesized in the same way.

2.2 Catalyst characterization

Powder X-ray diffraction (XRD) analysis was carried out on a Rigaku SmartLab III using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$, 40 mA and 40 kV) with a 2θ angle ranging from 10° to 80° and a scanning rate of $10^\circ \text{ min}^{-1}$. The gold content of in all catalysts was measured using an inductively coupled plasma-optical emission spectrometer (ICP-OES) with Agilent 5110 analyzer. The nitrogen adsorption-desorption isotherms were determined at -196°C on a Micromeritics ASAP2020HD with pretreatment at 200°C under vacuum for 3 h. Brunauer–Emmett–Teller (BET) equation was used to calculate the specific

surface area. Pore size distribution was obtained from the desorption branch using the Barrett–Joyner–Halenda (BJH) method. Transmission electron microscopy (TEM) images and high-resolution TEM (HRTEM) images were performed on an FEI Talos F200X at an accelerating voltage of 200 kV. X-ray photoelectron spectra (XPS) measurements were recorded on a Thermo Scientific Escalab 250Xi equipped with $\text{Al K}\alpha$ radiation (1486.6 eV). All binding energies were calibrated with the C 1s peak at 284.8 eV .

Pulse CO chemisorption carried out on Micromeritics AutoChem II 2920 was used to get the dispersion of Au. Prior to chemisorption, the catalysts were treated in the reaction gas (2 vol% CO and 10 vol% H_2O , N_2 balance) at 300°C for 2 h and then in a nitrogen stream at 200°C for 90 min to remove the adsorbed reaction gases, followed by cooling down to room temperature in Ar.

To be noticed, the samples were first treated in the reaction gas (2 vol% CO and 10 vol% H_2O) at 300°C for 2 h to stabilize their chemical state, and about 100 mg of catalysts were used for the following experiments. Hydrogen temperature-programmed reduction (H_2 -TPR) was measured on a Micromeritics AutoChem II 2920 apparatus with a thermal conductivity detector (TCD). In a typical process, about 100 mg of catalysts were sealed in a quartz tube reactor and purged in He (50 mL min^{-1}) atmosphere at 200°C for 90 min to remove impurities on the surface. Then, the temperature was raised to 300°C and pretreated in 20 vol% O_2/He (50 mL min^{-1}) for 60 min. After cooling down to room temperature, the analysis was carried out in a stream of 10 vol% H_2/He (50 mL min^{-1}) with a ramping rate of $10^\circ\text{C min}^{-1}$ up to 800°C .

The temperature-programmed CO reduction (CO-TPR) was carried out in Bel Cata II. A Bel mass spectrometer was used to monitor CO_2 ($m/z = 44$) and H_2 ($m/z = 2$) formation at the exit.

Table 1 Physicochemical properties of catalysts

Samples	ICP Au loading (wt%)	S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	XPS		Pr : Ti real ratio
			Pr (atomic%)	Ti (atomic%)	
Au/TiO_2	0.69	104	—	18.1	—
$\text{Au/Pr}_1\text{Ti}_4\text{O}_x$	0.46	135	2.5	7.5	1 : 3.0
$\text{Au/Pr}_1\text{Ti}_2\text{O}_x$	0.61	105	4.7	7.7	1 : 1.6
$\text{Au/Pr}_2\text{Ti}_1\text{O}_x$	0.24	2	4.9	2.7	1.8 : 1

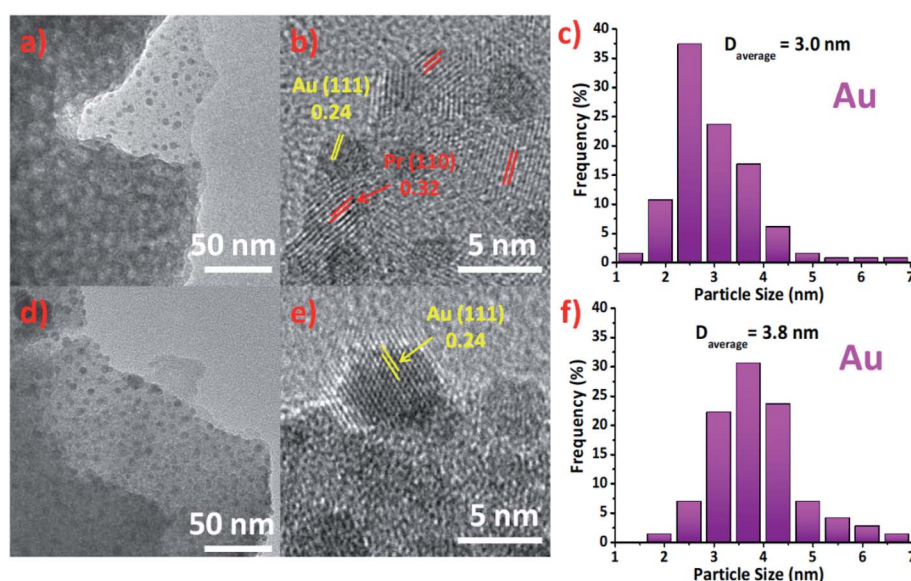


Fig. 2 TEM and HRTEM micro-graphs of $\text{Au/Pr}_1\text{Ti}_2\text{O}_x$ (a and b) and $\text{Au/Pr}_2\text{Ti}_1\text{O}_x$ (d and e). The size distributions of Au nano-particles for $\text{Au/Pr}_1\text{Ti}_2\text{O}_x$ and $\text{Au/Pr}_2\text{Ti}_1\text{O}_x$ are shown in (c and f), respectively. Images acquired after more than 10 h WGSF from 150°C to 400°C (feed-gas mixture: 2 vol% CO, 10 vol% H_2O , N_2 as carrier gas; total gas flow 45 mL min^{-1}).



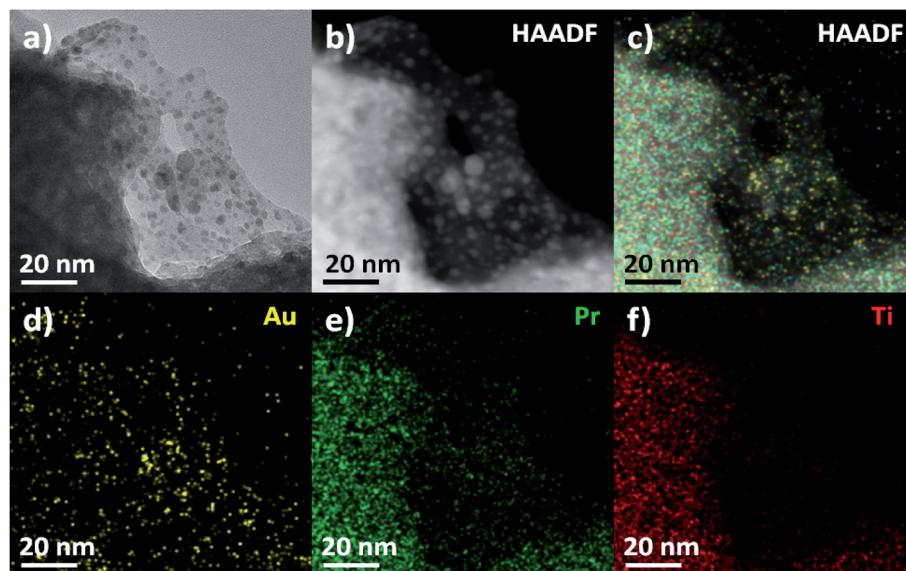


Fig. 3 (a) TEM and (b) HAADF-STEM image of Au/Pr₁Ti₂O_x, (c–f) elemental distributions maps. Au (yellow), Pr (green), Ti (red).

The catalysts were pretreated in He (30 mL min^{−1}) atmosphere at 200 °C for 90 min and then oxidized in 20 vol% O₂/He (30 mL min^{−1}) for 60 min. The analysis was carried out in a stream of 10 vol% CO/He (30 mL min^{−1}) from 50 to 800 °C at the rate of 10 °C min^{−1}.

CO-DRIFTS spectra were collected on a JASCO FT/IR-6100 spectrometer equipped with a diffuse reflectance accessory (ST Japan Heat Chamber HC-500) and MCT detector. CO-DRIFTS spectra were recorded by accumulating 128 scans with a resolution of 4 cm^{−1}. The sample was first purged under N₂ (50 mL min^{−1}) at the 120 °C for 1 h in the IR cell. After cooling down to −180 °C the background spectrum was recorded and subtracted. The CO adsorption was carried out at −180 °C with 3.84 vol% CO/He (50 mL min^{−1}) for 30 min. Then N₂ gas was introduced at −180 °C with a flow rate of 50 mL min^{−1} for 30 min to fully exclude the gas phase and weakly adsorbed CO species.^{36–38}

To be noted most of the characterizations are done for the spent catalyst in order to more precisely reflecting the properties of catalysts especially under steady-state conditions. According to McFarland and Metiu, heterogeneous catalytic reactions are run under steady-state conditions instead of at equilibrium.² It is difficult to accurately describe the catalytic performance of oxide catalysts using the property parameters of as-prepared catalysts, which are more likely to be in thermodynamic equilibrium during the preparation process.²

2.3 Catalyst evaluations

The water gas shift reaction (WGS) was performed under atmospheric pressure in a continuous flow reactor and a temperature range within 150–400 °C. About 50 mg of powder catalysts were packed to quartz wool in a U-shaped tube reactor (8 mm I.D.). An online Agilent 7820A gas chromatograph was used to detect the gas composition in feed and product gas streams by a thermal conductivity detector (TCD). The catalysts without pretreatment were tested under the

following condition: CO, 2 vol%; H₂O, 10 vol%; N₂ 88 vol%; total gas flow, 45 mL min^{−1}; gas hourly space velocity (GHSV), 54 000 mL g_{cat}^{−1} h^{−1}. Water vapor was fed into the reactor by a temperature-controlled saturator. The evaluations were maintained for 30 min to obtain catalyst performance. Reaction kinetics and stability test were performed under the same reaction conditions as catalytic evaluations. The kinetic studies were carried out at differential reaction conditions and by changing the amount of catalysts the conversion rate was kept below 20%.

The CO conversion (X_{CO}) was quantified using an area normalization method and determined by the degradation of CO gas following the equation:

$$X_{\text{CO}} = \left(\frac{\text{CO}_{\text{in}} - \text{CO}_{\text{out}}}{\text{CO}_{\text{in}}} \right) \times 100\%$$

where CO_{in} (CO_{out}) is the area percentage of CO concentration in inlet (outlet) gas composition.

The turnover frequencies (TOF) were calculated based on the following equation:

$$\text{TOF (s}^{-1}\text{)} = \frac{X_{\text{CO}} \times F_{\text{CO}} \times M_{\text{Au}}}{W_{\text{cat}} \times X_{\text{Au}} \times D_{\text{Au}}}$$

where X_{CO} is the CO conversion, X_{Au} is the Au loading in the catalyst, F_{CO} is the CO flow rate per unit time, D_{Au} is the dispersion of Au, M_{Au} is the molar weight of Au (197 g mol^{−1}).

3. Results and discussion

3.1 Structural and morphological studies

XRD investigation shows that only anatase phase TiO₂ is present in the Au/TiO₂. No diffraction peaks correspond to either praseodymia or titania are observed in the praseodymia–titania mixed oxides supported Au, with a broad peak present at 30°, which indicates the praseodymia–titania mixed oxides



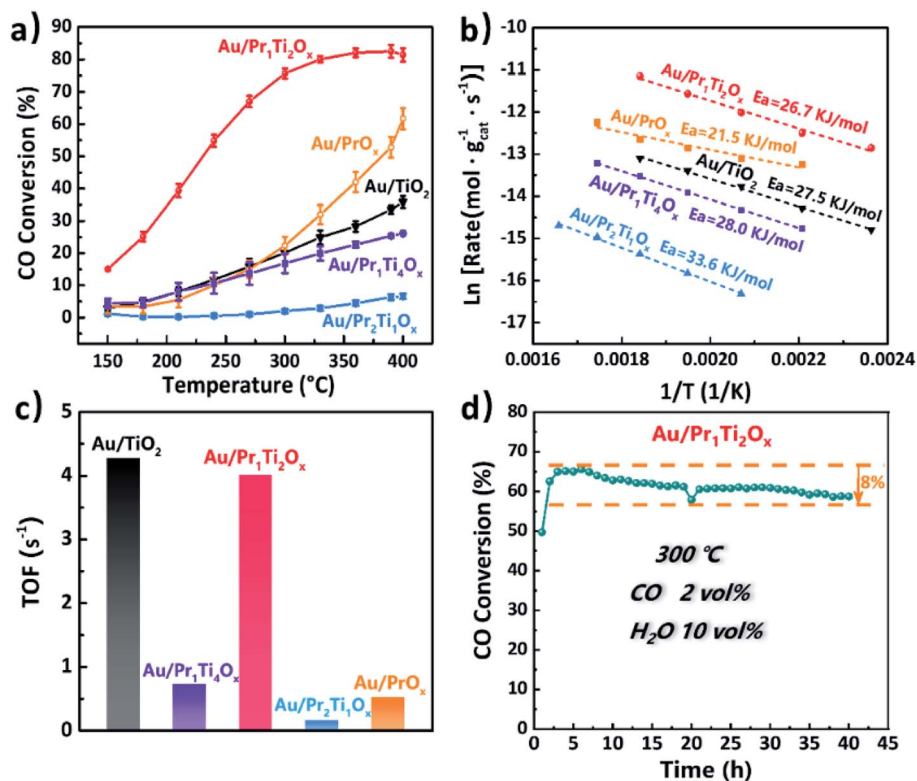


Fig. 4 (a) Steady-state test profiles of Au/TiO₂, Au/PrO_x and Au/Pr_aTi_bO_x catalysts for the WGS reaction (conditions: 2 vol% CO/10 vol% H₂O/N₂, 45 mL min⁻¹, m_{catal} = 50 mg, space velocity 54 000 mL h⁻¹ g_{cat}⁻¹). (b) Arrhenius plots of WGS over Au/TiO₂, Au/PrO_x and Au/Pr_aTi_bO_x. The space velocity is much higher than in steady-state to ensure reaction within the kinetic regime (conversion of CO < 20%). (c) Histogram of TOF values at 300 °C determined on Au/TiO₂, Au/PrO_x and Au/Pr_aTi_bO_x catalysts for the WGS reaction. (d) Long-term catalytic evaluation at 300 °C for Au/Pr₁Ti₂O_x (reaction conditions were the same as in steady-state).

mainly form an amorphous phase (Fig. S1†).^{12,39} Moreover, no distinct peaks of gold particles are observed on all samples, demonstrating the high Au dispersion (Fig. S1†). The BET data in Table 1 shows that the specific surface areas of Au/TiO₂, Au/Pr₁Ti₄O_x and Au/Pr₁Ti₂O_x are in the range of 104–135 m² g⁻¹, while the Au/Pr₂Ti₁O_x has a specific surface area of 2 m² g⁻¹. Such low surface area is also found on the Au/Pr₁Ti₁O_x sample (2.3 m² g⁻¹, Table S1†), it reveals when the atomic ratio of praseodymium is over a half in the praseodymia–titania mixed oxides, the specific surface area will decrease sharply. The low surface area also leads to few exposed catalytic active sites, therefore low catalytic activity as indicated in catalytic performance (below). The bulk Au concentration measured by ICP-OES shows the Au loading varies from 0.46 wt% to 0.69 wt% on Au/TiO₂, Au/Pr₁Ti₄O_x and Au/Pr₁Ti₂O_x, with Au/Pr₂Ti₁O_x shows the lowest loading of 0.24 wt%, which can also be attributed to the low specific surface area of Au/Pr₂Ti₁O_x result in few anchoring sites for Au. The XPS shows the surface atomic ratio of Pr : Ti for Au/Pr₁Ti₄O_x, Au/Pr₁Ti₂O_x and Au/Pr₂Ti₁O_x round 1 : 3, 1 : 1.6 and 1.8 : 1, respectively, which are close to the desired value (during synthesis), confirming the effectiveness of controlling the Pr : Ti ratio by using the sol–gel method.

TEM images in Fig. 2(a) and (d) corresponding to Au/Pr₁Ti₂O_x and Au/Pr₂Ti₁O_x. As we can see the former can maintain the porous structure and nanosheet morphology, while the

latter hardly have any pores. One explanation is that under the specific ratio (Pr : Ti = 2 : 1) the praseodymia–titania forming big aggregated particles. This is also in line with the nitrogen sorption analysis and explains why the Au/Pr₂Ti₁O_x exhibit such a small specific surface area (Fig. S2†). The HRTEM images of Au/Pr₁Ti₂O_x and Au/Pr₂Ti₁O_x in Fig. 2(b) and (e) display interplanar spacings of 0.24 nm and 0.32 nm, corresponding to the (111) plane of Au and (110) plane of Pr₆O₁₁, respectively.^{11,12,35,40–43} In addition, from Fig. 2(a) and (d) we can see the surface of nano-sheet are decorated with many small particles, which are attributed to be Au nanoparticles. The histogram analysis reveals that the Au nanoparticles have a mean size of about 3.0 ± 1.2 nm in the case of Au/Pr₁Ti₂O_x (Fig. 2(c)) and slightly bigger size of around 3.8 ± 1.5 nm in the case of Au/Pr₂Ti₁O_x (Fig. 2(f)). The Fig. 2(b) and (e) further indicates the arrangement of Au nanoparticles at the interfaces, with half of the Au atoms embedded into the supports. Similar to the observations on the nano-rod ceria supported Au catalyst, according to Shen *et al.*, the interfacial surface oxygen vacancies on oxide support work as anchoring sites for Au nanoparticles facilitating its stabilization.⁴⁴

A combined TEM (Fig. 3(a)), high-angle annular dark-field (HAADF) STEM images (Fig. 3(b)) and energy-dispersive spectroscopy (EDS) mapping (Fig. 3(c)–(f)) were used to determine the distribution of different components in Au/Pr₁Ti₂O_x



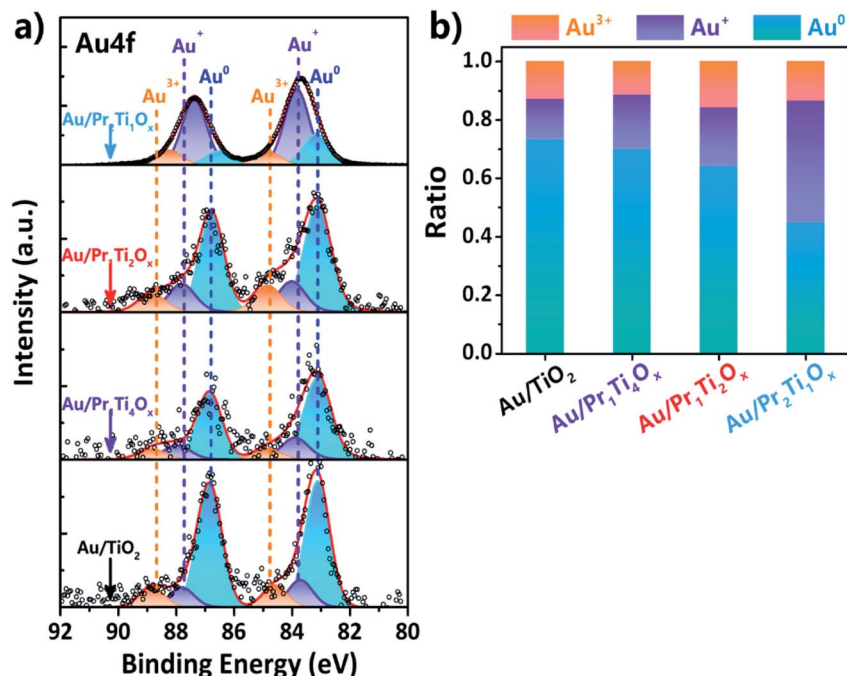


Fig. 5 Photoemission (XPS) spectra of (a) Au 4f over the Au/Pr_aTi_bO_x and Au/TiO₂ catalysts after WGS (2 vol% CO + 10 vol% H₂O/N₂, 10 h on-stream, 150 to 400 °C). (b) Plots of metallic and ionic Au ratios (peak area of Au⁰/or Au³⁺/or Au⁺ to total peak area).

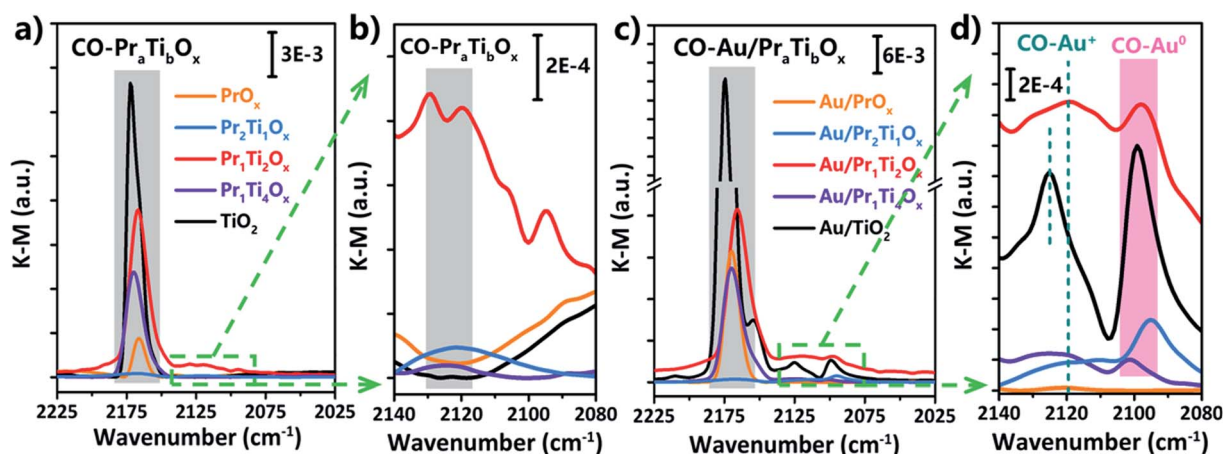


Fig. 6 DRIFT spectra of CO adsorption at −180 °C over the supports (a and b) and Au/TiO₂, Au/PrO_x, Au/Pr_aTi_bO_x catalysts (c and d) after WGS (2 vol% CO + 10 vol% H₂O/N₂, 10 h on-stream, 150 to 400 °C).

catalyst. The STEM-EDS mapping of Pr (Fig. 3(e)) and Ti (Fig. 3(f)) show a homogeneous distribution in the catalysts, indicates praseodymia was successfully mixed with titanium rather than separated mixture which is also in line with the XRD study. The signal of Au (Fig. 3(d)) corresponds well with the position of the nanoparticles in the HAADF-STEM (Fig. 3(b)), further confirming that they are Au nanoparticles.

3.2 Catalytic performance

Catalytic performances of the Au/Pr_aTi_bO_x (Au/Pr₁Ti₄O_x, Au/Pr₁Ti₂O_x, Au/Pr₁Ti₁O_x and Au/Pr₂Ti₁O_x) and Au/TiO₂ catalysts for WGS were studied with a continuous flow reactor in the

temperature range of 150–400 °C. The Au/Pr₁Ti₂O_x sample (Fig. 4(a)) exhibits exceptional high activities among the catalysts in the whole temperature range. Already at temperatures of 150 °C the catalytic conversion of water and CO is observed (Fig. 4(a)) over Au/Pr₁Ti₂O_x and around 15%. At 300 °C, the CO conversion rate over Au/Pr₁Ti₂O_x reached the highest point (75%), which is about 3.2 times that of Au/TiO₂ (25%) and 2.7 times that of Au/PrO_x (30%). The Au/Pr₁Ti₁O_x (Fig. S4†) and Au/Pr₂Ti₁O_x show very poor activity. Further increase the temperature to 400 °C instead leads to a slight decrease in the CO conversion rate. This is due to the WGS is an exothermic reaction, at a high temperature which is thermodynamically

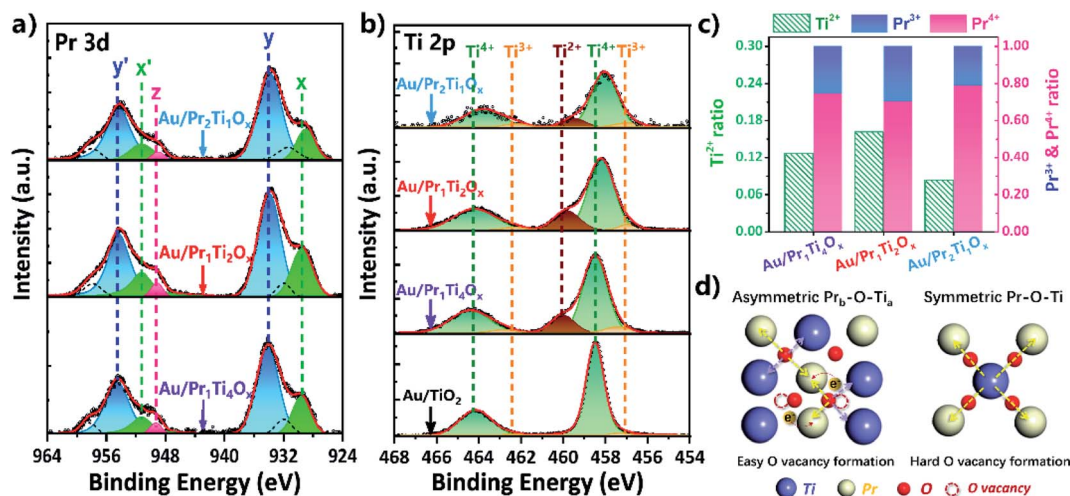


Fig. 7 XPS spectra of (a) Pr 3d, (b) Ti 2p of Au/Pr_xTi_{1-x}O_x and Au/TiO₂ catalysts after WGS (2 vol% CO + 10 vol% H₂O/N₂, 10 h on-stream, 150 to 400 °C) (the x/x' and z can be ascribed to Pr³⁺ and y/y' corresponds to Pr⁴⁺); (c) plots of Ti²⁺, Pr³⁺ and Pr⁴⁺ ratios (peak area of Ti²⁺/or Pr³⁺/or Pr⁴⁺ to total peak area); (d) schematic illustration of the formation of asymmetric site.

unfavorable.²⁵ In addition, after increasing or decreasing the atomic ratio of Pr in the praseodymia–titania mixed oxides corresponding to the Au/Pr₂Ti₈O_x and Au/Pr₁Ti₉O_x result in a drastically decrease in reactivity (Fig. 4(a)) of both catalysts. The control experiment pointed that pure Pr₆Ti₄O₁₀ and TiO₂ were inactive for WGS (CO conversion < 3%, 150–400 °C). We observed a similar behavior of catalysts in a simulate CO₂ laser conditioned CO oxidation (CO₂ 60 vol%, CO 1 vol%, O₂ 0.5 vol%, H₂O 0.5 vol%, N₂ balanced) reaction, with the Au/Pr₁Ti₉O_x shows the highest CO conversion rate of 75% at 120 °C, while Au/Pr₁Ti₄O_x of 9% and Au/Pr₂Ti₈O_x almost no reactivity at the same temperature (more details will be reported in another paper). The different behaviors of the catalysts suggest that the nature of the oxide support especially the atomic ratio of Pr : Ti plays a key role in determining the catalytic activities. Still, the high activity of Au/Pr₁Ti₉O_x must be a result of a synergistic effect of Au species and the oxide support.

The apparent activation energy (E_a , Fig. 4(b)) amounts to 21.5, 26.7, 27.5, 28.0, 33.6 kJ mol⁻¹ for Au/PrO_x, Au/Pr₁Ti₉O_x, Au/TiO₂, Au/Pr₁Ti₄O_x and Au/Pr₂Ti₈O_x, these values are comparable to the values reported by Fu *et al.* and Si *et al.*, with an E_a of 37 kJ mol⁻¹ on Au/CeO₂ and 32 kJ mol⁻¹ on Au/(Ti–Ce) O₂ mixed oxides, respectively.^{24,45} The relatively lower E_a on Au/Pr₁Ti₉O_x (26.7 kJ mol⁻¹) highlights the benefits of using Pr₁-Ti₉O_x mixed oxides as support.

The turn-over frequencies (TOF) were calculated to compare the WGS activities with other reported catalysts. We assume that all Au atoms are active sites (Au dispersion measured by pulsed CO chemisorption). The bar plot in Fig. 4(c) displays the TOFs of the four catalysts at 300 °C. The order of TOFs follow the sequences of Au/TiO₂ (4.27 s⁻¹) > Au/Pr₁Ti₉O_x (4.02 s⁻¹) > Au/Pr₁Ti₄O_x (0.72 s⁻¹) > Au/Pr₂Ti₈O_x (0.15 s⁻¹). The calculated TOF of Au/Pr₁Ti₉O_x is around 4.02 s⁻¹ (300 °C), which is even higher than the nanoparticulate Au/CeO₂ (1.27 s⁻¹, at 350 °C) reported by Fu *et al.*²⁴

In addition, we also tested the long-term stability of Au/Pr₁Ti₉O_x for WGS at 300 °C under steady-state conditions. As one major obstacle that limiting the practical applications of Au-based catalysts is rapid deactivation caused by aggregation of Au species and/or blocking of the active sites with the accumulation of intermediates (carbonates).^{12,35,42,46} As indicated in Fig. 4(d), after 40 h continued time-on-stream test, the CO conversion rate only decreased from 65% to 57%. Compared with the reported catalysts so far, the Au/Pr₁Ti₉O_x is among the most stable catalysts.⁴⁴ For example, Jia *et al.* found the reactivity of Au/CeO_x decreased from 83% to 59% within 50 h even at lower T (250 °C).²²

3.3 Investigations of electronic metal–support interaction

Fig. 5(a) shows the XPS spectra of Au 4f which is deconvoluted using a Gaussian fitting method. Two major peaks centered at 83.1 (Au 4f_{7/2}) and 86.8 eV (Au 4f_{5/2}) can be assigned to Au⁰.⁴⁷ The amounts of Au⁰ are higher than 40% in all the samples after reaction as a result of the strong reducing atmosphere of WGS, which is also in line with the findings of Si *et al.*^{45,48} The binding energy at 84.6 (Au 4f_{7/2}) & 88.3 (Au 4f_{5/2}) eV and 83.8 (Au 4f_{7/2}) & 87.7 (Au 4f_{5/2}) eV can be attributed to Au³⁺ and Au⁺, respectively.^{47,49} From Fig. 5(b) we can see the amount of ionic Au (Au⁺, 0.20; Au³⁺, 0.16) in Au/Pr₁Ti₉O_x is the higher compared with other samples (Au/Pr₁Ti₄O_x, 0.3; Au/TiO₂, 0.27). The positively charged Au indicates there is electron transfer from Au to the oxide (Pr₆Ti₄O₁₀ and TiO₂) support. According to Buerger *et al.* the charge state of gold plays a key role in influencing the binding of CO molecules, with cationic gold clusters can promote the CO adsorption through both an Eley–Rideal-like and Langmuir–Hinshelwood-like mechanism.⁵⁰ In this work we demonstrate that by changing the oxide composition (Pr : Ti ratio) one can modify the electron transfer between the support and Au, therefore, control the content of ionic gold. This provides a new way to modulate the active sites in catalysts.



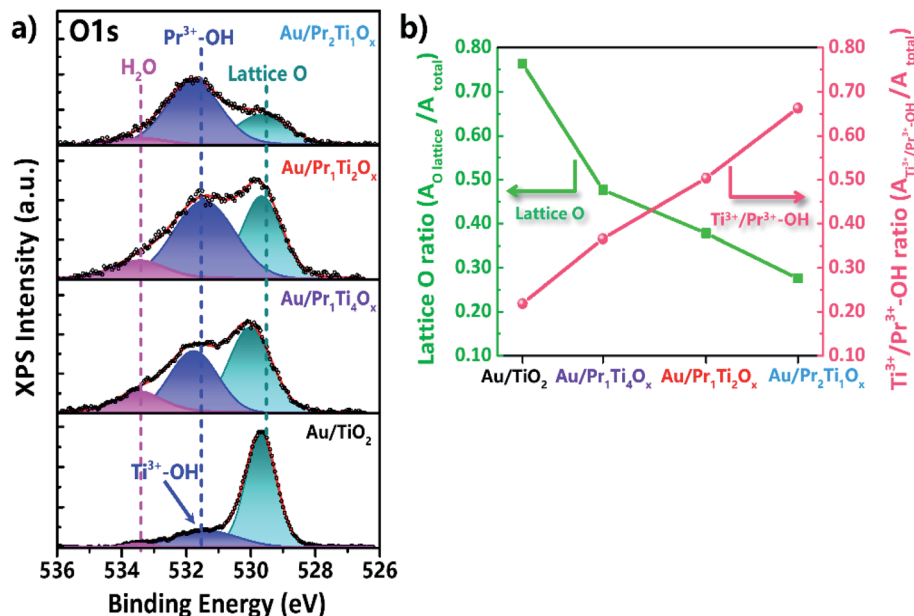


Fig. 8 Photoemission (XPS) spectra of (a) O 1s and (b) plots of lattice O and Ti³⁺/Pr³⁺-OH ratios (peak area of O lattice/O total or Ti³⁺/Pr³⁺-OH/O total peak area).

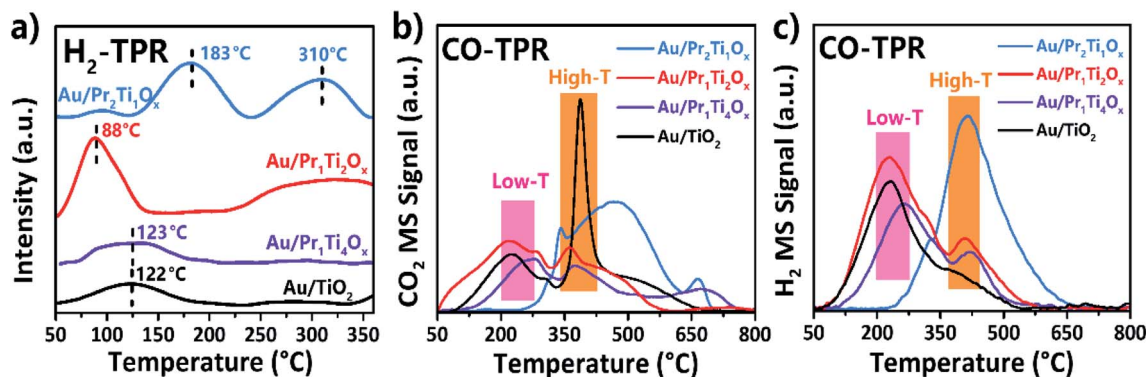


Fig. 9 (a) H₂-TPR (b and c) CO-TPR profiles of Au/TiO₂ and Au/Pr_aTi_bO_x catalysts.

The DRIFT spectra of CO adsorption on Au/TiO₂, Au/PrO_x and Au/Pr_aTi_bO_x catalysts were used to further confirm the oxidation state of Au. As shown in Fig. 6(a), the absorption bands observed at $\nu = 2168, 2166, 2170, 2174$ and 2172 cm^{-1} can be assigned to CO adsorbed on the oxide support (TiO₂, PrO_x and Pr_aTi_bO_x). The bands at 2095, 2097, 2101 and 2099 cm^{-1} can be assigned to CO adsorbed on Au⁰ (Fig. 6(d)). The bands at 2122, 2120, 2123 and 2125 cm^{-1} can be assigned to CO adsorbed on Au^{δ+} (Fig. 6(d)).³⁷ The CO adsorbed on Pr_a-Ti_bO_x also shows the band at 2122 cm^{-1} , after loading Au on it (Au/Pr_aTi_bO_x), the peak intensity further increased indicates it is overlapped with the CO-Au^{δ+} band. Fig. 6(d) shows the enlarged CO-Au^{δ+} and CO-Au⁰ band on all the samples. As we can see the intensity of CO-Au^{δ+} and CO-Au⁰ band on Au/TiO₂ are the highest followed by Au/Pr₁Ti₂O₆ > Au/Pr₂Ti₂O₆ > Au/Pr₁Ti₄O₆ > Au/PrO_x. From the literature we know it has been intensively

disputed whether metallic (Au⁰) or ionic gold (cationic Au^{δ+} or anionic Au^{δ-}) are the active site for WGS. For example, Stere *et al.* used the *in situ* DRIFTS coupled with plasma activation method and pointed that metallic Au was the most stable

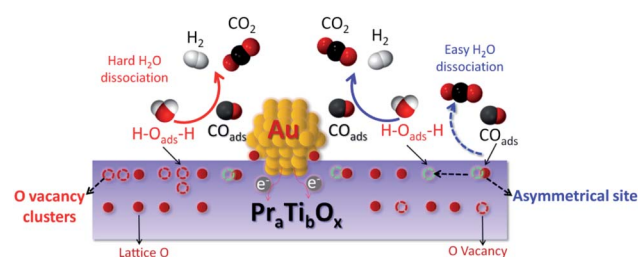


Fig. 10 Schematic illustration of the H₂O dissociation on the asymmetrical O vacancy site and the following steps for WGS.

Table 2 Comparison of catalytic performances toward WGS over various gold-based catalysts

Catalysts	Au (wt%)	Temp. (°C)	Gas feed composition	Reaction rate (mol _{CO} mol _{Au} ⁻¹ s ⁻¹)	Ref.
Au/TiO ₂	1	300	2% CO–10% H ₂ O–N ₂	0.077	This work
Au/Pr ₁ Ti ₄ O _x	1	300	2% CO–10% H ₂ O–N ₂	0.092	This work
Au/Pr ₁ Ti ₂ O _x	1	300	2% CO–10% H ₂ O–N ₂	0.327	This work
Au/Pr ₂ Ti ₁ O _x	1	300	2% CO–10% H ₂ O–N ₂	0.022	This work
Au/Pr(OH) _x –M	1	350	2% CO–10% H ₂ O–N ₂	0.502	12
Au/PrO _x	1	350	2% CO–10% H ₂ O–N ₂	0.024	12
Au/CeO ₂	4.7	250	11% CO–26% H ₂ O–26% H ₂ –7% CO ₂ –He	0.127	24
Au@TiO _{2-x} /ZnO	2	250	6% CO–25% H ₂ O–Ar	0.150	25
Au/TiO ₂	2	227	1% CO–3% H ₂ O–He	0.030	45
Au/CeO ₂	3	163	4.5% CO–13.5% H ₂ O–He	0.033	61
Au/TiO ₂	2.3	120	6.8% CO–11% H ₂ O–37.5% H ₂ –8.6% CO ₂	0.011	62
Au/α-Mo ₂ C	2	150	11% CO–26% H ₂ O–26% H ₂ –7% CO ₂ –N ₂	1.050	63
Au/Mo ₂ C	1.5	120	7% CO–22% H ₂ O–8.5% CO ₂ –37% H ₂ –Ar	0.020	64
Au/TiO _{2-x}	1.95	200	6% CO–25% H ₂ O–Ar	0.040	65
Au/ZrO ₂ –H ₂	3.8	210	6.25% CO–50% H ₂ O–N ₂	0.405	66
Au/CeFeAl	2.17	250	4.5% CO–30% H ₂ O–N ₂	0.026	67

and active species, the Au^{δ+} is less active for the WGS in the Au/CeZrO₄ catalyst.⁵¹ Jia *et al.* reported that CO–Au⁰ was not the active site for the WGS due to its inferior ability for CO adsorption under the WGS conditions. The CO–Au^{δ+} species at interfaces make the real contributions for the gold–ceria catalyst.²² While Wei *et al.* reported that the Au^{δ-} induced through a strong electronic metal–support interaction (EMSI) between Au and TiO_{2-x} acts as an active site for CO chemisorptions on the Au@TiO_{2-x}/ZnO catalyst in WGS.²⁵ Based on the current work, it's hard to say whether pure Au⁰, Au^{δ+} and Au^{δ-} are the active sites. But it can be sure that the CO adsorbed on Au or the Au-support interface indeed play an important role in WGS, as CO can also adsorb on the pure oxides but almost no WGS reactivity on the pure oxides. Although the intensity of CO on Au/Pr₁Ti₂O_x is in medium among all the catalysts, it shows the highest reactivity. One explanation is that following the “Sabatier principle”, the CO should have the “just right” interactions with Au or Au-support interface which should neither too strong nor too weak, can easily react with the OH group in the following steps.

To further clarify the electronic interactions between Ti and Pr, we explored the valence changes in both Ti and Pr caused by the mixing of them. Fig. 7(a) and (b) shows the Pr 3d and Ti 2p XPS spectra of the Au/Pr_aTi_bO_x and Au/TiO₂ catalysts after WGS. Due to the complex nature of final-state effects in the Pr 3d systems (hybridization of 4f² and 4f³L (L hole) and the multiple coupling of unpaired 4f electrons with 3d hole), distinguishing between Pr³⁺ and Pr⁴⁺ by XPS is challenging.^{9,13,14,52–54} The systematic studies of praseodymium oxides from Schaefer *et al.* point the peaks intensity increased at 973 and 949 eV after oxygen plasma treatment under UHV condition.⁵² The ratio of these peaks therefore can be used as a semi-quantitative probe for the amount of Pr³⁺ in the oxides (Fig. S3†). The two peaks centered at 954 and 934 eV due to hybridization of O 2p and Pr 4f can be attributed to Pr⁴⁺. The Ti 2p_{3/2} spectrum in Fig. 7(b) is deconvoluted into three peaks at

459.8, 458.5 and 457.2 eV, assigned to the Ti²⁺, Ti³⁺ and Ti⁴⁺ states, respectively.^{9,25,55,56}

Fig. 7(c) depicts changes of Ti²⁺, Pr³⁺ and Pr⁴⁺ content with the mixing of Pr : Ti from 1 : 4 to 1 : 2 and 2 : 1. As we can see, the ratios of Ti²⁺ and Pr⁴⁺ following the same trend, with the Au/Pr₁Ti₂O_x has the highest amount of Ti²⁺ (0.16) and Pr³⁺ (0.30), also corresponding the lowest amount of Pr⁴⁺ (0.70). This can be explained by the interaction between Pr and Ti. It is known that in TiO₂ the main cations are Ti⁴⁺, while in PrO_x the majority of cations are Pr³⁺. As Ti⁴⁺ (0.745 Å) is smaller than Pr³⁺ (1.266 Å), it should have a stronger affinity to electrons, when both Ti⁴⁺ and Pr³⁺ coordinate with O (Ti–O–Pr).^{6,13,25} Electrons of O may tend to move to Ti, leading to the reduction of Ti⁴⁺ → Ti²⁺ (accompanied by the creation of O vacancies). Simultaneously, the O attracts more electrons from Pr for compensation result in the oxidation of Pr³⁺ to Pr⁴⁺. However, the content of Ti²⁺ and Pr⁴⁺ doesn't monotonously increase with the amount of Ti in the mixed oxides. This can be explained by an asymmetry effect of the chemical bonds in Fig. 7(d). Recently, Zhou and co-workers proposed that the asymmetric A_{metal}–O–(B_{metal})_x led to easier O vacancy formation, which is accompanied by electron transformation between metals.¹⁷

XPS spectroscopy was also used to study changes in surface oxygen vacancies, induced by mixing of Ti and Pr. According to Hyuntae *et al.*, the O 1s could be deconvoluted into 3 peaks.⁵⁷ The binding energy of around 529.5 eV is attributed to the lattice oxygen of Ti⁴⁺–O₂ or Pr⁴⁺–O₂.^{12,25,56} The peak at 533.5 eV can be ascribed to adsorbed (molecular) H₂O (surface hydroxyl-like groups).⁵⁷ Features near 531.7 eV originate from Pr³⁺–OH or Ti³⁺–OH, *i.e.*, the reactant water dissociated on O vacancies (O[#]). As these species indicate the abundance of O[#], they have also been labeled O_v in the literature.^{57–59} In the current case, for the higher Pr amounts, the 531.7 eV peak mostly originates from Pr³⁺–OH (Fig. 8(a)).⁵⁷

The ratio of surface oxygen vacancies and lattice O is compared in Fig. 8(b). It can be seen that after adding



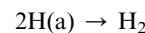
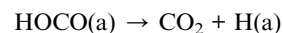
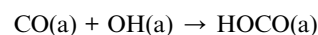
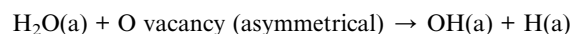
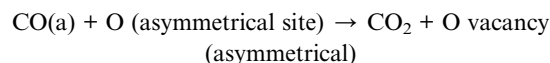
praseodymium into titanium oxide the O vacancies ratio increased greatly, meanwhile the ratio of lattice O decreased. With Au/Pr₂Ti₂O_x has the highest O vacancy ratio (0.68) followed by Au/Pr₁Ti₂O_x (0.50) > Au/Pr₁Ti₄O_x (0.38) > Au/TiO₂ (0.22). The theory study points that O vacancies play a key role in H₂O dissociation which is known as the limiting step for WGSR.⁶⁰ Our catalytic test shows that Au/Pr₁Ti₂O_x has the highest catalytic activity, however, the Au/Pr₁Ti₄O_x exhibits much lower activity and the Au/Pr₂Ti₂O_x has almost no reactivity, although the latter two catalysts also contain a high amount of oxygen vacancies. This indicates other factors such as the chemical environment of oxygen vacancies play a more important role in determining its reactivity. According to Zhou *et al.* in the mixed oxides such as Ce_{1-x}Bi_xO_{2-δ} the asymmetrical oxygen vacancies will be formed, which prefer to be filled by adsorbed oxygen species, due to a local charge balance or stable coordination for Ce⁴⁺.¹⁶ More importantly, the filled oxygen in these sites is also more easily to be released due to the asymmetric bonding effect.

The activity of surface O and OH was further investigated by H₂-TPR and CO-TPR. The H₂ TPR in Fig. 9(a) shows the H₂ consumption peak on four catalysts. The reduction peak on Au/Pr₁Ti₂O_x appears at 88 °C, which is much lower than other samples such as Au/Pr₂Ti₂O_x at 183 and 310 °C, Au/Pr₁Ti₄O_x and Au/TiO₂ at 123 °C. Moreover, the peak intensity is also much higher than other samples (2.4 times of Au/Pr₁Ti₄O_x and Au/TiO₂). The relatively low *T* of H₂ consumption on Au/Pr₁Ti₂O_x indicates the easy release of surface O. This can be attributed to two reasons: one is due to the weakening of Pr–O or Ti–O bond in Au/Pr₁Ti₂O_x caused by the asymmetrical chemical environment, the EXAFS and DFT studies by Dutta *et al.* show that substitution of Ce by another metal ion (Ti) can create disorder in the crystalline structure, resulting in the formation of weak long M–O bonds, similarly the distortion in Pr₁Ti₂O_x can also lead to the formation of long M–O bonds; the other one is the weakened O species bond contiguous to Au at the interface can further facilitates the O reduction.

After CO exposure, the CO-TPR (mass 44) in Fig. 9(b) shows that the CO₂ desorption peaks can be divided into two groups, the low-temperature group (50–350 °C) and the high-temperature group (350–800 °C), they are accompanied by the evolution of hydrogen in Fig. 9(b) (mass 2). The H₂ production can be ascribed to the WGSR from the adsorbed CO reacts with hydroxyl groups on the surface. As can be seen in Fig. 9(b) and (c), in the low-temperature range the amount of CO₂ and H₂ is also in line with catalytic test with Au/Pr₁Ti₂O_x is the highest followed with Au/TiO₂ > Au/Pr₁Ti₄O_x > Au/Pr₂Ti₂O_x. No obvious H₂ peak appears at the high-temperature range. Therefore, it could be due to the Au-catalyzed abstraction of the bulk lattice oxygen over oxides support by CO.

As illustrated in Fig. 10 after removing the active O species by CO (in WGSR) the asymmetrical O vacancy will be exposed. The asymmetrical O vacancy is energetically quite unstable tend to adsorb and dissociate H₂O more easily compared with other types of O vacancies (like O vacancy clusters). To be noted the experimentally directly distinguish the asymmetrical O vacancy site are difficult, more works are still needed to be done.

In WGSR, CO will first react with the active surface O species, thereby exposing the asymmetrical oxygen vacancies, and which will absorb water molecular and dissociate it into H and OH groups. The generated OH groups can react with CO, yielding CO₂ and H₂ (final products of WGSR). The entire pathway is summarized below:



4. Conclusions

In this work, praseodymia–titania solid solutions with different mixing ratios have been prepared *via* a sol–gel method. Au/Pr₁Ti₂O_x exhibits the better reaction rate (0.327 mol_{CO} mol_{Au}^{−1} s^{−1}) in comparison to gold-based catalysts reported previously (Table 2).^{15,45,61–67} The TOFs of Au/Pr₁Ti₂O_x is as high as 4.02 s^{−1} at 300 °C and it also exhibits good long-term stability within the 40 h continues test only lost 8% activity (300 °C) in WGSR. The HRTEM and STEM revealed that the Au nanoparticles with the mean size of 3.0 ± 1.2 nm in Au/Pr₁Ti₂O_x are half embedded in the Pr₂Ti₂O_x support. By varying the Pr ratio in the mixed oxides, the valence state of the supported Au species (Au⁺ and Au) and the amount of Ti²⁺, Pr³⁺, Pr⁴⁺ changed, which corresponds to an electronic interaction of Au and Pr_aTi_bO_x and a valence compensation effect between Ti and Pr, respectively. CO-DRIFT confirmed the adsorption CO on Au and Au–support interfacial sites. The XPS study demonstrates by increasing the amount of Pr doping the number of oxygen vacancies increase, however, don't lead to the corresponding increase of the catalytic activity of Au/Ce_aPr_bO_x. This proved that the nature of or chemical environment the vacancy sites plays a more important role in affecting the catalytic activity rather than just their abundance. The H₂-TPR confirms the easier removal of O species from Au/Pr₁Ti₂O_x due to the weakened Pr–O or Ti–O bond by the forming of an asymmetrical chemical environment. The exposed asymmetrical O vacancies due to reduction are more active, play a key role in the H₂O dissociation in WGSR. This research provides a new way to design and modulate the active sites in catalysts from the point of adjusting the chemical environment and gives a comprehensive understanding of the structure–function relation of mixed oxides supported Au catalysts.

Author contributions

Weixuan Zhao performed the preparation of catalysts, doing the catalysis test. The BET, ICP, TEM and XPS characterizations were performed in Shiyanjia Lab (<https://www.shiyanjia.com>).



Junjie Shi and Weixuan Zhao wrote the manuscript, prepared the figures and analyzed the data. Junjie Shi designed and supervised the project. MingYue Lin and Toru Murayama helped with CO-DRIFTS characterization and analysis. Libo Sun, Xun Sun and Huijuan Su helped modify the manuscript. Caixia Qi involved in the modification of the manuscript and provided great support for the project.

Conflicts of interest

The authors declare no conflict of interest.

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