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Article

On the mechanism of H₂ activation over single-atom catalyst: An understanding of Pt₁/WO_x in the hydrogenolysis reaction

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ABSTRACT

Owing to the atomic dispersion of active sites via electronic interaction with supports, single-atom catalysts (SACs) grant maximum utilization of metals with unique activity and/or selectivity in various catalytic processes. However, the stability of single atoms under oxygen-poor conditions, and the mechanism of hydrogen activation on SACs remain elusive. Here, through a combination of theoretical calculation and experiments, the stabilization of metal single atoms on tungsten oxide and its catalytic properties in H₂ activation are investigated. Our calculation results indicate that the oxygen defects on the WO₃(001) surface play a vital role in the stabilization of single metal atoms through electron transfer from the oxygen vacancies to the metal atoms. In comparison with Pd and Au, Pt single atoms possess greatly enhanced stability on the WO₃(001) surface and carry negative charge, facilitating the dissociation of H₂ to metal–H species (H^{δ−}) via homolytic cleavage of H₂ similar to that occurring in metal ensembles. More importantly, the facile diffusion of Pt–H to the WO_x support results in the formation of Brønsted acid sites (H^{δ+}), imparting bifunctionality to Pt₁/WO_x. The dynamic formation of Brønsted acid sites in hydrogen atmosphere proved to be the key to chemoselective hydrogenolysis of glycerol into 1,3-propanediol, which was experimentally demonstrated on the Pt₁/WO_x catalyst.

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1. Introduction

Single-atom catalysts (SACs), a new frontier in heterogene-

ous catalysis, have attracted intensive research interest in the past few years [1–11]. The single-atom dispersion of an active metal component allows maximal utilization efficiency of the

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metal atom, which is of particular importance for expensive and scarce platinum group metals (PGMs). Furthermore, the uniform structure of the active sites in SACs offers unrivalled selectivity for a variety of chemoselective transformations [12–15], which would be difficult to access using nanoparticle counterparts. With these unique advantages, SACs are expected to find wide application in heterogeneous catalysis, and even to act as a bridge between homogeneous and heterogeneous catalysis [3,11,16–19].

One of the challenges in practical application of SACs is the stability of single atoms. Although some SACs (e.g., Pt/CeO₂ [20–21], Pt/Fe₂O₃ [22], etc.) are reported to be highly stable under an oxidizing atmosphere, they barely survive under a reducing atmosphere, even at mild temperatures, due to the severe aggregation of single atoms, which greatly limits the application of SACs in hydrogen-involved reactions, such as hydrogenation, dehydrogenation, and hydrogenolysis. To fabricate stable SACs under hydrogen-involved reaction conditions, a fundamental understanding of the mechanism responsible for the stabilization of single atoms on the support is very important. In fact, for reducible oxide-supported single atoms, both the metal single atoms and the oxide supports are subject to reduction in the presence of hydrogen [12,23]. In this case, the oxide support forms non-stoichiometric sub-oxides with abundant oxygen vacancies. Therefore, the stability of single atoms on the nonstoichiometric sub-oxides will, to a certain extent, determine the stability of the SACs under a reducing atmosphere.

The activation of hydrogen is another important issue because it is associated with the application of SACs in hydrogen-involved reactions. It has been well established that the homolytic dissociation of H₂ can occur spontaneously to yield metal–H species on the multi-center ensembles of metal surfaces or nanoparticles [24–25]. However, such a process may be limited, due to the absence of contiguous metal atoms in SACs. In fact, when metal single atoms are bonded with the oxygen or nitrogen atoms of the supports, they are significantly positively charged, which provides an alternative pathway for hydrogen dissociation–heterolytic dissociation [26,27]. For example, when Pd single atoms were anchored to a C₃N₄ support, heterolytic dissociation of H₂ occurred, with one hydrogen atom bound to an N atom, and the other to a Pd atom [26]. In the Pd₁/TiO₂–EG single-atom catalyst, hydrogen was also heterolytically dissociated, leading to much higher hydrogenation activity in the unsaturated polar group than in the nonpolar group [27]. However, for single-atom alloy (SAA) catalysts such as Pd–Cu, hydrogen can be homolytically dissociated from the Pd monomers even at very low temperatures [28]. These results suggest that the activation mode of hydrogen on single atoms depends on the local coordination environment, just like the interplay between ligands and metal centers in homogeneous organometallic chemistry [3,11,19].

Pt/WO_x ($2 < x < 3$) is a typical strong metal support interaction (SMSI) system [29] and has been proven highly active and selective in a variety of hydrogen-involved reactions [23,30–32]. For the glycerol hydrogenolysis reaction in particular, Pt/WO_x catalysts showed unique chemoselectivity to

1,3-propanediol (1,3-PDO) [23,33,34]. In our previous experimental work [23], we compared Pt/WO_x and Pt/WO₃ and found that Pt single atoms can be stabilized on WO_x possessing abundant oxygen defects, but shows significant aggregation on well-crystallized WO₃. Moreover, hydrogen dissociation on the Pt/WO_x SAC formed in situ Brønsted acid, which was the key to the selective hydrogenolysis of glycerol to 1,3-PDO. However, an atomic level understanding of the mechanism is still lacking, such as how and where Pt single atoms are stabilized on the WO_x support, how hydrogen molecules are activated, and how Brønsted acids are formed.

In this contribution, by using density function theory (DFT) calculations we performed a comparative study of WO_x-supported Pt, Pd, and Au to address the above fundamental issues. Our DFT calculation results indicated that the oxygen defects in the WO_x play a vital role in the stabilization of Pt single atoms, and the SMSI on the defective site is favorable to maintaining the metallic nature of Pt single atoms. Consequently, unlike the positively charged single atoms, homolytic dissociation of H₂ is favored on metallic Pt single atoms. Meanwhile, the diffusion of H species from the metal active site to the surface oxygen of the support is also greatly favored, resulting in the formation of Brønsted acids on the WO_x. Consistent with the DFT calculations, we experimentally synthesized WO_x-supported Pt, Pd, and Au catalysts, which showed that only Pt could be atomically dispersed on the WO_x, while Pd formed small nanoparticles and Au formed large particles.

2. Computational and experimental details

2.1. Computational method

All calculations were performed with the Vienna ab initio simulation package (VASP) [35,36]. The generalized gradient approximation (GGA) parameterized by a Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional was employed, and core electrons were represented by the projector-augmented wave (PAW) method, with an energy cutoff for the plane waves of 430 eV. The geometric optimization of surfaces was performed using a $2 \times 2 \times 1$ Monkhorst–Pack mesh for the K-points sampling. The self-consistent iterations were converged within a criterion of less than 1×10^{-5} eV, and ionic optimization steps were converged at less than 0.02 eV/Å. To locate saddle points and calculate the reaction pathways, we used the climbing image nudged elastic band (CI–NEB) method to yield a minimum energy path. Atomic charge analysis was performed by Bader charge analysis [30,35].

With the optimized unit cell (Table S1), the WO₃ surface was built by cleaving the (001) surface on the O plane from a monoclinic or orthorhombic WO₃ supercell due to its comparable thermodynamic stability in experiments [36]. The O-terminated surface was used as the model of the catalyst surface, on which the oxidation/reduction was first performed by ab initio thermodynamics analysis under different oxygen chemical potentials, i.e., O-poor or O-rich conditions. As such, the WO₃(001) surface was modeled by a four-layer slab, with

the two bottom atomic layers frozen in the bulk configuration, and the top two atomic layers allowed to relax. A $p(2 \times 2)$ supercell with a 15 Å vacuum region between adjacent slabs was used to ensure that none of the adsorbate interacted with its periodic image [30,35].

2.2. Catalyst synthesis and characterization

WO_x was prepared using a modified procedure according to previous reports [37]. In detail, 3 g WCl_6 was dissolved into 100 mL ethanol while the mixture was stirred, and the solution was then transferred to a Teflon autoclave for heating in an oven at 433 K for 36 h. After cooling to room temperature, the dark blue precipitate was collected by filtration, washed with ethanol and water, and dried at 323 K for 6 h in a vacuum to obtain the WO_x support. Pt/WO_x was obtained by impregnation of WO_x with H_2PtCl_6 solution. After it was dried at 323 K for 6 h in a vacuum and reduced in flowing H_2 at 573 K for 1 h, the obtained Pt/WO_x catalyst was passivated using 1% O_2/N_2 for 4 h at room temperature before exposure to air. Pd/WO_x and Au/WO_x catalysts were prepared using a similar procedure.

X-ray powder diffraction (XRD) analysis was carried out on a Panalytical X'pert diffractometer using nickel-filtered $\text{Cu } K_\alpha$ radiation with scanning angle (2θ) in the range 10° – 80° , operated at 40 kV and 40 mA. High resolution transmission electron microscopy (HRTEM) images were obtained with a Tecnai G² Spirit (FEI) microscope operating at 200 kV. Prior to observations, the powder sample was ultrasonically dispersed in ethanol, and a few droplets of the suspension were put on copper grids covered with a holey carbon film and dried at room temperature. Hydrogen chemisorption was conducted on a Micromeritics AutoChem II 2920 chemisorber. Prior to H_2 adsorption at 323 K, the samples were degassed in Ar flow at 583 K for 30 min and reduced in H_2 flow at 573 K for 1 h.

The activity measurements for the hydrogenolysis of glycerol was performed at 413 K and 1 MPa H_2 for 12 h in a 75-mL autoclave with Teflon lining, as we reported earlier [34]. Prior to the reaction, the autoclave was flushed with H_2 several times, and then charged with 0.3 g of the catalyst and 12 g of an aqueous solution of 5 wt% glycerol. The liquid products were collected and analyzed with a GC equipped with an HP-INNO

Fig. 1. Top and side view of $\text{WO}_3(001)$ (a) and the oxygen vacancy (Ovac) in the $\text{WO}_x(001)$ (b) surface.

WAX capillary column (30 m $\times$ 0.32 mm $\times$ 0.5 μm , FID detector) using n -butanol as an internal standard.

3. Results and discussion

3.1. Stabilization of single metal atoms on WO_3 support

To model the possible exposed surface of WO_3 under a hydrogenolysis environment, i.e., the O-poor reaction condition, we first constructed a phase diagram of the W-terminated (001) surfaces (Figure 1a; denoted as $\text{WO}_3(001)$) with different coverages of oxygen adatoms or vacancies [38]. Two types of crystal-phase tungsten oxide, including orthogonal and monoclinic phases, were considered in our research, and these represent the two most common WO_3 phases observed under experimental conditions. Taking the orthogonal $\text{WO}_3(001)$ surface as a reference, as seen in Figure 2, the oxidation of $\text{WO}_3(001)$ through the formation of a terminal O (O_{it}) on the (001) surface is thermodynamically unfavorable (Table S2 and Figure S2). For example, the formation energy of an oxygen adatom is endothermic, with a value as high as 3.94 eV in

Fig. 2. Formation energy of oxygen vacancy at different coverages of oxygen vacancies as a function of oxygen chemical potential; (a) and (b) are orthogonal WO_3 and monoclinic WO_3 , respectively.

O-poor conditions. With full coverage of oxygen adatoms on the surface to form an O-terminated $\text{WO}_3(001)$ surface, the endothermicity shows a gradual increase, with an exothermic energy of 5.34 eV. On the other hand, the further removal of a bridged oxygen (O_{2b}) atom on $\text{WO}_3(001)$ to form a vacancy on the WO_3 surface is also not facile. The formation energy is endothermic with an energy of 0.60 eV in the O-poor condition, indicating the difficulty of deep reduction through the removal of bridging O atoms on the WO_3 surface. The surface formed by removing bridging O atoms is referred to as $\text{WO}_x(001)$ in the text (Figure 1b). This suggests that the terminal oxygen atoms on the O-terminated (001) surface of WO_3 are facile to remove to generate Lewis active sites under O-poor conditions, and the (001) surface of WO_3 without the terminal O is exposed in an O-poor, hydrogenation, or hydrogenolysis environment. In the case of the monoclinic $\text{WO}_3(001)$ surface, although it tended to be oxidized under O-rich conditions by forming oxygen adatoms on the surface, a similar preference to expose the W-terminated surface under O-poor conditions remained according to our thermodynamic calculations. Accordingly, the orthogonal WO_3 was used as the model surface in this research to obtain insight into the stabilization mechanism of single-atom active sites and its reactivity toward H_2 activation.

Subsequently, various sites on the $\text{WO}_3(001)$ and $\text{WO}_x(001)$ surfaces are considered for locating Pt single atoms through optimization with density functional theory (DFT) calculations (Figure S4). The most favorable geometric structures for Pt single atoms on the surface are schematically shown in Figure 3. As we can see, the O_{2c} site is the most favorable site for Pt location on the $\text{WO}_3(001)$ surface. The binding energy of the Pt single atom on the support, calculated as the energy difference between the Pt_1/oxide surface slab and the sum of energies of the free $\text{WO}_3(001)$ surface and the isolated Pt atom, is only -2.25 eV with a Pt–W bond length of 2.72 Å (Table 1), implying a relatively weak chemical interaction between the Pt single atom and the $\text{WO}_3(001)$ surface. It is noted, however, that the presence of the Pt single atom on the $\text{WO}_3(001)$ surface greatly promotes the reduction of the surface, i.e., the formation of a bridged oxygen vacancy on the $\text{WO}_3(001)$ surface is exothermic, with an energy of 1.51 eV in the O-poor condition. In this

Table 1

Binding energy, Bader charge, and bond length of Pt, Pd, and Au single atoms on the WO_x and $\text{WO}_3(001)$ surface.

Atoms		O_{2c} on WO_3	O_{vac} on WO_x
Pt	E_b/eV	–2.25	–4.36 (–4.65)*
	charge/ $ e $	0.13	–0.32
	Pt–W/Å	2.72	2.46
Pd	E_b/eV	–1.32	–2.34 (–2.81)*
	charge/ $ e $	0.26	0.10
	Pd–W/Å	2.77	2.59
Au	E_b/eV	–0.55	–2.38
	charge/ $ e $	1.53	0.73
	Au–W/Å	3.33	2.70

* Energy in parenthesis refers to metal atoms embedded in the oxygen vacancy.

regard, the presence of Pt single atoms on the WO_3 support leads to the reduction of O_{2c} site surface oxygen atoms, which can be ascribed to the much stronger interaction of Pt single atoms with the $\text{WO}_x(001)$ surface than with the $\text{WO}_3(001)$ surface. As shown in Table 1, the binding energy of Pt is calculated to be as high as -4.36 eV on the $\text{WO}_x(001)$ surface, which is nearly twice that of the $\text{WO}_3(001)$ surface. Geometrically, the Pt single atom prefers to be trapped in an oxygen vacancy by a slight deformation, and a great decrease in the Pt–W bond length to 2.45 Å was also observed. It was found that a Pt atom embedded in an oxygen vacancy was thermodynamically more favorable by 0.29 eV than a surface atom, and the diffusion barrier to the surface was 1.45 eV. In other words, a surface Pt atom was also unlikely to migrate to the subsurface (with a barrier of 1.16 eV, Figure S5). In addition, only surface Pt single atoms can be involved in the chemisorption of H_2 by an exothermic chemisorption energy as high as -1.37 eV. Therefore, surface Pt single atoms were thought to be predominant under reaction conditions.

For comparison, Pd and Au single atoms on both the $\text{WO}_x(001)$ and $\text{WO}_3(001)$ surfaces were also calculated. Similar to the case of Pt single atoms, oxygen vacancies on the $\text{WO}_x(001)$ surface showed much stronger binding energies than the O_{2c} on the $\text{WO}_3(001)$ surface towards both Pd and Au single atoms (-2.34 eV vs. -1.32 eV for Pd, -2.38 eV vs. -0.55 eV for Au), with a corresponding decrease in the Pd–W bond length from 2.77 to 2.59 Å, and in the Au–W bond length from 3.33 to 2.70 Å. Clearly, the generation of oxygen vacancies on the WO_3 support surface is crucial for stabilizing metal single atoms. Such a stabilization effect by oxygen vacancies was also reported previously on other supports for SACs, such as FeO_x and MnO_x [39]. However, the binding energy of the three different metal single atoms decreased in the order of Pt > Pd > Au, suggesting that Pt single atoms possess higher stability on the WO_x support than Au or Pd. It was also noted that both Pd and Pt single atoms adopted a similar geometry when they anchored on the $\text{WO}_x(001)$ and $\text{WO}_3(001)$ surfaces. That is, Pt was located on the O_{2c} site (a Pt–O distance of 1.96 Å) with neighboring Pt–W bond lengths of 2.72 Å and 3.36 Å on $\text{WO}_3(001)$, and preferred to be trapped in the hollow site near the oxygen vacancy on the $\text{WO}_x(001)$ surface by short Pt–W

Fig. 3. Most favorable geometric structures for Pt (a), Pd (b), and Au (c) single atoms on the WO_3 and $\text{WO}_x(001)$ surface.

distances (2.46 Å) and elongated Pt–O distances (2.38 Å). Such bonding geometry was also found for Pd on the WO₃ surface, but with increased Pd–W and Pd–O bond lengths due to their relatively weak interactions. In contrast, Au single atoms formed a different bonding geometry (Figure 3), by anchoring on top of the O_{2c} site of WO₃(001) and the bridge site of two neighboring W atoms on the WO_x(001) surface. This difference might have been caused by the different bonding natures of Pt, Pd, and Au single atoms, in which d-electron bonding is involved for Pt and Pd atoms, while s-electron bonding predominates for Au single atoms. In addition, the distinct metal/support interactions of different metals on a support also result in different charge states of metal single atoms, especially for the prominent anchoring of Pt single atoms on the WO_x support. As indicated by Bader charge analysis (Table 1), electron transfer occurs from oxygen vacancy to metal atoms, which is suggested by the enriched charges on Pt, Pd, and Au with the presence of oxygen vacancies on the WO_x support. In particular, due to the strong metal/support interaction, a negative charge as high as 0.32 |e| is found on the Pt atoms, which differs from the Pd and Au atoms on the WO_x surface. The charge difference between Pt and Pd may originate from the different electron affinity of these two metal atoms. According to previous studies, Pt single atoms possess a much higher electron affinity than Pd [39], which therefore leads to a different electron transfer between metal single atoms and WO_x. Due to the formation of oxygen vacancies on WO_x(001), residual electrons accumulate in the hollow sites neighboring the oxygen vacancies. This was confirmed by the differential electron density analysis on WO_x(001) (Figure 4a). As a result, a charge transfer to the Pt single atoms of Pt₁/WO_x was discovered, consistent with the previous report of single metal atoms on defective oxides [39]. However, the differential charge density analysis indicates that Pt single atoms are chemically bonded by an electron-enriched hollow site (Figure 4b). Meanwhile, the density of states (DOS) of Pt–5d for Pt₁/WO_x and the Pt(111) metal surface are shown in Figure 5. As we can see, the d-band density of Pt single atoms has a distribution similar to that on the Pt(111) surface, indicative of the similar electronic properties of these two different Pt active sites. Moreover, we also calculated the d-band center of the d-state, which was located at

Fig. 4. Differential charge density analysis of WO_x(001) (a) and Pt₁/WO_x (b), respectively (electron enrichment in green, electron deficiency in blue).

Fig. 5. Density of states of Pt–5d for Pt₁/WO_x and Pt(111) metal surface.

–2.01 and –2.37 eV for Pt₁/WO_x and Pt(111), respectively. This negative charge implies that Pt single atoms on the WO_x support can retain the metallic nature of Pt, which is quite different from most supported SACs, in which metal single atoms are usually positively charged [40–46].

3.2. Dissociation of hydrogen on M₁/WO_x(001)

Hydrogen activation is a key step in many hydrogenation and hydrogenolysis reactions. Particularly, when the active metal component is atomically dispersed, hydrogen activation may become a rate-determining step due to the absence of contiguous metal atoms [47]. Based on the above calculations, Pt single atoms are stabilized well on the oxygen vacancies of the WO_x(001) surface, and maintain the metallic nature of Pt, whereas Pd and Au are less stable on the same sites. We then studied the dissociation of H₂ on the Pt₁/WO_x(001) surface. Our DFT calculation indicated that as it moves closer to the Pt single atom, the gaseous H₂ molecule dissociates spontaneously into two hydrogen atoms with an exothermic energy of 1.37 eV by forming separated metal–H species on the Pt₁ active sites (Figure 6). Moreover, the two H atoms linked to the Pt metal site possess identical Pt–H bond lengths (1.57 Å) and charges (–0.10 |e|), similar to the H adatom on the Pt(111) surface. Clearly, the hydrogen molecule can proceed with homolytic dissociation on the Pt₁/WO_x(001), just like on the Pt(111) surface (1.56 Å). This result is in contrast to other SACs, for which heterolytic dissociation of hydrogen is preferred [26,27]. The facile dissociation of hydrogen on the Pt₁/WO_x(001) can be attributed to the negative charge of Pt single atoms due to the electron transfer from oxygen vacancies to the Pt single atoms. Furthermore, the low-coordination metal single atoms also offer the opportunity for multi-coordination toward adsorbates; that is, in the Pt₁/WO_x system, the Pt single atom active site can capture more than two metal–H species. As seen in Figure 7, our DFT calculation indicates that the Pt₁ single atom on WO_x can capture as many as three metal–H species, although the binding energy per metal–H shows a great decrease with the increase in metal–H bonds (from 1.25 eV to 1.37 eV and then to 0.87 eV). In this respect, the single atom catalyst

Fig. 6. Adsorption and dissociation of H₂ on Pt, Pd, and Au/WO_x(001) SACs.

behaves much like a homogeneous catalyst due to its tunable coordination environment on the support.

However, due to the maximized interface between metal single atoms and supports in SACs, the as-formed metal–H species on Pt single atoms is straightforward to transfer to the support via interface diffusion. As seen in Figure 8, the calculated energy barrier for metal–H diffusion to its neighboring O_{2c} is only 0.82 eV, with a slightly endothermic energy of 0.37 eV. This implies the facile spillover of H during reaction conditions. More importantly, the H atom on the O_{2c} site of the WO_x support behaves as a Brønsted acid site with a +0.69 |e| charge state (Table 2). As a result, we can conclude that both the metal–H (H^{δ−}) and Brønsted acid (H⁺) can form concurrently on the Pt₁/WO_x catalyst in the presence of H₂ gas. It is interesting that the Brønsted acid (H⁺) produced in situ by Pt single atoms possesses a stronger acidity than the intrinsic acid on the WO_x surface, as indicated by their different O–H frequency (3540 cm^{−1} vs. 3797 cm^{−1}). In other words, the Pt₁/WO_x surface behaves like a heterolytic cleave toward H–H, but it is the result of the homolytic cleavage with the further H spillover process. The H⁺ Brønsted acid is thought to play a key role in the hydrogenolysis reaction of polyols [23,34].

Unlike Pt₁/WO_x(001), gaseous H₂ cannot dissociate on the Pd₁/WO_x(001) surface to form metal–H species spontaneously. Instead, it can be chemisorbed and activated on Pd single atoms. The binding energy was calculated to be −0.76 eV with the H–H bond distance stretching from 0.75 to 0.92 Å. This is quite

Fig. 7. The capture of H atoms by Pt₁/WO_x(001) and binding energy on metal–H bonds.

Fig. 8. Dissociation of H₂ and migration of H atom on Pt₁/WO_x(001), Pd₁/WO_x(001), and Au₁/WO_x(001) surfaces.

different from that on the Pd(111) surface where the dissociation is barrierless with an exothermic energy 0.98 eV. The lower activity of the Pd₁/WO_x(001) for hydrogen dissociation can be ascribed to the less metallic nature of Pd single atoms on the WO_x support; in fact, different from Pt, the Pd single atoms on the WO_x support carry slightly positive charges (0.10 |e|), which leads to the dissociation of H₂ at the interface of Pd and WO_x to form metal–H and H⁺ on the O_{2c} site with the help of the support [27]. Obviously, such a process on Pd₁/WO_x causes a heterolytic cleavage of the H–H bond. The transition state calculations indicate that this process is very straightforward, with a barrier of 0.67 eV and a slight exothermic energy (0.05 eV). Unlike the Pt and Pd atoms, the Au single atom on the WO_x surface is completely inert toward the chemisorption of H₂. Accordingly, direct dissociation of H₂ cannot occur on the Au₁/WO_x surface. As calculated, the heterolytic cleavage mechanism requires an activation barrier of 1.07 eV with an endothermic energy of 0.39 eV, indicative of the lowest activity of an Au single atom for H₂ dissociation on the WO_x surface, similar to the inert property of Au(111) for hydrogen activation [48].

3.2. Experimental tests of Pt, Pd, and Au on WO_x

As predicted by our above DFT calculations, the stability of single atoms on the WO_x support decreases in the order of Pt > Pd > Au, and the hydrogen molecule can dissociate spontaneously on the Pt₁/WO_x, while it can only be heterolytically dissociated with the help of WO_x on the Pd₁/WO_x, and cannot dissociate at all on the Au₁/WO_x. To validate the DFT predictions, we experimentally prepared Pt/WO_x, Pd/WO_x, and Au/WO_x cata-

Table 2

Binding energy (*E*), H–H distance (*d*_{H–H}), and charge of H atoms on Pt, Pd, and Au/WO_x(001) surface.

Atom	Homolytic mechanism			Heterolytic mechanism	
	<i>E</i> /eV	<i>d</i> _{H–H} /Å	Charge/ e	<i>E</i> /eV	Charge/ e
Pt	−1.37	1.96	−0.10, −0.10	−1.00	−0.04, +0.69
Pd	−0.76	0.92	0.00, 0.03	−0.71	−0.13, +0.68
Au	N.A.	N.A.	N.A.	0.39	−0.16, +0.64

N.A.: not available.

Fig. 9. XRD patterns of Pt₁/WO_x (dark line), Pd/WO_x (red line), and Au/WO_x (blue line).

lysts using incipient wetness impregnation followed by reduction in hydrogen gas. The XRD patterns (Figure 9) of the three samples show the reflections of WO_{2.92} (PDF 00-030-1387), indicating the presence of oxygen vacancies. Moreover, there are no reflections of Pt or PtO_x species despite the relatively high Pt loading (2 wt%), indicative of highly dispersed Pt species. Considering that Pd and Au are predicted to be less stable on the WO_x support, we decreased the metal loading to 0.5 wt% for these two samples. In the case of Pd/WO_x, Pd species may still be highly dispersed, as suggested by the absence of any metal reflections in the XRD pattern. However, four typical reflection peaks of metallic Au can clearly be observed in the Au/WO_x sample, suggesting the formation of large particles of Au. In agreement with the XRD results, the TEM images (Figure 10) clearly show large Au particles on the WO_x surface, while no particles can be observed on either the Pt/WO_x or Pd/WO_x sample, assuming that Pt and Pd are atomically dispersed on the WO_x support. Unfortunately, the similarity of the atomic numbers of Pt and W does not allow us to distinguish them either through HAADF-STEM or X-ray absorption spectroscopy. In conclusion, both the XRD and TEM results agree with our DFT prediction about the stability of different metal atoms on the WO_x support, that is, Pt/WO_x > Pd/WO_x > Au/WO_x.

Subsequently, we performed hydrogen chemisorption on the three samples. As predicted by DFT calculations, the hy-

Fig. 10. TEM images for Pt₁/WO_x, Pd/WO_x and Au/WO_x.

Table 3

Hydrogenolysis of glycerol over tungsten oxide-supported Pt, Pd, and Au catalysts.

Catalyst	Conv. (%)	Selectivity (%)				
		1,3-PD	1-PO	2-PO	1,2-PD	Others
2 wt% Pt/WO _x	37.4	35.1	50.3	5.1	2.3	15.3
0.5 wt% Pd/WO _x	1.3	0.0	74.5	5.2	6.0	14.2
0.5 wt% Au/WO _x	1.8	0.0	87.7	5.2	0.0	7.1

Reaction conditions: 75 mL autoclave, catalyst 0.3 g, 12 g 5 wt% glycerol aqueous solution, 140 °C, 1 MPa, 800 rpm, 12 h.

drogen uptakes followed the order of Pt/WO_x (137 μmol/g-Pt) > Pd/WO_x (43 μmol/g-Pd) >> Au/WO_x (4 μmol/g-Au). However, hydrogen spillover can produce Brønsted acid sites, which enables the Pt/WO_x to function as a bi-functional catalyst. Therefore, we used glycerol hydrogenolysis as a probe reaction to test for bi-functionality. As shown in Table 3, among the three catalysts, only the Pt/WO_x sample was active in glycerol hydrogenolysis, affording a 37.4% glycerol conversion and 35.1% 1,3-PDO selectivity. Neither Pd nor Au was active on the WO_x. This result is in good agreement with the mode of hydrogen activation; the greater the hydrogen spillover and the more easily it happened, the higher the activity and selectivity. By stabilizing Pt single atoms on the oxygen vacancy of the WO_x support, hydrogen activation could proceed spontaneously and homolytically, producing two separate Pt-H[•] species, and one of them spilled over to the neighboring oxygen atom to form proton (H⁺). Such a pair of H⁺-H[•] is required for glycerol hydrogenolysis to form 1,3-PDO [23,34].

4. Conclusions

Using a combination of experimental and theoretical studies, the dispersion and stability of noble metals including Pt, Pd, and Au on tungsten oxides were investigated. Under oxygen-poor conditions, the formation of bridging oxygen vacancies was thermodynamically favored with the promotion of Pt single atoms, and the Pt single atoms preferred to be trapped into hollow sites near the oxygen vacancies on the WO_x(001) surface, resulting in a highly stable and negatively charged Pt site. Such a negatively charged Pt single atom facilitates the dissociation of H₂ into the metal-H species through the homolytic cleavage of the H-H bond, and leads to spillover of H to the WO_x to form Brønsted acid sites. The stability of the single atoms on the WO_x(001) surface decreases in the order of Pt > Pd >> Au, and hydrogen can only be heterolytically dissociated at the interface between Pd and WO_x, while it cannot dissociate at all on Au/WO_x. This accounts for the unique activity and selectivity of Pt₁/WO_x in the hydrogenolysis of glycerol. Our findings in the present study not only address the stabilization mechanism of metal single atoms on oxides under a reducing atmosphere, but also give new insight into the activation mechanism of H₂ on single-atom catalysts.

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Graphical Abstract

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On the mechanism of H₂ activation over single-atom catalyst: an understanding of Pt₁/WO_x in the hydrogenolysis reaction

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Pt single atoms possess a greatly enhanced stability on the WO_x(001) surface and carry negative charge, which facilitates the dissociation of H₂ to metal–H species (H^{δ-}) through the homolytic cleavage of H₂ like that which occurs on metal ensembles. More importantly, the facile diffusion of Pt–H to the WO_x support results in the formation of Brønsted acid sites (H^{δ+}), imparting bi-functionality to the Pt₁/WO_x.

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单原子催化剂活化氢气: Pt₁/WO_x催化氢解反应

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摘要: 单原子催化剂具有独特的结构位点, 能最大化利用贵金属原子, 在一系列化学转化反应中具有优异的活性和选择性。但单原子的稳定性是单原子催化剂应用的一个挑战, 特别是还原气氛下单原子的稳定性, 这极大地限制了单原子催化剂在加氢、脱氢和氢解反应中的应用。理解还原气氛下单原子的稳定机制和单原子催化剂活化氢气的反应机理对于扩大单原子催化剂的应用非常重要。Pt/WO_x (2 < x < 3) 是一种典型的金属-载体强相互作用体系, 在甘油氢解制1,3-丙二醇等一系列含氢反应中具有优异的活性和选择性。但原子层面的催化反应机理, 如Pt单原子在表面的位置、Pt单原子的稳定机理以及氢气在单原子上活化产生原位Brønsted酸的机制仍不清楚。

在本研究中, 我们结合密度泛函理论(DFT)和实验表征研究了WO_x负载Pt、Pd、Au三种单原子的稳定性和解离氢气的活性。DFT计算结果表明, 在还原气氛下Pt单原子能促进氧化钨表面形成桥式氧空位。WO_x表面的氧空位对于Pt单原子的稳定非常重要, 氧空位通过转移部分电子给Pt, 使Pt单原子带部分负电从而高效地稳定Pt单原子。不同于带正电单原子的非均相解离氢气, 带部分负电的Pt单原子保持一定的金属性, 能类似金属表面均相解离H₂产生金属氢物种(Pt-H)。同时Pt解离的H原子能容易地扩散到氧化钨载体上形成原位Brønsted酸, 从而使Pt₁/WO_x催化剂具有双功能催化性质。考察了Pt、Pd、Au三种单原子在WO_x(001)表面的稳定性, 三种单原子的稳定性顺序为Pt>Pd>Au。氢气能在Pd和WO_x界面非均相解离, 而Au/WO_x不能活化、解离氢气。

我们进一步采用实验表征验证了DFT理论计算的结果。实验合成了WO_x负载的Pt、Pd、Au三种催化剂, X射线衍射(XRD)和透射电子显微镜(TEM)结果表明, Pt能在WO_x表面原子级分散和稳定, 而Pd在WO_x表面形成较小的纳米颗粒, Au形成较大的纳米颗粒。采用氢气化学吸附研究了三种催化剂对氢气的活化能力, 结果表明三种催化剂的氢气活化能力顺序为Pt/WO_x (137 μmol/g-Pt) > Pd/WO_x (43 μmol/g-Pd) >> Au/WO_x (4 μmol/g-Au)。将三种催化剂用于甘油选择性氢解制备1,3-丙二醇的反应中, 只有Pt/WO_x催化剂对甘油氢解具有优异的活性和选择性。从而实验证实了氢气气氛下原位产生的Brønsted酸具有关键作用和Pt₁/WO_x催化剂具有双功能催化性质。

我们的研究不仅解释了还原气氛下金属单原子在氧化物表面的稳定机理, 而且对单原子催化剂活化解离氢气提供了新的认识。

关键词: 单原子催化剂; 铂; 密度泛函理论; 氢解离; 氧化钨

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