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Insight into the Nature of Brönsted Acidity of Pt-(WO_x)_n-H Model Catalysts in Glycerol Hydrogenolysis

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Abstract: In glycerol hydrogenolysis, the conventional preparation methods for Pt-WO_x catalysts on active supports usually result in the coexistence of various active sites, causing complex reaction network and declining the atom efficiency of W toward 1,3-propanediol (1,3-PDO) production. Herein, we report Pt-(WO_x)_n-H model catalyst prepared via strong metal–oxide interaction (SMOI) behavior on inert SiO₂ support, which shows both high performance and W efficiency for 1,3-PDO. The W efficiency as high as 5.786 h⁻¹ was obtained on 2W4Pt/SiO₂ at 160 °C under 8.0 MPa. Furthermore, these model catalysts also give the advantage in revealing the Brönsted acidity of Pt-(WO_x)_n-H sites. Structure characterizations and DFT calculation confirm the Brönsted acid strength of Pt-(WO_x)_n-H is significantly sensitive to both the polymerization and reduction degree of WO_x domains. The high catalytic efficiency of 2W4Pt/SiO₂ originates from the strong Brönsted acidity and its synergism with Pt metal. The correlation between Brönsted acidity and electronic state of Pt-(WO_x)_n-H is also discussed by electron density difference analysis and XPS.

Keywords: 1,3-propanediol, Brönsted acid, WOx domain, Pt, glycerol, hydrogenolysis

1. Introduction

The process for fuel and chemical production using biomass is attractive since it is environmental-friendly and sustainable. Because of the high oxygen content as feedstock, hydrodeoxygenation becomes one of the important reactions during the upgrading of biomass, including the C-O cleavage of ethers [1-3], esters [4,5], aromatic [6,7] and aliphatic [8-10] alcohols, et al. Glycerol is the simplest biomass platform compound containing both primary –OH and secondary –OH, and the hydrogenolysis of glycerol into useful C3 chemicals is gaining much attention [11,12]. Among these processes, selective C-O cleavage to 1,3-propanediol (1,3-PDO) is still one of the challenging problems. WO_x based materials have been widely investigated in this reaction because of its high selectivity on 1,3-PDO. As mentioned by many groups, Brönsted acid site is critical for 1,3-PDO formation [13-20]. However, as the lack of detail structural information on the active site, the nature of Brönsted acidity of Pt-WO_x catalysts is still not clear.

Recently, we found that 1,3-PDO formation rate can be adjusted by the size of WO_x species, and proposed the intrinsic active site of supported Pt-WO_x catalysts is Pt-(WO_x)_n-H structure with medium polymeric WO_x domains, which can provide both Pt metal and super strong Brönsted acid adjacent with each other [21]. Based on this viewpoint, some factors should be considered during the design of effective catalysts.

Firstly, for the construction of $Pt-(WO_x)_n$ -H site, ensuring WO_x domains on Pt surface is the prerequisite. However, in most reported methods, loading WO_x species on the support is the first step, and Pt metal is introduced after that. In consequence, only a few amounts of active sites could be formed during the heat treatment and reduction processes. Meanwhile, most WO_x species are existed on the catalysts without connecting with Pt metal, which may contribute to side reactions.

Secondly, the type of support affects much on the diversity of active sites on the catalyst surface. Our previous studies found that the independent Pt metal can catalyze 1,2-PDO formation and C-C cleavage reaction [22], while the independent WO_x species can't provide Brönsted acid with enough strength and excess WO_x domains give rise to deep hydrogenolysis to propanol [21]. Active supports such as ZrO_2 , Al_2O_3 and TiO_2 can be strongly interacted with both Pt and WO_x , and they also have original acid sites on their surface, leading to various kinds of active structures and intrinsically reducing the selectivity of 1,3-PDO. On the other hand, inert supports such as SiO_2 have much lower interaction with both Pt and WO_x , which improve the possibility of the interaction between Pt and WO_x during the preparation. Additionally, the structural sensitivity of Brönsted acidity on Pt-(WO_x)_n-H site should also be emphasized, which is not only related to the size, but also the reduction degree of WO_x . Because of the diversity of WO_x states and locations on the catalysts, results of characterization and catalytic performances usually do not reflect the natural properties of Pt-(WO_x)_n-H site.

Up to now, achieving a large amount of highly dispersed WO_x on the support seems to be the guideline of supported Pt-WO_x catalysts in glycerol hydrogenolysis, and the active supports are widely used, with a general loading sequence (WO_x before Pt) during catalyst preparation. Recently, Fan et al. broke the conventional idea from the preparation aspect. Before their impregnation, ZrO₂ was calcined at 600 °C for 5 h, which could reduce its surface –OH and other anchoring sites. Then Pt species was loaded on the ZrO₂ support, and after calcination, the WO_x precursor was subsequently impregnated. The reaction rate for 1,3-PDO over Pt-WO_x/t-ZrO₂ catalyst reached 0.102 $g_{1,3-PDO} \cdot g_{cat}^{-1} \cdot h^{-1}$ [20]. The passivation of ZrO₂ support under high temperature and the distinctive loading sequence both increased the amount of Pt-(WO_x)_n-H sites, which may contribute to its excellent catalytic performance. In another work, they synthesized W-

SBA-15 support with a very little W content using a modified sol-gel method, and applied it in glycerol hydrogenolysis after loading Pt. The selectivity of 1,3-PDO is 70.8%, which is the highest among Pt-WO_x catalysts [19]. It seems that inert SiO₂ always has a good effect on 1,3-PDO selectivity although it is not a popular support in WO_x based catalysts. In an earlier work, Gong et al. investigated different preparation conditions of Pt/WO₃/TiO₂/SiO₂ catalyst and found the SiO₂ support can improve 1,3-PDO selectivity than other supports [23]. Priya et al. impregnated WO_x and then Pt species to SBA-15 support and applied it in glycerol hydrogenolysis, the selectivity of 1,3-PDO reached 42% [24]. In addition, Zhu et al. [25] investigated the promoting of Pt/WO_x/ZrO₂ catalysts by SiO₂, and found a suitable amount of SiO₂ can improve 1,3-PDO selectivity from 44.3% to 52.0%. All the reports above demonstrates the diversity of active species on support dPt-WO_x catalysts can be significantly influenced by both the loading sequence and support types.

In their critical review [26], Tomishige et al. proposed the importance of strong metal–oxide interaction (SMOI) behavior in preparing various metal-oxophilic metal oxide catalysts, which have shown super performances in selective hydrogenolysis of biomass. Under this thought, they have applied a series of inert SiO₂ supported metal-ReO_x catalysts in glycerol hydrogenolysis [27]. The loading sequence in their preparation was always metal precursor before ReO_x species. In this work, SMOI behavior is also used in preparing Pt-WO_x catalysts on SiO₂ support. In order to exclude the independent WO_x species and ensure Pt-(WO_x)_n-H as the only active site, the mole ratio of W/Pt on the catalysts was kept below 1.0. By this way, we try to build the pure Pt-(WO_x)_n-H active sites and investigate the effects of WO_x structure and reduction degree on the catalytic performance. Combined with characterizations and DFT calculation, the nature of Brönsted acidity on Pt-(WO_x)_n-H is also revealed.

2. Experimental and Theoretical Methods

2.1. Catalyst Synthesis

The sequential incipient wetness impregnation was applied to synthesis the catalysts. Firstly, an appropriate amount of $Pt(NO_3)_2$ aqueous solution (10% Pt, Beijing HWRK Chem.) was dropped onto SiO₂ support, then they were well mixed. After drying at 100 °C overnight, the solid was pretreated in pure hydrogen for two hours at 250 °C. Then the $(NH_4)_6(H_2W_{12}O_{40}) \cdot nH_2O$ (>99.9%, J&K Chemical Corp.) aqueous solution was mixed with the dark sample, while the concentration of the solution was changed to achieve different mole ratios of W/Pt on the catalysts. After that, the sample was dried at 100 °C and calcined under air for 4 h at 500 °C. The obtained catalysts were named as xW4Pt/SiO₂, in which the Pt content was fixed to 4 wt% while the W/Pt mole ratio was x/4 (x = 0.5, 1, 2, 4).

For comparison, the normal impregnation process was also used and the corresponding sample was labelled as $4PtxW/SiO_2$ (x = 0.5, 1, 2, 4). Briefly, SiO₂ support was firstly impregnated with aqueous solution of ammonium metatungstate and dried at 100 °C. After the calcination for 4 h under air at 500 °C, the Pt(NO₃)₂ aqueous solution was impregnated to the sample and calcined again at 350 °C for 2 h.

2.2. Catalyst Characterization

The crystalline phase of catalysts was characterized by a Rigaku D/MAX-2500 diffractometer (Cu K $\alpha, \lambda = 1.5406$ Å) using a speed 8°/min. The catalyst powder was reduced at 180 °C under H₂ for 2 h before testing. The transmission electron microscopy (TEM) was performed under 200 kV on a JEM-2100F instrument. Sample was grinded and pretreated in hydrogen for 2 h at 180 °C. After that, it was dispersed in ethanol under ultrasonic for half an hour. Subsequently, the suspended sample was dropped onto an ultrathin carbon film supported on copper grid and dried

under the infrared lamp. Raman spectroscopy was used to determine the structure and polymerization degree of WO_x domains on the calcined catalysts. The instrument is a Renishaw inVia reflex Raman spectrometer and the wavenumber of the laser source is 532 nm. The result was accumulated by 3 scans, with the speed of 10 seconds/scan. The PHI 1600 ESCA spectrometer (PE Company) was applied to collect X-ray photoelectron spectroscopy of catalysts. The radiation source was an Al K α X-ray with the hv of 1486.6 eV. The dried sample was grinded to powder and pressed to a self-supporting wafer, and then it was reduced at 180 °C for 2 h and cooled to room temperature. Then the sample was sealed into centrifuge tube filled with Ar. After introduced into the sample chamber of the instrument within 5 minutes, the sample was degassed by evacuation. The C 1s peak (284.6 eV) was applied to calibrate the binding energy, within an error of ±0.2 eV.

The dispersion of Pt particles and H₂ adsorption capacity on catalyst were obtained from CO and H₂ chemisorption experiments over a Micromeritics Autochem 2910 analyzer. In CO chemisorption, about 50 mg (40–60 mesh) catalyst was pretreated in hydrogen for two hours at 180 °C. After purged by He flow, it was cooling to 50 °C. CO adsorption was carried out by pulses of 10% CO/He (1.076 mL) until the sample surface was saturated. The CO/Pt ratio of 1.0 was used for the dispersion calculation. During H₂ chemisorption, 10% H₂/Ar was used as the adsorption gas, and Ar is used as the purge/carrier gas. A H₂/Pt theoretical ratio of 0.5 was used, and the mole ratio of consumed H atoms amount to Pt atoms amount on the surface was labelled as H/Pt. H₂temperature programmed reduction (TPR) was also performed using the above instrument. The catalyst was degassed at 350 °C for one hour under Ar, then it was cooling to 50 °C. After the system became stable under 10% H₂/Ar, the TPR step began from 50 to 780 °C (10 °C/min). NH₃ temperature-programmed desorption (NH₃-TPD) was measured using a mass spectrometric

detector. Sample was degassed under He at 350 °C for one hour. Subsequently, the system was dropped to 50 °C and 10% NH₃/He was introduced for half an hour. After arriving a steady baseline under He, the system temperature was increased to 750 °C. To exclude the interference by H₂O, the signal of NH₃ with an m/z of 16 was used [28].

DRIFT spectra of CO adsorption under room temperature were determined on a Nicolet 6700 spectrometer. After reduction at 180 °C in the diffuse reflection cell, the catalyst was flushed under He flow. After recording the background, the gas was changed to 10% CO/He and kept for half an hour. Subsequently, He flow was introduced again and the result was obtained when the infrared signal was not changed. In addition, this characterization was also conducted at -130 °C to investigate the acid species on catalyst surface. The sample was degassed by N₂ at 350 °C for one hour, followed with an evacuation until the temperature was dropped to -130 °C. Subsequently, the background was record and CO pulse was introduced to the system until the adsorption spectrum was stable. Then the system was exposed to vacuum again and the spectrum was collected until it was stable.

2.3. Catalytic reactions

2.0 g glycerol, 18.0 g H₂O and 0.25 g catalyst were mixed in the autoclave with a volume of 100 ml. The hydrogen pressure was raised to 5.5 MPa after purging. Then, the temperature was increased to 180 °C, during which the consumed H₂ was replenished by pulse. The system was kept at 8.0 MPa and the stirring speed was 1000 rpm. After the reaction, the liquid product composition was analyzed by Agilent Micro GC 4890 with a DB-FFAP capillary column. Before the analysis, *n*-Butanol and 1,4-butanediol were added into the liquid as the internal standards. The

gas composition was analyzed using Agilent GC 7890B with a HP-AL/S column. The conversion was calculated as:

conversion (%) = (the consumed moles of glycerol) / (the initial moles of glycerol)

And the selectivity was calculated as:

selectivity (%) = (moles of specific product) / (the consumed moles of glycerol)

2.4. Theoretical Methods

DFT calculations were performed using the Material Studio 6.1 software with the Cambridge sequential total energy package (CASTEP), while plane-wave basis sets and ultrasoft pseudopotential were employed [29]. Generalized gradient approximation (GGA) method was applied to describe the electrons interaction with atomic cores, and Perdew-Burke-Ernzerhof (PBE) functional was chosen to describe the exchange and correlation energies [30]. The plane-wave energy cutoff was set as 400 eV, and the surface Brillouin zone was sampled with a $3\times3\times1$ Monkhorst-Pack k-point mesh [31,32]. The WO_x/Pt model was constructed with the HW_xO_y cluster supported on a (4 × 4) periodic Pt(111) slab of 4-layer. The vacuum space between two slabs along z-direction was 20 Å and the bottom two Pt atom layers were restrained to the optimized bulk Pt state. The convergence tolerance of energy change, maximum displacement and force in the geometry optimization and energy calculation were 2×10^{-5} eV/atom, 0.002 Å and 0.05 eV/Å.

The NH₃ adsorption energy (E_{ads}) on surface Brönsted acid site of the model was estimated by the equation: $E_{ads} = E(NH_3/HW_xO_y/Pt) - E(NH_3) - E(HW_xO_y/Pt)$, in which $E(NH_3/HW_xO_y/Pt)$, $E(NH_3)$ and $E(HW_xO_y/Pt)$ represent the total energy of HW_xO_y/Pt vacuum slab with adsorbed NH_3 , free NH_3 molecule and HW_xO_y/Pt vacuum slab, respectively.

3. Results and discussion

3.1. Advantage of SMOI on the preparation of highly efficient catalyst

Firstly, the performance of xW4Pt/SiO₂ prepared via SMOI in glycerol hydrogenolysis is studied. As shown in Fig. 1a, the conversion of glycerol over 4Pt/SiO₂ is 7.9%, and the corresponding selectivity of 1,3-PDO is only 13.2%. The main product is 1,2-PDO, with its selectivity of 63.0%, while the product selectivity from C-C cleavage is as high as 13.1%, which reflect a typical hydrogenolysis property on the independent Pt metal. With the W/Pt mole ratio increases from 0 to 1/4, the conversion is raised to 20.3%, accompanied by a 1.3-PDO selectivity development up to 36.5% and a drop of 1,2-PDO selectivity to 38.2%. The increased activity of C-O bond hydrogenolysis is ascribed to the acidity introduced by WO_x . Interestingly, when the W/Pt mole ratio reaches to 2/4, a sharp improvement of catalytic performance is obtained, with a 64.2% conversion and a 57.2% selectivity of 1,3-PDO. In addition, 1,2-PDO selectivity is dropped to only 10.5%, while 1-PO selectivity is increased obviously from 8.9% to 18.6%. The activity is increased for more than three times when W/Pt ratio increased from 1/4 to 2/4, and a much higher 1,3-PDO selectivity is also observed, indicating that not only the amount, but also the acidity of active site is enhanced on 2W4Pt/SiO₂. Further increment of W/Pt mole ratio to 4/4 has little effect on the product distribution, while the conversion is declined to 37.2%. The apparent activation energy (E_{app}) of 1,3-PDO formation over the three catalysts (W/Pt ratio of 1/4, 2/4 and 4/4) are also compared. As shown in Fig. 1b, 2W4Pt/SiO₂ has the lowest E_{app} for this reaction, indicating a stronger acidity on this catalyst for secondary C-O bond activation.



Fig. 1. (a) Glycerol hydrogenolysis performances and (b) apparent activation energies (Eapp) of 1,3-PDO formation over xW4Pt/SiO₂ catalysts. (c) Glycerol hydrogenolysis performances over 4PtxW/SiO₂ catalysts. (d) Trend of STYW with the increase of WOx loading. Reaction conditions: 2.0 g glycerol, 18.0 g water, 0.25 g catalyst, 180 °C, 8 MPa, 1000 rpm, 18 h. The catalyst was not reduced in H2 before reaction. 1,3-PDO: 1,3-propanediol; 1,2-PDO: 1,2-propanediol; 1-PO: 1-propanol; 2-PO: 2-propanol; others include ethylene glycol, ethanol, and methanol, et al.

For comparison, reaction results of $4PtxW/SiO_2$ catalysts prepared by the conventional method (introducing Pt after WO_x/SiO_2 is obtained) are given in Fig. 1c. The highest performance is also obtained on the catalyst with a W/Pt mole ratio of 2/4 ($4Pt2W/SiO_2$), with a 40% conversion and a 52.7% selectivity of 1,3-PDO. However, the activity and selectivity are both lower than those on $2W4Pt/SiO_2$. To evaluate W efficiency, the 1,3-PDO production rate based on WO_x mass (STY_W)

over the two series catalysts were presented in Fig. 1d. A volcano relationship was found between STY_W and WO_x loading over both series catalysts, reflecting the 1,3-PDO formation rate is structurally sensitive on WO_x polymerization degree, which is consistent with our previous study [21]. At WO_x loading of 2.4 wt.% (W/Pt = 2/4), STY_W over $2W4Pt/SiO_2$ is about two times of that over $4Pt2W/SiO_2$, confirming the advantage of SMOI behavior in the construction of $Pt-(WO_x)_n$ -H active site.

To further compare the catalytic performances of reported Pt-WO_x catalysts, Table S1 gives the activity values based on catalyst mass (STY), surface exposed Pt mass (STY_{Pt}) and WO_x mass (STY_W). Under a very low WO_x loading, the STY of 2W4Pt/SiO₂ reaches 0.135 $g_{1,3-PDO} \cdot g_{cat}^{-1} \cdot$ h⁻¹, ranking the top two among reported results. The dependence of STY_{Pt} and STY_W with STY is shown in Fig. 2a and b, respectively. The STY_{Pt} and STY_W of 2W4Pt/SiO₂ ranks top four and top two, respectively. Noted that a random distribution is presented between STY_{Pt} and STY, indicating that the activity based on surface exposed Pt sites is not suitable to evaluate the catalytic performance. On the other hand, the positive correlation is apparent between STY_W and STY, which means a catalyst with high activity usually shows a high STY_W value. The exception of Pt/W-SBA-15 sample is derived from its extremely low WO_x loading, leading to a high STY_W and STY values, revealing high W efficiency of this material among the reported catalysts. In addition, the statistical observation in Fig. 2 also demonstrates that WO_x state is more important than Pt state during 1,3-PDO formation on Pt-WO_x bifunctional system.



Fig. 2. The dependence of catalytic activity on surface Pt(a) or $WO_x(b)$ based STY values.

3.2. Catalytic performance of 2W4Pt/SiO₂ under various conditions

Wang et al. reported that the over reduction of WO_x species can "poison" the catalysts and decrease the activity [16]. It is predictable that besides the polymerization of WO_x domain, the reduction of WO_x can also influence the catalytic performance of Pt-(WO_x)_n-H. So the effect of reduction temperature of 2W4Pt/SiO₂ in H₂ was investigated. As shown in Table 1, with the increase of reduction temperature, both the conversion and 1,3-PDO selectivity are decreased, accompanied with a 1,2-PDO selectivity increment from 10.5% to 22.3%. The best performance of 2W4Pt/SiO₂ is achieved when it is directly used in the reaction without reduction pretreatment. Therefore, the reduction of WO_x on Pt-(WO_x)_n-H site is detrimental to 1,3-PDO production, which is ascribed to the weakening of Brönsted acidity as discussed below.

Daduction	Conversion ^b	Selectivity (%)				
Keduction.	(%)	1,3-PDO	1,2-PDO	1-PO	2-PO	Others
None	64.2	57.2	10.5	18.6	12.1	1.6
250 °C	20.5	51.0	20.0	16.2	10.3	2.5
400 °C	16.3	47.7	22.3	15.7	10.4	3.9

Table 1. The effect of reduction degree of 2W4Pt/SiO₂ in glycerol hydrogenolysis.

^a The 2W4Pt/SiO₂ catalyst was not reduced, reduced in H_2 at 250 °C and 400 °C before reaction, respectively.

^b Reaction conditions are the same as that in Fig. 1.

Considered that the reduction of Pt-(WO_x)_n-H may also occur during the reaction, the performance of 2W4Pt/SiO₂ was investigated in different reaction temperature and pressure. As shown in Fig. 3a, with the reaction temperature dropping from 180 °C to 160 °C, the activity drops from 64.2% to 58.2%, followed with an increment of 1,3-PDO selectivity from 57.2% to 64.9%. The decrease of reaction temperature results in a increment of 1,3-PDO STY from 0.135 to 0.139 $g_{1,3-PDO} \cdot g_{cat}^{-1} \cdot h^{-1}$. Although this is not such significant, it indicates that partial reduction of Pt-(WO_x)_n-H occurs under the reaction condition of 180 °C and 8 MPa, leading to a lower 1,3-PDO formation rate. Further declining the reaction temperature to 120 °C causes a gradual decrease of glycerol conversion from 58.2% to 19.2%, while the product distribution is not obviously influenced.



Fig. 3. Effects of (a) reaction temperature and (b) pressure on glycerol hydrogenolysis over $2W4Pt/SiO_2$ catalyst. The pressure effect was investigated at 140 °C, while other conditions were the same as that in Fig. 1.

The influence of reaction pressure at 140 °C was given in Fig. 3b. Above 5.2 MPa, the catalytic performance of $2W4Pt/SiO_2$ is not affected much by the reaction pressure. When the pressure drops to 2.5 MPa, the conversion of glycerol significantly decreased from 36.1% to 8.5%, while 1,3-PDO selectivity is not changed. At 0.5 MPa, the conversion drops to only 1.9%, while the primary C-O bond and C-C bond cleavage become the dominant reaction, with a total selectivity of 93.5%. 1,3-PDO is not formed at such low pressure. The observations above demonstrate that H₂ is critical for 1,3-PDO production. At 0.5 MPa, the concentration of active hydrogen species on the catalyst surface is too low, so 1,3-PDO is not formed. At 2.5 MPa, the dissolution of H₂ in the liquid is improved and active hydrogen species emerge on the catalyst surface, which promotes the generation of 1,3-PDO. With the raise of H₂ pressure to 5.2 MPa, the active hydrogen on the

catalyst surface is saturated and the formation of 1,3-PDO is near the top level. Therefore, further increment of the reaction pressure to 8 MPa does not contribute to the catalytic performance.

In our previous work, the reaction under different pressure was also studied on Pt/ZrW catalysts at 180 °C [22]. It was found that 1,3-PDO yield was decreased after 4.2 MPa, which was also ascribed to the destroy of WO_x structure under higher H₂ pressure. In addition, the conversion was the highest at low pressure of 0.7 MPa, with the main products of 1,2-PDO, C2 alcohols and hydroxyacetone. However, Fig. 3b shows that glycerol was almost not converted over 2W4Pt/SiO₂ at 140 °C under 0.5 MPa, and dehydration products (hydroxyacetone or 3-hydroxypropanal) were not detected, either. This confirms that glycerol dehydration route is not catalyzed by Pt-(WO_x)_n-H site at this mild condition, and 1,3-PDO is formed through the direct hydrodeoxygenation mechanism with the help of both strong Brönsted acid site and active hydrogen, consistent with the in situ FTIR studies [21].

3.3. Characterization of catalysts

Table 2 shows the physicochemical properties of the catalysts. The dispersion of Pt measured by CO chemisorption is decreased with WO_x increment, which can be ascribed to Pt metal aggregation or WO_x coverage over Pt surface. Meanwhile, the H/Pt ratio is increased from 4.5 to 6.6, demonstrating an enhancement of hydrogen spillover with the existence of WO_x domains [33].

Table 2. Phys	sicochemical pro	perties	of xW41	Pt/SiO_2	catalysts.
Catalyst	Dispersion ^a	Pt size ^b (nm)		_ II/D+c	
	(%)	d _{CO}	d _{XRD}	d_{TEM}	- п/РС

4Pt/SiO ₂	58.0	1.9	2.6	2.9	4.5
1W4Pt/SiO ₂	39.8	2.8	3.9	3.7	4.9
2W4Pt/SiO ₂	27.9	4.1	3.5	3.5	6.4
4W4Pt/SiO ₂	19.2	5.9	2.9	2.6	6.6

^a The dispersion of Pt was estimated from CO chemisorption.

^b The particle size of Pt was estimated from CO chemisorption, XRD and TEM characterizations.

^c The H/Pt ratio was derived from CO chemisorption and H₂ chemisorption results.

The crystalline structure of different catalysts is presented in Fig. S1. The wide diffraction peak at $2\theta = 22^{\circ}$ is assigned to amorphous SiO₂ support. In addition, the weak peaks of Pt metal are also observed on all catalysts ($2\theta = 39.8^{\circ}$ and 46.2°). The diffraction signals of WO₃ at about 24.0° and 34.0° are not found here, indicating WO_x are highly dispersed on these catalysts. The particle size of Pt metal is calculated by Scherrer equation and shown in Table 2. Different from the results from CO chemisorption, Pt particle size estimated from XRD ranges between 2.6 and 3.9 nm. To further determine the metal size, TEM was used to analyze Pt size distribution. As shown in Fig. 4, WO_x loading increment trend to slightly reduce Pt metal size. The mean particle size observed from TEM images is also consistent with XRD result (Table 2). Thus, the much lower dispersion derived from CO chemisorption is caused by the existence of WOx domains on Pt metal, indicating SMOI existed between Pt and WO_x clusters. This is also confirmed by the different CO adsorption states over catalysts in DRIFT spectra. As seen in Fig. S2, the bridge bonded CO is clearly shown at 1830 cm⁻¹ on Pt metal surface for 4Pt/SiO₂. However, on the catalyst 2W4Pt/SiO₂, this band is almost disappeared and only the linear CO species on Pt metal exists at 2080 cm⁻¹, which is caused by the significant loss of adjacent Pt atoms after partially covered by WO_x species. Line scanning curves of 2W4Pt/SiO₂ sample in Fig. 4d also confirms the close contact between Pt metal and WO_x domains.



Fig. 4. TEM images with Pt particle size distribution for 1W4Pt/SiO₂ (a), 2W4PtSiO₂ (b), 4W4PtSiO₂ (c), and HAADF-STEM image with line scanning of 2W4Pt/SiO₂ (d).

The structure of WO_x is characterized by Raman spectroscopy. For comparison, the sample of WO_x supported on SiO₂ without Pt element (2W/SiO₂) was also measured. As shown in Fig. 5, Raman bands of SiO₂ support are presented at about 450, 606 and 808 cm⁻¹, which are assigned to the D1 and D2 defect bands of tetra- and tri-cyclosiloxane rings, and Si-O-Si symmetrical stretching, respectively [34-36]. For 2W/SiO₂, a strong Raman band assigned to hydrated W=O

structure is emerged at 975 cm⁻¹, accompanied with a broad band of W-O-W stretching near 832 cm⁻¹ [37,38] which is overlapped with Si-O-Si symmetrical stretching at 808 cm⁻¹. However on 2W4Pt/SiO₂, the hydrated W=O band is redshifted from 975 cm⁻¹ to 947 cm⁻¹. This indicates a decrease of the WO_x domain size on Pt containing catalysts, which is caused by the interaction between WO_x and Pt. For 4W4Pt/SiO₂, a blueshift of hydrated W=O band is observed from 947 cm⁻¹ to 953 cm⁻¹, demonstrating a increment of WO_x polymerization with raising WO_x content. To elucidate the influence of impregnation order on the catalyst structure, XRD and Raman characterizations of 4Pt2W/SiO₂ are shown in Fig. S3. Large Pt particle size (11.8 nm) and bulk WO₃ phase are found on 4Pt2W/SiO₂, which results in a less amount of interacted Pt-WO_x species and a lower catalytic performance.



Fig. 5. Raman spectra of the calcined xW4Pt/SiO₂ catalysts.

The reducibility of different catalysts is shown in Fig. S4. Most of Pt species on $4Pt/SiO_2$ can be reduced before 100 °C, and the broad signal at about 390 °C is ascribed to the hydrogen consumption for small amount of PtO_x species with large particle size or interaction with SiO_2 support. With the introduction of WO_x, the intensity of reduction peak before 100 °C is weakened

and the main H_2 consumption signal is started after 120 °C, and the broad peak reflects a gradual reduction of both PtO_x and WO_x species on catalyst. The center of reduction peak is decreased from 390 °C to 308 °C as W/Pt mole ratio is increased to 4/4, reflecting an easier reduction of higher polymeric WO_x species [38]. The quantification analysis of TPR (Table S2) indicates the optimized average W valence of 2W4Pt/SiO₂ for this reaction is about $W^{5.48+}-W^{5.92+}$.

Fig. 6a gives NH₃-TPD curves of different catalysts, with the peak fitting results of strong acid region shown in Fig. 6b and Table S3. A peak with strong intensity is presented below 200 °C for all samples, which represents the desorption of weakly adsorbed NH₃ on the samples. For 4Pt/SiO₂, a small peak is also found at about 464 °C, which is ascribed to NH₃ desorption on Pt metal surface. With the W/Pt ratio increased to 1/4, the peak shifts from 464 °C to 407 °C, indicating a decrease of the adsorption strength of NH₃. This may be caused by a partial coverage of strong NH₃ adsorption sites on Pt after WO_x introduction, as the decline percent of peak area (27%) is similar to that of Pt dispersion (31%). In addition, as the reaction rate and 1,3-PDO selectivity increasing, the contribution of WO_x sites to the strong acid amount is also not excluded here. When the W/Pt ratio is increased to 2/4, a new type of acid site is emerged, with the corresponding NH₃ desorption peak at about 519 °C. Further increasing W/Pt ratio to 4/4 will weaken the strength of this type of acid as the NH₃ desorption temperature is dropped to 472 °C, meanwhile, the acid amount is also significantly reduced. For comparison, NH₃-TPD result of 2W/SiO₂ sample is also given here, and a desorption peak assigned to weaker acid sites is observed at about 300 °C. Thus, the strong acid is created only when WO_x species is connected to Pt metal, and is greatly affected by WO_x loading. On 2W4Pt/SiO₂, WO_x domains on Pt surface are medium polymeric and the corresponding acidity is the strongest, thus presenting the lowest apparent activation energy in the formation of 1,3-PDO (Fig. 1b). Fig. 6a and b also show that after reduction pretreatment at 250 °C, the strong acid



amount is obviously decreased on 2W4Pt/SiO₂, consistent with its catalytic activity decrease in Table 1.

Fig. 6. (a) NH_3 -TPD curves of $xW4Pt/SiO_2$ catalysts and (b) peak fitting results of the strong acid region. $2W4Pt/SiO_2$ (reduced) refers to the catalyst reduced at 250 °C before NH_3 -TPD measurement. DRIFT spectra of CO adsorption at low temperature: (c) spectra after 8 CO doses into the sample cell, (d) spectra after vacuum extraction.

Because of the darkness and low WO_x content of catalysts, pyridine adsorption FTIR is failed to characterize the acidity of catalysts. Instead, we carried out DRIFT experiments of CO adsorption under a low temperature of -130 °C to investigate the surface acids. The adsorbed CO

on Lewis acid sites gives characteristic peaks at above 2177 cm⁻¹, while bands at 2170 cm⁻¹ and 2156 cm⁻¹ are ascribed to CO adsorbed on strong and weak Brönsted acids, respectively [39-42]. As shown in Fig. 6c, all samples mainly exhibit Brönsted acids sites, and the bands correlated to Lewis acids are only presented as shoulder peaks in the spectra. Weak Brönsted acids are dominant on 4Pt/SiO₂. With the WO_x content increasing, the band correlated to strong Brönsted acids at 2170 cm⁻¹ develops and become stronger than the band at 2156 cm⁻¹. After exposed to vacuum, 2W4Pt/SiO₂ still remains a few of CO adsorbed on strong Brönsted acids, while signals on the other three samples almost disappear (Fig. 6d). Combined with NH₃-TPD results, this confirms the introduction of WO_x species to the catalysts mainly contributes to the formation Brönsted acids, and the Brönsted acidity on 2W4Pt/SiO₂ is stronger than that on other samples.

3.4. DFT study on the nature of Brönsted acid on WO_x/Pt model

Based on the experimental evidence, HW_xO_y cluster located on Pt(111) surface was built to simulate the structure of Brönsted acid site on $xW4Pt/SiO_2$ catalysts. The HW_xO_y cluster is considered as tetrahedral WO₄ units connected through W-O-W bond, and the Brönsted acid is a bridging –OH bonded with one W atom and one Pt atom simultaneously. Similar models were used to simulate WO_x supported on ZrO₂ or Pt surface [31,32]. The discussion of various proton positions and models with edge-share connection between WO₄ units is elucidated in Table S4 and Fig. S5, respectively. NH₃ adsorption energy was calculated to estimate the strength of Brönsted acid, and the effect of WO₄ unit amount on the acid strength is investigated. Fig. 7 gives the optimized structure and the NH₃ adsorption results. In all models, NH₄⁺ was formed after the adsorption on Brönsted acid site. For isolated HWO₄ cluster, the adsorption energy is -93.5 kJ/mol. With the cluster grows up to a dimeric HW₂O₇, NH₃ adsorption energy is decreased to -117.4 kJ/mol, indicating the Brönsted acid is stronger than that of HWO₄ cluster. For trimeric HW₃O₁₀,

two structures are investigated and the NH_3 adsorption energy is -113.2 and -111.4 kJ/mol, respectively, both of which are larger than the adsorption energy on HW_2O_7 . Although the difference is not such significant, it still reflects that HW_xO_y cluster with higher polymerization does not benefit the Brönsted acid strength.



Fig. 7. The optimized structure and NH₃ adsorption results of HW_xO_y/Pt(111) models. (a) HWO₄/Pt(111), (b) HW₂O₇/Pt(111), (c) linear HW₃O₁₀/Pt(111) and (d) angular HW₃O₁₀/Pt(111). NH₃ adsorption energies are given in kJ/mol.

To study the effect of reduction degree of HW_xO_y cluster on the Brönsted acid strength, one oxygen atom is moved from HW_2O_7 cluster. As shown in Fig. S6, the corresponding NH_3 adsorption energy is increased from -117.4 kJ/mol to -80.0 kJ/mol, and the H atom is still connected with surface oxygen, indicating that the partial reduction of HW_xO_y cluster can significantly weaken the Brönsted acid strength.



Fig. 8. H atom based electron density isosurface slice across surface Pt layer of $HW_xO_y/Pt(111)$ model: (a) $HWO_4/Pt(111)$ and (b) $HW_2O_7/Pt(111)$. In the color map, the red color represents the negative charge and the blue color means the positive charge.

The above theoretic studies of Brönsted acid strength on $HW_xO_y/Pt(111)$ models are consistent with the acid characterizations (Fig. 6) and catalytic performance results (Fig. 1 and Table 1). To further elucidate the different Brönsted acid strength of HW_xO_y clusters from electronic states, the electron density difference for HWO_4 and HW_2O_7 clusters on Pt(111) were calculated, in which the H atom was chosen to be one fragment and the rest of model (WO_4/Pt or W_2O_7/Pt) to be the other fragment. The top views of density isosurface slice across the surface Pt layer are shown in Fig. 8. The existence of Brönsted acid on HWO_4/Pt leads to the formation of a negative Pt atom under it, while the electron densities of the other two Pt atoms bonded with HWO_4 cluster are slightly decreased. However on HW_2O_7/Pt , the Pt atom under Brönsted acid becomes more negative compared with that on HWO_4/Pt , and the electron densities of some Pt atoms on the surface are also increased, even for those who are not connected with HW_2O_7 cluster. This indicates that Pt plays a role of electron acceptor on the formation of Brönsted acid, and WO_4 unit is a kind of electronic conductor. For HWO_4/Pt , the electron density is distributed mainly at the

narrow region of the Pt-O-H structure. Compared with that, the two adjacent WO_4 units of dimeric HW_2O_7 cluster can delocalize more negative charge to the wider Pt surface, leading to a much stronger Brönsted acid.

XPS of Pt4f over 4Pt/SiO₂ and 2W4Pt/SiO₂ are shown in Fig. S7. For 4Pt/SiO₂, the binding energy of Pt $4f_{7/2}$ is 70.7 eV, indicating metallic Pt on the catalyst. Meanwhile, the binding energy of Pt $4f_{7/2}$ on 2W4Pt/SiO₂ is obviously decreased to 69.9 eV, which reflects an increased electron density of Pt metal after loading of WO_x. The binding energy change observed here is consistent with the above electron density difference analysis of HW_xO_y/Pt(111) models.

It is not such clear why the Brönsted acid strength of trimer HW_3O_{10}/Pt is decreased. But from the geometric optimization results of the two $HW_3O_{10}/Pt(111)$ models in Fig. 7c and d, it can be seen that instead of bonding to Pt surface, the middle WO_4 unit is connected with the other two WO_4 units via W-O-W bonds, which can weaken the delocalization ability of negative charge to Pt surface. Such hanging structures for trimeric or highly polymerized WO_4 units were also reported by Wang et al. [31]

4. Conclusion

The SMOI behavior was applied for the preparation of $Pt-(WO_x)_n$ -H model catalysts, which can decrease the interference of other active sites and benefit the study of $Pt-(WO_x)_n$ -H structure in glycerol hydrogenolysis. $Pt-(WO_x)_n$ -H catalyst with medium polymeric WO_x domains shows the highest 1,3-PDO formation rate, but its activity can be significantly decreased after the WO_x domains partially reduced. Both high performance and high W efficiency toward 1,3-PDO are obtained over 2W4Pt/SiO₂ at 160 °C under 8.0 MPa. In addition, glycerol conversion occurs only

when the strong Brönsted acid site and active hydrogen are coexisted, indicating that 1,3-PDO is formed via a direct hydrodeoxygenation mechanism.

Characterizations and DFT studies reveal that both the polymerization and reduction degree of WO_x influence the Brönsted acidity of Pt-(WO_x)_n-H. Medium polymeric WO_x domains with no reduction shows the strongest Brönsted acidity and the lowest apparent activation energy in the formation of 1,3-PDO. Electron density difference analysis and XPS characterization confirm that in the formation of Brönsted acid, Pt and WO_4 unit play the role of electron acceptor and conductor, respectively. Compared with isolated HWO_4 , dimeric HW_2O_7 cluster can delocalize more negative charge to the wider Pt surface, leading to a much stronger Brönsted acidity. This work also demonstrates the advantage of SMOI behavior in construction and investigation of bifunctional active site than the conventional impregnation method.

Appendix A. Supplementary material

The supplementary data contain state of the art in glycerol hydrogenolysis to 1,3-PDO over Pt-WO_x catalysts, XRD profiles of the reduced xW4Pt/SiO₂ catalysts, DRIFT spectra of CO adsorbed on xW4Pt/SiO₂ catalysts, XRD profile of the reduced 4Pt2W/SiO₂ catalyst (a) and Raman spectra of the calcined 4Pt2W/SiO₂ catalyst (b), H₂-TPR curves of xW4Pt/SiO₂ catalysts, the consumed H₂ amount and quantification analysis from H₂-TPR, peak fitting results of the strong acid region in NH₃-TPD curves, the relative energy of models with various proton positions, the geometric optimization of models with edge-share connection, the optimized structure and NH₃ adsorption results of partially reduced HW₂O₆/Pt(111), and Pt 4f XPS results of the reduced xW4Pt/SiO₂ catalysts.

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Declaration of Competing Interest

The authors declare no competing financial interest.

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Declaration of interests

☑ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:



Graphical Abstract



- Strong metal-oxide interaction was applied to synthesize $Pt-(WO_x)_n$ -H active sites.
- The highest catalytic performance was obtained over 2W4Pt/SiO₂.
- The performance is affected by the impregnation order of Pt and W precursors.
- Besides polymerization, reduction degree of WO_x also affects the Brönsted acidity.
- Brönsted acidity is related to the electron delocalization ability from WO_x to Pt.