

# Glycerol Hydrogenolysis to 1,3-Propanediol on Pt/WO<sub>3</sub>/ZrO<sub>2</sub>: Hydrogen Spillover Facilitated by Pt(111) Formation

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**Abstract:** In glycerol hydogenolysis, the WO<sub>x</sub> or ReO<sub>x</sub> species of catalysts have been widely concerned because of their importance for the selectivity of 1,3-propanediol, but few studies are focused on the hydrogen spillover. In this work, the hydrogen spillover effect on the catalytic performance was investigated on a series of Pt/WO<sub>3</sub>/ZrO<sub>2</sub> nano-catalysts. The spillover capacities were tuned by changing tetragonal/monoclinic ZrO<sub>2</sub> composition and thermal treatment conditions of the Pt precursor. H<sub>2</sub>-O<sub>2</sub> titration and XPS confirm that all of the catalysts present a uniform Pt dispersion and a similar surface electron environment. DRIFT spectra of adsorbed CO and H<sub>2</sub> chemisorption reveal the strong correlation between the amount of Pt(111) terraces and spillover capacities. We demonstrate that the reaction rate is influenced by hydrogen spillover, but not the acid amount or acid strength of the catalysts in this case. The important roles of Pt(111) and WO<sub>3</sub> in the spillover process are discussed.

#### Introduction

As fossil resources are decreasing continuously, extensive efforts are focused on the conversion of biomass. Glycerol is a renewable resource that is readily available because of the rapid increase in biodiesel production. The conversion of glycerol to highly valuable products can expand the industrial chain of biomass and ease the pressure of the fossil resource crisis. Many processes have been reported so far such as glycerol esterification, etherification, reforming, dehydration and selective oxidation, among which propanediols (PDOs) production from glycerol hydrogenolysis is gaining more and more attention.<sup>[1]</sup>

The production of 1,2-PDO by glycerol hydrogenolysis has been extensively studied, and high yields more than 90% on Cubased catalysts have been reported by many groups.<sup>[2]</sup> However, the hydrogenolysis of glycerol to produce 1,3-PDO, which is a much more valuable commercial product than 1,2-PDO, remains a challenge. Generally, 1,3-PDO formation is based on bifunctional catalysts with both acid sites and metal sites. The acid sites enable the adsorption and dehydration of glycerol, and the metal sites provide active hydrogen for the hydrogenation step.

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 E-mail: xbma@tju.edu.cn Extensive research efforts have been devoted to understanding Re- and W-based catalysts. In the case of Re catalysts, Nakagawa et al.<sup>[3]</sup> conducted a comprehensive investigation and proposed that a Re<sup>n+</sup> coated metal structure is responsible for the efficient catalytic performance. In a recent study,<sup>[4]</sup> Re species were proved to be the source of acid site.

With respect to W-containing catalyst systems, Chaminand et al.<sup>[5]</sup> reported that tungstic acid improved the 1,3-PDO selectivity on Rh-based catalysts. Dam et al.<sup>[6]</sup> screened four commercial catalysts and four acidic additives for glycerol hydrogenolysis, and they achieved 28% 1,3-PDO selectivity with 49% conversion on Pt/Al<sub>2</sub>O<sub>3</sub> with silicotungstic acid as an additive. However, these additives are usually soluble in water and difficult to recycle. As a consequence, many researchers are engaged in the development of W-loaded solid catalysts. Zhu et al.<sup>[7]</sup> carried out a series of studies on metal-heteropolytungstic acid supported catalysts and observed that the Brønsted acid site is important for the formation of 1,3-PDO. For a better understanding of the catalytic roles of W species, WOx is loaded onto supports instead of heteropolyacids. Qin et al.<sup>[8]</sup> achieved 1,3-PDO yield as high as 32.0% with 70.2% conversion by tuning the tungsten loading and calcination temperature of Pt/WO<sub>3</sub>/ZrO<sub>2</sub> catalysts. Zhang et al.<sup>[9]</sup> fabricated mesoporous Ti-W oxides with tunable W/Ti ratios in a wide range for glycerol hydrogenolysis, and they concluded that the presence of Brønsted acid site and the synergy between the well-isolated WO<sub>x</sub> species and the highly dispersed Pt nanoparticles play important roles in the hydrogenolysis. Arundhathi et al.<sup>[10]</sup> obtained a high 1,3-PDO selectivity of 66% at 100% glycerol conversion using a boehmite-supported platinum/tungsten catalyst, and they attributed the superior performance to the AI-OH structure on the catalyst surface. Fernández et al.<sup>[11]</sup> studied Pt/WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts and observed that the interaction between Pt and WO<sub>x</sub> is also a key factor in addition to the Brønsted acid sites.

Regarding catalyst materials, both Re- and W-based catalysts can be classified as supported noble metal-oxophilic metal promoter model, the acid strength and bifunctional catalytic behavior of which have been systematically studied bv Hibbitts et al. using density functional theory (DFT) calculations.<sup>[12]</sup> In the hydrogenolysis of glycerol, the oxophilic metal promoter provides the site to activate C-O bonds of glycerol, while the noble metal is responsible for dissociating the hydrogen molecule. Most of the researchers have focused on the former site in attempts to obtain highly dispersed oxophilic sites or Brønsted acid sites by optimizing the promoter loading, heat treatment conditions or the structure of the support.<sup>[8-9, 13]</sup> By contrast, few reports have been focused on the hydrogen activation.

The dissociative adsorption of hydrogen usually occurs at the metal site and is known to be especially facile on a noble metal. However, an important phenomenon known as hydrogen spillo-

ver could affect the hydrogenation system. Hydrogen spillover was first reported by Khoobiar et al. and then it was enforced with the work of Pajonk and Teichner.<sup>[14]</sup> This concept is fully developed and gained application in the field of hydrogen storage. Pevzner et al.<sup>[15]</sup> studied solid-phase hydrogenation kinetics on different carbonaceous allotrope spillover agents, and they found a dimensionality effect of the support on the hydrogen transport rate. Wang et al.<sup>[16]</sup> prepared a series of Pt-doped IRMOF-8 samples via organometallic chemical-vapor deposition and studied their hydrogen storage capacities. They claimed that the Pt catalyst size is a crucial factor in hydrogen spillover. Thus, hydrogen spillover has been proved to be influenced by the properties of both metal and support.

Although there are still arguments on this phenomenon, many excellent works have been carried out to demonstrate the importance of hydrogen spillover in catalysis. Taniya et al.<sup>[17]</sup> designed a Sn-modified SiO<sub>2</sub>-coated Pt catalyst and applied it in crotonaldehyde hydrogenation. In the absence of crotonaldehyde—metal contact, they achieved a crotyl alcohol selectivity of 100% through hydrogen spillover. Im et al.<sup>[18]</sup> revealed the important catalytic functions of hydrogen spillover using a Pt encapsulated model catalyst. Lee et al.<sup>[19]</sup> investigated the effects of physical diluents and concluded that Lewis acid sites on the aluminosilicate surface can enhance hydrogen spillover. In fact, hydrogen spillover has also been proposed in glycerol hydrogen dite in genolysis by many investigators, but direct evidences of its influence on catalytic activity have not yet been reported.<sup>[8, 10, 13, 20]</sup>

In this work,  $WO_3/ZrO_2$ , a type of ceramic acid, was chosen as the support in view of its good stability in hydrothermal environment. Because of the low surface area of  $ZrO_2$ , a solvothermal method was applied to prepare a nano- $ZrO_2$  precursor, on which  $WO_3$  could be loaded as much as possible while maintaining a high dispersion. To reveal the spillover effect of the catalysts on glycerol hydrogenolysis, the monoclinic/tetragonal crystalline composition of  $ZrO_2$  and thermal treatment conditions of Pt precursor were changed, from the respects of support and metal sites respectively mentioned above. Finally, a mechanism of hydrogen spillover facilitated by Pt(111) formation was proposed for the Pt/WO<sub>3</sub>/ZrO<sub>2</sub> catalyst system.

#### **Results and Discussion**

#### Characterization and Catalytic performance

The crystalline structures of the supports and reduced catalysts are presented in Figure 1(a) and (b), respectively. For comparison, *m*-ZrO<sub>2</sub> and *t*-ZrO<sub>2</sub> without WO<sub>3</sub> were also prepared by calcination of the precursors at 700 °C in air and nitrogen, respectively. As shown in Figure 1(a), pure phases of *m*-ZrO<sub>2</sub> and *t*-ZrO<sub>2</sub> can be prepared by the solvothermal method, and the particle sizes of both samples are approximately 12 nm, as calculated by the Scherrer equation. Moreover, the crystalline phases of ZrO<sub>2</sub> were remained after WO<sub>3</sub> species were loaded. When the ZrO<sub>2</sub> precursors were physically mixed before impregnation, WO<sub>3</sub>/ZrO<sub>2</sub> with heterogeneous crystalline phases was al-



Intensity

20



Figure 1. XRD patterns of the (a) supports and (b) reduced catalysts.





Table 1. Physicochemical properties of various Pt/ZrW catalysts.						
Catalyst	S <sub>BET</sub> <sup>[a]</sup> [m <sup>2</sup> g <sup>-1</sup> ]	D <sub>pore</sub> <sup>[a]</sup> [nm]	V <sub>pore</sub> <sup>[a]</sup> [cm <sup>3</sup> g⁻¹]	Dispersion <sup>[b]</sup> [%]	d <sub>Pt</sub> <sup>[b]</sup> [nm]	H/Pt <sup>[c]</sup>
Pt/ZrW(m)	65.3	15.7	0.27	35.6	3.2	1.02
Pt/ZrW(mt)	63.4	11.5	0.21	34.6	3.3	1.35
Pt/ZrW(t)	49.6	6.2	0.10	31.5	3.6	1.11
Pt/ZrW(m-350)	66.2	12.7	0.25	36.0	3.2	1.97
Pt/ZrW(mt-350)	71.6	12.1	0.21	36.4	3.1	2.00
Pt/ZrW(t-350)	54.2	6.0	0.10	38.1	3.0	2.03

[a] Obtained by N<sub>2</sub> adsorption/desorption analysis. [b] Calculated from  $H_2$ -O<sub>2</sub> titration. [c] Calculated from  $H_2$  chemisorption.

so obtained successfully. Using a previously reported method,<sup>[21]</sup> the volume ratio of m/t phases in this sample was calculated to be 1.2, which is similar to the designed value of 1.0. In addition, the diffraction peaks of WO<sub>3</sub> at  $2\theta$  = 23.5° and 33.3° are not observed in the XRD patterns of all the samples, indicating that WO3 is highly dispersed on these ZrO2 supports. Meanwhile, the particle sizes of ZrO<sub>2</sub> decreased from 12 to 7 nm after the loading of WO<sub>3</sub>, regardless of the crystalline structures. The addition of WO<sub>3</sub> apparently prevented the aggregation of ZrO<sub>2</sub> nanoparticles by reacting with the surface hydroxyl groups during calcination, consistent with the observations of Song et al.<sup>[22]</sup> Figure 1(b) shows that the diffraction peaks of reduced catalysts are nearly the same as those of WO<sub>3</sub>/ZrO<sub>2</sub> samples, except for a weak peak characteristic of Pt(111) at 40° in the case of Pt/ZrW(t). This result indicates that Pt addition doesn't change the crystalline structures of the supports.

Table 1 shows the textural properties of the reduced catalysts. The specific surface area of the catalysts is increased with the increment of m-ZrO<sub>2</sub> in the supports, which is in agreement with the pore volume trend. Pore distributions of the catalysts are presented in Figure 2. Interestingly, *t*-ZrO<sub>2</sub> based catalysts possess pores of 3.5 and 6 nm in diameter, whereas *m*-ZrO<sub>2</sub> based catalysts exhibit only one type of pores, which is 19 nm in diameter.



Figure 3. NH<sub>3</sub>-TPD curves of ZrW supports.

eter. In addition, the thermal pretreatment has little effect on pore distributions of the catalysts. According to the  $H_2$ - $O_2$  titration results, the dispersion of Pt is slightly higher on the ZrW support with larger specific surface area. Moreover, the Pt dispersion was further improved when Pt/ZrW catalysts were calcined before the reduction. But in fact, it can be observed from Table 1 that average Pt particle sizes for all the catalysts ranged from 3.0 to 3.6 nm. Direct reduction or thermal treatment at a low temperature does not obviously affect the Pt particle size.

The acid strength distribution of the ZrW supports was obtained by  $NH_3$ -TPD. The profiles were normalized by sample weight for comparison with each other. It is known that  $NH_3$ -TPD peaks at <200 °C, 200-350 °C, and 350-450 °C represent the weak,

medium and strong acid sites, respectively.<sup>[23]</sup> As shown in Figure 3, ZrW(t) exhibits the most intense TCD signal among the samples, indicating that this support contains the most acidic sites. Additionally, some strong acid sites were observed on ZrW(t) and ZrW(mt), while ZrW(m) contained the fewest acid sites which are mainly presented as weak acids, with a small amount of medium-strength sites. Therefore, the presence of *t*-ZrO<sub>2</sub> promotes the acid properties of the supports.

The surface chemical states of various catalysts were identified by XPS and Pt 4f, Zr 3d and W 4f lines are shown in Figure 4. For comparison, Pt/ZrO<sub>2</sub>(m-350) was also analyzed. Two peaks at 74.5 eV and 71.0 eV are observed in the spectrum of Pt/ZrO<sub>2</sub> (Figure 4(a)), which are assigned to Pt 4f<sub>5/2</sub> and Pt 4f<sub>7/2</sub> signals of Pt<sup>0</sup> species, respectively.<sup>[24]</sup> When W species were introduced into the support, the binding energies of Pt<sup>0</sup> shifted to lower values, demonstrating an electron-rich Pt state and a less interaction between Pt and ZrO<sub>2</sub>.<sup>[25]</sup> This effect was accompanied by a broadened FWHM and a slight shift of Zr<sup>4+</sup> peaks toward higher binding energies (Figure 4(b)). As Jacome et al.<sup>[26]</sup> analyzed, these changes may be caused by a strong interaction between Zr and W atoms and the formation of a few deformed Zr<sup>4+</sup> cations on the surface. In Figure 4(c), the two peaks at 37.3

 Table 2. The deconvolution results of elemental peaks in the band region of CO linear adsorption.

Catalyst	Peak position	Height	FWHM	Area	A <sub>2088</sub> /A <sub>total</sub> <sup>[a]</sup>	
	[cm <sup>-1</sup> ]					
Pt/ZrW(m)	2074	0.15	24	3.74	0.029	
	2088	0.03	15	0.48	0.036	
Pt/ZrW(t)	2072	0.11	22	2.69	0.027	
	2087	0.03	12	0.35	0.037	
Pt/ZrW(mt)	2072	0.07	17	1.52	0 172	
	2088	0.06	13	0.85	0.172	
Pt/ZrW(m-350)	2074	0.03	15	0.65	0.344	
	2090	0.05	15	0.96	0.344	
Pt/ZrW(t-350)	2074	0.05	17	1.02	0.261	
	2089	0.07	18	1.50	0.301	
Pt/7rW/(mt.250)	2076	0.04	11	0.52	0.310	
FVZIVV (ML-350)	2091	0.05	13	0.77	0.310	

[a] A<sub>total</sub> is the total area of IR peaks of CO chemisorption on Pt.

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Figure 4. XPS of the reduced catalysts: (a) Pt 4f, (b)Zr 3d, (c)W 4f.

eV and 35.3 eV are assigned to W 4f<sub>5/2</sub> and W 4f<sub>7/2</sub> signals of W<sup>6+</sup>species. But the FWHM values are wider than the reported ones,<sup>[26]</sup> which indicates the co-existence of the W<sup>5+</sup> species. For all of the samples containing WO<sub>3</sub>, it should be noticed from Figure 4 that the binding energies of the three elements remain



Figure 5. (a) DRIFT spectra of CO adsorbed on reduced catalysts and (b) the deconvoluted band region of CO linear adsorption.

constant, implying similar electron environments on these catalysts.

 $\rm H_2$  chemisorption is an important method to reveal the effect of hydrogen spillover, and the H/Pt ratio is often introduced to evaluate the spillover capacity of materials.<sup>[27]</sup> Because one H atom is adsorbed onto one Pt atom, the H/Pt value is usually higher than the Pt dispersion when hydrogen spillover occurs. As listed in Table 1, all the catalysts exhibit a spillover capacity

Table 3. Catalytic performance of glycerol hydrogenolysis on Pt/ZrW cat	alvsts. <sup>[a]</sup>

Catalyst	Conversion	Selectivity <sup>[b]</sup> [%]					
	[%]	1,3-PDO	1,2-PDO	1-PO	2-PO	others	
Pt/ZrW(m)	6.7	32.2	24.2	35.8	7.7	0.1	
Pt/ZrW(mt)	15.2	32.5	21.1	36.1	8.3	2.0	
Pt/ZrW(t)	7.0	34.1	30.6	27.9	7.4	0.0	
Pt/ZrW(m-350)	20.4	23.8	25.4	40.3	10.4	0.1	
Pt/ZrW(mt-350)	19.3	30.7	12.7	42.4	9.9	4.3	
Pt/ZrW(t-350)	21.9	35.1	12.4	42.9	9.6	0.0	
Pt/ZrW(t) <sup>[c]</sup>	53.4	36.0	14.6	44.8	3.3	1.3	
Pt/ZrW(t-350) <sup>[d]</sup>	77.7	29.7	10.6	48.1	10.4	1.2	

[a] Reaction conditions: 4.0 g glycerol, 36.0 g water, 1.0 g catalyst, 180 °C, 8 MPa, 1000 rpm, 24 h. [b] 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. [c] The input glycerol is 2.0 g, catalyst 1.25 g and reaction time is 78 h. [d] The input glycerol is 2.0 g and reaction time is 50 h.

to some extent, as H/Pt is much higher than Pt dispersion. Calcination of the Pt precursor and the m/t-phase mixture of  $ZrO_2$ facilitate the hydrogen spillover on the catalysts, and the effect of the former is more significant. In addition, H/Pt values are nearly the same for the pure *m*-ZrO<sub>2</sub> and *t*-ZrO<sub>2</sub> based catalysts when the same preparation conditions are applied.

As it is sensitive to the noble metal particle size, crystal plane, and electronic states, CO chemisorbed DRIFT spectra was performed for a better understanding of Pt states of the catalysts. The results are shown in Figure 5(a). All of the catalysts present an absorption band corresponding to linear adsorption of CO on Pt ( $\nu_{CO} = 2070-2094 \text{ cm}^{-1}$ ) and a low frequency band at about 1850 cm<sup>-1</sup> corresponding to bridge adsorption of CO on Pt.<sup>[28]</sup> In the spectra of Pt/ZrW(m) and Pt/ZrW(t), an obvious shoulder peak is observed at approximately 2045 cm<sup>-1</sup>, which represents the linear adsorption of CO on Pt<sup>0</sup> of smaller size.<sup>[29]</sup>

Additionally, the band in the linear adsorption region is divided into two peaks, as clearly observed in the cases of Pt/ZrW(mt), Pt/ZrW(m-350), Pt/ZrW(mt-350) and Pt/ZrW(t-350). For a better analysis, deconvolution of the absorption band in this region was taken and the results are shown in Figure 5(b). As previously reported,<sup>[30]</sup> the elemental band at 2073 cm<sup>-1</sup> can be assigned to less packed terraces or step sites such as Pt(100), and the elemental band at about 2088 cm<sup>-1</sup> represents close packed terraces such as Pt(111). In this way, a semi-quantitative analysis of Pt(100) and Pt(111) can be carried out on the basis of the intensity ratio between these two bands. Table 2 lists the deconvolution data and area ratio of elemental bands, and it is indicated that using heterogeneous ZrO<sub>2</sub> phase based support and calcination of Pt precursor before reduction can lead to more Pt(111) terraces for the catalysts, and the effect of the later method is stronger.

Table 3 lists the reaction results of the glycerol hydrogenolysis on these catalysts. Compared with the performances of Pt/ZrW(m) and Pt/ZrW(t), the catalyst with heterogeneous  $ZrO_2$  as support exhibited a better activity, and the conversion of glycerol reached 15.2%. Moreover, when a thermal treatment was conducted on the three catalysts, further increases of the glycerol conversion were obtained, with the highest conversion being 21.9%. At high glycerol conversion of 77.7% on Pt/ZrW(t-350), the selectivity of 1,3-PDO was decreased and more 1-PO was formed because of deep hydrogenolysis.

Mass balance was well achieved for all of the reactions within a deviation of  $\pm 2\%$ , thus very few gaseous or coke products were formed. The main products were 1,3-PDO 1,2-PDO and 1-PO, with a small amount of 2-PO. The product distribution appears to have no clear relationship with the catalysts because of the complicated reaction system, which involves both parallel reactions and deep hydrogenolysis. Although the selectivity of 1,3-PDO is greater than that of 1,2-PDO (except in the case of Pt/ZrW(m-350)), the advantage is not significant compared with the reported results.<sup>[11, 13]</sup> Even at low conversion, the formation of 1-PO is large, consistent with the results reported by Li et al.<sup>[8]</sup>

The effect of hydrogen spillover on the catalytic activities

To elucidate the influence of hydrogen spillover, some factors should be excluded first. In our case, a large change in Pt size was avoided by a relatively mild thermal treatment during the Pt loading process, and Pt particle sizes only ranged from 3.0 to 3.6 nm (Table 1). In addition, a clear difference was observed in glycerol conversion between Pt/ZrW(m) and Pt/ZrW(m-350), even though they had similar Pt particle sizes. Therefore, the size effect is not the dominant factor in the catalytic activity.

As mentioned in the introduction, acid properties of the supports play an important role in glycerol hydrogenolysis, and a better catalytic activity can usually be ascribed to more acid sites especially strong acid sites. However,  $NH_3$ -TPD results (Figure 3) show that although the acid amount and strength of ZrW(t) exceed those of ZrW(m), the corresponding catalysts perform a similar conversion (Table 3). Therefore, glycerol activation on the catalysts should not be the main reason for the different catalytic performances, and other factors should be highlighted.

We thus focus on the activation of hydrogen. H<sub>2</sub> chemisorption demonstrates that hydrogen spillover occurs on all of the catalysts. As shown in Table 1, the spillover effect is the most significant on Pt/ZrW(t-350), on which the conversion of glycerol is also the highest (Table 3). A further revelation is presented in Figure 6. It is clear that H/Pt has a liner relationship with glycerol conversion, which illustrates that hydrogen spillover plays an important role in the catalytic activity.



Figure 6. The correlation between H/Pt and glycerol conversion.

In the hydrogenolysis of other reactants, the roles of spillover hydrogen and the reaction models were discussed. Shin et al.<sup>[31]</sup> studied the gas phase hydrodechlorination of chlorobenzene and 3-chlorophenol on Ni/SiO2 catalysts. They found that the hydrodechlorination proceeds via the electrophilic attack of the adsorbed aromatic by surface dissociated hydrogen, possibly spillover hydronium ions. And the Kinetic parameters reflect that spillover hydrogen and the adsorbed aromatic do not compete for the same adsorption site on the catalyst surface. This model is consistent with the hydrodesulfurization reactions.<sup>[32]</sup> In the case of hydrodeoxygenation, Ranade et al.[33] investigated the hydrogenolysis of benzylic alcohols on rhodium catalysts, and they concluded that direct hydrogenolysis occurs on the carbon support because of the formation of a better leaving group  $(OH_2)$ from the benzylic hydroxy group and its subsequent substitution by spillover hydrogen. However, Thakar et al.<sup>[34]</sup> argued that the model depends on the nature of the support. They found that both hydrogenolysis and the dehydration-hydrogenation route were observed over Pd/C, which was attributed to the acidic nature of the carbon support. But hydrogen spillover was not involved in the direct hydrogenolysis of the C-O bond on Pd/SiO<sub>2</sub> because the reactant was only adsorbed on Pd metal in this case, which was proved by the same initial reaction rate on Pd black and Pd/SiO<sub>2</sub>. These reports demonstrate that hydrogen spillover is important when the adsorption of the organic reactant mainly occurs on the support.

Based on these researches, we also proposed here the role of spillover hydrogen in the glycerol hydrogenolysis. Generally, dehydration is a reversible process and hydrogenation of the adsorbed intermediate species plays a role in breaking this balance in aqueous system. In this way, spillover effect is the key for the activated hydrogen atoms to reach the sites where glycerol is adsorbed. However, tremendous physical/energy barriers impede the surface diffusion of hydrogen atoms from one material to another,<sup>[35]</sup> and inter-particle H spillover is only enhanced in some cases.<sup>[19]</sup> This fact implies that in the case of the nano-ZrO<sub>2</sub> based Pt/ZrW catalysts, the enhanced hydrogen

spillover capacity ensures the hydrogenation of adsorbed glycerol far away from Pt particles, thus increased the conversion.

It should be pointed out that by a simple impregnation method, the composition of WO<sub>3</sub> could reach 38 wt.% on the nano-ZrO<sub>2</sub> support, which is higher than those reported for many other catalysts.<sup>[8, 10-11, 13, 25]</sup> A novel two-phase interface hydrolysis method was used by Song et al. to prepare WO<sub>x</sub>/ZrO<sub>2</sub> nanosized catalysts with a similar WO<sub>3</sub> loading, but their process was complicated.<sup>[22]</sup> As mentioned in the introduction, WO<sub>3</sub> plays an important role on the formation of acid sites and the activation of glycerol. But in our case, the conversion of glycerol is not affected by the acid amount or strength, no matter the hydrogen spillover capacity is high or low. So we propose that the acid amount and acid strength of the catalysts have nothing to do with the activation step of glycerol, and other factors should be investigated.

# The role of Pt(111) structure and $WO_3$ on the hydrogen spillover

Using heterogeneous  $ZrO_2$  as support and thermally treating Pt precursor, hydrogen spillover and glycerol conversion were both improved (Table 1 and 3). Interestingly, the signal changes in the CO chemisorbed DRIFT spectra appear to be consistent with such improvements (Figure 5 and Table 2). To better illustrate it, the relationship between  $A_{2088}/A_{total}$  and H/Pt is given in Figure 7. H/Pt is clearly proportional to the  $A_{2088}/A_{total}$  value, which indicates that the formation of Pt(111) terraces can facilitate hydrogen spillover on the catalysts, thereby increasing their catalytic activity.



Figure 7. The relationship between  $A_{2088}/A_{total}$  and H/Pt.

To further confirm the importance of heterogeneous  $ZrO_2$  and Pt precursor pretreatment for the Pt(111) formation, Pt/ZrO<sub>2</sub> (m, mt and m-350) samples were prepared by the same method without W loading. CO chemisorbed DRIFT spectra of the samples are presented in Figure 8. Compared with the Pt/ZrW catalysts, the spectra differ substantially. The band of bridge CO

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species is strengthened and red shifted from 1850 cm<sup>-1</sup> to 1837 cm<sup>-1</sup>. This change also occurs in the case of the band of CO adsorbed on smaller sized Pt at 2037 cm<sup>-1</sup>. The bands of CO linear adsorption on Pt(100) and Pt(111) are blue shifted to 2077 cm<sup>-1</sup> and 2093 cm<sup>-1</sup>, respectively. This shift is ascribed to a decrease of Pt electron density caused by the interaction between Pt and ZrO<sub>2</sub>,<sup>[36]</sup> which is consistent with the XPS results in Figure 4. In addition, a weak band at 2129 cm<sup>-1</sup> corresponding to CO adsorption on Pt<sup>6+</sup> is observed in the spectra of Pt/ZrO<sub>2</sub>(m), further confirming the interaction between Pt species and ZrO<sub>2</sub>.



Figure 8. DRIFT spectra of CO adsorbed on reduced Pt/ZrO<sub>2</sub> samples.

Because of the interference of the broad band at 2037 cm<sup>-1</sup>, the deconvolution of the region corresponding to CO linear adsorption and semiquantitative analysis of Pt(100) and Pt(111) are difficult. However, as evident in Figure 8, the bands at 2093 cm<sup>-1</sup> for Pt/ZrO<sub>2</sub>(mt) and Pt/ZrO<sub>2</sub>(m-350) are both distinguished compared with those for Pt/ZrO<sub>2</sub>(m). Therefore, the heterogeneity of ZrO<sub>2</sub> crystalline structure and Pt precursor thermal treatment can provide more Pt(111) sites on the catalysts, regardless of the presence of WO<sub>3</sub>.

H<sub>2</sub> chemisorption was also carried out for Pt/ZrO<sub>2</sub> catalysts, and H/Pt values are given in Table 4. The H/Pt values of Pt/ZrO<sub>2</sub>(mt) and Pt/ZrO<sub>2</sub>(m-350) are higher than that of Pt/ZrO<sub>2</sub>(m), consistent with the trend of the intensity of the DRIFT band at 2093 cm<sup>-1</sup> (Figure 8). This result again demonstrates that Pt(111) formation can facilitate the spillover of hydrogen on catalysts.

Notably, as shown in Table 4, the H/Pt values are significantly lower for Pt/ZrO<sub>2</sub> catalysts than for W-containing catalysts,<sup>[28]</sup> which imply much weaker spillover capacities. Thus, WO<sub>3</sub> must play a certain role in hydrogen spillover. As Prins reviewed,<sup>[14]</sup> for Pt/WO<sub>3</sub> and Pt/WO<sub>3</sub>–ZrO<sub>2</sub> catalysts, hydrogen atoms on Pt move to the WO<sub>3</sub> surface and become a combination of protons and electrons. Then the electrons reduce WO<sub>3</sub> and migrate by  $W^{5+}-W^{6+}$  exchange, while the protons are solvated in water and transport rapidly via hydrogen bonding. However, in the case of

Table 4. H/Pt values of $\text{Pt/ZrO}_2$ samples and the corresponding $\text{WO}_3\text{-}$ containing catalysts				
Catalyst	H/Pt	Catalyst	H/Pt	
Pt/ZrO <sub>2</sub> (m)	0.34	Pt/ZrW(m)	1.02	
Pt/ZrO <sub>2</sub> (mt)	0.38	Pt/ZrW(mt)	1.35	
Pt/ZrO <sub>2</sub> (m-350)	0.53	Pt/ZrW(m-350)	1.97	

 $Pt/ZrO_2$ , the proton–electron migration may be limited to the interface between the Pt particle and the metal oxide particle because of the difference in crystal lattices and the low reducibility and conductibility of  $ZrO_2$  compared to those of WO<sub>3</sub>.

Finally, how Pt(111) terraces can enhance hydrogen spillover is an open question. Gee et al.<sup>[37]</sup> studied the dynamics of hydrogen dissociation on Pt(533) by temperature programmed desorption and time-of-flight technique. They observed from H<sub>2</sub>-TPD that the associative desorption of H<sub>2</sub> on Pt(100) step sites occurs at 375 K, while H<sub>2</sub> desorption from Pt(111) terraces takes place below 300 K with a broad peak. These results indicate that H<sub>2</sub> desorption from Pt(111) terraces is easier than that from Pt(100) steps. In addition, they compared two channels for H<sub>2</sub> dissociation on Pt and found that Pt(100) step sites are responsible for the low energy component to dissociation on Pt(533), and the high energy component is a result of a direct dissociation channel on Pt(111) terraces. This was also proved by van Duin et al.<sup>[38]</sup> using molecular dynamics and the reactive force field ReaxFF.

Considering that high pressure and high concentration conditions are generally applied in industry. Under such conditions, the indirect channel is significantly diminished because the Pt surface is often littered with adatoms.<sup>[38-39]</sup> Therefore, we propose that the direct H<sub>2</sub> dissociation channel on Pt(111) terraces is dominant on the Pt/WO<sub>3</sub>/ZrO<sub>2</sub> catalysts in glycerol hydrogenolysis, and the advantages of dissociation and desorption of H<sub>2</sub> on Pt(111) both enhance the hydrogen spillover capacity.

#### Conclusions

In this study, Pt/ZrW nano-catalysts with highly dispersed  $WO_3$ and uniform Pt dispersion were used in glycerol hydrogenolysis, and the hydrogen spillover capacity was tuned by changing nano-ZrO<sub>2</sub> crystalline structures and thermal treatment conditions of Pt precursor. A linear relationship was observed between H/Pt and glycerol conversion, which confirms that hydrogen spillover is important for glycerol hydrogenolysis on these  $WO_3$  rich nano-catalysts. The acid strength and total amount of acid sites of supports seem to have no influence on the glycerol conversion, so further works should be done to reveal the essential catalyst properties for the glycerol activation step.

When a heterogeneous  $ZrO_2$  phase based support was used or a thermal treatment of Pt precursor was performed before reduction, the amount of Pt(111) terraces was increased and the effect of hydrogen spillover was also enhanced. The important role of Pt(111) terraces on hydrogen spillover is proposed from two aspects. One aspect is that H<sub>2</sub> dissociation preferentially occurs on Pt(111) terraces via the direct dissociation channel during glycerol hydrogenolysis. The other aspect is that H<sub>2</sub> desorption is easier on close packed Pt(111) terraces than on less packed sites such as Pt(100) steps, which ensures a faster spillover pathway from the Pt particle to the support.

### **Experimental Section**

#### Chemicals

Zirconyl nitrate (ZrO(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, >45.0% ZrO<sub>2</sub>) was purchased from Tianjin Guangfu Fine Chemical Research Institute. Urea (CO(NH<sub>2</sub>)<sub>2</sub>, >99.0%) and methanol (CH<sub>3</sub>OH, >99.0%) were obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. Ammonium metatungstate ((NH<sub>4</sub>)<sub>6</sub>(H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>)·nH<sub>2</sub>O, >99.9%) was provided by J&K Chemical Corp. Chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, >37.0% Pt) was purchased from Real&Lead Co., Ltd.

#### **Catalyst preparation**

Monoclinic (m) and tetragonal (t)  $ZrO_2$  precursors were prepared by the solvothermal method of Li et al.<sup>[40]</sup> A mixture phase of the  $ZrO_2$  precursors was also prepared via physical mixing of the two aforementioned pure precursors, such that the m/t  $ZrO_2$  ratio was 1:1 after calcination.

Pt/WO<sub>3</sub>/ZrO<sub>2</sub> catalysts were prepared by the sequential impregnation method. Briefly, the ZrO<sub>2</sub> precursors were impregnated with a suitable amount of ammonium metatungstate dissolved in deionized water, ensuring a WO<sub>3</sub> loading of 38 wt.%. The samples were dried at 100 °C overnight and then calcined at 700 °C for 4 h, with a heating rate of 2 °C/min. After cooling to room temperature, the white samples were impregnated with an aqueous solution of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (corresponding to 2 wt.% Pt loading in the catalysts) and dried at room temperature. Before the reaction, the powder was directly reduced or reduced after calcination at 350 °C for 2 h with a ramping rate of 2 °C/min. The obtained catalysts were labelled as Pt/ZrW(m), Pt/ZrW(t), Pt/ZrW(mt), Pt/ZrW(m-350), Pt/ZrW(t-350) and Pt/ZrW(mt-350), where the information in parentheses represents the ZrO<sub>2</sub> crystalline state and the calcination temperature for Pt precursor after drying.

#### **Catalytic reactions**

Typically, the catalysts were reduced at 150 °C for 2 h under pure H<sub>2</sub>. The reduction temperature was increased to 250 °C when the calcined catalysts were used. All of the reduction conditions were identical, unless noted otherwise. The reduced catalyst (1.0 g) was introduced into 10 wt.% glycerol aqueous solution (40 mL) in a stainless steel autoclave (100 mL). The system was purged five times with H<sub>2</sub>, and the pressure was increased to 5.5 MPa. The reactor was then heated to 180 °C and maintained at this temperature for 24 h, during which the pressure of the reaction system was maintained at 8 MPa by pulsing H<sub>2</sub>. After the reaction, the products were cooled and liquid samples were analyzed using a gas chromatograph (Agilent Micro GC 4890) equipped with a flame ionization detector and an HP-INNOWAX capillary column (Hewlett–Packard Company, 30 m  $\times$  0.32 mm  $\times$  0.50 m). *n*-Butanol and 1,4-butanediol were added as internal standards. The conversion of the glycerol and the selectivity toward each product are defined as follows:

conversion (%) = (moles of converted glycerol) / (moles of inlet glycerol) selectivity (%) = (moles of glycerol required for specific product) / (moles of converted glycerol)

#### Catalyst characterization

Nitrogen adsorption/desorption isotherms were obtained at -196 °C on a Micromeritics Tristar II 3000 analyzer. The X-ray powder diffraction (XRD) patterns of the catalysts were recorded on a Rigaku D/MAX-2500 diffractometer equipped with a Cu K $\alpha$  radiation source ( $\lambda$  = 1.5406 Å). The scanning angle (2 $\theta$ ) ranged from 20° to 90°, and the scanning speed was 10°/min. X-ray photoelectron spectroscopy (XPS) was performed on a PHI 1600 ESCA spectrometer (PE Company) equipped with an Al K $\alpha$  X-ray radiation source (hv = 1486.6 eV). The powder was pressed into a self-supporting wafer and reduced in a quartz tube. It was then preserved in a centrifuge tube filled with Ar and introduced into the testing chamber. The measurement was taken at 10<sup>8</sup> Torr, and the binding energy values were calibrated by the C 1s peak at 284.6 eV within an error of ±0.2 eV.

 $H_{2}\mathchar`-O_{2}$  titrations were carried out on a Micromeritics Autochem II 2920 chemisorption analyzer to measure the dispersion of Pt<sup>0</sup> on the reduced catalysts.<sup>[41]</sup> Briefly, the sample (about 100 mg) was put into a U-shaped quartz tube and reduced in 10% H<sub>2</sub>/Ar mixed gas under the aforementioned reduction condition, and then purged with He. After the temperature was decreased to 45 °C, the catalyst was oxidized by 10%(vol.) O<sub>2</sub>/He (0.5082 mL) pulse injection until the TCD peaks became stable. H<sub>2</sub> titrations were subsequently performed under the same condition. The adsorption stoichiometry factor of Pt/H<sub>2</sub> was 2/3. H<sub>2</sub> chemisorption was measured to evaluate the levels of hydrogen spillover on the catalysts. The sample was reduced and then purged with He at 300 °C to remove chemisorbed hydrogen. After cooling to 45 °C, H<sub>2</sub> chemisorption uptakes were measured by pulses of 10% H<sub>2</sub>/Ar. The H/Pt value is defined as the moles of adsorbed H atoms per mole Pt on the catalyst. Ammonia temperature-programmed desorption (NH<sub>3</sub>-TPD) of the acid support was also carried out using the same instrument. The sample was pretreated in He flow at 300 °C for 1 h and cooled to 50 °C. Then it was treated in NH<sub>3</sub> flow for 0.5 h. After adsorption, the sample was purged in He until the baseline was stable. Subsequently, it was heated to 800 °C at a ramping rate of 10 °C/min. The desorbed NH<sub>3</sub> was monitored by a TCD detector.

Diffuse reflectance infrared Fourier transform (DRIFT) spectra of adsorbed CO were collected on a Nicolet 6700 spectrometer equipped with an MCT/A detector. The powder sample was put into a high temperature cell, reduced in situ by flowing H<sub>2</sub>, and then purged with He for 30 min. After the sample cooled to 30 °C, the background spectrum was recorded and CO chemisorption was subsequently carried out for 30 min. Then the sample was purged again and desorption spectra were obtained with the background subtracted. The result was acquired when the spectra were stable.

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**Keywords:** glycerol • heterogeneous catalysis • hydrogenolysis • hydrogen spillover • platinum

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**Structure-spillover relationship:** The spillover capacities on Pt/ZrW catalysts were tuned and they were investigated in glycerol hydrogenolysis. The formation of Pt(111) terraces facilitates both  $H_2$  dissociation and desorption steps, thus enhances the capacity of  $H_2$  spillover and the conversion of glycerol.

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Glycerol Hydrogenolysis to 1,3-Propanediol on Pt/WO<sub>3</sub>/ZrO<sub>2</sub>: Hydrogen Spillover Facilitated by Pt(111) Formation