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# Selective hydrogenolysis of glycerol to 1,3-propanediol: manipulating the “frustrated Lewis pairs” by introducing gold to Pt/WO<sub>x</sub>

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**Abstract:** WO<sub>x</sub> supported highly dispersed Au and Pt catalyst were developed for high performance in selective hydrogenolysis of glycerol to 1,3-propanediol under very mild reaction conditions (81.4% glycerol conversion, 51.6% of 1,3-PD selectivity at 413K, 1MPa H<sub>2</sub>). The highly dispersed Au decreased the original surface Lewis acid sites on Pt/WO<sub>x</sub> but greatly increased its *in-situ* generated Brønsted acid sites with the assistance of H<sub>2</sub> *via* the formation of frustrated Lewis pair (FLP). Such *in situ* formed and spatially separated pair of H<sup>+</sup> and H<sup>-</sup> functions as the active sites in glycerol conversion to 1,3-propanediol.

Selective cleavage of secondary C-O bonds in polyols and carbohydrates is an important strategy in the transformation of biomass to value-added chemicals.<sup>[1]</sup> Experimental practices of this strategy, however, have met significant challenges due to steric hindrance and unfavourable thermodynamics in access to secondary C-O bonds. As a typical example, chemoselective hydrogenolysis of glycerol to 1,3-propanediol (1,3-PD) has attracted intensive interests in the past decade, from both academia and industry, as it provides an opportunity to upgrade crude glycerol, a byproduct in the production of biodiesel by transesterification of vegetable oils, into highly value-added 1,3-PD, which is widely used as a monomer in polyester industry.<sup>[2]</sup> Unfortunately, over most supported metal catalysts, 1,2-propanediol (1,2-PD) is the predominant product as a consequence of cleavage of primary C-O bond of glycerol molecule. To date, only the combination of PGM and oxophilic metal oxide catalysts, e.g. Ir-ReO<sub>x</sub> and Pt-WO<sub>x</sub> exhibited preferential selectivity towards 1,3-PD, although the selectivity in most cases is not satisfactory yet (< 50% at high conversion levels).<sup>[3]</sup> Therefore, it is keenly desired to develop a highly chemoselective catalyst for production of 1,3-PD from glycerol, which critically rely on the understanding of reaction mechanism at a molecular level.

The hydrogenolysis of glycerol is usually understood as a concerted work of acid sites and metal sites, with the former catalyzing dehydration and the latter for hydrogenation reaction.<sup>[2a]</sup> Nevertheless, how the two types of sites cooperate in catalysis and what factors dictate the 1,3-PD selectivity are not clear yet. While substantial works have focused on correlating acidity of the supports with catalytic performances, the correlations,<sup>[3a, 3d, 4]</sup> if any, were subtle in most cases. Moreover, without H<sub>2</sub> the glycerol could not be converted at all on either Ir-ReO<sub>x</sub> or Pt-WO<sub>x</sub> catalyst systems, which implies that hydrogen

is not only involved in the hydrogenation step but also in the dehydration step. Indeed, in our recent work on atomically dispersed Pt/WO<sub>x</sub> catalyst, which gave a promising activity and moderate selectivity (59.8 % of glycerol conversion, 36.3% of 1,3-PD selectivity) under relatively mild conditions (1 MPa H<sub>2</sub>, 413K),<sup>[5]</sup> experimental evidences suggest that H<sub>2</sub> is dissociated heterolytically at the interface of Pt and WO<sub>x</sub>, and the resulting protons and hydrides are supposed to be responsible for dehydration and hydrogenation, respectively. This scenario is reminiscent of a frustrated Lewis pair (FLP) which was first developed in homogenous catalysis but rarely demonstrated in heterogeneous catalysis.<sup>[6]</sup> The unique properties of the Pt/WO<sub>x</sub> enable the formation of spatially separated pair of H<sup>+</sup> and H<sup>-</sup>, speed up the neutralization of dehydrated secondary carboxylic acid before it transforms to thermodynamically favoured acetol, and hence lead to a high selectivity towards 1,3-PD. However, just like a double-edged sword, the employment of WO<sub>x</sub> support, on the one hand benefits the formation of FLP; on the other hand, serves as a Lewis acid owing to the richness of oxygen vacancies, and consequently tends to do the catalysis via traditional dehydration-hydrogenation pathway with 1,2-PD or 1-PO as the dominant products. Therefore, manipulating the ratio of FLPs to Lewis acid sites is expected to provide an opportunity to simultaneously enhance the activity and selectivity in the hydrogenolysis of glycerol to 1,3-PD.

Gold (Au), bearing a full d-band, has shown distinctive performances in chemoselective hydrogenations when modelled into nanocatalysts.<sup>[7]</sup> Theoretical calculations indicated that low coordinated Au atoms can heterolytically dissociate H<sub>2</sub>,<sup>[8]</sup> and the concept of FLPs has been recently used to interpret the distinctive chemoselectivity on gold surface,<sup>[9]</sup> suggesting Au might be a proper candidate to facilitate the FLPs on Pt/WO<sub>x</sub>. In addition, since Au prefers depositing on the defects or oxygen vacancies of MoO<sub>x</sub>,<sup>[10]</sup> introduction of Au to WO<sub>x</sub>, congener of Mo, might occupy the oxygen vacancies and hence decrease the Lewis acid sites of WO<sub>x</sub> support. Meanwhile, Au atoms/clusters were also reported to significantly promote the activity of PGMs, even with extremely low loading.<sup>[11]</sup> Therefore, introducing highly dispersed Au to Pt/WO<sub>x</sub> might be a reasonable attempt to enlarge FLPs and reduce Lewis acid sites, and thus enhance the selectivity to 1,3-PD meanwhile suppress the formation of 1,2-PD or 1-PO.

Hitherto, however, Au has never been reported promoting the production of 1,3-PD, although alkali and transition metals were widely investigated but showing limited promotional effect.<sup>[12]</sup> This is probably because the well dispersion of Au on Pt/WO<sub>x</sub> is rather difficult owing to the low isoelectric point (<2) of WO<sub>x</sub> support<sup>[13]</sup> and a large miscibility gap between Au and Pt *fcc* phases.<sup>[14]</sup> However, the bulk phase relation might be considerably altered for nano-sized particles. Taking the advantage of utmost Pt dispersion, herein we introduce Au to

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Pt/WO<sub>x</sub><sup>[5]</sup> via a selective deposition procedure and the obtained AuPt/WO<sub>x</sub> catalysts exhibited unprecedented high glycerol conversion (81.4%) and 1,3-PD selectivity (51.6%) under quite mild reaction conditions (413K, 1MPa H<sub>2</sub>). The superior activity

and chemoselectivity were attributed to the increase of FLPs after Au introduction, providing more *in-situ* Brønsted acid sites and hydrides to carry out the chemoselective catalysis.

**Table 1.** Hydrogenolysis of glycerol over different catalysts

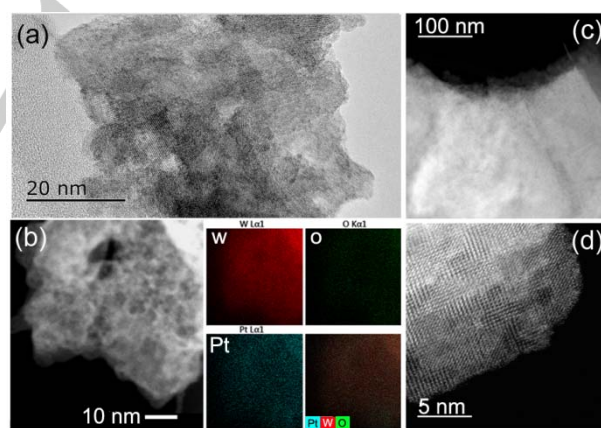
Entry	Catalyst	Conv. (%)	Selectivity (%)					Yield (%)
			2-PO	1-PO	1,2-PD	1,3-PD	Others <sup>[b]</sup>	
1	Pt/WO <sub>x</sub>	35.7	4.3	49.9	2.5	36.1	7.2	12.9
2	0.010AuPt/WO <sub>x</sub>	37.7	5.0	36.5	1.5	47.4	9.6	17.9
3	0.025AuPt/WO <sub>x</sub>	46.3	3.6	30.4	2.9	51.9	11.2	24.0
4	0.050AuPt/WO <sub>x</sub>	47.1	3.7	34.3	3.0	54.6	4.4	26.2
5	0.10AuPt/WO <sub>x</sub>	52.0	3.8	33.7	5.4	56.3	0.8	29.3
6	0.25AuPt/WO <sub>x</sub>	45.2	2.6	31.4	5.6	57.1	3.3	25.8
7	0.40AuPt/WO <sub>x</sub>	36.0	5.4	27.3	6.1	58.6	2.6	21.1
8	0.50AuPt/WO <sub>x</sub>	27.9	3.9	26.3	2.4	60.4	7.0	16.9
9	0.10AuPt/WO <sub>x</sub> <sup>[a]</sup>	81.4	5.8	30.8	1.5	51.6	10.3	42.0
10	Pt/WO <sub>x</sub> -HCl	35.5	4.2	50.1	1.4	35.1	9.2	12.5
11	Pt/WO <sub>x</sub> +0.50Au/TiO <sub>2</sub> <sup>[c]</sup>	33.4	4.8	50.4	1.7	33.1	10.0	11.1
12	0.50Au/TiO <sub>2</sub>	3.2	7.5	47.6	39.8	0.0	5.1	0
13	0.18AgPt/WO <sub>x</sub>	1.7	0	18.6	27.5	20.3	33.6	0.4
14	0.31CuPt/WO <sub>x</sub>	4.5	2.6	49.8	4.8	35.2	9.5	1.6

The loading of Pt for all catalysts is 2 wt.%, the loading of promoter is presented with molar ratio to Pt in nomination. Reaction condition: 12g 5wt% glycerol aqueous solution in 75mL autoclave with Teflon lining, 0.3 g of catalyst, 800rpm, 413K, 1MPa, 12h. <sup>[a]</sup>the amount of catalyst is 0.6g. <sup>[b]</sup>Others include propane, ethylene glycol, ethanol, methanol, methane, and ethane. The deviation of carbon balance is ±4%. <sup>[c]</sup>0.3 g Pt/WO<sub>x</sub> + 0.06 g 0.5Au/TiO<sub>2</sub> so that the amounts of Pt and Au are equal to those of 0.1 AuPt/WO<sub>x</sub>.

Employing Pt/WO<sub>x</sub><sup>[5]</sup> as the mother catalyst, AuPt/WO<sub>x</sub>s were prepared by selective deposition of Au on the pre-formed Pt/WO<sub>x</sub> with tetrachloroaurate (HAuCl<sub>4</sub>) as the gold precursor and NaBH<sub>4</sub> as the reducing agent. Attempts other than this selective deposition procedure failed (Table S1), suggesting Pt single/pseudo-single atoms altered the surface chemistry of the WO<sub>x</sub> support and thereby made it favourable to gold deposition. The glycerol hydrogenolysis reaction test was performed under mild conditions (413 K, 1 MPa H<sub>2</sub>) as we reported previously.<sup>[5]</sup> As shown in Table 1, in comparison with the mother catalyst 2wt%Pt/WO<sub>x</sub> (referred to as Pt/WO<sub>x</sub> for clarity), introducing Au, even as low as 0.01 molar ratio, resulted in significant increase in 1,3-PD selectivity and suppression of 1-PO formation (entry 1-2). More intriguing, with an increase of Au ratio from 0.01 to 0.10, both the glycerol conversion and the 1,3-PD selectivity were enhanced concurrently (entry 2-5). Further increasing the Au ratio to 0.50 led to the decrease of glycerol conversion although the 1,3-PD selectivity remained going up slightly (entry 6-8). The best performance regarding the yield of 1,3-PD was achieved with 0.10AuPt/WO<sub>x</sub>, which afforded 1,3-PD selectivity of 51.6% at glycerol conversion of 81.4% with a doubled catalyst amount (entry 9). Evidently, gold functions as a remarkable promoter of Pt/WO<sub>x</sub> for the chemoselective hydrogenolysis of glycerol to 1,3-PD, being capable of enhancing both activity and selectivity as desired, which has never been reported before.

The critical role of gold was further confirmed with the following control experiments. First, Pt/WO<sub>x</sub>-HCl was prepared by substituting HAuCl<sub>4</sub> with HCl, and it exhibited similar performance to that of Pt/WO<sub>x</sub> (Table 1, Entry 10), ruling out the possible role of NaBH<sub>4</sub>. Second, the mixture of Pt/WO<sub>x</sub> and Au/TiO<sub>2</sub> showed no obvious promotion (Table 1, Entry 11-12), indicating synergy between Au and Pt/WO<sub>x</sub> is required. Third,

other IB group metal promoted Pt/WO<sub>x</sub> (CuPt/WO<sub>x</sub>, AgPt/WO<sub>x</sub>) demonstrated hardly activity (Table 1, Entry 13, 14), suggesting the distinctive characteristic of Au in promoting the chemoselective hydrogenolysis of glycerol.



**Figure 1.** TEM (a), EDS mapping (b), and HAADF-STEM (c,d) images for 0.025AuPt/WO<sub>x</sub>

In order to get an insightful understanding of the synergy between Au and Pt/WO<sub>x</sub>, extensive characterizations of the catalysts were performed. Initially, the best-performance catalyst 0.10AuPt/WO<sub>x</sub> was examined by STEM, however, no discernible particle was observed except for very few large Au particles (5–10 nm) accompanied with smaller but detectable Pt particles (1–2 nm) (Figure S1). Since the performance for Au catalysis is sensitive to the particle size,<sup>[7c, 7d]</sup> such few and large Au particles are improbable to improve the reactivity so greatly. On the contrary, the undetectable Au species, which are probably highly

dispersed on Pt/WO<sub>x</sub>, are supposed to drastically modify the chemistry for Pt/WO<sub>x</sub> and its resultant performance for glycerol hydrogenolysis. The electron micrographic characterizations of the 0.025AuPt/WO<sub>x</sub> proved our assumption. As shown in Figure 1, no particles of either Pt or Au were observed in STEM or HAADF images of 0.025AuPt/WO<sub>x</sub>, certifying highly dispersed Au species the genuine promoters for Pt/WO<sub>x</sub> in the chemoselective hydrogenolysis of glycerol.

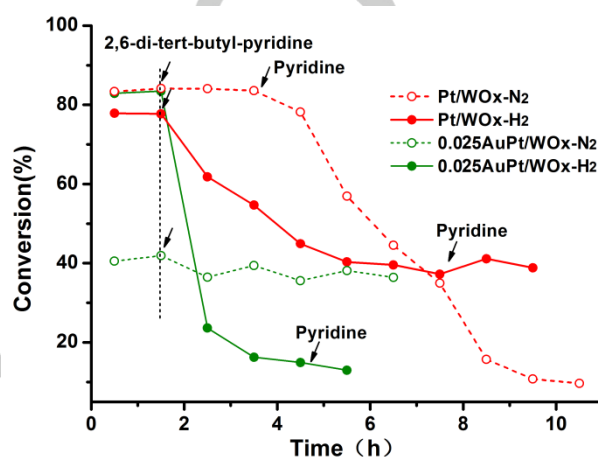
Since Au species cannot be well dispersed on WO<sub>x</sub>, the highly dispersed Au species are supposed to deposit at the defects/vacancies of Pt-WO<sub>x</sub> ensembles, adjacent to Pt in particular, concerning the surface free energy. Surface science studies demonstrated that Au-Pt hetero-bond in well defined Pt surface will induce significant changes in catalytic performance of Pt<sup>[15]</sup>. Consistently, we found that only 0.025 ratio of Au introduction led to a drastic decrease of H<sub>2</sub> adsorption (145.8 μmol/g to 10.4 μmol/g) with much lower adsorption heat (60 KJ/mol) (Figure S2) due to the inert nature of gold towards H<sub>2</sub> adsorption. On the other hand, WO<sub>x</sub> support can also be considerably modified by the introduction of Au. As shown in H<sub>2</sub>-TPR experiment (Figure S3, Table 2), the introduction of Au, even in a tiny amount, resulted in W reduction peaks shifting to lower temperatures accompanied with an increase in H<sub>2</sub> uptakes, indicating W-O bonding is weakened and more W species is activated in AuPt/WO<sub>x</sub> catalysts. Besides, a decrease of edge energy (E<sub>g</sub>) with low transmittance was observed in the UV-vis diffuse reflectance spectra of AuPt/WO<sub>x</sub>s (Figure S4, Table 2), suggesting the electronic properties of the WO<sub>x</sub> support were modified by Au introduction.

To quantitatively correlate the surface modifications of Pt/WO<sub>x</sub> by Au with the catalytic performance, we measured the capability for heterolytically dissociation of H<sub>2</sub> and the consequent formation of H<sup>+</sup>. To this end, dehydration of 2-butanol was tested with/without H<sub>2</sub> using 2,6-di-*tert*-butylpyridine as a selective titrant (Figure 2). In contrast to pyridine, which titrates all types of acids, 2,6-di-*tert*-butylpyridine titrates only Brønsted acid sites owing to steric hindrance.<sup>[16]</sup> In absence of H<sub>2</sub>, the initial reactivity of Pt/WO<sub>x</sub> is much higher than that of 0.025AuPt/WO<sub>x</sub>, and no obvious decline was observed after 2,6-di-*tert*-butylpyridine titration, indicating the dehydration reactivity was mainly attributed to the presence of Lewis acid sites, the amount of which was greatly decreased on the 0.025AuPt/WO<sub>x</sub> (Table 2). By contrast, in the presence of H<sub>2</sub>, the 2-butanol conversion declined upon titration with 2,6-di-*tert*-butylpyridine, indicating Brønsted acid sites were in situ formed with the assistance of H<sub>2</sub>, probably *via* the heterolytic dissociation of H<sub>2</sub>. In comparison with Pt/WO<sub>x</sub>, the initial 2-butanol conversion over AuPt/WO<sub>x</sub> was significantly increased from 40.5% to 82.9%, and could be titrated by 2,6-di-*tert*-butylpyridine more sharply to a conversion of 14.9%. This result strongly suggested that more and stronger Brønsted acid sites were in-situ generated after Au introduction. Therefore, the introduction of Au to Pt/WO<sub>x</sub> decreased the Lewis acid sites on the one hand, and improved greatly the capability for in-situ Brønsted acids generation with the assistance of H<sub>2</sub> on the other hand.

**Table 2.** Chemical and physical properties of AuPt/WO<sub>x</sub> and Pt/WO<sub>x</sub>

Sample	ICP <sub>Au</sub> (wt %)	H <sub>2</sub> uptake <sup>[a]</sup> (mmol/g)	E <sub>g</sub> (eV)	Acid content <sup>[b]</sup> (mmol/g)
Pt/WO <sub>x</sub>	--	1.98	2.5	0.65
0.025AuPt/WO <sub>x</sub>	0.05	2.76	2.4	0.53
0.10AuPt/WO <sub>x</sub>	0.16	2.64	1.9	0.57

[a] The H<sub>2</sub> uptake is for W reduction at 910K–960K, [b] Acid contents were calculated by the amount of adsorbed NH<sub>3</sub>.



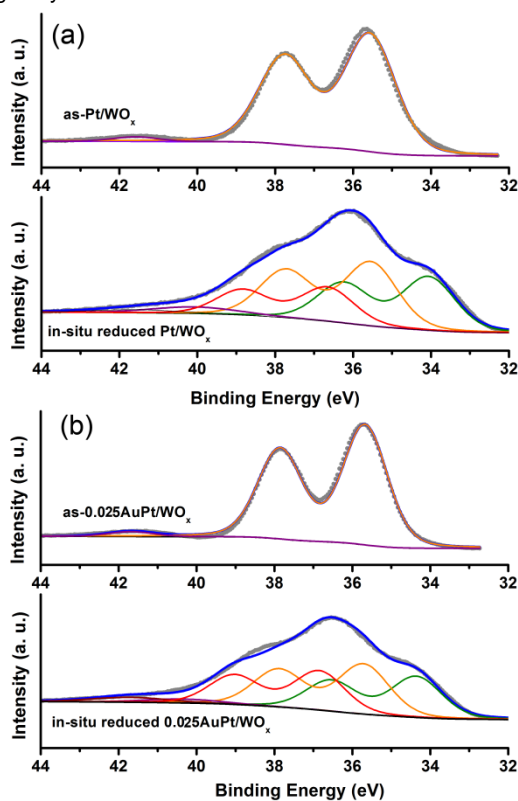
**Figure 2.** Catalytic titration of 0.025AuPt/WO<sub>x</sub> and Pt/WO<sub>x</sub>: the 2-butanol dehydration activity as a function of time at 413K. Arrow indicated the time of titrant addition (details in ESI).

In good agreement with previous studies,<sup>[3a]</sup> the presence of Lewis acid sites on the Pt/WO<sub>x</sub> was demonstrated unfavourable to the selective formation of 1,3-PD (entry 1, 2 in Table 1). More importantly, positive correlations were established between the in-situ generated Brønsted acid (IGBA) sites and the superior performance of AuPt/WO<sub>x</sub>, implying IGBA sites should be the active acid sites for chemoselective hydrogenolysis of glycerol to 1,3-PD. On the ensemble of metal-WO<sub>x</sub>, H<sub>2</sub> can heterolytically dissociate to H<sup>+</sup> and H<sup>-</sup> and spillover to a certain domain of WO<sub>x</sub>, forming the IGBAs responsible for dehydration and the hydrides responsible for hydrogenation. Moreover, thanks to the community of neighbored IGBAs and hydrides, the secondary carbonation can be fast neutralized and transformed to 1,3-PD; which perfectly explained the synchronized increase of glycerol conversion and 1,3-PD selectivity over AuPt/WO<sub>x</sub>, bearing more IGBA sites than Pt/WO<sub>x</sub>.

The XPS results for in-situ reduced catalysts (Figure 3) confirmed the presence of H<sup>+</sup> and H<sup>-</sup> and the consequential proposed mechanism. In comparison with the as-0.025AuPt/WO<sub>x</sub>, two new W species were detected on in-situ reduced 0.025AuPt/WO<sub>x</sub>. The new oxidized and reduced W species were generated owing to their interactions with the H<sup>+</sup> and H<sup>-</sup>, respectively. It should be noted that H<sup>+</sup> and H<sup>-</sup> can easily neutralize/interact with each other and is usually undetectable, unless analogies of “frustrated Lewis pair” (FLP) are formed.<sup>[6, 17]</sup> Therefore, the formation of “FLP” structure was evidenced by the detection of oxidized W species after H<sub>2</sub> reduction, thanks to the oxo nature of the support,<sup>[18]</sup> and perfected the aforementioned mechanism. In heterogeneous catalysis, only NaY zeolite



supported Pt has been unambiguously demonstrated the formation of FLPs before.<sup>[19]</sup> In this regard, the proportion of oxidized W species (W<sub>2</sub>), mirroring the amount of “FLP” structure, can not only be detected but also calculated according to XPS results. As shown in Table S3, the FLPs for 0.025AuPt/WO<sub>x</sub> (30.1%) is more than that of Pt/WO<sub>x</sub> (22.7%), indicating more IGBA sites were provided by 0.025AuPt/WO<sub>x</sub> with assistance of H<sub>2</sub>, consistent with the evaluated acidity and the glycerol chemoselective hydrogenolysis performances. Meanwhile, chemisorption of H<sub>2</sub> was conducted at reaction temperature (413K) to provide better estimate of the reactive surface H. Consistent with the acidity results, H<sub>2</sub> chemisorption was significantly enlarged from 8.8 umol/g over Pt/WO<sub>x</sub> to 17.0 umol/g over 0.025AuPt/WO<sub>x</sub> (Figure S5), indicating more surface H was activated/ stabilized on the AuPt/WO<sub>x</sub> via FLPs, conducted the bi-functional catalysis, and hence resulted in superior chemoselective performance for glycerol hydrogenolysis.



**Figure 3.** XPS for W4f for (a) as-prepared Pt/WO<sub>x</sub> and in-situ reduced Pt/WO<sub>x</sub>, (b) as-prepared 0.025AuPt/WO<sub>x</sub> and in-situ reduced 0.025AuPt/WO<sub>x</sub>

**Table 3.** Hydrogenolysis of propanediols over 0.025AuPt/WO<sub>x</sub> and Pt/WO<sub>x</sub>

Sample	Sub.	Conv. (%)	Selectivity (%)			
			2-PO	1-PO	C <sub>3</sub> H <sub>8</sub>	Others
AuPt/WO <sub>x</sub>	1,2-PD	26.8	7.3	89.1	--	3.6
	1,3-PD	8.6	--	94.7	--	5.3
Pt/WO <sub>x</sub>	1,2-PD	15.6	7.1	87.0	3.3	2.6
	1,3-PD	6.6	--	95.2	--	4.8

To verify the crucial role “FLP” playing in chemoselective hydrogenolysis of glycerol, 1,3-PD and 1,2-PD were employed

as the substrate to substitute glycerol. In principle, if the increase of 1,3-PD selectivity was caused by suppressing over-hydrogenolysis, the activity for propanediol hydrogenolysis over AuPt/WO<sub>x</sub> should be decreased compared to Pt/WO<sub>x</sub>, which is contradictory to the results in Table 3, ruling out the influence of depressing overreaction. On the other hand, the results can be explained well by “FLP” hypothesis: increasing “FLP” induced more active protons and hydrides for the hydrogenolysis of propanediol, in particular 1,2-PD, and hence increasing the activity of propanediol hydrogenolysis. This result further verified that the performance improvement over AuPt/WO<sub>x</sub> was achieved by enlarging the “FLP” domains, the catalytic sites for chemoselective hydrogenolysis of glycerol to 1,3-PD.

Furthermore, to explore the fraction of Au that forms FLP, the yield of 1,3-PD was plotted as a function of the molar ratio of Au/Pt (Figure. S6). When Au/Pt was below 0.025, a linear increase of 1,3-PD yield was found, indicating almost 100% of the introduced Au was active in improving the catalytic performance; meanwhile no Au particles were observed in the HAADF-STEM images (Figure. 1), implying that Au was most probably atomically dispersed when Au/Pt was below 0.025, as aforementioned. In contrast, when the molar ratio of Au/Pt was above 0.10, large Au particles were detected (Figure. S1), indicating that some Au species have been aggregated. In agreement with the change of Au dispersion, the yield of 1,3-PD levelled off when the Au/Pt ratio was greater than 0.025, indicating it was the highly (probably atomically) dispersed Au species that contributed to the formation of FLP and significantly promoted the selective hydrogenolysis of glycerol to 1,3-PD. This also explained the deterioration of 1,3-PD productivity as the Au ratio increased (Table 1), for excessive Au concentration could promote the Au agglomeration.

In summary, highly dispersed Au promoted Pt/WO<sub>x</sub> catalysts were developed for chemoselective hydrogenolysis of glycerol to 1,3-PD. Under relatively mild conditions, 81.4% of glycerol conversion, with 51.6 % selectivity towards 1,3-PD, were obtained on 0.10AuPt/WO<sub>x</sub>, among the best catalysts to our knowledge (Table S2). The highly dispersed Au species significantly modified the structure of Pt/WO<sub>x</sub> ensemble, and provided more activated W species for the formation of “FLP” analogies. In presence of H<sub>2</sub>, more “FLP”'s accounted for more catalytic IGBA sites, thus endowed superior performance of AuPt/WO<sub>x</sub> for chemoselective hydrogenolysis of glycerol to 1,3-PD. This work disclosed a crucial role of IGBA sites playing in chemoselective hydrogenolysis, uncovered the reason for oxophilic oxide as an indispensable component in selectively producing 1,3-PD, and allowed mechanistic insight into catalyst requirements. It also provides a new avenue of catalysts design for the selective cleavage of secondary C-O bonds in the biomass-derived polyols and sugars.

## Experimental Section

In a typical experiment for the preparation of the Au-Pt/WO<sub>x</sub>, 1 g of prepared Pt/WO<sub>x</sub><sup>[5]</sup> was suspended in 167 ml distilled water, then 1 mL of HAuCl<sub>4</sub> solution (10<sup>-2</sup> mol/ dm<sup>3</sup>) was added slowly with continuous stirring. After stirring for 0.5h, a solution of NaBH<sub>4</sub> (10<sup>-2</sup> mol/ dm<sup>3</sup>) was added

under vigorous stirring till the solution pH turned to ca. 4.6. The suspension was aged for 4 h before the solid was recovered by filtering and washing. The solid was dried at 393K, reduced in flowing H<sub>2</sub> at 573 K for 1 h, and passivated with O<sub>2</sub>/N<sub>2</sub> for 4 h at room temperature before exposure to air. The molar ratio of Au:Pt varied from 0.010 to 0.50, while the loading of Pt was 2.0 wt. %.

The reaction tests were carried out in a 75 mL of autoclave with Teflon lining. Typically, 0.3 g of catalyst and 12 g of glycerol aqueous solution (5 wt.%) were put into the autoclave and flushed by H<sub>2</sub> for several times. Typically, the reaction was conducted at 413 K and 1 MPa H<sub>2</sub> for 12 h. The gas and the liquid products were collected and analyzed separately.

The conversion of glycerol and the selectivity of each liquid product (including 1,3-PD, 1,2-PD, 1-PO, and 2-PO) were calculated by the following equations:

$$\text{Conversion of glycerol (\%)} = \frac{\text{mole of glycerol consumed}}{\text{mole of glycerol initially added}} * 100$$

$$\text{Selectivity (\%)} = \frac{\text{mole of carbon in specific product}}{\text{mole of carbon in consumed glycerol}} * 100$$

Others include products of propane, ethanol, methanol, methane, ethane, and ethylene glycol.

$$\text{Selectivity}_{\text{others}} (\%) = 100 - \text{Sum selectivity of (1,3-PD +1,2-PD +1-PO +2-PO)}$$

## Acknowledgements

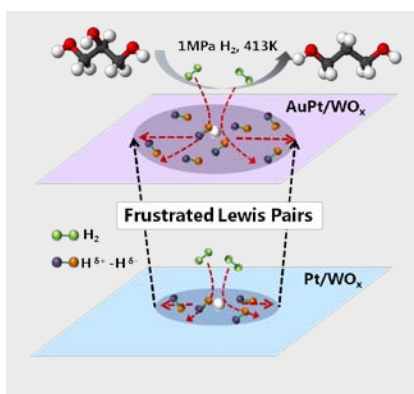
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**Keywords:** glycerol • hydrogenolysis • 1,3-propanediol • Au promotion • frustrated Lewis pair

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## COMMUNICATION

Pt/WO<sub>x</sub> catalysts were greatly promoted by highly dispersed Au via manipulating the “frustrated Lewis acid pair” sites. The resulting AuPt/WO<sub>x</sub> catalysts are highly active and selective for hydrogenolysis of glycerol to 1,3-PD under mild conditions.



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Selective hydrogenolysis of glycerol to 1,3-propanediol: manipulating the “frustrated Lewis pairs” by introducing gold to Pt/WO<sub>x</sub>