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Article

Understanding the promotional effect of Au on Pt/WO₃ in hydrogenolysis of glycerol to 1,3-propanediol

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ABSTRACT

Pt/Au/WO₃ bimetallic catalysts were prepared by impregnation of Pt onto preformed Au/WO₃, obtained by a hexadecyl trimethyl ammonium bromide (CTAB)-assisted one-pot synthesis method. The resulting Pt/Au/WO₃ catalysts exhibited remarkable synergistic effects for selective hydrogenolysis of glycerol to 1,3-propanediol. The characterization results showed that doping of Au promoted the reduction of both Pt and W at low temperatures and uniform dispersion of Pt on the WO₃ support. Furthermore, more low-valence Pt species were produced on the WO₃ surface after introduction of Au. These changes in electronic properties resulted in enhancement of both glycerol conversion and selectivity for 1,3-propanediol.

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1. Introduction

Selective hydrogenolysis of glycerol to 1,3-propanediol (1,3-PDO) is an important reaction in terms of both fundamental and applied catalysis [1–15]. On one hand, this reaction involves selective cleavage of secondary C–O bonds in polyols, which requires sophisticated design of an acid-metal bifunctional catalyst in order to engineer the activation energy such that the reaction proceeds towards 1,3-PDO rather than the parallel reaction to 1,2-PDO or the sequential one to 1-propanol (1-PO). On the other hand, the reaction allows the conversion of cheap and surplus glycerol to highly valued 1,3-PDO, which is widely used as the monomer for the production of high-quality polyester polytrimethylene terephthalate (PTT). Moreover, the

similar hydrodeoxygenation (HDO) strategy should have wide applications in the upgrading of biomass [16,17]. However, the selective formation of 1,3-PDO from glycerol remains a challenge because of the unfavorable thermodynamics and steric hindrance. Among various catalyst compositions, only Pt–W [1–7] and Ir–Re [8–11] bifunctional systems are able to provide moderate-to-good selectivity (30–70%), depending on the reaction conditions and the nature of the catalyst support. The cooperative mechanism involving the metallic component (Pt or Ir) and the oxophilic metal oxide (low-valence WO_x or ReO_x) is yet to be clarified, although there have been experimental reports implying that glycerol is adsorbed and activated on the surface of the oxophilic metal oxides, while hydrogen is heterolytically dissociated at the interface of the metal and oxide

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[18,19].

In our earlier studies [20–24], we synthesized mesoporous WO_x ($2.5 < x < 3.0$), which has abundant oxygen vacancies, and found that the WO_x -supported Pt catalyst was superior to WO_3 -supported one for the hydrogenolysis of glycerol to 1,3-PDO because of the improved dispersion of Pt on the WO_x support. In the Pt/WO_x system, Pt was probably dispersed as single atoms or fine clusters of only a few atoms because of the stabilization effect of oxygen vacancy on Pt atoms. Moreover, by introducing a small amount of Au (0.1%–0.2%) to the pre-formed Pt/WO_x , both glycerol conversion and 1,3-PDO selectivity were greatly enhanced [24]. The promotional effect of gold was attributed to the production of more *in-situ* Brønsted acid sites and hydrides due to gold deposition. In this case, gold is supposed to deposit on the Pt atoms because it could not be deposited on the surface of acidic WO_x without Pt. However, if it was true, the exposed Pt surface would be reduced, which would hinder the dissociation of hydrogen, which conflicted with the experimental results. Therefore, there might be another pathway explaining the promotional effect of gold.

To provide an insightful understanding of the promotional effect of gold, we report here an inverse catalyst system, $\text{Pt}/\text{Au}/\text{WO}_3$, in which Pt was deposited on the pre-formed Au/WO_3 . The $\text{Pt}/\text{Au}/\text{WO}_3$ system provides almost 2-fold increase in space time yield (STY) of 1,3-PDO compared with the $\text{Au}-\text{Pt}/\text{WO}_x$ catalyst we reported earlier [24], and 4-fold increase in STY compared with the Pt/WO_3 catalyst [20]. The superior performance is attributed to the higher dispersion, higher surface enrichment and increased electron density of Pt due to the doping of Au into the WO_3 .

2. Experimental

2.1. Catalyst preparation

The Au/WO_3 catalyst was prepared by a surface-modified deposition method. In detail, 2.7 g of ammonium paratungstate was first dissolved in 90 mL of water at 90 °C and stirred magnetically. After cooling down to room temperature, a certain amount of aqueous solution of HCl was added dropwise to adjust the solution pH to 0.9. After continuous stirring for 0.5 h, 1.2 g of CTAB was added and stirred for another 30 min. Then, an aqueous solution of HAuCl_4 was added to the above solution. The suspension was aged for 24 h before the solid was recovered by filtering and washing. The solid was further dried at 110 °C overnight, and calcined at 500–650 °C for 3 h to obtain Au/WO_3 -*T* (*T* refers to calcination temperature, °C) samples where the Au content was fixed at 0.1 wt%. Subsequently, the Au/WO_3 -*T* samples were impregnated with an aqueous solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, followed by calcination at 300 °C for 1 h and reduction in flowing H_2 at 300 °C for 1 h to obtain the $\text{Pt}/\text{Au}/\text{WO}_3$ -*T* catalysts, where the Pt content was fixed at 2 wt%.

2.2. Reaction test

The reaction tests were performed in a Teflon-lined 75-mL

stainless steel autoclave. 12 g of glycerol aqueous solution (5 wt%) and 0.3 g of catalyst were loaded into the reactor. The autoclave was purged three times with H_2 , then pressurized to 5 MPa, and heated to a certain reaction temperature. After the reaction, the autoclave was cooled to room temperature and the liquid was collected for analysis using a gas chromatograph (Agilent 7890 B) equipped with a flame ionization detector (FID) and a FFAP capillary column. *n*-Butanol was used as an internal standard for analysis.

2.3. Characterization

The crystalline phase of the catalyst was identified with X-ray diffraction (XRD) on a PANalytical X'pert Pro Super X-ray diffractometer using $\text{Cu } K\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$). The tube voltage and current were 40 kV and 40 mA, respectively, and the scanning angle ranged between 10° and 80°.

Hydrogen temperature-programmed reduction (H_2 -TPR) was performed on a Micromeritics Autochem II 2920. 100 mg of the calcined sample was placed in the U-shaped quartz reactor and heated to 120 °C in Ar for 30 min to remove the physically adsorbed water and other contaminants. After cooling to –50 °C, the gas was switched to 10% H_2/Ar , and the sample was heated to 800 °C at a ramp rate of 10 °C/min for reduction. The H_2 consumption during the sample reduction was monitored with TCD.

Transmission electron microscopy (TEM) images were obtained on a JEM-2100F microscope operating at acceleration voltage of 200 kV.

X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250 instrument equipped with an Al $K\alpha$ X-ray radiation source (1486.6 eV). Binding energies were calibrated using the C 1s peak at 284.6 eV.

Surface areas of the catalysts were measured on a Micromeritics ASAP 2460 instrument. Before the measurements, the samples were degassed at 110 °C for 1 h, followed by 300 °C for 4 h. The N_2 adsorption was performed at –196 °C. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method.

3. Results and discussion

Usually, Au is difficult to deposit on the WO_3 surface via conventional deposition-precipitation or co-precipitation method because of low isoelectric point of WO_3 (< 2) [25]. Herein we developed a new CTAB-assisted deposition approach (Fig. 1), which resulted in quantitative deposition of Au up to an amount of 0.5 wt%.

Table 1 shows the performance of the $\text{Pt}/\text{Au}/\text{WO}_3$ in com-

Fig. 1. A new CTAB-assisted deposition approach to prepare Au/WO_3 .

Table 1Catalytic performances of Pt/Au/WO₃ catalysts in comparison with reference samples.

Catalyst	Reaction temperature (°C)-Time (h)	Conv. (%)	Selectivity (%)				STY (g _{1,3-PDO} /(g _{cat} ·h))	Ref.
			1,3-PDO	1-PO	1,2-PDO	2-PO		
Pt/m-WO ₃ ^a	180-12	18.0	39.3	33.8	4.1	7.1	0.019	[20]
Pt/WO _x ^b	160-12	49.5	28.1	52.3	6.5	4.1	0.019	[23]
Pt/WO ₃ ^b	160-12	33.7	56.9	29.7	2.9	3.0	0.026	This work
0.1Au-Pt/WO _x ^b	140-12	52.0	56.3	33.7	5.4	3.8	0.040	[24]
Pt/WO ₃ ^c	155-12	37.5	32.4	46.3	4.0	6.4	0.033	This work
Pt/Au/WO ₃ -500 ^c	155-7	30.0	43.2	36.0	2.2	5.4	0.061	This work
Pt/Au/WO ₃ -550 ^c	155-5.3	33.1	37.8	51.2	3.2	9.3	0.078	This work
Pt/Au/WO ₃ -600 ^c	155-7.5	30.7	54.3	34.8	3.3	5.0	0.073	This work
Pt/Au/WO ₃ -650 ^c	155-9	17.8	54.4	43.8	0	6.5	0.036	This work

^a Reaction conditions: 1.0 g catalyst, 40 g glycerol aqueous solution (10 wt%), H₂ pressure 5.5 MPa.^b Reaction conditions: 0.3 g catalyst, 12 g glycerol aqueous solution (5 wt%), H₂ pressure 1.0 MPa.^c Reaction conditions: 0.3 g catalyst, 12 g glycerol aqueous solution (10 wt%), H₂ pressure 5.0 MPa.

parison with the reference samples for the glycerol hydrogenolysis. The Pt/WO₃ catalyst provided a glycerol conversion of 33.7% and 1,3-PDO selectivity of 56.9% after reaction at 160 °C for 12 h, while the Pt/WO_x catalyst gave 49.5% glycerol conversion and 28.1% 1,3-PDO selectivity under identical conditions [23]. Clearly, the Pt/WO₃ catalyst is less active but more selective than the Pt/WO_x catalyst we reported earlier for the glycerol conversion to 1,3-PDO, which agrees well with the much lower surface area of WO₃ than WO_x (17.7 m²/g vs. 126 m²/g). In terms of STY of 1,3-PDO, however, the Pt/WO₃ catalyst is superior to Pt/WO_x (0.026 vs. 0.019 g_{1,3-PDO}/(g_{cat}·h)). The superior performance of the Pt/WO₃ catalyst may arise from the suitable interaction between Pt and WO₃. Considering that the hydrogenolysis of glycerol is a consecutive reaction, we controlled the glycerol conversion at ~30% by varying the reaction time and then compared the 1,3-PDO selectivity between different catalysts. As shown in Table 1, when the reaction temperature was fixed at 155 °C and the glycerol feed concentration was raised to 10 wt%, the Pt/WO₃ catalyst provided a glycerol conversion of 37.5% and 1,3-PDO selectivity of 32.4% after reaction for 12 h. Compared with Pt/WO₃, the Pt/Au/WO₃-500 catalyst gave rise to both activity (as indicated

by the shorter reaction time) and 1,3-PDO selectivity, and the STY was almost doubled. Moreover, the performance could be further tailored by changing the calcination temperature of the Au/WO₃. The activity of the resultant Pt/Au/WO₃ decreased and the 1,3-PDO selectivity increased with increasing calcination temperature of the Au/WO₃ precursor (as indicated by a longer reaction time to reach comparable conversion of glycerol). Such a trend can be explained by the decrease in surface area (14.0, 10.6, 11.2 m²/g for Au/WO₃-500, Au/WO₃-550, and Au/WO₃-600, respectively) with increasing calcination temperature. Consequently, the dispersion of Pt may decrease, which in turn results in decrease in activity. When Au/WO₃ was calcined at 600 °C, the resultant Pt/Au/WO₃ gave the highest 1,3-PDO selectivity (54.3%), and the STY was higher than that of the Au-Pt/WO_x catalyst reported earlier [24]. Further increasing of the calcination temperature to 650 °C led to the decrease in activity, though the 1,3-PDO selectivity remained unchanged.

Fig. 2 illustrates the glycerol conversion and product selectivity as a function of temperature and H₂ pressure. The glycerol conversion increases with increasing reaction temperature; concomitantly, the 1,3-PDO selectivity decreases, demonstrat-

Fig. 2. Catalytic performance of Pt/Au/WO₃-500 at different reaction temperatures and H₂ pressures. Reaction conditions: 0.3 g catalyst, 12 g glycerol solution (5 wt%), *P* = 5 MPa (a) and *T* = 155 °C (b).

Fig. 3. XRD patterns of the freshly reduced and passivated Pt/WO₃ and Pt/Au/WO₃ catalysts.

ing the typical feature of consecutive reactions. The major side product that competes with 1,3-PDO is 1-PO, which could be produced from further hydrogenolysis of diols or directly from the hydrogenolysis of glycerol, based on previous reports [4,26]. In contrast to 1-PO, only a marginal amount of 1,2-PDO was formed using this catalyst system. The pressure-dependence of the glycerol conversion is similar to the temperature dependence, increasing with increasing H₂ pressure, while the 1,3-PDO selectivity does not change much with increasing H₂ pressure. This trend is quite different from the inverse dependence on H₂ pressure observed for the Au-Pt/WO_x catalyst [24]. The underlying reason might be the structural difference between the two catalysts.

To understand the superior performance of the Pt/Au/WO₃ catalyst, we performed extensive characterizations using XRD, TEM, H₂-TPR, and XPS. Fig. 3 shows that both the freshly reduced and passivated Pt/WO₃ and Pt/Au/WO₃-600 catalysts presented the typical XRD pattern of WO₃; no Pt or Au phase

Fig. 4. H₂-TPR profiles of the calcined Pt/WO₃ and Pt/Au/WO₃ samples.

was detected by XRD, suggesting that both components were highly dispersed on the WO₃ support. Furthermore, compared with the Pt/WO₃ catalyst, the Pt/Au/WO₃ XRD peaks are shifted towards lower angles. Considering that Au³⁺ is bigger than W⁶⁺ (0.85 vs. 0.60 Å), the peak shift of the Pt/Au/WO₃ catalyst may be due to the replacement of W⁶⁺ with Au³⁺. In fact, in the field of semiconductors, doping of Au into WO₃ was also used to modify the properties [27].

The H₂-TPR profiles show that the introduction of Au facilitated the reduction of both Pt⁴⁺ and W⁶⁺, shifting their reduction peak temperature towards lower temperatures (Fig. 4). The calculation of the amount of hydrogen consumed below 300 °C indicates WO₃ → WO_{2.96} in the Pt/WO₃ catalyst and WO₃ → WO_{2.91} in the Pt/Au/WO₃-600 catalyst. Therefore, there are more oxygen vacancies in the reduced Pt/Au/WO₃ catalyst than in the Pt/WO₃ sample.

Fig. 5 presents the typical TEM images of the two catalysts. While the Pt particles in the Pt/WO₃ catalyst are irregular, they are nearly spherical and more finely and uniformly dispersed in

Fig. 5. TEM images of Pt/WO₃ (a) and Pt/Au/WO₃ (b) catalyst.

Fig. 6. W 4f and Pt 4f XPS spectra of freshly reduced and passivated Pt/WO₃ and Pt/Au/WO₃ catalysts.

Table 2

XPS analysis result for Pt/WO₃ and Pt/Au/WO₃ catalysts.

Catalyst	XPS	W 4f _{7/2}			Pt 4f _{7/2}			Pt/W
		W1	W2	W3	Pt1	Pt2	Pt3	
Pt/WO ₃	Binding energy (eV)	34.0	35.5	36.2	70.9	71.5	72.3	1/8.3
	Content (%)	12.1	79.1	8.8	39.0	40.7	20.3	
Pt/Au/WO ₃	Binding energy (eV)	34.0	35.5	36.2	71.0	71.6	72.4	1/7.9
	Content (%)	16.5	74.6	8.9	48.2	35.6	16.2	

the Pt/Au/WO₃ catalyst, with a mean particle size of 2.36 nm. This result indicates that the doping of Au on WO₃ promotes the dispersion of the active component, Pt.

The electronic properties of Pt and W were studied with XPS. As shown in Fig. 6 and Table 2, in comparison with the Pt/WO₃, the Pt/Au/WO₃ catalyst showed a remarkable surface enrichment of Pt; the surface ratio of Pt to W is 1/8.3 in Pt/WO₃ while it is 1/7.9 in the Pt/Au/WO₃ catalyst. Au induces this effect because it weakens the interaction between Pt and WO₃. Pt/WO₃ is a typical strong metal-support interaction (SMSI) system [28–30], and the fact that both Pt and WO₃ could be reduced simultaneously (Fig. 4) provides evidence for the SMSI. However, Au belongs to the IB group on the periodic table and its doping will inevitably weaken the interaction between Pt and WO₃. More than one peak below 300 °C in the H₂-TPR profiles of the three Pt/Au/WO₃ samples supports this conclusion. The XPS spectrum of W_{4f} can be deconvoluted into three sets of doublets with the W_{4f7/2} binding energies at 34.0 eV (W1), 35.5

eV (W2) and 36.2 eV (W3), which can be ascribed to W^{5-δ}, W⁶⁺, and W^{6+δ} [31], respectively. In comparison with Pt/WO₃, the percentage of W^{5-δ} in the Pt/Au/WO₃ is much higher, in agreement with the H₂-TPR result that Au facilitated W⁶⁺ reduction. For the oxidation state of Pt, a trend similar to that of W was obtained, i.e. low-valence state of Pt is more abundant on Pt/Au/WO₃ than that on Pt/WO₃. The increased electron density of Pt favors the dissociation of H₂ in a heterolytic way, providing more protons and hydrides for the selective hydrogenolysis of glycerol to 1,3-PDO based on our previous studies [20–24].

4. Conclusions

Pt/Au/WO₃ catalysts were successfully prepared via a CTAB-assisted deposition method. The doping with Au resulted in partial replacement of W⁶⁺ with Au³⁺, which altered the surface properties of WO₃. Consequently, the interaction between

Graphical Abstract

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Understanding the promotional effect of Au on Pt/WO₃ in hydrogenolysis of glycerol to 1,3-propanediol

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In selective hydrogenolysis of glycerol to 1,3-propanediol, the Pt/Au/WO₃ catalyst affords almost 2.4-fold STY of 1,3-propanediol than the Pt/WO₃ catalyst due to Au doping.

Pt and WO₃ was weakened, and the reduction of both Pt and W became easier, resulting in more low-valence state of W and Pt. Such a change in the electronic state is beneficial to the conversion of glycerol to 1,3-PDO, leading to enhancement in both glycerol conversion and 1,3-PDO selectivity compared with Pt/WO₃. Such a strategy should find wide application in other HDO reactions.

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Au促进Pt/WO₃催化甘油氢解制1,3-丙二醇

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摘要: 近年来, 以生物质为基础的生物柴油得到了迅速发展, 导致了粗甘油过剩. 通过甘油选择性氢解制1,3-丙二醇, 进而被用于合成高价值的聚对苯二甲酸丙二醇酯被认为是最具工业应用潜力的反应之一, 对于提高生物柴油的利用效率有着极其重要的意义. 但由于反应空间位阻和热力学上的限制给甘油氢解制1,3-丙二醇带来了很大的挑战, 因此需要设计高活性的金属-酸双功能催化剂以降低甘油第二个C-O键断裂的活化能和减少其他副反应的发生. 目前Pt-W和Ir-Re双功能催化剂可高选择性制得1,3-丙二醇, 但仍需较严苛的反应条件实现对氢气的活化和解离. 本课题组曾将准单原子/单原子Pt高度分散于具有大量氧空位和酸位点的WO_x载体上, 十分有利于甘油选择性氢解制1,3-丙二醇反应; 在Au-Pt/WO_x催化剂中添加Au可促进B酸产生, 进而提高了甘油转化率和1,3-丙二醇的选择性.

为了进一步研究Au对Pt/WO_x催化剂结构和催化性能的影响, 本文利用CTAB辅助吸附法制备了Au/WO₃, 再浸渍Pt制得Pt/Au/WO₃双金属催化剂. 在甘油选择性氢解制1,3-丙二醇反应中, 所制催化剂表现出比Au-Pt/WO_x更好的催化活性, 1,3-丙二醇时空收率为0.078 g_{1,3-PDO}/(g_{cat}·h), 是后者的1.95倍. 值得一提的是, Au-Pt/WO_x催化剂在低压时活性较高, 而Pt/Au/WO₃催化剂活性则在压力的升高而提高; 另外反应温度的升高导致副产物正丙醇的选择性上升, 1,3-丙二醇的选择性降低. 因此, 适宜的反应条件为155 °C和5 MPa. 与Pt/WO₃和Pt/WO_x相比, Pt/Au/WO₃表现出了更优异的催化性能, 其1,3-丙二醇的时空收率是Pt/WO₃的2.36倍和Pt/WO_x的4倍.

为了探究Au的掺入对Pt/WO_x催化剂性能的影响, 通过XRD, TEM, H₂-TPR和XPS等技术对催化剂进行了深入表征. 结果表明, 与Pt/WO₃相比, Pt/Au/WO₃-600催化剂的XRD衍射峰向小角度偏移, 其原因是Au³⁺离子半径(0.85 Å)比W⁶⁺的(0.60 Å)大, Au³⁺以取代晶格W⁶⁺形式进入WO₃晶格中; 对H₂-TPR前300 °C耗氢量的计算可知: Pt/WO₃可被还原至Pt/WO_{2.96}, 而Pt/Au/WO₃可被还原至Pt/Au/WO_{2.91}. 因此与Pt/WO₃相比, Pt/Au/WO₃表面氧空位更加丰富. TEM和XPS表征可知, 添加0.1 wt% Au后, 促进了更低价态的Pt均匀分散在WO₃载体上, 其平均粒径为2.36 nm.

综上所述, Au的掺杂改变了Pt/Au/WO₃双金属催化剂的结构, 不仅降低了Pt和W的还原温度, 削弱了Pt和W之间的相互作用, 也促进了更低价态的Pt均匀分散于WO₃载体上, 使得Pt/Au/WO₃双金属催化剂在甘油氢解制1,3-丙二醇反应中具有更为优异的活性和产物选择性. 该催化剂有望被广泛运用于其他生物质平台化合物加氢脱氧的反应中.

关键词: 双金属; Pt/Au/WO₃; 甘油; 1,3-丙二醇; 氢解作用

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