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Article

Understanding the deactivation behavior of Pt/WO₃/Al₂O₃ catalyst in the glycerol hydrogenolysis reaction

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ABSTRACT

The selective hydrogenolysis of glycerol to 1,3-propanediol is a highly important reaction for both improving the profitability of biodiesel and valorization of biomass. While intensive research efforts have been devoted to enhancing the catalytic activity and selectivity, little is focused on the stability although the latter is of paramount importance to practical applications. In this work, we investigated the stability of Pt/WO₃/Al₂O₃ and observed a continuous deactivation trend during a 700 h time-on-stream run. Neither the leaching of active W nor the coking was responsible for the deactivation. Instead, XRD, HAADF-STEM and CO chemisorption results clearly showed the occurrence of significant aggregation of Pt particles, which caused a remarkable decrease of Pt-WO_x interfacial sites. As a consequence, strong Brønsted acid sites which were in situ formed by H₂ dissociation at the Pt-WO_x interfacial sites were reduced, leading to the deactivation of the catalyst.

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1. Introduction

Glycerol, as a byproduct in the production of biodiesel, is being considered as an ideal renewable feedstock for production of high-value important chemicals due to its availability at large volume and low cost [1,2]. Among various potential products from glycerol, 1,3-propanediol (1,3-PDO) is the most important one as it has been widely used as the monomer for production of polytrimethylene terephthalate (PTT), a high-performance polyester [3,4]. For glycerol transformation into 1,3-PDO, it is required to selectively cleave the secondary C–O bond. The steric hindrance, however, along with the similar reactivities between primary and secondary –OH groups, poses a significant challenge for the selective hydrogenolysis of glycerol to 1,3-PDO [5]. In order to selectively cleave the sec-

ondary C–O bond of glycerol, bi-functional catalysts which are comprised of a noble metal like Pt, Ir, Rh and an acidic metal oxide such as WO_x and ReO_x have been developed [6–40]. For example, Ir-ReO_x/SiO₂ catalyst, which was first reported by Tomishige and coworkers, could afford 1,3-PDO yield of 38% at 81% glycerol conversion at 120 °C and 8 MPa H₂. Nevertheless, such a good performance was only achieved with the promotion of liquid sulfuric acid (H⁺/Re = 1) [6,7], which would cause equipment corrosion and environmental problems. Compared with Ir-ReO_x system [6–16], Pt-WO_x based catalysts have shown a greater potential for practical applications because they could give promising 1,3-PDO selectivity (40%–70%) at moderate glycerol conversions without addition of any promoters [19–34]. Moreover, the activity and selectivity of the Pt-WO_x combination can be tuned by interaction with the oxide

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support as well as the preparation procedures. For example, Pt/WO₃/ZrO₂ catalyst was reported in 2008 to show 1,3-PDO yield up to 24% in DMI (1,3-dimethyl-2-imidazolidinone) solvent at 170 °C [19]. Quite different from this early report, later studies revealed that water was the best solvent, and Pt/WO₃/ZrO₂ could give 1,3-PDO yield of 32% when the reaction was conducted in water at 130 °C and 4 MPa H₂ [20]. By doping a suitable amount of Mn, the turnover frequency of 1,3-PDO could be increased by 2.6 times than the non-doped Pt/WO₃/ZrO₂ catalyst [21]. In addition to Pt/WO₃/ZrO₂ system, other catalysts systems have also been investigated for the reaction, including Pt/WO₃/TiO₂/SiO₂ [22,23], Pt/WO₃/Al₂O₃ [24–26], Pt/W-SBA-15 [27], Pt-WO_x/SAPO-34 [28], and even non-supported Pt-WO_x system [30–33]. Among them, Pt/WO₃/AlOOH showed the best performance, giving 1,3-PDO yield of 66% after reaction at 180 °C and 5 MPa H₂ for 12 h [34].

Although intensive efforts have been invested towards enhancing the catalytic activity and 1,3-PDO selectivity, little attention has been paid to the catalyst stability. In fact, catalyst durability is a paramount factor to be considered for practical applications. In this work, we investigated the stability of Pt/WO₃/Al₂O₃ catalyst during the long-term continuous reaction, and observed a clear deactivation trend. By characterization of both fresh and spent catalysts using X-ray diffraction (XRD), chemical adsorption, High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), thermogravimetric (TG), as well as 2-butanol dehydration/dehydrogenation as the probe reaction, we are able to provide an insightful understanding of the deactivation behavior.

2. Experimental

2.1. Catalyst preparation

The Pt/WO₃/Al₂O₃ catalyst was prepared by a sequential impregnation method according to our previous report [26]. In brief, WO₃ was first supported on a home-made alumina ($A_{\text{BET}} = 151 \text{ m}^2/\text{g}$) with ammonium metatungstate (AMT) as the precursor followed by calcination at 700 °C for 3 h. Then, Pt was loaded onto the as-prepared WO₃/Al₂O₃ by using hydrochloroplatinic acid (H₂PtCl₆·6H₂O) as the precursor. After drying at 110 °C for 12 h and calcination in air at 300 °C for 3 h, the Pt/WO₃/Al₂O₃ catalyst was obtained. ICP analysis showed the loadings of W and Pt were 9.1 wt% and 4.6 wt%, respectively.

2.2. Reaction test

The reaction for glycerol hydrogenolysis was conducted in a fixed-bed reaction system at 180 °C and 5 MPa H₂. Prior to the reaction, the catalyst sample (2.0 mL, 20–40 mesh) was loaded into a stainless steel reactor (400 mm × 9 mm) at the center position between two beds of quartz sands, and then was in situ reduced in flowing H₂ at 300 °C for 1 h. After cooling to the desired temperature (180 °C), an aqueous solution of glycerol (50 wt%) was fed into the reactor through a high-pressure

liquid pump, affording a liquid-hour space velocity (LHSV) of 1 h^{−1}, while H₂ was co-fed at a flow rate of 33 mL/min, corresponding to a gas-hour space velocity (GHSV) of 1000 h^{−1}. The effluent gas and liquid were separated by a condenser, and the liquid product was sampled at a certain interval and then analyzed on a gas chromatograph (Agilent 7890B) equipped with an HP-INNO WAX capillary column (30 m × 0.32 mm × 0.5 μm) and FID detector using *n*-butanol as internal standard. The conversion of glycerol and the selectivity of products were calculated based on the following equations:

Conversion of glycerol (%) = (mole of glycerol in – mole of glycerol out) / (mole of glycerol in) × 100%.

Selectivity (%) = (mole of carbon in specific product) / (mole of carbon in consumed glycerol) × 100%.

2.3. Characterization

Nitrogen adsorption-desorption measurements were conducted at −196 °C on a Micromeritics ASAP 2460 instrument. Before the measurements, the sample was firstly dehydrated at 110 °C for 1 h and then degassed at 300 °C for at least 4 h. The specific surface areas (A_{BET}) were calculated from the N₂ adsorption isotherm with BET equation, and the pore size distributions were obtained using desorption branch of the isotherms and BJH method.

Powder XRD patterns of the reduced samples were acquired on a PW3040/60 X'Pert PRO (PANalytical) diffractometer equipped with a Cu K_α radiation source ($\lambda = 0.15432 \text{ nm}$) operated at 40 kV and 40 mA, in the 2 θ range from 10° to 80°.

HAADF-STEM images were obtained on a JEM-2100F transmission electron microscope operated at 200 kV and equipped with EDS microanalysis system. The reduced powder sample was ultrasonically dispersed into ethanol solvent and deposited on a holey carbon/copper TEM grid prior to the observations.

CO chemisorption and temperature-programmed oxidation (TPO) were conducted on a Micromeritics AutoChem II 2920 chemisorber. In CO chemisorption measurements, the samples were first pre-reduced at 300 °C under a stream of pure H₂ for 1 h, and then purged under He gas flow for 30 min at 310 °C. After being cooled down to 50 °C, pulses of 5% CO/He were introduced to the reactor for CO chemisorption until saturation was reached.

In TPO measurements, the spent catalyst was first treated at 150 °C under He for 1 h. After being cooled down to 40 °C, the sample was heated from 40 to 800 °C in 2% O₂/He at ramp of 10 °C/min, while the consumed O₂ and the oxidative products were online monitored by a mass spectrometer system.

Thermogravimetric (TG) analysis was performed on a SDT Q600 analyser in a flowing air (100 mL/min) at a heating rate of 10 °C/min up to 900 °C.

The dehydration/dehydrogenation of 2-butanol was used as a model reaction to probe the acid sites of the catalysts, which was carried out at 140 °C in a quartz flow reactor. Prior to the reaction test, the sample (0.030 g) was reduced in flowing H₂ (20 mL/min) at 300 °C for 1 h. After being cooled down to the reaction temperature, liquid 2-butanol was bubbled with flow-

ing N₂ or H₂ (20 mL/min) into the reaction system at 1 bar and 60 °C. Reactant and product concentrations were measured by Agilent 7890B GC with a HP-INNO WAX capillary column (30 m × 0.32 mm × 0.5 μm, FID detector). The conversion of 2-butanol and the selectivity of products were calculated based on the following equations:

Conversion of 2-butanol (%) = (mole of 2-butanol in – mole of 2-butanol out) / (mole of 2-butanol in) × 100.

Selectivity (%) = (mole of specific product) / (mole of consumed 2-butanol) × 100.

3. Results and discussion

To better assess the potential for practical applications, we here evaluated the catalyst using a relatively high concentration of glycerol solution, which is distinct from most of the previous reports where an extreme dilute glycerol solution was used as the feedstock [34–40]. Fig. 1(a) shows the glycerol conversion and product selectivity with time on stream for a continuous running of 700 h. The catalyst exhibited a high initial activity and promising 1,3-PDO selectivity, with glycerol conversion of 57.5% and 1,3-PDO selectivity of 40.4%, which was similar to our previous reports [26]. Besides the target product 1,3-PDO, there were also 1,2-PDO, 1-propanol (1-PO) and 2-propanol (2-PO) whose initial selectivities were 6.3%, 36.7%, and 11.5%, respectively. The much higher selectivity of 1,3-PDO than 1,2-PDO suggests that the catalyst possesses the higher intrinsic activity for cleaving the secondary C–O bond than the primary C–O bond. However, the glycerol conversion declined remarkably with the time on stream, from the initial 57.5% to 44.9% at 100 h. The deactivation rate can be further estimated by fitting the data with three-stage lines (Fig. 1(b)). The first-stage line fits to the initial reaction time of 100 h, which has the highest slope, corresponding to a deactivation rate of 0.111 %/h. After that, the catalyst began to deactivate at a slower rate, 0.037 %/h, until the time on stream for 600 h. In the last stage from 600 to 700 h, the glycerol conversion appeared stable. Contrary to the obvious drop of glycerol conversion in the initial stage, the 1,3-PDO selectivity kept rather stable over the whole reaction duration. Interestingly, the selectivity of 1,2-PDO had a gradual increase with the reaction time, and as a consequence, the selectivity of 1-PO decreased slightly.

This result suggests that the activity for cleaving the secondary C–O bond had a gradual decrease, if it is assumed that at least a part of 1-PO results from cleavage of the secondary C–O bond of 1,2-PDO [41]. Overall, the glycerol conversion dropped by more than half in the whole process, from the initial 57.5% to 25.1% at 700 h.

In order to understand the mechanism for the deactivation behavior, both the fresh and spent catalysts were characterized. First, the textural properties of the catalysts were analyzed. As shown in Fig. 2 and Table 1, the adsorption-desorption isotherms of the spent catalyst are almost identical to the fresh one; the BET surface area, the pore volume, and the pore size distribution kept essentially unchanged after the long-term reaction. This result clearly indicated that the deactivation was not caused by the textural change of the support, confirming that the WO₃/Al₂O₃ was robust enough to endure the hydrothermal conditions. It was reported that the doping of WO₃ or TiO₂ on the alumina supports can greatly improve their hydrothermal stability [42–45], in agreement with our present finding.

Subsequently, elemental analysis was performed to check whether the active components were leached out during the long-term reaction. As shown in Table 1, both the Pt and the W contents had a slight decrease after the long-term reaction. In particular, the W content dropped more obviously, from 9.1 to 7.8 wt%, a decrease by 14%. The reason of W leaching is not clear yet, it might be related with the ligating interaction of WO_x with glycerol [24]. In order to figure out if the leaching of W component was responsible for the deactivation of the catalyst, we further analyzed the W concentration in the liquid product at various reaction time. As shown in Table 2, the deactivation rate could be hardly correlated with the W leaching, suggesting that the loss of W during the reaction was not the dominant reason for the deactivation of the Pt/WO₃/Al₂O₃ catalyst. Nevertheless, the continuous leaching of W might cause the aggregation of Pt nanoparticles due to the destruction of Pt–WO_x interaction to some extent. It should also be noted that we did not detect any Pt species in the liquid product, indicating that Pt was not leached out during the reaction.

The XRD patterns of the fresh and spent catalysts are shown in Fig. 3. In addition to the three peaks assigned to reflections of γ-Al₂O₃, a new peak at 2θ = 39.8° assignable to reflection of Pt

Fig. 1. Stability test of Pt/WO₃/Al₂O₃ catalyst for glycerol hydrogenolysis. (a) Glycerol conversion and products selectivity with time on stream; (b) Fitting of the deactivation curve with three-stage lines. Reaction conditions: 180 °C, 5.0 MPa H₂, 50 wt% glycerol aqueous solution, GHSV = 1000 h⁻¹, LHSV = 1.0 h⁻¹.

Fig. 2. Adsorption-desorption isotherms (a) and BJH pore size distributions (b) of fresh and spent Pt/WO₃/Al₂O₃ catalysts.

Table 1

Physical and chemical properties of the fresh and spent Pt/WO₃/Al₂O₃ catalysts.

Sample	<i>A</i> _{BET} (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)	Pt content ^a (wt%)	W content ^a (wt%)	CO uptake ^b (μmol/g)	Dispersion ^c (%)
Fresh	127	0.21	5.4	4.6	9.1	68.6	29.1
Spent	139	0.21	5.1	4.2	7.8	21.7	10.1

^a Detected by ICP-AES. ^b Detected by CO chemisorption. ^c Determined by CO uptake based on CO/Pt = 1.

(111) appeared in the spent catalyst whereas it was absent in the fresh catalyst. The emergence of this peak in the spent catalyst suggested the occurrence of aggregation/agglomeration of Pt particles during the long-term reaction. The HAADF-STEM images in Fig. 4 further confirmed this point. In accordance with our previous report [26], the Pt nanoparticles were finely dispersed onto the WO₃/Al₂O₃ support, with a mean size of 1.9 nm (Fig. 4(a) and (b)). After the reaction, the growth of Pt particles are prominent, with the formation of some irregular-shaped large particles (Fig. 4(c) and (d)). The mean particle size of the spent catalyst is 3.1 nm. Since Pt and W have close atomic number, it is difficult to distinguish Pt and W from HAADF-STEM images. Then we conducted elemental mapping of Pt and W in the spent catalyst using EDS. The result showed

that the images of Pt and W were well overlapped (Fig. 4(e) and (f)), suggesting that most of the Pt species were still dispersed on the WO_x after the long-term reaction.

Chemisorption of CO is very useful to quantitatively measure the change of Pt dispersion. The data in Table 1 revealed that the fresh catalyst had a CO uptake of 68.6 μmol/g, corresponding to the Pt dispersion of 29.1% if assuming CO/Pt molar ratio of 1/1 [46]. After the reaction it dropped down to 21.7

Table 2

W concentration in the liquid product at various time as well as the deactivation rate.

Sample	W concentration (10 ⁻⁶)	Deactivation rate (%/h)
100 h	0.54	0.111
200 h	0.71	0.037
300 h	0.85	0.037
400 h	0.94	0.037

Fig. 3. XRD patterns of the fresh and spent Pt/WO₃/Al₂O₃ catalysts.

Fig. 4. HAADF-STEM images and Pt particle size distributions of Pt/WO₃/Al₂O₃ catalyst before (a, b) and after (c, d) stability test, as well as EDS analysis of Pt/WO₃/Al₂O₃ catalyst after stability test (e, f).

Fig. 5. TG (a) and TPO (MS signal) (b) profiles of the spent Pt/WO₃/Al₂O₃ catalyst.

μmol/g and the Pt dispersion decreased to 10.1%. This result is in good agreement with the HAADF-STEM, pointing to the occurrence of significant aggregation/agglomeration of Pt nanoparticles. Consequently, the surface Pt sites decreased, resulting in the activity decline.

In addition to the aggregation of Pt particles, coking is another possible reason for deactivation. To address this issue, we performed TG analysis and TPO for the spent catalyst. As shown in Fig. 5(a), there are two weight-loss stages in the TG profile. The first weight loss (1.5 wt%) occurred below 150 °C due to the evaporation of physically adsorbed water on the surface. The second weight loss (3.6 wt%) occurred between 200–500 °C, which can be ascribed to combustion of coke on the surface. Benjamin et al. studied the chemical nature of the coke which was formed in the glycerol dehydration, and found that the coke was aromatic and aliphatic C_xH_yO_z species [47]. The TPO profile of the spent catalyst (Fig. 5(b)) showed that both H₂O and CO₂ were formed at 320 °C, confirming that the coke contained both C and H. Nevertheless, after removing the coke by feeding 3% O₂/He to the spent catalyst at 500 °C for 3 h, the activity was not recovered; instead, it dropped further (Fig. 1(a)). This result suggests that coking is not the major reason for the catalyst deactivation, in agreement with the literature reports [37,48].

Based on the mechanism understanding of the glycerol hydrogenolysis, the formation of 1,3-PDO is closely related to the strong Brønsted acid, which is in situ formed via hydrogen dissociation at Pt-WO_x interface [26,32]. We have known from the

above characterizations that neither the W leaching nor the coking could be responsible for the continuous deactivation of the Pt/WO₃/Al₂O₃ catalyst; instead, the aggregation/agglomeration of Pt nanoparticles decreased the interfacial sites between Pt and WO_x, which most likely decreased the number of the strong Brønsted acid sites. In order to prove this point, we subsequently used 2-butanol dehydration and dehydrogenation as the probe reaction to study the change of strong Brønsted acid sites before and after the reaction [49,50]. As shown in Fig. 6, in N₂ atmosphere, the 2-butanol mainly underwent dehydrogenation reaction to form 2-butanone, and dehydration reaction occurred only to a minor extent. Compared to the fresh catalyst on which dehydrogenation/dehydration ratio was about 4/1, the spent catalyst led to a greater dehydrogenation/dehydration ratio (10/1), indicating the growth of Pt particles caused the decrease of Brønsted acid sites and thus decreased the dehydration activity. When the reaction proceeded in H₂, dehydration, instead of dehydrogenation, became dominated, indicating that new strong Brønsted acid sites were created in H₂. Moreover, compared with the fresh catalyst, the dehydration activity of the spent catalyst decreased almost by 50%, showing a strong implication that the growth of Pt particles brought about a sharp decrease of the in situ formed strong Brønsted acid sites. As a consequence, the activity for cleaving the second C–O bond decreased. This result demonstrated that the reaction for glycerol hydrogenolysis to 1,3-PDO is structure-sensitive, and the high dispersion of Pt is a prerequisite for obtaining the high 1,3-PDO yield.

Fig. 6. The performance of 2-butanol dehydration/dehydrogenation in the presence of N₂ or H₂ over both fresh and spent Pt/WO₃/Al₂O₃ catalysts.

4. Conclusions

In summary, long-term stability is of paramount importance for practical applications of glycerol hydrogenolysis into 1,3-PDO. Pt/WO₃/Al₂O₃ is one of the most active and selective catalysts for this reaction, however, its long-term stability is not satisfactory. By using various techniques, we for the first time revealed that the aggregation/agglomeration of Pt nanoparticles took place with time on stream, and it caused significant decrease of Pt dispersion. As a result, the interfacial sites between Pt and WO_x, which were the active sites for the reaction, were reduced remarkably, leading to the deactivation of the catalyst. In order to alleviate or even prevent the deactivation, new catalyst formulations and preparation methods must be developed to strengthen the interaction between Pt and WO_x and consequently to limit the growth of Pt particles.

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Graphical Abstract

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Understanding the deactivation behavior of Pt/WO₃/Al₂O₃ catalyst in the glycerol hydrogenolysis reaction

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A continuous deactivation trend was observed during the stability test of glycerol hydrogenolysis over Pt/WO₃/Al₂O₃ catalyst. Characterization results suggested that the aggregation of Pt particles and decrease of Pt-WO_x interfacial sites were responsible for the deactivation.

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甘油氢解反应中Pt/WO₃/Al₂O₃催化剂的失活行为

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摘要: 随着生物柴油产业的高速发展, 其副产物甘油大量过剩, 亟需寻找高效的甘油高值化利用途径来提高整个生物柴油产业链的经济性。在各种甘油转化路线中, 甘油选择性氢解制备1,3-丙二醇可用作高端聚酯PTT的单体, 因而成为最具应用潜力的高质化路线之一。同时, 该反应涉及到仲羟基的选择性脱除, 对其它生物质加氢脱氧反应也具有普遍意义。目前, 在提高甘油氢解反应活性和1,3-丙二醇选择性方面已经做了大量的研究工作, 但是关于催化剂稳定性的研究却鲜有报道, 而后者对于整个过程的工业应用是必不可少的。鉴于此, 我们以Pt/WO₃/Al₂O₃为催化剂, 在连续运行的固定床反应器上对其甘油氢解反应的长期稳定性以及其失活的机理进行了详细的考察。

Pt/WO₃/Al₂O₃催化剂表现出较高的初始活性: 甘油的转化率为57.5%, 目标产物1,3-丙二醇的选择性可达40.4%, 主要副产物1,2-丙二醇、正丙醇和异丙醇的选择性分别为6.3%, 37.3%和11.5%。在长达700 h的稳定性测试中, Pt/WO₃/Al₂O₃催化剂呈现缓慢失活趋势: 甘油转化率从57.5%下降到25.1%, 而1,3-丙二醇选择性基本不变。通过对失活曲线进行拟合可以得出催化剂的失活呈现三个阶段: 第一阶段内(0–100 h)催化剂的失活速率最快, 甘油转化率由57.5%降至44.9%, 失活速率为0.111%/h; 第二阶段内(100–600 h)催化剂的失活明显变缓, 失活速率降至0.037%/h; 第三阶段内(600–700 h)甘油转化率基本保持不变。

N₂物理吸附、电感耦合等离子体原子发射光谱、热重和程序升温氧化等表征结果显示, 活性组分(铂, 氧化钨)的流失或积炭都不是催化剂失活的主要原因。同时X射线衍射、高角环形暗场扫描透射电子显微镜和CO化学吸附等表征结果表明, 反应过程中Pt/WO₃/Al₂O₃催化剂上Pt颗粒发生了明显的聚集长大, 使得Pt的分散度由29.1%降至10.1%。仲丁醇脱水/脱氢探针反应的结果显示, 稳定性测试后催化剂在氢气气氛下产生原位B酸的能力显著降低。由此可以得出, 反应过程中Pt/WO₃/Al₂O₃催化剂失活的主要原因是催化剂表面Pt颗粒的聚集长大, 而引起催化剂加氢能力的降低, 同时Pt-WO_x界面位点的数量下降, 使得在氢气气氛下催化剂产生原位B酸的能力大大降低, 从而导致了催化剂的失活。

关键词: 甘油; 氢解; 1,3-丙二醇; 失活; 聚集

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