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Article

Effect of promoters on the selective hydrogenolysis of glycerol over Pt/W-containing catalysts

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ABSTRACT

Diverse promoters, including noble metals (such as Ru, Ir and Rh) and transition metal oxides (such as Re, La, Fe, Zr, Sn and Ce oxides) were introduced into Pt/WO_x and Pt/WO_x/Al_2O_3 catalysts to investigate the ability of these promoters to modify activity and selectivity during glycerol hydrogenolysis to 1,3-propanediol. Among these, La exhibited the greatest promotional effect; the introduction of 0.1% La to the Pt/WO_x improved activity, selectivity and stability, although the significant increase in selectivity came at the cost of a slight activity loss in the case of the Pt/WO_x/Al_2O_3 catalyst. Transmission electron microscopy, high angle annular dark field scanning tunneling electron microscopy and NH_3-temperature programmed desorption all demonstrated that the introduction of La generates a greater quantity of acidic sites on the catalyst surface, and that the majority of the La species are associated with Pt particles. Most of the other additives resulted in only minimal improvements or even detrimental effects with regard to both activity and selectivity, although some appear to improve the stability of the catalyst.

1. Introduction

Advances in the biodiesel industry have resulted in the production of large amounts of glycerol as a byproduct of the transesterification of vegetable oils. Adding value to surplus glycerol by chemical transformations has attracted significant attention in recent decades [1]. Among the various transformation routes such as dehydration [2–4], oxidation [5,6], and reforming [7,8], the selective hydrogenolysis of glycerol to 1,3-propanediol (1,3-PD) is highly desirable, owing to the widespread use of 1,3-PD in the polyester industry for the production of polytrimethylene terephthalate (PTT) [9,10]. Whereas the synthesis of 1,2-propanediol (1,2-PD) can be accomplished with a wide range of catalysts, only Pt-W catalysts [11–13] and Ir-Re catalysts [14–16] can selectively cleave the secondary –OH group of the glycerol molecule to obtain high yields of 1,3-PD. Very recently, our group developed a novel Pt single/pseudo-single atom catalyst deposited on a mesoporous tungsten oxide [17]. The optimized interface between the Pt and the WO_x, as well as the mesoporous structure of the material, result in outstanding activity by this catalyst under relatively low H_2 pressures (i.e. 1MPa), as well as a high space-time yield of 1,3-PD. Even under mild reaction conditions, however, the undesirable formation of 1-propanol as a result of over-hydrogenolysis is still the dominant reaction, with approximately 50% selectivity for this product. Therefore, there

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is a requirement to further enhance the selectivity for 1,3-PD by suppressing the formation of 1-propanol, and the addition of small amounts of promoters to the present Pt/WO_x catalyst appears promising in this regard.

The introduction of a promoter is generally used to improve catalyst performance and stability *via* controlling and/or modulating the electronic structure of the noble metal [18], covering unfavorable sites [19], or modifying the surface chemistry of the support and its consequent interaction with the noble metal [20,21]. Because the selective hydrogenolysis of glycerol to 1,3-PD is a synergistic process based on concerted dehydration and hydrogenation, modification of the catalyst with a promoter could definitely tune both the catalytic performance and the distribution of products. Therefore, an investigation of promoter effects on Pt-W catalysts will be crucial to future breakthroughs in catalyst design. In previous studies, AlO_x promoters [22] and Al_2O_3 supports [11] have both demonstrated promising promotional effects during the selective hydrogenolysis of glycerol to 1,3-PD (90% and 100% glycerol conversions with 44% and 66% 1,3-PD selectivities, respectively). It is likely that the AlO_x support inhibits the over-hydrogenolysis reaction, although the mechanism is still unclear. Moreover, in contrast to Pt/WO_x, supported catalysts are more desirable in practical applications owing to their favorable mechanical and shaping properties. Despite this, positive promoters that work for Pt/WO_x might not function with supported catalysts, because the different chemical properties of Al_2O_3 and WO_x may affect the action of the promoters. To examine such effects, the present work employed both Pt/WO_x and Pt/WO_x/Al_2O_3 as the mother catalysts, and introduced transition metal (such as Re, La, Fe, Zr, Sn and Ce) oxides and noble metals (such as Ru, Ir and Rh) as promoters, and investigated the role of the promoters in modifying the hydrogenolysis reactivity. Among these catalysts, La and Fe showed positive promotional effects on Pt/WO_x, while Re showed a similar effect on Pt/WO_x/Al_2O_3.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of a promoted Pt/WO_x catalyst

The Pt/WO_x was prepared according to a previously reported method [17]. Briefly, 3 g of WCl_6 was added to 100 mL of ethanol with stirring at 500 r/min for 20 min, and then transferred to a Teflon-lined autoclave and heated in an oven at 433 K for 36 h. After cooling to room temperature, the solution was filtered and the recovered WO_x was washed with ethanol and water, then dried at 323 K for 6 h under vacuum. This material is denoted simply as WO_x herein. Pt/WO_x was prepared by impregnating this material with an aqueous solution of H_2PtCl_6, followed by drying at 323 K for 6 h under vacuum.

Noble metal promoted catalysts were prepared by impregnating the Pt/WO_x in $RhCl_3·3H_2O$, $RuCl_3·3H_2O$, or H_2IrCl_6 solutions overnight, with subsequent drying at 383 K for 12 h. The as-prepared catalysts were calcined at 673 K for 1 h at a heating rate of 2 K/min.

Transition metal promoted catalysts were prepared using the incipient wetness impregnation method. The metal precursors used included NH_4ReO_4, $La(NO_3)_3·6H_2O$, $Zr(NO_3)_2·5H_2O$, $Al(NO_3)_3·9H_2O$, $Fe(NO_3)_3·9H_2O$, $Zn(NO_3)_2·6H_2O$, $Ce(NO_3)_3·6H_2O$, $SnCl_4·5H_2O$, $Ga(NO_3)_3·4.5H_2O$, and ammonium paratungstate (APT). After impregnation, the samples were dried at 383 K for 12 h and then calcined at 673 K for 1 h at a heating rate of 2 K /min. These materials are denoted as M/Pt/WO_x. The M loading was fixed at 0.1 wt% and was calculated based on the mass of the mother catalyst. All the catalysts were reduced in H_2 at 573 K prior to reaction trials.

2.1.2. Preparation of the promoted Pt/WO_x/Al_2O_3 catalyst

The Pt/WO_x/Al_2O_3 catalyst was prepared using a sequential impregnation method. WO_x/Al_2O_3 was initially synthesized according to a previously published procedure [11]. In this process, 1.248 g of APT was dissolved in distilled water at 363 K. The solution was then cooled to room temperature, after which 10 g of Al_2O_3 was added, followed by additional stirring at room temperature for 16 h. The solid was subsequently filtered off, dried at 383 K for 12 h, and calcined at 1073 K for 3 h to obtain WO_x/Al_2O_3. This material was then impregnated with an aqueous solution of $H_2PtCl_6·6H_2O$, followed by drying at 383 K for 12 h and calcination at 573 K for 3 h to obtain the Pt/WO_x/Al_2O_3 catalyst. Analysis by inductively coupled plasma-atomic emission spectroscopy showed that the catalyst contained 7.0 wt% tungsten and 2.0 wt% platinum.

The introduction of promotors to the Pt/WO_x/Al_2O_3 catalyst was performed in a manner similar to that applied in the case of the Pt/WO_x, except for the use of a calcination temperature of 573 K. The promoted catalysts are referred to herein as M/Pt/WO_x/Al_2O_3, where the M loading was fixed at 0.1 wt% as calculated based on the mother catalyst.

For comparison purposes, M-Pt/WO_x/Al_2O_3 catalysts were also prepared by co-impregnation of WO_x/Al_2O_3 using a solution of $H_2PtCl_6·6H_2O$ and the corresponding metal precursor. The resulting solids were dried at 383 K and calcined at 573 K for 3 h. In addition, Pt/M/WO_x/Al_2O_3 catalysts were prepared by sequential incipient wetness impregnation of WO_x/Al_2O_3 with solutions of the corresponding metal precursor and $H_2PtCl_6·6H_2O$.

The WO_x/Pt/Al_2O_3 catalyst was prepared via a sequential impregnation method. The initial Pt/Al_2O_3 catalyst was prepared by impregnation of Al_2O_3 samples with an aqueous solution of $H_2PtCl_6·6H_2O$, after which the impregnated sample was dried at 383 K for 12 h and subsequently calcined at 673 K for 3 h. WO_x/Pt/Al_2O_3 was prepared by impregnation of Pt/Al_2O_3 samples with an aqueous solution of ammonium metatungstate (AMT). Impregnated samples were dried at 383 K for 12 h and subsequently calcined at 823 K for 3 h. The platinum content was fixed at 2 wt%, while the tungsten content was varied between (0.1 and 8) wt%.

2.2. Catalytic reactions and product analysis

Glycerol hydrogenolysis trials over Pt/WO_x were conducted in a 75-mL autoclave with a Teflon lining. Typically, 0.3 g of catalyst and 12 g of an aqueous glycerol solution (5 wt%) were transferred into the autoclave, after which the chamber was flushed several times with H_2 and then filled with H_2 to a pressure of 1.0 MPa. The reactor was subsequently sealed and heated to 413 K and the reaction proceeded at a stirring speed of 800 r/min for 12 h. The same conditions were applied in the performance tests over $Pt/WO_x/Al_2O_3$, except using a 3 wt% glycerol solution, an initial H_2 pressure of 5.0 MPa and a reaction temperature of 453 K.

After each reaction, the gaseous and liquid products were collected separately. The liquid phase products were analyzed with an Agilent 7890B gas chromatograph with an HP-INNOWAX capillary column (30 m × 0.32 mm × 0.5 μm, flame ionization detector) using *n*-butanol as the internal standard, while the gaseous products were analyzed online using the same instrument with a HayeSep Q packed column (3 m × 1/8", thermal conductivity detector). The conversion of glycerol and the selectivity for each liquid product were calculated using the following equations.

Conversion of glycerol (%) = (moles of glycerol consumed)/(moles of glycerol initially added) × 100.

Selectivity (%) = (moles of carbon in a given product)/(moles of carbon in glycerol consumed) × 100

Deactivation rate (% h^{-1}) = $(\mathrm{Conv.}_{\max} - \mathrm{Conv.}_{\mathrm{final}}) \times 100 / (t \times \mathrm{Conv.}_{\max})$

2.3. *Catalyst characterization*

High resolution transmission electron microscopy (HRTEM) and high angle annular dark field scanning tunneling electron microscopy (HAADF-STEM) images were obtained on a JEM-2100F instrument operating at 200 kV. The samples were prepared by ultrasonically dispersing the finely powdered catalysts in ethanol and the dropping each solution onto a C/Cu TEM grid.

NH_3-adsorption data were obtained using a Micromeritics AutoChem II 2920 chemisorber to measure the acidity of catalysts. The samples were degassed in He flow at 393 K for 1 h and then cooled to 373 K prior to pulse adsorption trials. After adsorption saturation, the amount of NH_3 adsorption was calculated accordingly.

H_2 adsorption trials were conducted with the same instrument to measure the H_2 uptake of catalysts. The samples were reduced in H_2 flow at 573 K for 1 h after being degassed in Ar flow at 583 K for 30 min, then cooled to 323 K in preparation for pulsed adsorption. After adsorption saturation, the amount of H_2 adsorption was calculated accordingly.

3. Results and discussion

3.1. *The effects of transition metal promoters*

As noted, transition metal promoters can drastically change the activity and selectivity of noble metal supported catalysts. Thus the effects of transition metal promoters during the hydrogenolysis of glycerol were examined in the present work, with the results shown in Table 1. In the case of Pt/WO_x, the additions of Re, Sn, Zn, and Ga (Entries 5–8) decreased glycerol conversion but increased 1,3-PD selectivity, while Zr (Entry 4) had the opposite effect. During the sequential glycerol hydrogenolysis reaction, it is usually difficult to simultaneously enhance both glycerol conversion and selectivity for 1,3-PD, because a highly active catalyst often generates over-hydrogenolysis, thus decreasing the selectivity, and vice versa. However, when promoted by La or Fe (Entries 2 and 3), the glycerol conversion was increased from 37.4% to 39.9% or 41.6%, respectively, while the 1,3-PD selectivity was improved from 35.1% to 41.3% or 37.8%. These slight enhancements resulted in a higher yield of 1,3-PD compared with that obtained with Pt/WO_x. Moreover, the incorporation of La obviously improved the stability of the mother catalyst. The $0.1La/Pt/WO_x$ had an average 0.13% activity loss per hour during an 85-h stability test (Fig. 1), while the activity loss of the Pt/WO_x was 0.33% per hour over a 70-h stability test [17]. In the case of the $Pt/WO_x/Al_2O_3$, the addition of La or Fe also

Table 1
Results obtained with transition metal promoters on Pt-W catalysts during the hydrogenolysis of glycerol.

Entry	Catalyst	Conv. (%)	Selectivity (%)					Yield (%)
			2-PO	1-PO	1,2-PD	1,3-PD	Others [a]	
1	Pt/WO_x	37.4	5.1	50.3	2.3	35.1	7.2	13.1
2	$0.1La/Pt/WO_x$	39.9	4.80	44.7	2.8	41.3	6.4	16.5
3	$0.1Fe/Pt/WO_x$	41.6	6.1	50.5	2.4	37.8	3.2	15.8
4	$0.1Zr/Pt/WO_x$	40.2	5.7	46.9	4.5	33.3	9.6	13.4
5	$0.1Re/Pt/WO_x$	18.1	5.2	46.1	4.0	38.4	6.3	7.0
6	$0.1Sn/Pt/WO_x$	29.8	5.8	40.8	8.5	39.6	5.3	11.8
7	$0.1Zn/Pt/WO_x$	16.2	4.7	40.0	6.3	44.2	4.8	7.2
8	$0.1Ga/Pt/WO_x$	25.0	6.1	44.0	6.1	36.5	7.3	9.1
9	$0.1Ce/Pt/WO_x$	4.0	6.6	54.4	4.8	24.6	9.6	1.0
10	$Pt/WO_x/Al_2O_3$	65.4	7.4	23.2	7.2	48.2	14.0	31.5
11	$0.1La/Pt/WO_x/Al_2O_3$	47.4	9.5	24.1	12.5	56.9	1.3	27.0
12	$0.1Fe/Pt/WO_x/Al_2O_3$	38.3	6.2	21.8	12.2	57.0	2.8	21.8
13	$0.1Zr/Pt/WO_x/Al_2O_3$	55.9	7.1	26.4	5.8	49.1	11.6	27.4
14	$0.1Re/Pt/WO_x/Al_2O_3$	67.9	10.6	29.6	8.7	49.0	2.1	33.3
15	$0.1Sn/Pt/WO_x/Al_2O_3$	21.0	9.7	32.4	16.0	32.6	9.3	6.8
16	$0.1Ce/Pt/WO_x/Al_2O_3$	32.7	9.4	16.5	19.2	51.5	3.4	16.8

[a] This category included propane, ethylene glycol, ethanol, methanol, methane and ethane.

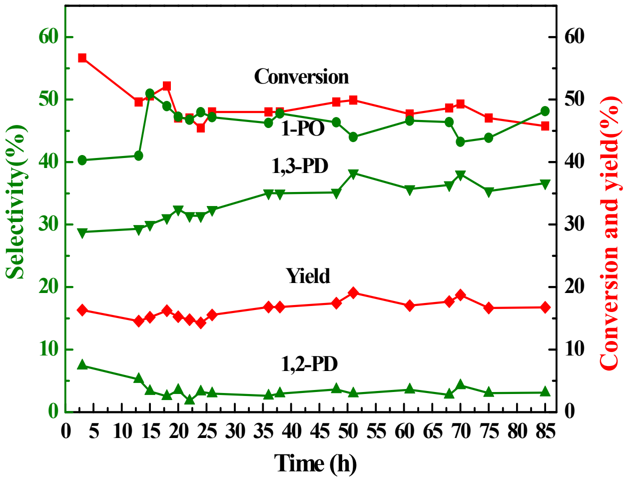


Fig. 1. Stability of 0.1La/Pt/WO$_x$ over time. Conditions: fixed-bed reactor at 413 K, 1.0 MPa, gas hourly space velocity of 1000 h^{-1}, liquid hourly space velocity of 1 h^{-1}, 5 wt% glycerol.

remarkably enhanced the 1,3-PD selectivity (from 48.2% to 57.0%) although the glycerol conversion decreased to some extent. We assume that the inherently higher activity of the Pt/WO$_x$/Al$_2$O$_3$ was responsible for the lesser extent of activity enhancement on adding the promoters. It should be noted that improved selectivity at the cost of a slight loss of activity is the most acceptable scenario with regard to practical applications. In this regard, La is the better promoter.

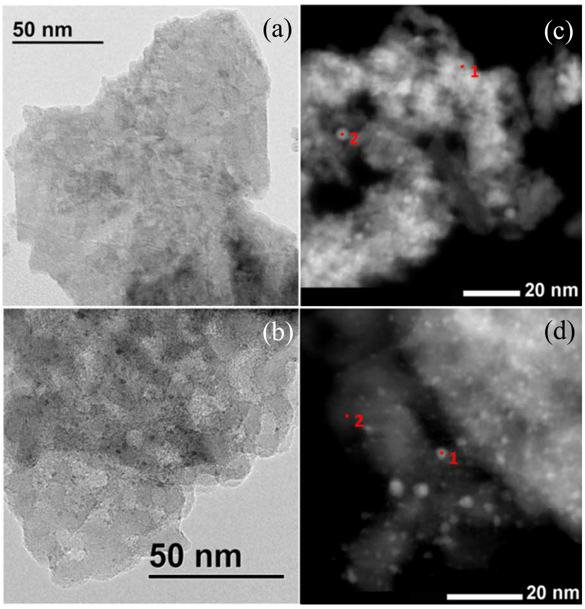
To illustrate the effects of promoters on hydrogenolysis performance with or without the Al$_2$O$_3$ support, further investigations were performed, using La as a model promoter.

In principle, hydrogenolysis requires acidic sites for dehydration and metallic sites for hydrogenation, and the selective hydrogenolysis of glycerol to 1,3-PD involves the concerted functioning of these two types of sites. For this reason, the acidity of a catalyst is widely accepted as playing a crucial role in glycerol conversion and product selectivity [23, 24]. According to the NH$_3$ adsorption results (Table 2), the addition of La did indeed generate a greater quantity of acidic sites on both the 0.1La/Pt/WO$_x$ and 0.1La/Pt/WO$_x$/Al$_2$O$_3$. In addition to these surface acid sites, as determined by NH$_3$ adsorption, we propose that acid sites could also have originated from Brønsted acid sites generated *in situ* by the heterolytic dissociation of H$_2$ on metal sites with subsequent spillover to the support [17]. In addition to the increased acid site concentration, the Brunauer-Emmett-Teller (BET) surface area and pore structure of the original Pt/WO$_x$ were both greatly decreased after the introduction of La, possibly due to partial collapse of the mesoporous WO$_x$ structure during calcination. In the case of the Pt/WO$_x$/Al$_2$O$_3$, however, the BET surface area and pore structure were almost unchanged after La introduction, indicating the superior mechanical strength of the Al$_2$O$_3$ support compared to the WO$_x$.

Table 2
Textural parameters and acid properties of La-promoted catalysts and reference catalysts.

Catalyst	Acid content (mmol/g)	BET (m^2/g)	D_p (nm)
Pt/WO$_x$	0.65	82	6.5
0.1La/Pt/WO$_x$	0.86	62	5.0
Pt/WO$_x$/Al$_2$O$_3$	0.40	105	9.0
0.1La/Pt/WO$_x$/Al$_2$O$_3$	0.50	101	9.3

TEM and HAADF-STEM images demonstrated aggregations of Pt single/pseudo-single atoms after La introduction (Fig. 2), which may have been caused by the high temperature calcination following impregnation. In contrast, EDS results showed that Pt species were only partially aggregated, and that there were still a large number of single/pseudo-single Pt atoms highly dispersed on the W species. In addition, the majority of the La species were found to be associated with Pt species, in



Element (%)	Position 1	Position 2
La	0.3	0
Pt	2.4	24.3
W	93.9	72.1

Element (%)	Position 1	Position 2
La	0.71	0
Pt	21.4	0.7
W	22.2	16.2

Fig. 2. TEM images of (a) 0.1La/Pt/WO$_x$ and (b) 0.1La/Pt/WO$_x$/Al$_2$O$_3$, and HAADF-STEM images of (c) 0.1La/Pt/WO$_x$ and (d) 0.1La/Pt/WO$_x$/Al$_2$O$_3$. The tables present STEM-EDS elemental analysis data for positions 1 and 2.

accordance with the deposition sequence of each component.

It has been reported that La possesses unique properties for catalytic cellulose conversion [25]. In the present study, La also exhibited a superior promotional effect for Pt-W catalysts during the selective hydrogenolysis of glycerol to 1,3-PD, thus it was thought that optimization of the La content might provide opportunities to further improve the hydrogenolysis performance. However, additional evaluation (Table 3) demonstrated that the use of a greater quantity of La both lowered glycerol conversion and decreased 1,3-PD selectivity, likely due to over-coverage of the active Pt sites by La species. Further investigation of the deposition sequence of La relative to Pt on the WO_x/Al_2O_3 sample showed that La must be introduced after Pt loading, otherwise the activity is greatly decreased upon introduction of the La. This result suggests that the coverage of the highly active Pt sites by a very small amount of La tends to enhance selectivity without much activity loss.

3.2. The effects of noble metal promoters

Ru, Ir, and Rh were introduced to Pt/WO_x and $Pt/WO_x/Al_2O_3$ with a loading of 0.1 wt %, respectively, and the promotional effects were examined during the hydrogenolysis of glycerol under optimized reaction conditions (Table 4). In the case of the Pt/WO_x, the Ru promoted material showed similar performance to the mother catalyst (Entry 2), while Ir and Rh promoters significantly decreased the glycerol conversion (from 37.4% to approximately 26.3%) but maintained the 1,3-PD selectivity at approximately 35.0% (Entries 3 and 4). Similarly, no obvious effect was identified when using the $Ru/Pt/WO_x/Al_2O_3$, indicating that Ru has the same function with and without a support. In contrast, the negative effect of Rh was eliminated when employing Al_2O_3 as the support, and the yield of 1,3-PD returned to 32.4%. In addition, introducing Ir to the $Pt/WO_x/Al_2O_3$ decreased not only the glycerol conversion but also the 1,3-PD selectivity, indicating the negative effects were more pronounced on supported catalysts. Chemical adsorption results demonstrated that variation in the initial acid amounts over the Al_2O_3 supported catalysts (from 0.40 to 0.39 mmol/g) was less than that over the Pt/WO_x (from 0.65 to 0.55 mmol/g) after Ir introduction, suggesting that the hydrogenolysis reactivity is not highly correlated with the initial acid amount. As well, compared with the transition metal promoted catalysts, that decreased the H_2 uptake from 0.067 to the range of 0.046 to 0.049 mmol/g, the use of Ir greatly decreased the H_2 uptake, from 0.067 to 0.024 mmol/g. This effect most likely was responsible for the inferior performance of this catalyst during the hydrogenolysis of glycerol to 1,3-PD.

Electron microscopy (Fig. 3) shows significant aggregation of Pt on the Pt/WO_x after Ir introduction, consistent with the H_2 adsorption results, and presumably responsible for the low activity of this material during the hydrogenolysis reaction. The Pt particle sizes were maintained over the supported catalysts, indicating that the presence of an Al_2O_3 support may facilitate the stabilization of these particles. Taking the chemical H_2 adsorption results into account, the significant decrease in the H_2 uptake over the Ir promoted $Pt/WO_x/Al_2O_3$ is attributed to the change in electronic structure, rather than particle size, of the active Pt species, which greatly influenced the performance of this material during the selective hydrogenolysis of glycerol.

Table 3
The effects of La on Pt-W catalysts during hydrogenolysis of glycerol.

Entry	Catalyst	Conv. (%)	Selectivity (%)					Yield (%)
			2-PO	1-PO	1,2-PD	1,3-PD	Others [a]	
1	Pt/WO_x	37.4	5.1	50.3	2.3	35.1	7.2	13.1
2	$0.1La/Pt/WO_x$	39.9	4.8	44.7	2.8	41.3	6.4	16.5
3	$0.2LaPt/WO_x$	28.6	5.9	45.2	5.7	38.5	4.7	11.0
4	$0.4LaPt/WO_x$	17.0	5.9	47.1	4.1	37.3	5.6	6.3
5	$0.5LaPt/WO_x$	14.8	6.1	45.4	4.0	37.7	6.8	5.6
6	$Pt/WO_x/Al_2O_3$	65.4	7.4	23.2	7.2	48.2	14.0	31.5
7	$0.1La/Pt/WO_x/Al_2O_3$	47.4	9.5	24.1	12.5	56.9	1.3	27.0
8	$Pt/0.1La/WO_x/Al_2O_3$	37.5	4.2	12.2	14.0	51.1	18.5	19.2
9	$Pt\text{-}0.1La/WO_x/Al_2O_3$	32.9	7.3	17.2	14.9	50.0	10.6	16.4

[a] This category included propane, ethylene glycol, ethanol, methanol, methane and ethane.

Table 4
The effects of noble metal promoters on Pt-W catalysts during hydrogenolysis of glycerol.

Entry	Catalyst	Conv. (%)	Selectivity (%)					Yield (%)
			2-PO	1-PO	1,2-PD	1,3-PD	Others [a]	
1	Pt/WO_x	37.4	5.1	50.3	2.3	35.1	7.2	13.1
2	$0.1Ru/Pt/WO_x$	33.6	5.1	49.9	2.6	35.5	6.9	12.0
3	$0.1Ir/Pt/WO_x$	25.6	5.6	53.0	4.5	34.4	2.5	8.8
4	$0.1Rh/Pt/WO_x$	26.3	5.9	50.2	4.0	33.1	6.8	8.7
5	$Pt/WO_x/Al_2O_3$	65.4	7.4	23.2	7.2	48.2	14.0	31.5
6	$0.1Ru/Pt/WO_x/Al_2O_3$	58.1	7.7	26.2	9.2	50.0	6.9	29.1
7	$0.1Ir/Pt/WO_x/Al_2O_3$	55.7	6.4	33.1	6.1	41.1	13.3	22.9
8	$0.1Rh/Pt/WO_x/Al_2O_3$	67.7	5.2	19.8	9.3	47.8	17.9	32.4

[a] This category included propane, ethylene glycol, ethanol, methanol, methane and ethane.

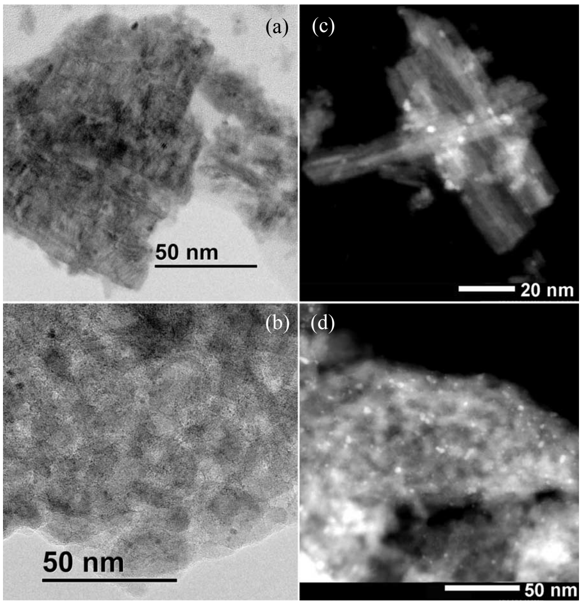


Fig. 3. TEM images of (a) $0.1Ir/Pt/WO_x$ and (b) $0.1Ir/Pt/WO_x/Al_2O_3$, and HAADF-STEM images of (c) $0.1Ir/Pt/WO_x$ and (d) $0.1Ir/Pt/WO_x/Al_2O_3$.

3.3. *The effect of impregnation sequence*

Previous studies have demonstrated that the addition sequence of the AlO_x promoter strongly influences the hydrogenolysis reactivity and the product selectivities [22]. Therefore, taking Pt/WO_x and $Pt/WO_x/Al_2O_3$ as reference catalysts, the effects of varying the Al and W impregnation sequence were investigated (Table 5). The introduction of either W or Al species to the Pt/WO_x resulted in lower reactivity (glycerol conversion decreased from 37.4% to 27.1 % or 17.0%, respectively), owing to the coverage of active sites, while no significant improvements were identified in the selectivity for 1,3-PD. Similar effects were observed when introducing W to the $Pt/WO_x/Al_2O_3$ catalyst. These results imply that merely covering the active Pt sites by other species cannot enhance the selectivity for 1,3-PD, although it does decrease the glycerol conversion. To probe the interactions between Pt and WO_x, we deposited a small amount of WO_x species on the Pt/Al_2O_3 mother catalyst (Entries 6 and 7). In this case, the predominant product from glycerol hydrogenolysis was 1,2-PD rather than 1,3-PD. However, further increasing the amount of WO_x (Entries 8 and 9) led to more 1,3-PD and less 1,2-PD, akin to the results obtained from a typical $Pt/WO_x/Al_2O_3$ catalyst. These results strongly suggest that the interface between the Pt and WO_x determines the selective hydrogenolysis of glycerol to give 1,3-PD, irrespective of their deposition sequence. Therefore, future work may focus on the design of more selective catalysts by maximizing the Pt/WO_x interface.

4. Conclusions

In summary, a diverse range of promoters, including transition and noble metals, was introduced to Pt/WO_x and $Pt/WO_x/Al_2O_3$. La was the most effective promoter, and the introduction of 0.1% La improved catalytic activity and selectivity for 1,3-PD, as well as the stability of Pt/WO_x. However, the significant increase in 1,3-PD selectivity came at the cost of a slight activity loss in the case of the $Pt/WO_x/Al_2O_3$. In some instances, the same promoter exhibited different effects with or without an Al_2O_3 support. Fe promoted Pt/WO_x and Re promoted $Pt/WO_x/Al_2O_3$ both demonstrated superior 1,3-PD productivity relative to the unpromoted catalysts, while the opposite effect was observed when varying the mother catalysts. In addition, some other promoted catalysts, such as Zr and Sn promoted Pt/WO_x and Fe and Zr promoted $Pt/WO_x/Al_2O_3$, showed slightly decreased production of 1,3-PD but still have significant potential in practical applications. This is because the introduction of promoters sometimes enhances the stability of the catalysts, which might be even more significant than the reactivity itself. Characterization of selected catalysts implied that the promotion mechanism likely results from modifying the electronic structure of the active Pt species. Hydrogenolysis performance is not highly correlated with original acid amounts, and therefore measurements of acidic sites generated *in situ* will be of great importance in future work to provide insight into the reaction mechanism and allow the rational design of such catalysts.

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Table 5
The effect of impregnation sequence and WO_x amount on hydrogenolysis of glycerol over Pt-W catalysts.

Entry	Catalyst	Conv. (%)	Selectivity (%)					Yield (%)
			2-PO	1-PO	1,2-PD	1,3-PD	Others [a]	
1	Pt/WO_x	37.4	5.1	50.3	2.3	35.1	7.2	13.1
2	$0.1W/Pt/WO_x$	27.1	5.6	46.2	8.0	30.0	10.2	8.2
3	$0.1Al/Pt/WO_x$	17.0	5.5	45.9	4.7	35.5	8.4	6.1
4	$Pt/WO_x/Al_2O_3$	65.4	7.4	23.2	7.2	48.2	14.0	31.5
5	$0.1W/Pt/WO_x/Al_2O_3$	44.1	8.2	24.1	10.0	47.1	10.6	20.8
6	$0.5W/Pt/Al_2O_3$	5.4	1.8	5.9	68.9	3.0	20.4	0.2
7	$1W/Pt/Al_2O_3$	6.5	2.5	9.9	56.0	2.8	28.8	0.2
8	$4W/Pt/Al_2O_3$	10.1	4.7	12.9	32.6	34.8	15.0	3.5
9	$8W/Pt/Al_2O_3$	8.7	7.5	16.6	17.5	43.9	14.5	3.8

[a] This category included propane, ethylene glycol, ethanol, methanol, methane and ethane.

Graphical Abstract

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Effect of promoters on the selective hydrogenolysis of glycerol over Pt/W-containing catalysts

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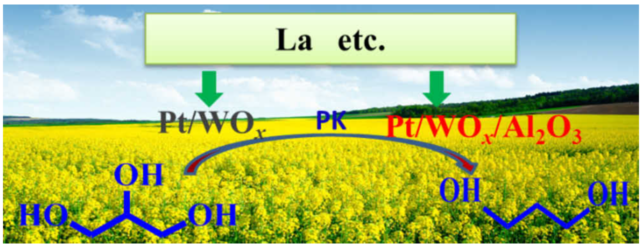

Different promoters were introduced to Pt/WO_x and $Pt/WO_x/Al_2O_3$ catalysts for the selective hydrogenolysis of glycerol to 1,3-propanediol. The effects of these promoters on the hydrogenolysis performance and product selectivity were investigated and detailed comparisons were made both with and without Al_2O_3 supports.

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