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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/Al₂O₃ 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/Al₂O₃ catalyst. Transmission electron microscopy, high angle annular dark field scanning tunneling electron microscopy and NH₃-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.

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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 poly(trimethylene terephthalate) (PTT) [9,10]. Whereas the synthesis of 1,2-propanediol (1,2-PD) can be ac-

complished 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 H₂ pressures (i.e. 1 MPa), 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 Al₂O₃ 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 Al₂O₃ 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/Al₂O₃ 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/Al₂O₃.

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 WCl₆ 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 H₂PtCl₆, followed by drying at 323 K for 6 h under vacuum.

Noble metal promoted catalysts were prepared by impregnating the Pt/WO_x in RhCl₃·3H₂O, RuCl₃·3H₂O, or H₂IrCl₆ 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 NH₄ReO₄, La(NO₃)₃·6H₂O, Zr(NO₃)₂·5H₂O, Al(NO₃)₃·9H₂O, Fe(NO₃)₃·9H₂O, Zn(NO₃)₂·6H₂O, Ce(NO₃)₃·6H₂O, SnCl₄·5H₂O, Ga(NO₃)₃·4.5H₂O, 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 H₂ at 573 K prior to reaction trials.

2.1.2. Preparation of the promoted Pt/WO_x/Al₂O₃ catalyst

The Pt/WO_x/Al₂O₃ catalyst was prepared using a sequential impregnation method. WO_x/Al₂O₃ 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 Al₂O₃ 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/Al₂O₃. This material was then impregnated with an aqueous solution of H₂PtCl₆·6H₂O, followed by drying at 383 K for 12 h and calcination at 573 K for 3 h to obtain the Pt/WO_x/Al₂O₃ 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 promoters to the Pt/WO_x/Al₂O₃ 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/Al₂O₃, where the M loading was fixed at 0.1 wt% as calculated based on the mother catalyst.

For comparison purposes, M-Pt/WO_x/Al₂O₃ catalysts were also prepared by co-impregnation of WO_x/Al₂O₃ using a solution of H₂PtCl₆·6H₂O 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/Al₂O₃ catalysts were prepared by sequential incipient wetness impregnation of WO_x/Al₂O₃ with solutions of the corresponding metal precursor and H₂PtCl₆·6H₂O.

The WO_x/Pt/Al₂O₃ catalyst was prepared via a sequential impregnation method. The initial Pt/Al₂O₃ catalyst was prepared by impregnation of Al₂O₃ samples with an aqueous solution of H₂PtCl₆·6H₂O, 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/Al₂O₃ was prepared by impregnation of Pt/Al₂O₃ 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 H₂ and then filled with H₂ 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/Al₂O₃, except using a 3 wt% glycerol solution, an initial H₂ 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) = (Conv._{max} – Conv._{final}) × 100 / (t × 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.

NH₃-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 NH₃ adsorption was calculated accordingly.

H₂ adsorption trials were conducted with the same instrument to measure the H₂ uptake of catalysts. The samples were reduced in H₂ 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 H₂ 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/Al₂O₃, 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 ₂ O ₃	65.4	7.4	23.2	7.2	48.2	14.0	31.5
11	0.1La/Pt/WO _x /Al ₂ O ₃	47.4	9.5	24.1	12.5	56.9	1.3	27.0
12	0.1Fe/Pt/WO _x /Al ₂ O ₃	38.3	6.2	21.8	12.2	57.0	2.8	21.8
13	0.1Zr/Pt/WO _x /Al ₂ O ₃	55.9	7.1	26.4	5.8	49.1	11.6	27.4
14	0.1Re/Pt/WO _x /Al ₂ O ₃	67.9	10.6	29.6	8.7	49.0	2.1	33.3
15	0.1Sn/Pt/WO _x /Al ₂ O ₃	21.0	9.7	32.4	16.0	32.6	9.3	6.8
16	0.1Ce/Pt/WO _x /Al ₂ O 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/Al₂O₃ 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 Al₂O₃ 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

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

glycerol conversion and product selectivity [23, 24]. According to the NH₃ 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/Al₂O₃. In addition to these surface acid sites, as determined by NH₃ adsorption, we propose that acid sites could also have originated from Brønsted acid sites generated *in situ* by the heterolytic dissociation of H₂ 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/Al₂O₃, however, the BET surface area and pore structure were almost unchanged after La introduction, indicating the superior mechanical strength of the Al₂O₃ support compared to the WO_x.

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

Fig. 2. TEM images of (a) 0.1La/Pt/WO_x and (b) 0.1La/Pt/WO_x/Al₂O₃, and HAADF-STEM images of (c) 0.1La/Pt/WO_x and (d) 0.1La/Pt/WO_x/Al₂O₃. The tables present STEM-EDS elemental analysis data for positions 1 and 2.

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

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 $\text{WO}_x/\text{Al}_2\text{O}_3$ 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 $\text{Pt}/\text{WO}_x/\text{Al}_2\text{O}_3$ 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

$\text{Ru}/\text{Pt}/\text{WO}_x/\text{Al}_2\text{O}_3$, 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 $\text{Pt}/\text{WO}_x/\text{Al}_2\text{O}_3$ 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 $\text{Pt}/\text{WO}_x/\text{Al}_2\text{O}_3$ 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	$\text{Pt}/\text{WO}_x/\text{Al}_2\text{O}_3$	65.4	7.4	23.2	7.2	48.2	14.0	31.5
7	0.1La/ $\text{Pt}/\text{WO}_x/\text{Al}_2\text{O}_3$	47.4	9.5	24.1	12.5	56.9	1.3	27.0
8	Pt/0.1La/ $\text{WO}_x/\text{Al}_2\text{O}_3$	37.5	4.2	12.2	14.0	51.1	18.5	19.2
9	Pt-0.1La/ $\text{WO}_x/\text{Al}_2\text{O}_3$	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	$\text{Pt}/\text{WO}_x/\text{Al}_2\text{O}_3$	65.4	7.4	23.2	7.2	48.2	14.0	31.5
6	0.1Ru/ $\text{Pt}/\text{WO}_x/\text{Al}_2\text{O}_3$	58.1	7.7	26.2	9.2	50.0	6.9	29.1
7	0.1Ir/ $\text{Pt}/\text{WO}_x/\text{Al}_2\text{O}_3$	55.7	6.4	33.1	6.1	41.1	13.3	22.9
8	0.1Rh/ $\text{Pt}/\text{WO}_x/\text{Al}_2\text{O}_3$	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/Al₂O₃, and HAADF-STEM images of (c) 0.1Ir/Pt/WO_x and (d) 0.1Ir/Pt/WO_x/Al₂O₃.

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/Al₂O₃ 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/Al₂O₃ 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/Al₂O₃ 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/Al₂O₃ 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. Conclusion

In summary, a diverse range of promoters, including transition and noble metals, was introduced to Pt/WO_x and Pt/WO_x/Al₂O₃. 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/Al₂O₃. In some instances, the same promoter exhibited different effects with or without an Al₂O₃ support. Fe promoted Pt/WO_x and Re promoted Pt/WO_x/Al₂O₃ 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/Al₂O₃, 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 ₂ O ₃	65.4	7.4	23.2	7.2	48.2	14.0	31.5
5	0.1W/Pt/WO _x /Al ₂ O ₃	44.1	8.2	24.1	10.0	47.1	10.6	20.8
6	0.5W/Pt/Al ₂ O ₃	5.4	1.8	5.9	68.9	3.0	20.4	0.2
7	1W/Pt/Al ₂ O ₃	6.5	2.5	9.9	56.0	2.8	28.8	0.2
8	4W/Pt/Al ₂ O ₃	10.1	4.7	12.9	32.6	34.8	15.0	3.5
9	8W/Pt/Al ₂ O 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/Al₂O₃ 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 Al₂O₃ supports.

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助剂对铂-钨催化剂体系催化氢解甘油制1,3-丙二醇性能的影响

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摘要: 甘油作为生物柴油产业的副产物大量过剩, 通过甘油氢解制备具有高附加值的丙二醇既符合原子经济的原则, 又具有重要的学术意义和应用价值。尤其是选择氢解制得 1,3-丙二醇, 因其产物在新型聚酯材料合成中不可替代的作用而备受关注, 被认为是最具工业应用潜力的甘油转化工艺之一。目前, 可高选择性制得 1,3-丙二醇的催化剂体系主要是为铈-铈催化剂和铂-钨催化剂两类。前期工作表明, 氧化钨负载的铂单原子/准单原子催化剂 (Pt/WO_x) 具有优异的低压活性 (1 MPa 氢气) 和 1,3-丙二醇时空收率。然而在该温和条件下, 催化产物仍然以过度氢解的产物正丙醇为主。一般来讲, 引入助剂可以通过改变活性组分的电子结构、覆盖不利反应位点、调变载体表面化学性质等来改变催化剂的催化活性、选择性和稳

定性. 我们以单原子/准单原子催化剂 Pt/WO_x 和担载型催化剂 $\text{Pt}/\text{WO}_x/\text{Al}_2\text{O}_3$ 为催化剂母体, 引入过渡金属和贵金属助剂, 考察助剂对氢解反应活性和选择性的影响, 并对比有无氧化铝载体时助剂对反应活性的影响.

对于 Pt/WO_x 体系, La 和 Fe 的引入有助于甘油转化率和 1, 3-丙二醇选择性的提高, 同时也明显地提高了催化剂的稳定性. 其中 0.1% La 是最佳引入量. 然而, 对于担载型催化剂 $\text{Pt}/\text{WO}_x/\text{Al}_2\text{O}_3$, La 的引入在提高 1,3-丙二醇选择性的同时, 甘油的转化率也有一定程度下降. 但由于 $\text{Pt}/\text{WO}_x/\text{Al}_2\text{O}_3$ 催化剂的本征活性较高, 通过加入助剂提高 1, 3-丙二醇的选择性在实际应用中更为重要. 表征分析表明, 无论对于 Pt/WO_x 还是 $\text{Pt}/\text{WO}_x/\text{Al}_2\text{O}_3$ 催化剂, 大部分的 La 都在 Pt 颗粒上; 同时 La 的引入提高了催化剂的酸量.

在贵金属助剂中, Ru , Ir 改性的 Pt/WO_x 和 $\text{Pt}/\text{WO}_x/\text{Al}_2\text{O}_3$ 催化剂上, 1,3-丙二醇的收率均有所降低, Ru 助剂的降低幅度较小. 相反, 助剂 Rh 对 Pt/WO_x 和 $\text{Pt}/\text{WO}_x/\text{Al}_2\text{O}_3$ 催化剂上反应性能的影响截然不同: $\text{Rh}/\text{Pt}/\text{WO}_x$ 催化剂上 1,3-丙二醇的收率从 13.1% 降到 8.7%, $\text{Rh}/\text{Pt}/\text{WO}_x/\text{Al}_2\text{O}_3$ 的 1,3-丙二醇收率从 31.5% 略升到 32.4%.

另外, 由于前期研究表明助剂铝的担载顺序对催化活性有重要影响, 因此我们对铂、钨、铝的担载顺序进行了考察. 研究表明, 在活性组分铂上担载铝或钨物种对催化活性有一定程度的抑制; 催化剂体系中钨的含量直接影响甘油的转化率和产物的选择性; 含量过少时, 甘油转化率极低并以 1,2-丙二醇为主要产物.

虽然大部分助剂对铂-钨催化剂体系没有明显的促进作用, 但是助剂的添加通常可以抑制活性组分的烧结、提高催化剂的稳定性; 因此, 我们筛选出的 La , Fe , Re , Ru , Rh 等助剂仍具有深入研究的价值和工业应用的潜力.

关键词: 甘油; 氢解; 1,3-丙二醇; 氧化钨; 助剂

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