available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

Pt/Nb-WO_x for the chemoselective hydrogenolysis of glycerol to 1,3-propanediol: Nb dopant pacifying the over-reduction of WO_x supports

Man Yang^{a,b}, Xiaochen Zhao^{a,*}, Yujing Ren^{a,b}, Jia Wang^c, Nian Lei^{a,b}, Aiqin Wang^{a,#}, Tao Zhang^a^a State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China^b University of Chinese Academy of Science, Beijing 100049, China^c College of Forestry, Northwest A&F University, Yangling 712100, Shaanxi, China

ARTICLE INFO

Article history:

Received 2 March 2018

Accepted 10 April 2018

Published 5 June 2018

Keywords:

Nb-doped WO_x

Glycerol

1,3-propanediol

Selective hydrogenolysis

ABSTRACT

Selective hydrogenolysis of glycerol to 1,3-propanediol (1,3-PD) is an important yet challenging method for the transformation of biomass into value-added chemicals due to steric hindrance and unfavorable thermodynamics. In previous studies, chemoselective performances were found demanding and sensitive to H₂ pressure. In this regard, we manipulate the chemical/physical characteristics of the catalyst supports via doping Nb into WO_x and prepared 1D needle-, 2D flake-, and 3D sphere-stack mesoporous structured Nb-WO_x with increased surface acid sites. Moreover, Nb doping can successfully inhibit the over-reduction of active W species during glycerol hydrogenolysis and substantially broaden the optimal H₂ pressure from 1 to 5 MPa. When Nb doping is 2%, supported Pt catalysts showed promising performance for the selective hydrogenolysis of glycerol to 1,3-PD over an unprecedentedly wide H₂ pressure range, which will guarantee better catalyst stability in the long run, as well as expand their applications to other hydrogen-related reactions.

© 2018, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Tungsten oxide, which shares perovskite units, has attracted much attention for thermocatalysis, photocatalysis, and photoelectrocatalysis [1,2]. Tungsten oxide is well known for its oxophilic nature, which renders the lattice capable of withstanding numerous oxygen deficiencies in the bulk without compromising the crystal phase stability and allows the formation of a series of tungsten sub oxides (WO_x such as WO_{2.92}, WO_{2.84}, and WO_{2.72}) [3–5]. Intriguingly, WO_x is favored for a variety of applications, as oxygen vacancies can serve as shallow donors

and modify the electronic structure of tungsten oxide, thus enhancing the dispersion of supported active metal sites [6] and adsorption of surface species (H₂, CO₂, alcohols etc.) [7]. Recently, WO_x was found to be catalytically active in the hydrogenation of olefins and aryl nitro groups with a linear activity dependence on oxygen vacancies [8], which indicates their crucial role in H₂ activation. Moreover, the acidity of tungsten oxide can also be adjusted via a slight reduction of W species accompanied by H^{δ+} release. Therefore, WO_x-containing catalysts were found to be of high value in a series of H₂-related biomass conversion processes [9–17].

* Corresponding author. Tel: +86-411-84379416; E-mail: zxc@dicp.ac.cn

Corresponding author. Tel: +86-411-84379348; Fax: +86-411-84685940; E-mail: aqwang@dicp.ac.cn

This work was supported by the National Natural Science Foundation of China (2169008, 21690084, 21673228, 21303187, 21403218), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB17020100), Key Projects for Fundamental Research and Development of China (2016YFA0202801), and DICP ZZBS 201612.

DOI: 10.1016/S1872-2067(18)63074-8 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 6, June 2018

For instance, in the selective hydrogenolysis of glycerol, WO_x , together with Pt species, was found to be active in producing 1,3-propanediol (1,3-PD) [18–25]. The production of 1,3-PD is rather challenging due to steric and thermodynamic reasons [26,27], but it is of great value and widely used in the polyester industry. As the hydrogenolysis reaction greatly relies on the participation and activation of H_2 , a high H_2 pressure was taken for granted in previous studies, till we reported a novel single/pseudo-single Pt atom catalyst (Pt-SAC) with promising performance for 1,3-PD production at a very low H_2 pressure [6]. However, its support, WO_x , exhibited a poor pressure-bearing capacity, which is the primary reason for catalyst deactivation in the long run. Moreover, the outstanding performance of Pt-SACs reduced greatly as H_2 pressure fluctuated, thus limiting their long-run applications as well as their significance in biomass conversion.

On WO_x -containing catalysts, a redox cycle between W^{5+} and W^{6+} was detected during the selective hydrogenolysis of glycerol [28]. This cycle, resulting from H_2 activation and spillover, is essential for 1,3-PD production by stabilizing active in-situ generated Brønsted acid sites and hydrides as analogs of frustrated Lewis pairs [29]. Nevertheless, the severe conditions required for H_2 activation, on the other hand, may cause a slight over-reduction of the active W species beyond the redox cycle, thus rendering the hydrogenolysis performance sensitive to H_2 pressure when compared to conventional nano-catalysts. Similarly, conflicts between H_2 activation and W over-reduction also occurred on Pt-SACs [6]. The only difference is that the Pt-SACs cut both ways in using H_2 , the pros in easy H_2 activation and the cons in easy W-species over-reduction. Therefore, a rational design of a H_2 -tolerating WO_x support, without sacrificing its role in H_2 activation, may suppress the catalyst deactivation caused by W over-reduction and guarantee superior hydrogenolysis performance in the long run, which is highly desirable in both practical applications and academic studies.

Doping, defined as the incorporation of foreign atoms or ions into host lattices, is one of the most effective methods to modify the electronic structure and chemical properties of functional metal oxides [28,30–34]. Recently, Te-doped tungsten oxide wires were found to exhibit high thermal and hydrothermal stability [35]. Therefore, in this investigation, we explored the idea of introducing a dopant, in particular Nb, into WO_x via a facile solvothermal strategy and investigated the structure, chemistry, and performance of the doped catalyst in the selective hydrogenolysis of glycerol. The obtained Nb-doped WO_x maintained a high surface area (above $130 \text{ m}^2/\text{g}$) when the Nb doping concentration was as high as 5 wt%; the morphology transformed to 2D flake-stack and 3D sphere-stack clusters from 1D needle-stack clusters as Nb doping increased. When Nb doping is above 2 wt%, the over-reduction of W species can be greatly inhibited on Pt/Nb- WO_x . The optimized Nb doping is ca. 2 wt%, at which conflicts between H_2 activation and W over-reduction were successfully eased. The optimized catalyst, 2%Nb- WO_x , supported highly dispersed Pt catalysts, leading to promising hydrogenolysis performance (ca. 40% glycerol conversion and ca. 30% 1,3-PD selectivity) over an unprecedentedly wide opera-

tion window (1 to 5 MPa H_2).

2. Experimental

2.1. Chemicals

WCl_6 (Aladdin, >99.0%), NbCl_5 (Aladdin, >99.0%), absolute ethanol (Tianjin Damao Chemical Reagent Technologies Co., Ltd., >99.7%), H_2PtCl_6 solution (Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd., >37.0%), glycerol (Tianjin Kermel Chemical Reagent Co., Ltd., >99.0%), and cellobiose (J&K Scientific, >98.0%) were used in this study. All the chemicals were used as-received without further purification. Deionized water was used in all experiments.

2.2. Preparation of $n\%\text{Nb-WO}_x$ oxides

Nb-doped WO_x was prepared via a modified solvothermal procedure [6]. In detail, WCl_6 (3 g) and NbCl_5 ($\text{mol}_{\text{Nb}}:\text{mol}_{\text{W}} = 0.1, 2, \text{ and } 5$) were added to ethanol (100 mL) while stirring at 500 r/min for 20 min and then transferred to a 150 mL Teflon-lined autoclave and heated at 160°C for 36 h in an oven. After cooling to room temperature, dark blue products were obtained, which were washed separately with ethanol and water thrice. Nb-doped WO_x was obtained by drying the as-prepared samples at 50°C for 6 h in vacuum. The samples are denoted as $n\%\text{Nb-WO}_x$, where $n\%$ represents the molar ratio of Nb to W.

2.3. Preparation of catalysts

Pt/Nb- WO_x was prepared by incipient wetness impregnation with a H_2PtCl_6 solution (Pt = 2 wt%), followed by drying at 50°C for 6 h in vacuum, reduction in flowing H_2 at 300°C for 1 h, and then passivated by 1% O_2/N_2 for at least 4 h at room temperature.

The reference catalyst, Pt/ WO_3 , was prepared by incipient wetness impregnation with H_2PtCl_6 solution (Pt = 2 wt%) on commercial WO_3 , followed by drying at 50°C for 6 h in vacuum, reduction in flowing H_2 at 300°C for 1 h, and then passivated by 1% O_2/N_2 for at least 4 h at room temperature.

2.4. Characterization

Nitrogen adsorption-desorption measurements were performed at -196°C on a Micromeritics ASAP2010 instrument. The specific surface areas (A_{BET}) were calculated from the N_2 adsorption isotherm using the BET equation. The average pore diameter was estimated from the adsorption branches of the isotherms using the Barrett-Joyner-Halenda (BJH) method. The sample was firstly dehydrated at 110°C for 1 h and then degassed at 200°C for at least 4 h.

X-ray diffraction (XRD) patterns were obtained on a PANalytical X'pert diffractometer equipped with a $\text{Cu } K_\alpha$ radiation source. The instrument was operated in the continuous mode at 40 kV and 40 mA to collect data in the 2θ range of 10° to 80° .

High-resolution transmission electron microscopy (HRTEM) and high-angle annual dark-field scanning transmission elec-

tron microscopy (HAADF-STEM) images were acquired on a JEM-2100F Transmission Electron Microscope operating at 200 kV. The samples were prepared by ultrasonically dispersing the fine powders in ethanol and dripping them on porous C/Cu TEM grids.

Scanning electron microscopy (SEM) experiments were performed on a JSM-7800F electron microscope operating at 3.0 kV. The samples were pasted on a conductive carbon tape.

Raman spectra were generated using a Jobin Yvon HR 800 Dispersive Raman Spectrometer, operating at a resolution better than 2 cm^{-1} . Raman scattering was collected at room temperature in a static-scan mode in the $150\text{--}1200\text{ cm}^{-1}$ range at an excitation wavelength of 532 nm and power of ca. 0.1 mW, which was mild enough to avoid changes in the surface information.

Temperature-programmed desorption of NH_3 (NH_3 -TPD) was carried out on a Micromeritics Auto Chem II 2920 chemisorber equipped with a mass spectra detector. The samples were degassed in flowing He at $150\text{ }^\circ\text{C}$ for 1 h and then cooled down to $100\text{ }^\circ\text{C}$ to be ready for pulse adsorption. After adsorption saturation, the samples were heated from 100 to $800\text{ }^\circ\text{C}$ in a He stream at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$, while the desorbed NH_3 was monitored by a mass spectrometer system. During measurement, $m/e = 16$ was monitored to analyze desorbed NH_3 to avoid the interference of water.

Temperature-programmed reduction of hydrogen (H_2 -TPR) was performed on an Auto Chem II 2920 apparatus. In each measurement, the as-synthesized sample ($\sim 100\text{ mg}$) was loaded into a U-shaped quartz reactor and pretreated with Ar at $150\text{ }^\circ\text{C}$ for 1 h to remove adsorbed carbonates and hydrates. Next, after the sample cooled down to $-50\text{ }^\circ\text{C}$, the flowing gas was switched to 10% H_2/Ar and the sample was heated to $900\text{ }^\circ\text{C}$ at a ramping rate of $10\text{ }^\circ\text{C}/\text{min}$. The amount of H_2 consumed was monitored by a thermal conductivity detector (TCD), while a cold trap (a mixture of isopropanol and liquid nitrogen) was placed to remove generated water.

H_2 chemisorption was performed on an Auto Chem II 2920 apparatus. The samples were first dried at $150\text{ }^\circ\text{C}$ in Ar flow for 1 h. Subsequently, the samples were cooled down to $50\text{ }^\circ\text{C}$ in Ar and the flowing gas was switched to 10% H_2/Ar at $50\text{ }^\circ\text{C}$ for H_2 chemisorption.

X-ray photoelectron spectroscopy (XPS) was conducted on an ESCALAB 250 X-ray photoelectron spectrometer with a monochromated Al K_α anode. All the binding energies were calibrated for surface charging by referencing them to the energy of the C 1s peak at 284.6 eV .

2.5. Activity test

2.5.1. Selective hydrogenolysis of glycerol over Pt/Nb- WO_x

Hydrogenolysis of glycerol was carried out in a stainless-steel autoclave (Parr Instrument Company, 75 mL) with Teflon lining typically at 1 or 5 MPa H_2 pressure (measured at room temperature) and $160\text{ }^\circ\text{C}$ for 12 h, while stirring at 800 r/min. For each reaction, 0.3 g of the catalyst and 12 mL of glycerol aqueous solution (5 wt%) were placed in the autoclave and subjected to several cycles of flushing with H_2 to drive off

the air in the autoclave. After the reaction, the gas and liquid products were collected separately and analyzed by a gas chromatograph (GC, Agilent 7890B) equipped with a flame ionization detector (FID). A DB-FFAP capillary column (diameter 0.32 mm , length 30 m) was used for separation and 1-butanol was used as the internal standard. The conversion of glycerol (X_{glycerol}) and the selectivity (S) of each product were calculated using the following equations:

$$X_{\text{glycerol}} (\%) = (\text{mol}_{\text{glycerol consumed}}) / (\text{mol}_{\text{glycerol initially added}}) \times 100$$

$$S(\%) = (\text{mol}_{\text{carbon in specific product}}) / (\text{mol}_{\text{carbon in consumed glycerol}}) \times 100$$

$$S_{\text{others}} (\%) = 100 - \sum S(1,3\text{-PD} + 1,2\text{-PD} + 1\text{-PO} + 2\text{-PO})$$

Others include acetone, ethylene glycerol, ethanol, methanol, methane, ethane, and propane.

2.5.2. Hydrolysis of cellobiose over Nb- WO_x

Hydrolysis of cellobiose was performed in an autoclave of 20 mL capacity with Teflon lining, typically at an auto-generated pressure. The catalyst (50 mg) and 2 mL of a cellobiose aqueous solution (5 wt%) were placed in the autoclave and heated at $120\text{ }^\circ\text{C}$ for 1 h while stirring. The liquid products were collected and analyzed using a high-performance liquid chromatograph (HPLC, Agilent 1200) equipped with a refractive index detector (RID). A SUGER SC1011 capillary column (diameter 8.0 mm , 300 mm) was used for separation. An external standard method was employed. The conversion of cellobiose ($X_{\text{cellobiose}}$) and the selectivity of each liquid product were calculated using the following equations:

$$X_{\text{cellobiose}} (\%) = (\text{mol}_{\text{cellobiose consumed}}) / (\text{mol}_{\text{cellobiose initially added}}) \times 100$$

$$S_{\text{glucose}} (\%) = (\text{mol}_{\text{carbon in glucose}}) / (\text{mol}_{\text{carbon in consumed cellobiose}}) \times 100$$

3. Results and discussion

3.1. Mesoporous Nb-doped WO_x

The pore structures of Nb- WO_x oxides were analyzed by N_2 adsorption-desorption isotherms (Fig. 1). The type-IV isotherms indicated that slit mesopores were formed in Nb- WO_x oxides at Nb doping levels from 0.1% to 5.0%. As shown in Table 1, when the doping of Nb increased from 0.1% to 5%, the surface area of Nb- WO_x slightly increased from 126 to 144

Fig. 1. Nitrogen adsorption-desorption isotherms of WO_x , 0.1%Nb- WO_x , 2%Nb- WO_x , and 5%Nb- WO_x .

Table 1
Textural parameters of Nb-WO_x.

Material	Surface area (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)
WO _x	126	3.4	0.07
0.1%Nb-WO _x	130	4.9	0.08
2%Nb-WO _x	136	4.1	0.06
5%Nb-WO _x	144	3.2	0.06

m²/g, while the pore size increased at first and then decreased but generally was around 3–5 nm (Table 1). The maintaining effect in terms of the surface area and porosities is interesting and desirable in catalysis, because significant alterations in surface area and structural porosity, which usually occur during doping, might deteriorate the consequent catalytic performance [33,36]. Upon comparing the isotherm profiles, it is obvious that when the doping of Nb was above 2%, the hysteresis loop changed from type H₃ to H₄, while 0.1%Nb-WO_x shared a similar H₃ hysteresis with WO_x, indicating that large amounts of

Nb doping led to an alteration in the pore morphology.

The SEM images of Nb-WO_x (Fig. 2 and Fig. S1) demonstrate that the morphologies changed greatly with an increase in the doping amount of Nb. WO_x without doping showed a needle-stack morphology (Fig. 2(a)) [6] and this morphology did not change much after doping with a small amount of Nb (<1%, Fig. S1). In contrast, when the Nb content was between 1% and 2%, the samples exhibited flake-stack clusters (Fig. 2(d) and Fig. S1), while 5%Nb-doped WO_x formed sphere-stack clusters (Fig. 2(g)). Furthermore, in the HRTEM images (Fig. 2(b), and (c)), clear lattice fringes with a spacing of 0.377 nm (010) could be observed on WO_x (Fig. 2(c)), forming needle-shaped structures. On the other hand, the crystallization of 2%Nb-WO_x (Fig. 2(e), and (f)) and 5%Nb-WO_x (Fig. 2(h) and (i)) was greatly reduced and numerous amorphous clusters were found in the 2D flake-shaped and 3D sphere-shaped structures, which is consistent with the results of SEM analysis. To explore the introduction of Nb, as well as its dispersion, EDS mapping was conducted on both 2%Nb-WO_x and 5%Nb-WO_x and the results

Fig. 2. SEM images of WO_x (a), 2%Nb-WO_x (d), and 5%Nb-WO_x (g); HRTEM images of WO_x (b, c), 2%Nb-WO_x (e, f), and 5%Nb-WO_x (h, i); (j) EDS mapping images of W, O, and Nb corresponding to 2%Nb-WO_x.

Fig. 3. XRD patterns of WO_3 , 0.1%Nb- WO_3 , 2%Nb- WO_3 , and 5%Nb- WO_3 .

demonstrated that Nb was highly dispersed in doped WO_3 (Fig. 2(j), Fig. S2).

From the XRD patterns (Fig. 3), undoped WO_3 could be indexed as $\text{WO}_{2.72}$ (01–073–2177); its main peak centered at $2\theta = 23.4^\circ$ was assigned to the (010) lattice plane, which is consistent with the results of HRTEM. In the XRD patterns of Nb- WO_3 oxides, no niobium oxide phase could be found. The (010) peak located at around 23.4° and (020) peak located at around 47.9° slightly shifted toward lower angles, suggesting that Nb was inserted into the lattice, leading to lattice deformation, because the ionic radius of Nb^{5+} is greater than that of W^{5+} and W^{6+} [31]. In addition, the peaks at $2\theta = 24.4^\circ$, 34.2° , and 50.1° disappeared, while the peaks at 26.7° and 55.6° weakened when Nb doping was above 2%, indicating that the crys-

tallinity of WO_3 was greatly decreased and more amorphous clusters were formed in 2%Nb- WO_3 and 5%Nb- WO_3 , which is consistent with the HRTEM images (Fig. 2(e), (f), (h), and (i)).

To explore the formation mechanism of Nb- WO_3 , TEM images of 2%Nb- WO_3 and reference WO_3 were captured as functions of the solvothermal synthesis time. On the basis of the aforementioned characterization procedures, a formation mechanism is proposed (Fig. 4). (a) In the absence of Nb species, the W precursor formed amorphous WO_3 species, crystallized in the same direction, and consequently formed needle-like crystals. (b) In the presence of Nb species, Nb species might occupy W positions along the [010] direction, thus inhibiting 1D crystallization and promoting the crystallization of Nb- WO_3 in the form of a 2D flake structure.

To evaluate the vibration of W–O–W bonds, Raman spectroscopy was conducted on Nb- WO_3 . As shown in Fig. 5, peaks centered at around 975 cm^{-1} increased with an increase in the doping amount of Nb; these peaks are assigned to the stretching mode of the distorted terminal W=O bond on the surface and can extract protons in many surface reactions [6]. The bands at around 714 and 807 cm^{-1} were assigned to the stretching vibration of W–O–W bonds and they both shifted to lower wavenumbers with an increase in Nb doping, indicating that the stretching vibrations of the W–O–W bonds were weakened. As the vibration peak of Nb–O bonds appears at around 680 cm^{-1} [37], the red-shift of W–O–W after doping was attributed to the formation of W–O–Nb. Moreover, the relative intensity of these two stretching vibrations, W–O–W and W=O, increased with an increase in the amount of Nb used for doping, suggesting that the vibrations of planar modes increased [38].

The chemical states of W and Nb after Nb doping were determined by XPS (Fig. 6). In the tungsten core level (W 4f)

Fig. 4. Process of crystallization in WO_3 and Nb-doped WO_3 at various times during solvothermal treatment.

Fig. 5. Raman spectra of WO_x , 0.1%Nb- WO_x , 2%Nb- WO_x , and 5%Nb- WO_x .

spectrum (Fig. 6(a)), no obvious shift was observed in Nb- WO_x when compared to WO_x , indicating that the chemical state of W species remained unchanged after Nb doping. Besides, the peaks suggested a combination of W^{6+} (35.8 eV ($\text{W } 4f_{7/2}$) and 37.9 eV ($\text{W } 4f_{5/2}$)) and W^{5+} (34.9 eV ($\text{W } 4f_{7/2}$) and 37.0 eV ($\text{W } 4f_{5/2}$)) in the obtained WO_x and Nb- WO_x , respectively [31]. Fig. 6(b) shows the Nb 3d spectrum of 2%Nb- WO_x . Though the intensity was poor, the doublet peaks of Nb $3d_{5/2}$ and Nb $3d_{3/2}$ could be observed ambiguously, which confirmed that Nb was successfully introduced in WO_x in the form of Nb^{5+} (207.5 eV (Nb $3d_{5/2}$) and 210.2 eV (Nb $3d_{3/2}$)) [30].

3.2. Pt/Nb- WO_x catalysts

For the selective hydrogenolysis of glycerol, Pt-W-containing catalysts were found to be one of the few catalyst systems that could effectively produce 1,3-propanediol [6,39]. In our previous study, highly dispersed Pt was prepared on mesoporous WO_x and it yielded a promising performance under relatively mild conditions (140 °C, 1 MPa H_2). Neverthe-

Fig. 6. XPS spectra of W 4f of WO_x and 2%Nb- WO_x (a), Nb 3d of 2%Nb- WO_x (b).

less, the W species were over-reduced during the hydrogenolysis reaction, which is unfavorable in practical applications. In this regard, Nb doping on one hand led to significant morphological changes in WO_x from 1D needle-stack structures to 2D flake-stack and 3D sphere-stack structures; on the other hand, it might influence H_2 -spillover. Therefore, employing Nb- WO_x as the support might lead to a distinctive performance from Pt/ WO_x .

To investigate the dispersion of Pt on the obtained Nb- WO_x , XRD (Fig. 7), STEM, and HRTEM (Fig. 8, Fig. S3) were conducted. In Fig. 7, a new broad peak at $2\theta = 40.1^\circ$ appeared in the pattern of Pt/Nb- WO_x when compared to that of Nb- WO_x supports. To identify the affiliation of this new peak, Pt/ WO_3 and Pt/ WO_x were also analyzed as references. Over the conventional Pt/ WO_3 , split peaks (39.8° and 40.8°) were observed at around 40° , assigned to Pt (01-070-2057) and WO_x (00-030-1387) respectively, while over Pt/ WO_x only one broadened peak (40.3°) was observed, embarrassing the discrimination of Pt and WO_x due to the overlap of these two species. However, a discernible shift towards lower angles was observed in Pt/Nb- WO_x when compared to Pt/ WO_x , suggesting the possibility of slight Pt agglomeration or Nb insertion into the lattice. On the other hand, in the TEM measurements, no obvious Pt particles were observed (Fig. 8 and Fig. S3), probably due to the low contrast between Pt and W elements as well as the high dispersion of Pt species, indicating that Pt dispersion was hardly influenced by Nb doping.

According to our previous study [6], the activation of H_2 played a crucial role in the catalysis of the selective hydrogenolysis reaction. In particular, owing to its intrinsic oxophilic nature, WO_x was distinctive in H_2 dissociation and H stabilization. To evaluate the influence of Nb doping on H_2 adsorption and activation, H_2 -TPR of the as-synthesized samples and chemisorption of H_2 on the reduced samples were conducted. According to the H_2 chemisorption measurements, the H_2 -uptake increased as a function of Nb doping, from 137 $\mu\text{mol/g}$ (Pt/ WO_x) to 155 $\mu\text{mol/g}$ (Pt/0.1%Nb- WO_x) and 179 $\mu\text{mol/g}$ (Pt/2%Nb- WO_x). Because a good dispersion of Pt over

Fig. 7. XRD patterns of Pt/0.1%Nb- WO_x , Pt/2%Nb- WO_x , Pt/5%Nb- WO_x , Pt/ WO_x , and Pt/ WO_3 .

Fig. 8. HRTEM images of Pt/0.1%Nb-WO_x (a) and Pt/2%Nb-WO_x (b). HAADF-STEM images of Pt/0.1%Nb-WO_x (c) and Pt/2%Nb-WO_x (d).

WO_x was demonstrated by TEM images, the increase of H₂ uptake can be explained by a more pronounced spillover effect rather than differences in Pt dispersion.

In the H₂-TPR profiles (Fig. 9), two peaks were observed below 180 °C, wherein the peak at around 60 °C was assigned to the reduction of PtO₂ to Pt (based on the amount of consumed hydrogen), while the peak at around 80 °C was assigned to the reduction of W⁶⁺ close to Pt. In comparison to Pt/WO_x, these two peaks shifted to lower temperatures, indicating that the reduction of Pt was facilitated by doping with Nb. Furthermore, with an increase in the amount of doped Nb, the reduction peak of Pt shifted to higher temperatures and closer to Pt/WO_x. In particular, a very sharp peak at 80 °C was observed in the pattern of Pt/5%Nb-WO_x, which could be ascribed to the co-reduction of both Pt and WO_x (or NbO_x). This result suggests that the introduction of a very little amount of Nb (0.1%) facilitates the reduction of Pt and WO_x, while greater amounts of Nb strengthened the interaction between Pt and the support (Nb-WO_x). Besides, when Nb doping was greater than 2%, further reduction of W species from WO_x (2 < x < 3) to WO₂ shifted

Fig. 9. H₂-TPR profiles of the as-synthesized Pt/WO_x and Pt/Nb-WO_x samples.

to higher temperatures (from 675 to 737 °C at 2%Nb content), indicating that introducing greater amounts of Nb makes WO_x more stable against H₂ reduction, which is expected to yield promising results at high H₂ pressures and superior stability in H₂-related reactions.

3.3. Selective hydrogenolysis of glycerol over Pt/Nb-WO_x

In our previous work, highly dispersed Pt/WO_x catalysts showed promising performance in the selective hydrogenolysis of glycerol under relatively mild reaction conditions (140 °C, 1 MPa); the conversion of glycerol was 37.4%, while the selectivity was 35.1% [6]. However, when the pressure of H₂ increased from 1 to 5.5 MPa, glycerol conversion over Pt/WO_x decreased from 37.4% to 14.2%, while the yield of 1,3-PD decreased from 13.9% to 4.7%, owing to the over-reduction of active W species [6]. Because the reduction of W was greatly suppressed on Pt/Nb-WO_x when the Nb doping amount was >2%, the support morphology varied from 1D needle-structure (WO_x) to a 2D flake-structure and 3D sphere structure; we then further evaluated their catalytic performance for the selective hydrogenolysis of glycerol under diverse conditions (Table 2). As shown in Table 2, when the reaction was performed at 1 MPa H₂, the introduction of Nb in the WO_x support resulted in a decrease in the activity (Entries 1–4). Meanwhile, the 1,3-PD selectivity

Table 2

Selective hydrogenolysis of glycerol over niobium-doped tungsten oxide-supported Pt catalysts ^a.

Entry	Catalyst	P (MPa)	Conv. (%)	Sel. (%)					1,3-PD Yield (%)
				1,3-PD	1,2-PD	1-PO	2-PO	Others ^b	
1	2%Pt/WO _x	1	49.5	28.1	6.5	52.3	4.1	9.0	13.9
2	2%Pt/0.1%Nb-WO _x		44.7	27.6	2.5	64.9	0.5	4.5	12.3
3	2%Pt/2%Nb-WO _x		40.0	29.7	2.5	42.7	3.0	22.1	11.9
4	2%Pt/5%Nb-WO _x		29.2	25.7	2.2	42.6	3.3	26.2	7.5
5	2%Pt/WO _x	5	23.2	35.7	2.0	52.9	4.7	13.2	8.3
6	2%Pt/0.1%Nb-WO _x		11.6	37.7	4.6	28.9	2.7	26.1	4.4
7	2%Pt/2%Nb-WO _x		40.3	27.5	1.7	52.9	5.1	12.8	11.1
8	2%Pt/5%Nb-WO _x		27.0	20.6	2.7	34.5	4.4	37.8	5.6

^a Reaction conditions: 75 mL autoclave, catalyst 0.3 g, 12 g of 5 wt% glycerol aqueous solution, 800 r/min, and 160 °C for 12 h. ^b Others include acetone, ethylene glycerol, ethanol, methanol, methane, ethane, and propane.

was nearly unchanged. The greater the amount of Nb introduced into the system, the greater is the loss of activity. However, when the reaction was conducted under elevated pressures, the results were quite different (Entries 5–8). In the case of the Pt/WO_x catalyst, glycerol conversion decreased from 49.5% to 23.2% when hydrogen pressure was increased from 1 to 5 MPa; meanwhile, 1,3-PD selectivity increased from 28.1% to 35.7%, leading to a reduction in the 1,3-PD yield from 13.9% to 8.3%. The catalytic behavior of Pt/0.1%Nb-WO_x was quite similar to that of Pt/WO_x; this is to be expected because their morphologies are similar. In contrast, in the case of the Pt/2%Nb-WO_x catalyst, both glycerol conversion and 1,3-PD selectivity remained almost unchanged when the hydrogen pressure was raised from 1 to 5 MPa. 1,3-PD yield was maintained at 11.1%, higher than that obtained on Pt/WO_x under identical conditions. A similar trend was observed in the case of the Pt/5%Nb-WO_x catalyst. Evidently, doping a suitable amount of Nb into WO_x could, to a certain extent, overcome the susceptible nature of WO_x and yield superior H₂-tolerance performance across a wide operation window (H₂ pressure: 1–5 MPa).

To justify this unexpectedly high stable performance, we conducted XPS on Pt/WO_x and Pt/2%Nb-WO_x before and after the hydrogenolysis reaction (Fig. 10). In fact, even at 1 MPa H₂, an obvious shift was detected in the binding energy of W 4f (W 4f_{7/2} shifts from 35.9 to 35.5 eV) in the spectrum of Pt/WO_x (Fig. 10(a)), indicating the reduction of W species during glycerol hydrogenolysis, which in turn deteriorated the stability of

the catalyst. In contrast, no obvious shift could be found in the W 4f_{7/2} peaks in Pt/2%Nb-WO_x before and after the reaction at 5 MPa (Fig. 10(b)), suggesting that doping Nb into WO_x led to superior catalyst stability towards H₂ reduction, which is consistent with the H₂-TPR results.

This scenario suggested that a balance between H₂ dissociation and W-reduction was achieved successfully on Pt/2%Nb-WO_x, which may benefit catalyst stability in the long run and broaden its practical applications in other H₂-related reactions.

3.4. The acidity of Nb-WO_x

Catalyst acidity is essential for hydrogenolysis and may provide an insight into the mechanism of a catalyst's diverse chemoselectivity; hence, acidity variation in WO_x after Nb doping was thoroughly exploited. In NH₃ adsorption studies, 2%Nb-WO_x showed increased acid density (0.46 mmol/g) when compared to WO_x (0.36 mmol/g), although both of them shared similar weak and medium acid sites according to the NH₃-TPD results (Fig. 11). To confirm the measured acidity, cellobiose hydrolysis was also conducted [35]. Consistent with the NH₃ adsorption results, Nb-WO_x exhibited a slight improvement in cellobiose hydrolysis when compared to WO_x and both of them exhibited relatively high reactivity and glucose selectivity (Table 3). However, the performance of selective glycerol hydrogenolysis over Pt/2%Nb-WO_x bearing more acid sites, was slightly lower than that of Pt/WO_x (Table 2, entries 1

Fig. 10. XPS patterns of W 4f of fresh and used 2%Pt/WO_x (a) and 2%Pt/2%Nb-WO_x (b).

Fig. 11. NH_3 -TPD ($m/e = 16$) curves of WO_x and 2%Nb- WO_x .

and 3) under mild conditions. The discrepancy between hydrogenolysis performance and catalyst acidity suggested that the active acid sites might not be the measured surface acid sites, but in-situ Brönsted acids formed with the assistance of H_2 [29].

From a mechanistic point of view, an optimum balance between acid and metal sites is necessary for efficient dehydration (despite the aqueous reaction system), followed by fast hydrogenation to stable products. Because dehydration is more likely to be the rate-determining step, a high H_2 -pressure dependence seems unnecessary in this step, unless it is used to obtain active acid sites. In combination with the aforementioned results, we tentatively assumed that a high H_2 pressure is required to provide active in-situ formed acid sites in the rate-determining dehydration step, rather than for fast hydrogenation. Consequently, the outstanding low-pressure performances of Pt/ WO_x [6] systems can be explained by their superior H_2 dissociation over atomically dispersed Pt species to in-situ generated Brönsted acid sites. However, even with improved dispersion and stabilization of metal components, the defect-rich WO_x supports were easily over-reduced, thus resulting in a sharp activity loss as H_2 pressure increased. In contrast to conventional volcano-profiled performance towards H_2 , Pt/Nb- WO_x , in this regard, demonstrated a terrace-profiled performance as a function of H_2 pressure, indicating that a high H_2 pressure is not indispensable or beneficial when H_2 can be sufficiently dissociated to provide active acid sites. It should be admitted that in this work, the doping of Nb, to some extent, might impair the capacity of WO_x to dissociate H_2 and generate in-situ acid sites, thus leading to a decrease in the activity as the Nb doping amount increased. Though 2% Nb was found optimal for WO_x doping for the selective hydrogenolysis of glycerol,

more experimental studies to optimize the reaction conditions over the optimal catalyst (Pt/2%Nb- WO_x) are being undertaken.

4. Conclusions

In summary, mesoporous Nb-doped WO_x oxides were successfully synthesized by a solvothermal method in ethanol with a uniform pore size of ca. 4.0 nm and high surface area of 130–144 m^2/g . The morphology of WO_x substantially evolved from 1D needle-stack structures to 2D flake-stacks and 3D sphere-stack clusters when the Nb doping amount increased to 2 and 5 wt%, respectively. Highly dispersed Pt catalysts were prepared on the obtained Nb- WO_x supports. During the selective hydrogenolysis of glycerol to 1,3-PD, Nb introduction can successfully inhibit the over-reduction of active W species at high H_2 pressures. An optimal catalyst was obtained when the Nb doping was 2 wt% and the optimized catalyst demonstrated promising performance in a wide operating window (1 to 5 MPa H_2), which guarantees superior stability towards H_2 pressure. The unique features brought about by Nb-doping may also enlarge the applications of Pt/ WO_x catalysts in other hydrogen-involved reactions, particularly under more severe conditions. Moreover, the possibility to reconcile the conflicts in H_2 usage is soundly validated by modifying catalyst supports, although the 1,3-PD yield is far from satisfactory currently. Instead of pursuing high performance, we took a quite different approach in this regard and manipulated the supports to endow the catalyst with longevity with respect to H_2 pressure; we strongly believe that this will provide novel ideas and shed light on the design of highly stable catalysts, which is desirable for practical applications.

References

- [1] W. H. Yu, P. P. Wang, C. H. Zhou, H. B. Zhao, D. S. Tong, H. Zhang, H. M. Yang, S. F. Ji, H. Wang, *Chin. J. Catal.*, **2017**, 38, 1087–1100.
- [2] H. D. Zheng, J. Z. Ou, M. S. Strano, R. B. Kaner, A. Mitchell, K. Kalantar-zadeh, *Adv. Funct. Mater.*, **2011**, 21, 2175–2196.
- [3] C. Di Valentin, G. Pacchioni, *Acc. Chem. Res.*, **2014**, 47, 3233–3241.
- [4] H. Bai, W. C. Yi, J. Y. Liu, Q. Lv, Q. Zhang, Q. Ma, H. F. Yang, G. C. Xi, *Nanoscale*, **2016**, 8, 13545–13551.
- [5] X. X. Guo, X. Y. Qin, Z. J. Xue, C. B. Zhang, X. H. Sun, J. B. Hou, T. Wang, *RSC Adv.*, **2016**, 6, 48537–48542.
- [6] J. Wang, X. C. Zhao, N. Lei, L. Li, L. L. Zhang, S. T. Xu, S. Miao, X. L. Pan, A. Q. Wang, T. Zhang, *ChemSusChem*, **2016**, 9, 784–790.
- [7] Z. F. Huang, J. J. Song, L. Pan, F. L. Lv, Q. F. Wang, J. J. Zou, X. W. Zhang, L. Wang, *Chem. Commun.*, **2014**, 50, 10959–10962.
- [8] J. J. Song, Z. F. Huang, L. Pan, J. J. Zou, X. W. Zhang, L. Wang, *ACS Catal.*, **2015**, 5, 6594–6599.
- [9] C. W. Liu, C. H. Zhang, S. L. Hao, S. K. Sun, K. K. Liu, J. Xu, Y. L. Zhu, Y. W. Li, *Catal. Today*, **2016**, 261, 116–127.
- [10] J. Y. Zhang, B. L. Hou, A. Q. Wang, Z. L. Li, H. Wang, T. Zhang, *AIChE J.*, **2015**, 61, 224–238.
- [11] Y. B. Huang, L. Yan, M. Y. Chen, Q. X. Guo, Y. Fu, *Green Chem.*, **2015**, 17, 3010–3017.
- [12] K. Fabricovicova, M. Lucas, P. Claus, *Green Chem.*, **2015**, 17, 3075–3083.

Table 3
Hydrolysis of cellobiose over WO_x and Nb- WO_x .

Catalysts	Con. (%)	Glucose Sel. (%)
WO_x	46.0	>99.0
2%Nb- WO_x	59.6	>99.0

Reaction conditions: 20 mL autoclave, catalyst 50 mg, 2 g of 5 wt% cellobiose aqueous solution, 800 r/min, 120 °C for 1 h.

Graphical Abstract

Chin. J. Catal., 2018, 39: 1027–1037 doi: 10.1016/S1872-2067(18)63074-8

Pt/Nb-WO_x for the chemoselective hydrogenolysis of glycerol to 1,3-propanediol: Nb dopant pacifying the over-reduction of WO_x supports

Man Yang, Xiaochen Zhao*, Yujing Ren, Jia Wang, Nian Lei, Aiqin Wang*, Tao Zhang

Dalian Institute of Chemical Physics, Chinese Academy of Sciences; University of Chinese Academy of Sciences; Northwest A&F University

Pt/2%Nb-WO_x successfully reconciled the conflicts between H₂ activation and W-reduction and demonstrated a promising performance in the selective hydrogenolysis of glycerol to 1,3-propanediol across an unprecedentedly wide H₂ pressure range.

- [13] M. Y. Zheng, J. F. Pang, A. Q. Wang, T. Zhang, *Chin. J. Catal.*, **2014**, 35, 602–613.
- [14] J. Wang, N. Lei, C. J. Yang, Y. Su, X. C. Zhao, A. Q. Wang, *Chin. J. Catal.*, **2016**, 37, 1513–1520.
- [15] Y. K. Hong, D. W. Lee, H. J. Eom, K. Y. Lee, *Appl. Catal. B*, **2014**, 150, 438–445.
- [16] A. Q. Wang, T. Zhang, *Acc. Chem. Res.*, **2013**, 46, 1377–1386.
- [17] R. W. Gosselink, D. R. Stellwagen, J. H. Bitter, *Angew. Chem. Int. Ed.*, **2013**, 52, 5089–5092.
- [18] S. García-Fernández, I. Gandarias, J. Requies, M. B. Güemez, S. Ben-nici, A. Auroux, P. L. Arias, *J. Catal.*, **2015**, 323, 65–75.
- [19] R. Arundhathi, T. Mizugaki, T. Mitsudome, K. Jitsukawa, K. Kaneda, *ChemSusChem*, **2013**, 6, 1345–1347.
- [20] J. ten Dam, K. Djanashvili, F. Kapteijn, U. Hanefeld, *ChemCatChem*, **2013**, 5, 497–505.
- [21] Y. Nakagawa, X. H. Ning, Y. Amada, K. Tomishige, *Appl. Catal. A*, **2012**, 433–434, 128–134.
- [22] C. H. Deng, L. Leng, X. Z. Duan, J. H. Zhou, X. G. Zhou, W. K. Yuan, *J. Mol. Catal. A*, **2015**, 410, 81–88.
- [23] C. H. Deng, L. Leng, J. H. Zhou, X. G. Zhou, W. K. Yuan, *Chin. J. Catal.*, **2015**, 36, 1750–1758.
- [24] W. Zhou, Y. J. Zhao, Y. Wang, S. P. Wang, X. B. Ma, *ChemCatChem*, **2016**, 8, 3663–3671.
- [25] Y. Q. Fan, S. J. Cheng, H. Wang, D. H. Ye, S. H. Xie, Y. Pei, H. R. Hu, W. M. Hua, Z. H. Li, M. H. Qiao, B. N. Zong, *Green Chem.*, **2017**, 19, 2174–2183.
- [26] Y. Nakagawa, M. Tamura, K. Tomishige, *J. Mater. Chem. A*, **2014**, 2, 6688.
- [27] J. ten Dam, U. Hanefeld, *ChemSusChem*, **2011**, 4, 1017–1034.
- [28] Y. H. Zhang, X. C. Zhao, Y. Wang, L. K. Zhou, J. Y. Zhang, J. Wang, A. Q. Wang, T. Zhang, *J. Mater. Chem. A*, **2013**, 1, 3724.
- [29] X. C. Zhao, J. Wang, M. Yang, N. Lei, L. Li, B. L. Hou, S. Miao, X. L. Pan, A. Q. Wang, T. Zhang, *ChemSusChem*, **2017**, 10, 819–824.
- [30] W. J. Mu, X. Xie, X. L. Li, R. Zhang, Q. H. Yu, K. Lv, H. Y. Wei, Y. Jian, *RSC Adv.*, **2014**, 4, 36064.
- [31] D. M. Kabtamu, J. Y. Chen, Y. C. Chang, C. H. Wang, *J. Mater. Chem. A*, **2016**, 4, 11472–11480.
- [32] C. Zhang, W. Zhang, W. T. Zheng, *Chin. J. Catal.*, **2018**, 39, 4–7.
- [33] H. S. Wei, Y. J. Ren, A. Q. Wang, X. Y. Liu, X. Liu, L. L. Zhang, S. Miao, L. Li, J. Y. Liu, J. H. Wang, G. F. Wang, D. S. Su, T. Zhang, *Chem. Sci.*, **2017**, 8, 5126–5131.
- [34] Z. J. Li, S. Y. Wu, Z. G. Wang, Y. Q. Fu, *J. Alloys Compd.*, **2016**, 672, 155–160.
- [35] Z. X. Zhang, M. Sadakane, N. Hiyoshi, A. Yoshida, M. Hara, W. Ueda, *Angew. Chem. Int. Ed.*, **2016**, 55, 10234–10238.
- [36] R. Solarzka, B. D. Alexander, A. Braun, R. Jurczakowski, G. Fortu-

- nato, M. Stiefel, T. Graule, J. Augustynski, *Electrochim. Acta*, **2010**, 55, 7780–7787.
- [37] A. H. Yan, C. S. Xie, F. Huang, S. P. Zhang, S. L. Zhang, *J. Alloys Compd.*, **2014**, 610, 132–137.
- [38] K. Kalantar-zadeh, A. Vijayaraghavan, M. H. Ham, H. D. Zheng, M. Breedon, M. S. Strano, *Chem. Mater.*, **2010**, 22, 5660–5666.
- [39] L. J. Liu, Y. H. Zhang, A. Q. Wang, T. Zhang, *Chin. J. Catal.*, **2012**, 33, 1257–1261.

Pt/Nb- WO_x 催化甘油选择氢解制1,3-丙二醇: Nb掺杂抑制 WO_x 的过度还原

杨 曼^{a,b}, 赵晓晨^{a,*}, 任煜京^{a,b}, 王 佳^c, 雷 念^{a,b}, 王爱琴^{a,#}, 张 涛^a

^a中国科学院大连化学物理研究所催化基础国家重点实验室, 辽宁大连116023

^b中国科学院大学, 北京100049

^c西北农林科技大学林学院, 陕西杨凌712100

摘要: 随着生物柴油产业的快速发展, 甘油作为副产物大量过剩, 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, 又具有重要的学术研究意义和应用价值。其中选择氢解制备1,3-丙二醇, 因其产物在新型聚酯材料合成中的重要应用而备受关注, 被认为是最具工业应用潜力的甘油转化工艺之一。但是由于反应空间位阻效应和热力学上的限制, 甘油氢解制备1,3-丙二醇仍存在很大的挑战。目前, 可高选择性制得1,3-丙二醇的催化剂体系主要是铌-铈催化剂和铂-钨催化剂两类; 且反应通常需要较苛刻的压力。在我们的前期工作中, 单原子/准单原子Pt催化剂(Pt/WO_x)成功突破了这一压力壁垒, 实现了在较低(1 MPa)氢气压力下优异的甘油选择氢解制1,3-丙二醇活性; 但是该催化剂的耐压性能较差, 是长期反应后失活的一个主要原因, 且随着氢气压力的进一步升高, Pt/WO_x 催化剂活性大幅下降。研究发现, 在高压氢气下, 单原子/准单原子催化剂 Pt/WO_x 中的 WO_x 易被过度还原, 导致催化剂失活, 大大限制了该系列单原子催化剂在涉氢催化反应中的应用。因此, 通过载体改性设计制备具有良好氢气稳定性的载体, 有可能拓宽催化反应的氢压窗口。

一般来讲, 可以通过掺杂来改变载体的电子结构、表面化学性质等, 进而改变催化剂活性、选择性和稳定性。为了提高单原子/准单原子催化剂(Pt/WO_x)在高压氢气中的稳定性, 本文采用原位掺杂法制备了一系列具有不同掺杂量、结构、及物化性质的Nb- WO_x 载体, 并通过物理吸附, XRD, SEM, HRTEM, Raman, XPS对其进行表征。结果发现Nb掺杂的介孔 WO_x 仍保持较高的比表面积($\sim 136 \text{ m}^2/\text{g}$); 且当Nb掺杂量增加至2 wt%时, WO_x 由一维针状堆积转变为二维片状堆积; 至5 wt%时, 变为三维球状堆积。以所得的Nb- WO_x 为载体, 我们制备了一系列Pt高度分散的Pt/Nb- WO_x 催化剂, 并考察了其在甘油选择性氢解制备1,3-丙二醇反应中的催化性能。结果表明, 当 H_2 压力由1 MPa升到5 MPa后, Pt/WO_x 催化剂上1,3-丙二醇的收率由13.9%急剧下降到8.3%; 但随着Nb掺杂量的增加(>2wt%), 1,3-丙二醇的收率随压力升高并没有明显变化, 说明该催化剂在高压氢气下的过度还原被有效抑制, 反应的最佳氢气压力由1 MPa拓宽到5 MPa。其中, Nb的最佳掺杂量为2 wt%, 在Pt/2%Nb- WO_x 催化剂上1 MPa甘油氢解转化率为40.0%, 1,3-丙二醇收率11.9%; 当氢气压力为5 MPa时, 甘油氢解转化率为40.3%, 1,3-丙二醇收率11.1%。值得一提的是, 虽然Nb的掺杂使 WO_x 的表面酸量增加, 并且表现出了更优的酸催化纤维二糖水解活性, 但是在甘油氢解制备1,3-丙二醇的反应中Pt/Nb- WO_x 催化剂的性能并没有得到提升反而略有下降, 进一步证实了催化剂本身的表面酸性位并不是催化甘油选择氢解的活性中心, 真正的活性中心很可能是氢气辅助下原位产生的B酸。

对 WO_x 载体进行Nb的掺杂改性, 显著提高了单原子/准单原子Pt/ WO_x 催化剂在高压氢气反应条件下的稳定性, 进而在更宽压力范围内实现了甘油氢解制1,3-丙二醇的高效催化转化。同时, 载体的改性也拓宽了该系列催化剂在其他涉氢反应中的应用范围, 尤其是需要较高氢气压力的反应。

关键词: Nb掺杂 WO_x ; 甘油; 1,3-丙二醇; 选择性氢解

收稿日期: 2018-03-02. 接受日期: 2018-04-10. 出版日期: 2018-06-05.

*通讯联系人. 电话: (0411)84379416; 电子信箱: zxc@dicp.ac.cn

#通讯联系人. 电话: (0411)84379348; 传真: (0411)84685940; 电子信箱: aqwang@dicp.ac.cn

基金来源: 国家自然科学基金(2169008, 21690084, 21673228, 21303187, 21403218); 中国科学院战略重点研究项目(XDB17020100); 国家重点基础研究发展计划(2016YFA0202801); 中国科学院大连化学物理研究所自主部署青年基金(DICP ZZBS 201612).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).