Chinese Journal of Catalysis 39 (2018) 1027–1037

available at www.sciencedirect.com

ScienceDirect

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 H_2 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 H_2 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 H_2 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 (H_2, CO_2, 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 H_2 activation. Moreover, the acidity of tungsten oxide can also be adjusted via a slight reduction of W species accompanied by $H^{\delta+}$ release. Therefore, WO_x-containing catalysts were found to be of high value in a series of H_2-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 Brönsted 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 m^2/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 operation 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%Nb-WO_x oxides

Nb-doped WO_x was prepared via a modified solvothermal procedure [6]. In detail, WCl_6 (3 g) and $NbCl_5$ (mol_{Nb}:mol_W = 0.1, 2, 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%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 Cu K_α 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-

Download English Version:

https://daneshyari.com/en/article/6505643

Download Persian Version:

https://daneshyari.com/article/6505643

Daneshyari.com