Chinese Journal of Catalysis 37 (2016) 1513–1519

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Article

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

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ARTICLE INFO

Article history:
Received 5 April 2016
Accepted 26 May 2016
Published 5 September 2016

Keywords:
Glycerol
Hydrogenolysis
1,3-propanediol
Tungsten oxide
Promoter

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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This work was supported by the National Natural Science Foundation of China (21176235, 21373206, 21303187).
DOI: 10.1016/S1872-2067(16)62479-8 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 9, September 2016

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