



Sustainable production of acrolein: Catalytic gas-phase dehydration of glycerol over dispersed tungsten oxides on alumina, zirconia and silica



Song-Hai Chai, Bo Yan, Li-Zhi Tao, Yu Liang, Bo-Qing Xu*

Innovative Catalysis Program, Key Lab of Organic Optoelectronics & Molecular Engineering Department of Chemistry, Tsinghua University, Beijing 100084, China

ARTICLE INFO

Article history:

Received 11 November 2013
Received in revised form 17 January 2014
Accepted 8 February 2014
Available online 11 March 2014

Keywords:

Glycerol dehydration
Acrolein
Tungsten oxide
Solid acids
Green chemistry
Catalyst support

ABSTRACT

Tungsten oxides dispersed on Al_2O_3 , ZrO_2 , and SiO_2 supports were investigated for catalytic dehydration of glycerol (GL) to form acrolein (AC) in the gas phase at 315°C with aqueous GL (GL concentration: 36.2 wt% or 10 mol%, molar $\text{GL}/\text{H}_2\text{O} = 1/9$) as the feed ($\text{GHSVGL} = 400\text{ h}^{-1}$). The $\text{WO}_3/\text{Al}_2\text{O}_3$ and WO_3/ZrO_2 catalysts are found much more effective than WO_3/SiO_2 in catalyzing the reaction in terms of the selectivity (ca. 70 mol% vs. 60 mol%) and yield (49–58% vs. 11–32%) for AC production. Optimization of the WO_3 loading (5–40 wt%) and calcination temperature (550–900 $^\circ\text{C}$) of the $\text{WO}_3/\text{Al}_2\text{O}_3$ and WO_3/ZrO_2 catalysts identifies that the calcination at 800°C of a 30 wt% $\text{WO}_3/\text{Al}_2\text{O}_3$ sample would generate the most efficient catalyst that offers an AC yield as high as 61% AC for longer than 10 h (AC selectivity: 69 mol%). Correlating the catalytic performance with the density of W atoms at the surfaces of $\text{WO}_3/\text{Al}_2\text{O}_3$ and WO_3/ZrO_2 samples discloses that those catalysts having the intermediate numbers for the surface density of W atoms (3.5–7.6 W nm^{-2} or 0.5–1.0 monolayer), either on Al_2O_3 or on ZrO_2 , would offer the highest AC selectivity (69–72 mol%). The catalytic results obtained in the temperature range of 280–400 $^\circ\text{C}$ uncover 315°C as the optimum reaction temperature; significant derivation from this temperature would lead to faster catalyst deactivation and lower AC selectivity.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Much attention has been paid recently to the utilization of renewable biomass and its derivatives for the production of fuels, chemicals and materials because the products of biomass-origin are widely considered as carbon (or CO_2) neutral [1–4]. One of the biomass derivatives is glycerol (GL). Starting from about two decades ago, GL has been excessively produced as a co-product of biodiesel in the transesterification of vegetable oils with methanol and ethanol [5,6], entitling GL a promising low-cost sustainable feedstock for producing value-added chemicals and materials [7,8]. Acrolein (AC), which is an important intermediate in the chemical industry, is currently manufactured by gas-phase oxidation of petroleum-based propylene over a mixed Bi–Mo oxides catalyst. The production of AC from catalytic double dehydration of GL would lead to a potentially practical route to sustain the AC production on recycling bio-resources. As the selectivity of alcohol dehydration reaction depends critically on the function of acid catalysts, both liquid and solid acids have been screened as

the catalyst for AC production from GL dehydration [9–29]. We have previously reported the catalytic performance of a wide variety of solid acids and bases for the gas-phase dehydration of GL using an aqueous feed containing 36.2 wt% GL (10 mol% GL or molar $\text{GL}/\text{H}_2\text{O} = 1/9$) mostly at 315°C and GL space velocity of $\text{GHSVGL} = 400\text{ h}^{-1}$ [12–14,19,26–28]. The identified selective catalysts (AC selectivity > 50 mol%) include supported phosphoric acid [12], and heteropolyacids [12,14,19], mixed oxides [26], zirconia-supported tungsten oxide (or tungstated zirconia, WO_3/ZrO_2) [12,28], hydrated niobium oxide ($\text{Nb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$) [12,13], and tantalum oxide ($\text{Ta}_2\text{O}_5 \cdot x\text{H}_2\text{O}$) [27]. The last catalyst could produce AC selectivity as high as 74–76 mol% and its catalytic life can be longer than 85 h.

The potential of WO_3/ZrO_2 catalyst toward the selective dehydration of aqueous GL for AC production was also explored in other laboratories [21,30–32], using an aqueous feed of 20 wt% (4.6 mol%) GL. The highest selectivity for AC was documented at the levels of 62–79 mol%, being similar to or slightly higher than the data in our work [12,28]. The results gained from Raman and FTIR measurements of adsorbed pyridine pointed toward that the catalytically active surface structure was related with the highly dispersed WO_x species having acidic W–OH groups, up to a monolayer on the surface of ZrO_2 [31]. In this work, tungsten oxides

* Corresponding author. Tel.: +86 10 62792122; fax: +86 10 62771149.
E-mail address: [bxqu@mail.tsinghua.edu.cn](mailto:bqxu@mail.tsinghua.edu.cn) (B.-Q. Xu).

dispersed on Al_2O_3 , ZrO_2 , and SiO_2 supports were prepared and employed to catalyze the gas-phase dehydration of aqueous glycerol (GL) for selective AC production, aiming to understand the effects of supporting materials and WO_3 dispersion (or density of W atoms at the support surface) on the catalyst performance. Variation in the density of W atoms at the support surface was made in the range of $0\text{--}17\text{ W nm}^{-2}$ by changing the WO_3 loading and its subsequent calcination temperature during the preparations or employing commercially available supports (SiO_2 and Al_2O_3) of varying surface areas. Moreover, a $\text{WO}_3/\text{Al}_2\text{O}_3$ catalyst with the optimized WO_3 loading and calcination temperature was selected to show the effect of reaction temperature on the formation of AC from GL.

2. Materials and methods

2.1. Samples and their preparations

$\text{WO}_3/\text{Al}_2\text{O}_3$ and WO_3/SiO_2 catalysts were prepared by impregnation of commercial Al_2O_3 ($341\text{ m}^2\text{ g}^{-1}$, Fushun Research Institute of Petroleum Processing (FRIPP), SINOPEC) and SiO_2 ($370\text{ m}^2\text{ g}^{-1}$, Beijing Chemical Reagent Co.) with an aqueous solution of ammonium metatungstate ($(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40}$, Shanghai Chemical Reagent, AR). After the removal of excess water in a rotary evaporator at $50\text{--}60^\circ\text{C}$, the remaining powders were dried overnight at 110°C and then calcined in flowing air at elevated temperature for 4 h. According to the WO_3 loading (x , the weight percentage (wt%) of WO_3 in relation to the total weight of WO_3 and its support in the catalyst) and calcination temperature (T in $^\circ\text{C}$), the final catalyst samples were denoted as $x\text{WAl-T}$ ($x=8\text{--}40$, $T=700\text{--}900$) and $x\text{WSi-T}$ ($x=9$ and 23 , $T=650$).

Similarly, WO_3/ZrO_2 catalysts were prepared by impregnation of a $\text{ZrO}(\text{OH})_2$ alcogel ($\text{ZrO}(\text{OH})_2\text{-AN}$) with an aqueous solution of $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40}$. This alcogel was prepared by extensive washing of a $\text{ZrO}(\text{OH})_2$ hydrogel with anhydrous ethanol according to the method described previously [19,33,34]. After removal of excess water in a rotary evaporator at ca. 60°C , the remaining powders were dried at 110°C overnight and then calcined in flowing air at elevated temperature for 4 h. The final catalyst samples were denoted as $x\text{WZ-AN-T}$ ($x=5\text{--}40$ wt%, $T=550\text{--}900^\circ\text{C}$). The calcined powder catalysts were pressed, crushed, and sieved to 20–40 mesh (ca. $0.43\text{--}0.85$ mm) before use.

2.2. Experimental methods for the catalytic reactions

The gas-phase dehydration reaction of GL was carried out at 315°C (unless specified otherwise) under atmospheric pressure in a vertical fixed-bed tubular quartz reactor (i.d. 9 mm, length 50 cm), which was heated by a tubular furnace in a height of 40 cm. A constant volume (0.63 mL) of the catalyst bed was sandwiched in the middle of the reactor with quartz wool. 2 mL quartz sand (2 cm in height) was placed above the catalyst bed for complete evaporation of the reactant. Prior to the reaction, the catalyst was pretreated at the reaction temperature for 1.5 h in flowing dry nitrogen (30 mL min^{-1}). The reaction feed, an aqueous solution of GL (36.2 wt%, molar GL/ H_2O ratio of 1/9) was fed continuously into the reactor inlet (at the top of the reactor) by a micro-pump. The catalytic performance of the solid catalysts was evaluated at a gas hourly space velocity (GHSV) of 400 h^{-1} by GL [19,26–28].

The reaction products were condensed in an ice-water trap (0°C) and collected hourly for off-line analysis on a HP6890 GC equipped with a HiCap CBP20-S25-050 (Shimadzu) capillary column (i.d. $0.32\text{ mm} \times 25\text{ m}$) and an FID detector [12–14,26–28]. The reaction was continued for 10 h. The GL conversion and product

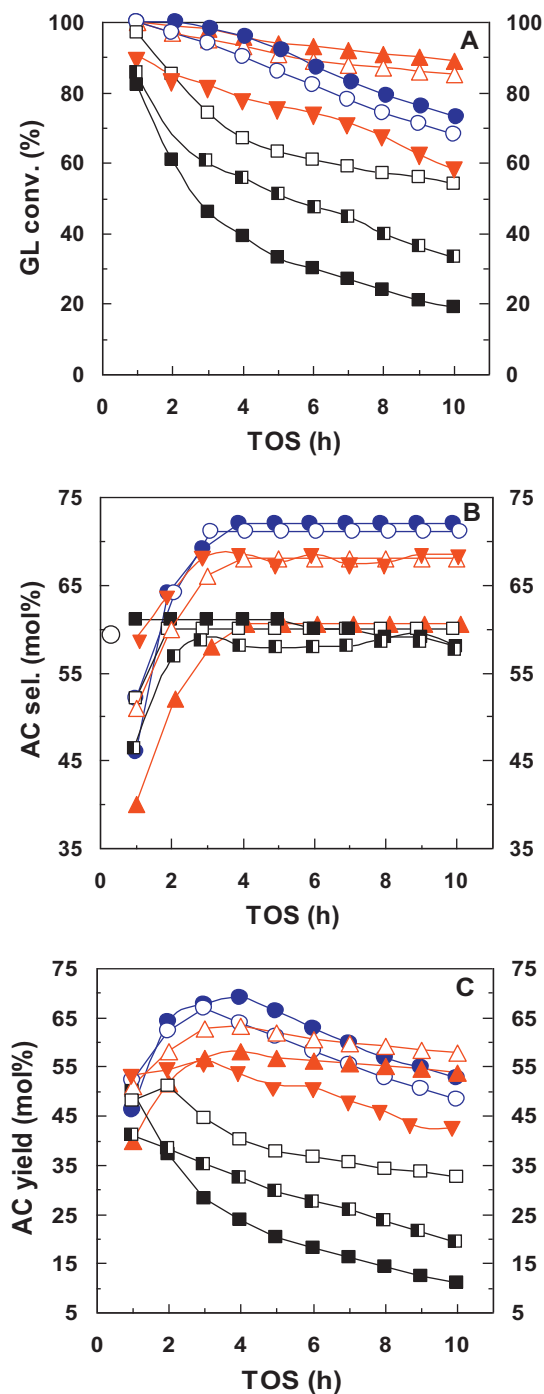


Fig. 1. Performance of (▲) 15WAl-700, (△) 30WAl-700, (▼) 15WAl-700-Sasol, (●) 15WZ-AN-650, (○) 30WZ-AN-650, (■) 9WSi-650, (□) 23WSi-650, and (◻) 23WSi-650-Degussa catalysts by the time courses of (A) glycerol conversion, (B) acrolein selectivity and (C) acrolein yield. Rxn conditions: 315°C , 10 kPa GL, 90 kPa H_2O , $\text{GHSV}_{\text{GL}} = 400\text{ h}^{-1}$.

selectivity data were calculated according to the following equations:

$$\text{Glycerol conversion (\%)} = \frac{\text{Moles of glycerol reacted}}{\text{Moles of glycerol in the feed}} \times 100$$

Product selectivity (mol%)

$$= \frac{\text{Moles of carbon in a product defined}}{\text{Moles of carbon in glycerol reacted}} \times 100$$

Download English Version:

<https://daneshyari.com/en/article/54265>

Download Persian Version:

<https://daneshyari.com/article/54265>

[Daneshyari.com](https://daneshyari.com)