Hydrothermally stable regenerable catalytic supports for aqueous-phase conversion of biomass

Jinzhao Duan [a,b,1], Yong Tae Kim [a,1], Hui Lou [b], George W. Huber [a,*]

[a] Department of Chemical and Biological Engineering, University of Wisconsin-Madison, Madison, WI 53706, USA
[b] Institute of Catalysis, Department of Chemistry, Zhejiang University, Hangzhou 310028, PR China

ARTICLE INFO

ABSTRACT

The hydrothermal stability of TiO_2- and ZrO_2-based materials was studied by exposing the samples to liquid water at 523 K for 60 h in a batch reactor. No phase transformation or loss in BET surface area was observed for TiO_2-based materials that had initial BET surface area of less than $52 \, m^2/g$. In contrast, the BET surface area decreased and the primary crystallite size increased for all ZrO_2-based materials tested. The BET surface area decreased and the primary crystallite size increased for high BET surface area TiO_2 ($156 \, m^2/g$) and ZrO_2 ($246 \, m^2/g$). Silica-containing TiO_2 only lost 30% of its high BET surface area (from 128 to $90 \, m^2/g$). In contrast a material composed of silica–phosphate–ZrO_2 lost 56–72% of its BET surface area. Using the crystalline TiO_2 as a support, we prepared and tested a Pt–ReO_x/TiO_2 catalyst for hydrodeoxygenation of sorbitol. Pt–ReO_x/TiO_2 was almost 2 times more active on a total Pt basis than Pt–ReO_x/C catalyst. Between 0.1 and 0.9 wt% of coke formed on the catalyst surface after reaction depending on the reaction conditions. The coke could be removed and the catalyst activity completely regenerated by an oxidation-reduction treatment. The catalyst showed only minimal change in BET surface area, TiO_2 phase and TiO_2 crystallite size after more than 163 h of time on stream. The CO chemisorption of Pt–ReO_x/TiO_2 increased after reaction which was probably due to migration of ReO_x species away from the Pt during the reaction.

1. Introduction

Diminishing petroleum reserves and the growing demand for energy make biomass-based energy resources a promising alternative for the production of renewable, sustainable, and carbon neutral fuels and chemicals [1–3]. Biomass feedstocks typically contain a large number of hydroxyl functional groups making them both highly reactive and highly soluble in water. A number of reactions involving biomass conversion occur in the aqueous phase including aqueous-phase hydrodeoxygenation (APHDO) [2,4–6], aqueous-phase reforming [7,8], aqueous-phase dehydration [9–11], and aqueous-phase hydrogenation [4,12].

APHDO reacts biomass feedstocks with hydrogen producing deoxygenated products such as alkanes, alcohols and polyols. One of the challenges with working in the water phase is that conventional catalytic supports such as SiO_2 [13], Al_2O_3 [14,15], SiO_2–Al_2O_3 [16], Nb_2O_5 [17], and zeolites [18] are not

hydrothermally stable. For instance, alumina undergoes a phase transformation from γ-Al_2O_3 to boehmite (AlOOH) with a 64% loss of surface area under the conditions utilized for aqueous-phase reforming (e.g., 473 K and autogenic pressure) [14,15]. SiO_2-based materials also lose surface area under hydrothermal conditions via a collapse of mesopores [19]. The loss of the surface area of supports under the aqueous-phase reaction conditions negatively affects metal performance, resulting in metal sintering [17]. We have recently used a zirconium phosphate-supported platinum catalyst (Pt/Zr-P) to convert C5–C6 sugar alcohols to high octane gasoline products in water condition with a high yield (~70%) in 6.21 MPa at 518 K [5]. During APHDO of sorbitol, the Pt/Zr-P undergoes a phase transformation of amorphous Zr-P into crystalline Zr-P, leading to a 97% loss in BET surface area, 86% loss of Pt surface sites, and 95% loss of surface acid sites [4]. High surface area activated carbon does not lose surface area in hot water [4,20]. Different types of carbon such as carbon nano-tubes [21], carbon black [22], and mesoporous carbon [23] have also been used as hydrothermally stable supports for aqueous phase reactions. We also found that the Pt–ReO_x/C catalyst was stable in APHDO of sorbitol for 140 h time on stream [4]. However, the carbon deposition on the Pt–ReO_x/C catalyst was 6.8 wt% after the APHDO of sorbitol,

* Corresponding author. Tel.: +1 608 262 1092; fax: +1 608 262 5434.
  E-mail address: huber@engr.wisc.edu (G.W. Huber).
[1] These authors contributed equally to this work.

leading to a decreased reaction rate for sorbitol conversion under steady-state condition [4]. Catalysts often need to be regenerated by oxidation to remove deposited carbon species from the catalyst surface [24,25]. Catalysts supported on carbon cannot be regenerated by calcination because the treatment will burn the carbon. The formation of humin and other coke species is common in biomass conversion reactions and has been reported in the conversion of sugars [6], sugar alcohols [4,26] and bio-oils [7].

TiO$_2$- and ZrO$_2$-based materials have been reported to be hydrothermally stable at temperatures up to 623 K in aqueous environments by Elliott and co-workers [20,27]. These catalytic supports also showed high activity without coking, though a phase transformation above 623 K in the aqueous-phase reaction was noted [20]. Removal of the OH groups from amorphous TiO$_2$ or ZrO$_2$ by thermal treatment leads to a crystalline structure [28,29]. TiO$_2$ exhibits two common crystal phases (i.e., anatase and rutile), and the rutile phase is thermally stable [30]. The metastable ZrO$_2$ crystalline phase (i.e., tetragonal) undergoes a phase transformation to monoclinic ZrO$_2$ upon thermal treatment [31]. Addition of silica or phosphate to TiO$_2$ and ZrO$_2$ can increase the surface area and is reported to inhibit the phase transformation [32,33]. Silica-modified TiO$_2$ and ZrO$_2$ have been reported to be thermally stable at temperatures up to 1173 K [34,35]. The details of the hydrothermal stability of TiO$_2$- and ZrO$_2$-based materials have not been explored. TiO$_2$- and ZrO$_2$-based materials may be suitable supports for long-term biomass conversion. These hydrothermally stable materials can be regenerated and are preferred for the development of biomass conversion.

In this paper we first study the hydrothermal stability of TiO$_2$- and ZrO$_2$-based materials to find hydrothermally stable materials that could be used as supports for biomass conversion in the aqueous phase. We then prepare catalysts on the most hydrothermally stable materials and test their regenerability in APHDO of sorbitol.

2. Experimental

2.1. Catalyst preparation

Microcrystalline TiO$_2$ (P25) was supplied by Aldrich. TiO$_2$ was calcined in air at 673 K and 973 K for 4 h (ramping rate of 4 K min^{-1}) in order to change crystallinity. The obtained materials were denoted as TiO$_2$-673 and TiO$_2$-973. High surface area TiO$_2$ with a rutile phase (TiO$_2$-HSA) was prepared by homogeneous precipitation of TiOCl$_4$ solution at 338 K [36]. The aqueous TiOCl$_4$ solution was prepared by hydrolysis of TiCl$_4$ solution (Aldrich) at 273 K. The precipitates were filtered out, washed with deionized water, and dried at 373 K overnight. The obtained solid was calcined in air at 773 K for 4 h at a ramping rate of 4 K min^{-1}.

Zirconium hydroxide (Zr(OH)$_4$) was prepared from ZrOCl$_2$·8H$_2$O (Aldrich) by the precipitation method using ammonia solution as a precipitant according to the reference [37]. The precipitates were filtered out, and washed with deionized and dried at 373 K overnight. The obtained solid was divided to two equal parts. Some of the material (ZrO$_2$-773) was calcined in air at 773 K for 4 h (ramping rate of 4 K min^{-1}) to form zirconium oxide. The other part of the material (ZrO$_2$-HSA) was hydrothermally treated with water at 433 K for 14 h in a Parr reactor (Parr Instrument Company, series 4560), filtered out, washed with deionized water and then dried at 373 K overnight according to the reference [38].

TiO$_2$–SiO$_2$ was prepared from TiCl$_4$ (Aldrich) and tetraethyl orthosilicate (Aldrich) by co-precipitation method using ammonia solution as a precipitant [39]. The precipitates were filtered out, washed with deionized water, dried at 373 K overnight and then calcined in air at 773 K for 4 h at a ramping rate of 4 K min^{-1}. The content of SiO$_2$ was 5 wt% for TiO$_2$–SiO$_2$.

ZrO$_2$–SiO$_2$ was prepared from ZrOCl$_2$·8H$_2$O (Aldrich) and tetraethyl orthosilicate (Aldrich) by co-precipitation method using ammonia solution as a precipitant. The precipitates were filtered out and washed with deionized water, dried at 373 K overnight. The solid was calcined in air at 773 K for 4 h at a ramping rate of 4 K min^{-1}. The content of SiO$_2$ was 5 wt% for ZrO$_2$–SiO$_2$.

Zirconium phosphate (Zr-P) was prepared by co-precipitating ZrCl$_2$O·8H$_2$O (Aldrich) and NH$_4$H$_2$PO$_4$ (Aldrich) aqueous solutions at a molar ratio of Pt/Zr = 2, as described by Kamiya et al. [40]. The precipitates were aged at room temperature for 30 min, filtered, washed with deionized water until the pH was 5, dried at 373 K overnight, and then calcined in air at 673 K for 4 h at a ramping rate of 4 K min^{-1}.

Pt–ReO$_x$/TiO$_2$ catalyst was prepared from H$_2$PtCl$_6$ (Aldrich) and NH$_4$ReO$_4$ (Aldrich) by sequential incipient wetness impregnation. P25 was hydrothermally treated with deionized water in hydrogen gas at 6.0 MPa (partial pressure of hydrogen is 2.0 MPa) for 100 h at 523 K prior to impregnation of the noble-metal precursors. The solid was then dried at 373 K overnight and calcined in air at 723 K for 4 h (ramping rate of 4 K min^{-1}). The content of Pt was 0.86 wt% and that of Re was 1.2 wt% (Re/Pt = 1.5) for Pt–ReO$_x$/TiO$_2$. The Pt–ReO$_x$/TiO$_2$ catalyst was reduced in situ at 723 K for 2 h (heating rate of 1 K min^{-1}) in hydrogen before APHDO of sorbitol.

2.2. Hydrothermal studies

The hydrothermal tests were done in a Parr reactor (Parr Instrument Company, series 4560). Half a gram of support and 60 g deionized water were added to the reactor. The reactor was then pressurized with hydrogen to a pressure of 2.0 MPa at 298 K. The reactor was heated to 523 K to start the test with continuous stirring at 600 rpm. The final pressure was reached to 6.0 MPa at 523 K. After the desired reaction time, the reactor was cooled, and the slurry was removed from the reactor. The solid was then filtered, washed with deionized water and dried at 373 K overnight.

2.3. Characterizations

XRD patterns were acquired on a X-ray diffraction instrument (RAPID$^{\text{TM}}$ II X-ray instrument) in the scan range of 0.5–45° at a scan rate of 0.02° min^{-1} using a Mo source. The assignment of the crystalline phases was carried out in JADE 5.0 software. Peak intensities for quantitative analysis were determined by measuring integrated areas using Jade® software.

The crystallite size was calculated via Scherrer equation as shown in Eq. (1). In this equation L denotes the average crystallite size, 0.9 is a value when $B_{(2\theta)}$ is the full width at half maximum (FWHM) of the peak broadening in radians, $\lambda_{K\alpha1}$ is the wavelength of the X-ray radiation (0.0709 nm), and $\theta_{\max}$ is the angular position at the (1 1 1) peak maximum of ZrO$_2$, or the (1 0 1) peak maximum of TiO$_2$.

$$L = \frac{0.9\lambda_{K\alpha1}}{B_{(2\theta)} \, COS \, \theta_{\max}} \tag{1}$$

The crystalline volume fraction of anatase phase in TiO$_2$ (X_A) and the tetragonal phase in ZrO$_2$ (X_T) are calculated based on the crystalline peak intensity as shown in Eqs. (2) [41] and (3) [42], respectively. In Eq. (2), I_R and I_A represent the integral intensities of the rutile ($2\theta = 12.554°$) and anatase ($2\theta = 11.601°$) planes, respectively. In Eq. (3), I_T and I_M represent the integral intensities of the tetragonal ($2\theta = 13.812°$) and monoclinic ($2\theta = 12.894°$) planes, respectively.

$$X_A (\%) = \frac{1}{1 + 1.26(I_R/I_A)} \times 100 \tag{2}$$