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# Improved hydrothermal stability of niobia-supported Pd catalysts

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ABSTRACT

Aqueous-phase reactions at elevated temperatures can cause significant loss of surface area in oxide supports. Addition of a second component can help improve the hydrothermal stability of the support and retain a more open, porous structure. Here we show that small amounts of silica (5 wt%) help improve the activity and stability of Pd/niobia–silica catalysts used for pentanoic acid formation from γ-valerolactone. At the end of the run, the Pd/Nb–Si oxide catalysts showed significantly higher activity than catalysts where the Pd was deposited on commercial niobia (HY-340). Loss of surface area occurred for all of the catalysts; however, surface area loss occurred to lesser extents for the Pd/Nb–Si oxide catalysts. In these samples, the regions that contained more silica retained their porous structure and maintained smaller Pd crystallite sizes after reaction while those areas with depleted silica content transformed into crystalline niobia along with significant metal particle growth. We conclude that addition of silica to niobia not only improves the stability of the support but also helps retain smaller crystallite sizes for the Pd phase, resulting in improved catalytic performance in the bi-functional aqueous-phase conversion of γ-valerolactone into pentanoic acid.

## 1. Introduction

Unlike petroleum feedstocks, biomass derivatives are typically highly functionalized molecules with high reactivity and high solubility in water, which are more suitably processed in the aqueous phase at moderate temperatures [1]. However, conventional catalysts and supports designed over the last 100 years for gas phase reactions (such as those involved in the petrochemical industry) may not be suitable for such conditions, particularly aqueous phase reactions at temperatures in excess of 473 K. Consequently, a central challenge for production of biorenewable fuels and chemicals is the development of catalytic materials that are hydrothermally stable during aqueous-phase reactions [2]. Unlike typical supports such as mesoporous silica which are not stable when exposed to hydrothermal conditions, these new materials should operate efficiently at moderate temperatures under high-water environments, with high activity and, most importantly, high stability. One approach that has been demonstrated to be effective in improving the hydrothermal stability of classical supports, such as silica, consists of doping the material with small amounts of alumina or zirconia, which assists to stabilize the silica framework under the hydrothermal conditions [3].

Herein, we have tried to improve the hydrothermal stability of an important catalytic solid acid such as niobia by using the same approach. Niobia has been shown to be useful as a catalyst and support for a variety of important reactions [4,5]. Niobia has high acidity, which, remarkably, is maintained under aqueous environments. This behavior of niobia is valuable to carry out deoxygenation of biomass derivatives in the aqueous phase through dehydration reactions [6,7]. Furthermore, aldol-condensation [8] and ketonization [9] reactions have been carried out over niobia-based catalysts to upgrade biomass derivatives into larger molecular weight compounds. However, commercial niobia (HY-340 supplied by CBMM) suffers from poor hydrothermal stability resulting in a low surface area after use and, consequently, low catalytic stability. In the case of niobia-supported metallic catalysts, the loss of surface area of the niobia support under hydrothermal conditions negatively affects the metal performance, favoring sintering and decreasing the catalytic activity. We report here improved catalytic performance of Pd catalysts supported on niobia–silica for the transformation of aqueous solutions of an important biomass derivative, γ-valerolactone (GVL) [10], into pentanoic acid (PA) (Fig. 1). In this bifunctional catalyst, the acidic niobia catalyzes the ring-opening of GVL to produce pentenoic acid, which is subsequently hydrogenated over Pd yielding hydrophobic pentanoic acid. This reaction has interest since pentanoic acid can

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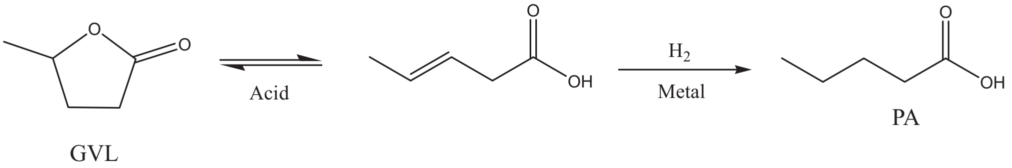

**Fig. 1.** Reaction scheme for the conversion of γ-valerolactone to pentanoic acid (PA) over a niobia-supported palladium catalyst.

be used as a platform molecule for the production of gasoline, diesel and jet fuels components for the transportation sector [11,12] by means of ketonization reactions [13,14].

## 2. Experimental

### 2.1. Catalyst Preparation

Catalysts were prepared with 1 wt% Pd supported on commercial niobia (HY-340, CBMM), as well as 1 wt% Pd supported on two different silica-modified niobia samples prepared with organic and water soluble precursors (Nb–Si oxide_ETO and Nb–Si oxide_ANO, respectively). The niobia–silica oxides contained 5 wt% silica incorporated into the niobia framework.

95 wt% Nb–Si oxide_ANO was prepared using Ammonium Niobium Oxalate (ANO) and Cetyl Tetramethyl Ammonium Bromide (CTAB) as the surfactant template, with a molar ratio of CTAB:$H_2O$ = 1:284 and a molar ratio of $SiO_2$:ANO = 0.1:1. CTAB was dissolved in water followed by the addition of ANO. Sodium silicate was added dropwise to the solution in order to obtain a homogeneous mixture. The pH was then slowly adjusted to 7 by adding 1 M $NH_4OH$. The mixture was heated at 353 K for 7 h in a water bath, cooled to room temperature, and then kept at ambient temperature overnight. The mixture was filtered, washed with water, vacuum dried, and calcined in air at 773 K for 12 h to remove the CTAB template.

95 wt% Nb–Si oxide_ETO was prepared using tetraethyl orthosilicate (TEOS) as the silica precursor [15]. For this preparation, tetradecylamine (1.7 g, 7.9 mmol) was dissolved in a mixture of niobium(V) ethoxide ($Nb(EtO)_5$) (ETO) (4.2 g, 13.3 mmol) and tetraethyl orthosilicate (0.28 g, 1.32 mmol) in the absence of water. The solution was stirred until homogeneous, then 5 mL of ethanol and 15 mL of water were added to the mixture; this causing the precipitation of a white solid. The mixture was left at ambient temperature for 1 day and then aged at 353 K, 373 K, and 453 K for 1, 1, and 7 days respectively. The product was filtered and washed with 500 mL of water and 500 mL of ethanol. After drying of the product, the surfactant was removed by an acid reflux treatment with 70% nitric acid at pH 0.5 in a 4:1 (v:v) mixture of isopropanol and water for 24 hr. The product was filtered, washed and dried in a vacuum oven at 353 K overnight.

Pd nanoparticles on niobia (HY-340, Nb–Si oxide_ANO, Nb–Si oxide_ETO) were prepared by incipient wetness impregnation with an aqueous solution of $Pd(NO_3)_2{\cdot}xH_2O$ (Aldrich). The niobia-supported Pd catalysts (1 wt%) were dried at 380 K overnight, followed by calcination at 538 K in flowing air (250 $cm^3$ (STP) $min^{-1}$, 1 K $min^{-1}$ ramp) for 2 h.

### 2.2. γ-valerolactone reaction

A feed composed of a 50 wt% solution of GVL in water and a co-feed of both $H_2$ and He at 25 mL $min^{-1}$ ($H_2$:GVL molar ratio of 2.2) was used for all the experiments herein described. The apparatus used for kinetic experiments was an up-flow reactor described in detail elsewhere [16]. Before reaction, the catalysts were reduced at 538 K under flowing $H_2$ (100 mL $min^{-1}$) for 3 h (3 h ramping time). The liquid effluents were drained from the separator and analyzed by GC (Shimadzu GC-2010, FID, SHRX5 column) and by GC-MS (Shimadzu GC-2010 SHRX1-5MS column). Gas effluents were analyzed with a Carle GC (Series 400 AGC, TCD, Porapak Q column) for CO, $CO_2$ and a Varian GC (Saturn 3, FID, GS-Q column (J&W Scientific)) for gaseous hydrocarbons.

### 2.3. Catalyst characterization

Catalyst samples were dispersed in ethanol and mounted on holey carbon grids for examination in a JEOL 2010F 200 kV transmission electron microscope equipped with Oxford Energy Dispersive Spectroscopy system for elemental analysis. Images were recorded in bright field high resolution (HRTEM) mode as well as in high angle annular dark field (HAADF) mode. Surface area was measured using $N_2$ adsorption at 77 K in a Micromeritics Gemini 2360 multipoint BET analyzer. Nitrogen sorption isotherms and pore size distributions were measured at 77 K in a Quantachrome Autosorb-1 analyzer. X-ray powder diffractions (XRD) were recorded using Scintag Pad V diffractometer (Cu Kα radiation) with DataScan 4 software (MDI, Inc.).

CO adsorption isotherms were collected using a Micromeritics ASAP 2020 apparatus. Prior to chemisorption measurements, the catalysts were reduced in flowing $H_2$ (100 $cm^3$ (STP) $min^{-1}$) for 3 h at 538 K (1.5 K $min^{-1}$). The samples were then purged with UHP helium to clean the metallic surface (200 $cm^3$ (STP) $min^{-1}$) for 1 hr at 538 K. After cooling the samples to 300 K subsequently, small amounts of CO were dosed onto the catalysts. Two isotherms were collected and irreversible probe molecule uptake was calculated by subtracting the reversible uptake from the total uptake measured in the first isotherm.

Temperature-programmed desorption of ammonia was used to measure acid sites. The reactor consisted of a tube furnace connected to a variable power-supply and PID temperature controller (Love Controls) with a K-type thermocouple (Omega). The effluent was monitored by a mass spectrometer system comprising a quadruple residual gas analyzer (Stanford Instruments RGA 200) inside a vacuum chamber. Vacuum was provided by a diffusion pump backed by a rotary pump. The effluent was introduced into the vacuum chamber via a constricted quartz capillary tube, creating a pressure of $5 \times 10^{-5}$ Torr inside the chamber. Dried, unreduced catalysts (100 mg) were loaded into a 12.6 mm outer diameter, fritted quartz tube. Prior to TPD measurements, the catalysts were reduced in flowing $H_2$ (100 $cm^3$ (STP) $min^{-1}$) for 3 h at 538 K (1.5 K $min^{-1}$). The samples were degassed with flowing helium for 1 h at the reduction temperature (200 $cm^3$ (STP) $min^{-1}$), and then cooled to 423 K. $NH_3$ was adsorbed onto the catalysts by exposure to flowing 1 mol % $NH_3$ in helium gas mixture (100 $cm^3$ (STP) $min^{-1}$) for 45 min at 423 K. Residual $NH_3$ was removed by purging the catalyst with helium (200 $cm^3$ (STP) $min^{-1}$) at 423 K for 1 h. Desorption of $NH_3$ was performed by heating the catalyst at a rate of 10 K $min^{-1}$ under flowing helium (50 $cm^3$ (STP) $min^{-1}$) from room temperature to 1073 K.

CO oxidation was performed under flowing CO (1.5 $cm^3$ (STP) $min^{-1}$), $O_2$ (1 $cm^3$ (STP) $min^{-1}$) and He (75 $cm^3$ (STP) $min^{-1}$). Reactivity measurements for the sam-