Applied Catalysis B: Environmental 202 (2017) 446–453

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Hydrodeoxygenation of 3-pentanone over bifunctional Pt-heteropoly acid catalyst in the gas phase: Enhancing effect of gold

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ARTICLE INFO

Article history:
Received 10 August 2016
Received in revised form
15 September 2016
Accepted 22 September 2016
Available online 23 September 2016

Keywords:
Hydrodeoxygenation
3-Pentanone
Bifunctional catalysis
Platinum
Gold
Heteropoly acid

ABSTRACT

Hydrodeoxygenation (HDO) of 3-pentanone to yield *n*-pentane was carried out using bifunctional metal-acid catalysis at a gas-solid interface at 40–80 °C and 1 bar H_2 pressure in a fixed-bed microreactor. The bifunctional catalysts studied comprised Pt as the metal component and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW), an acidic Cs salt of Keggin-type heteropoly acid $H_3PW_{12}O_{40}$, as the acid component. The bifunctional HDO pathway included hydrogenation of ketone to secondary alcohol on metal sites followed by dehydration of the alcohol to alkene on acid sites and finally alkene hydrogenation to alkane on metal sites. Addition of gold to the Pt/CsPW was found to increase both catalyst hydrogenation activity (turnover rate at Pt sites) and catalyst stability to deactivation, although the Au alone without Pt was almost totally inert. The enhancement of catalyst performance is suggested to be caused by PtAu alloying. Scanning transmission electron microscopy–energy dispersive X-ray spectroscopy (STEM-EDX) and X-ray diffraction (XRD) analysis of the PtAu/CsPW catalysts indicated the presence of bimetallic PtAu nanoparticles with a wide range of Pt/Au atomic ratios (0.5–7.7).

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1. Introduction

Biomass-derived oxygenated organic molecules, such as ketones, carboxylic acids, alcohols, phenols, esters, etc., readily available from fermentation, acid-catalyzed hydrolysis, and fast pyrolysis of biomass, are attractive as renewable raw materials for the environment-friendly production of value-added chemicals and bio-fuels [1,2]. For fuel applications, these oxygenates require reduction in oxygen content to increase their caloric value. Therefore, much current research worldwide is focused on the deoxygenation (hydrodeoxygenation) of renewable organic oxygenates using heterogeneous catalysis [3–11].

Previously, this group and others have reported that platinum on acidic supports, especially, Pt on heteropoly acids (HPA), is a highly active bifunctional metal-acid catalyst for hydrodeoxygenation (HDO) of a wide range of oxygenates in the gas and liquid phases under mild conditions [12–17]. On the other hand, bimetallic PdAu and PtAu catalysts have attracted much attention because of their enhanced performance in comparison to monometallic Pd and Pt catalysts [18–29] (and references therein). Bimetallic enhancement of catalyst performance has been attributed to Au alloying through geometric (ensemble) and electronic (ligand) effects of the constituent elements [28,29]. The ensemble effect, often considered to be more important one [29], can cause structural modifications in the surface metal atom geometry to generate specific isolated surface sites that are highly active for certain reactions. The ligand effect can alter the strength of metal-adsorbate bonds as a result of electronic perturbations of platinum group metal due to heteronuclear metal–metal bond formation, which can also lead to increased catalyst activity in certain reactions. Bimetallic PdAu catalysts have been extensively investigated and employed for many important applications, including, among others, the industrial vinyl acetate synthesis [23,24], low-temperature CO oxidation [25,26], and direct H_2O_2 synthesis from H_2 and O_2 [19]. PtAu bimetallics have been widely used for electrocatalysis in fuel cells [27], but scarcely documented for environment-friendly synthetic applications.

Here, we report the enhancing effect of Au on the gas-phase HDO of a ketone, 3-pentanone, over bifunctional metal-acid catalysts comprising Pt as the metal component and a cesium acidic salt of tungstophosphoric HPA, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW), as the acid component. This catalyst has been shown to be highly efficient in a wide range of HDO reactions [13–15]; it has the highest activity in

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http://dx.doi.org/10.1016/j.apcatb.2016.09.044
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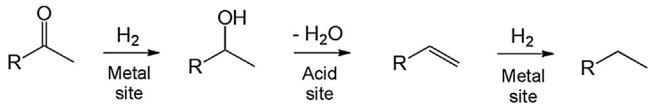

Scheme 1. Ketone hydrodeoxygenation via bifunctional metal-acid catalysis.

the HDO of anisole [15] and aliphatic ketones [13,14] for a gas-phase catalyst system reported so far. The HDO of ketones via bifunctional metal-acid catalysis occurs through a sequence of steps involving hydrogenation of ketone to secondary alcohol on metal sites followed by dehydration of the alcohol to alkene on acid sites and finally hydrogenation of the alkene to alkane on metal sites (Scheme 1) [12–15]. The bifunctional metal-acid catalyzed pathway has been demonstrated to be much more efficient compared to the monofunctional metal-catalyzed ketone-to-alkane hydrogenation [12–14]. It is now demonstrated that modification of the Pt/CsPW catalyst with gold increases the turnover rate of ketone hydrogenation at Pt surface sites and decreases the rate of catalyst deactivation. These effects, however, are dependent on the catalyst formulation and preparation technique. It is suggested that the catalyst enhancement is caused by PtAu alloying. STEM-EDX and XRD analysis of the PtAu/CsPW catalysts indicates the presence of bimetallic PtAu nanoparticles with a wide range of Pt/Au atomic ratios.

2. Experimental

2.1. Chemicals and catalysts

3-Pentanone (98%), $HAuCl_4{\cdot}3H_2O$, H_2PtCl_6 hydrate, $H_3PW_{12}O_{40}$ hydrate, and Darco KB-B activated carbon (150 μm particle size) were all purchased from Sigma-Aldrich. H_2 gas cylinders (>99%) were supplied by the British Oxygen Company.

Cesium tungstophosphate $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW) was prepared according to the literature procedure [30] by adding drop-wise the required amount of aqueous solution of cesium carbonate to aqueous solution of $H_3PW_{12}O_{40}$ to afford CsPW as a white precipitate. The material was isolated, oven dried and calcined at 150 °C/10^{-3} kPa for 1.5 h; finally, it was ground to 45–180 μm particle size. The CsPW thus prepared had a single point BET surface area of 133 $m^2\,g^{-1}$, a single point total pore volume of 0.085 $cm^3\,g^{-1}$, and an average pore diameter of 2.5 nm.

CsPW-supported bifunctional metal-acid catalysts were prepared by wet impregnation of CsPW powder with aqueous solutions of H_2PtCl_6 and/or $HAuCl_4$. This involved stirring the aqueous slurry at 50 °C for 2 h followed by rotary evaporation to dryness and reduction with H_2 flow at 250 °C for 2 h. These catalysts had metal loadings between 0.3–6 wt% and hereafter referred to as Pt/CsPW and Au/CsPW. The bimetallic PtAu/CsPW catalysts were prepared similarly; PtAu/CsPW-CI was prepared by co-impregnation, whereas PtAu/CsPW-SI by sequential impregnation of CsPW with H_2PtCl_6 and $HAuCl_4$. The sequential procedure included preparation of Pt/CsPW with reduction by H_2 at 250 °C/2 h followed by impregnation of the Pt/CsPW thus made with $HAuCl_4$ aqueous solution and subsequent reduction (H_2/250 °C/2 h), i.e. in this case, the Pt was treated twice with H_2 at 250 °C. The metal loadings quoted were confirmed by ICP-AES elemental analysis. Supporting Pt and/or Au had little effect on the texture of CsPW, only slightly decreasing the surface area.

Carbon-supported 5%Pt/C and 5%Au/C catalysts were prepared by wet impregnation of Darco KB-B activated carbon with aqueous solutions of H_2PtCl_6 and $HAuCl_4$ at 50 °C for 2 h followed by rotary evaporation to dryness and reduction by H_2 flow as above. Bimetallic PtAu/C catalysts were prepared similarly by wet co-impregnation of the Darco KB-B carbon with H_2PtCl_6 and $HAuCl_4$ (Pt/Au = 1:1 and 1:2 mol/mol); these are hereafter referred to as 5%Pt/5%Au/C-CI and 5%Pt/10%Au/C-CI, respectively. PtAu/C catalysts were also prepared by sequential impregnation either by wet-impregnating the pre-made 5%Pt/C with the required amount of $HAuCl_4$ followed by reduction with H_2 at 250 °C/2 h (referred to as 5%Pt/5%Au/C-SI and 5%Pt/10%Au/C-SI) or the other way around by wet-impregnating the pre-made 5%Au/C with H_2PtCl_6 (referred to as 5%Pt/5%Au/C-SI* and 5%Pt/10%Au/C-SI*). Physically mixed metal-acid bifunctional catalysts 5%Pt/C + CsPW, 5%Au/C + CsPW, 5%Pt/5%Au/C + CsPW, and 5%Pt/10%Au/C + CsPW with 0.5% Pt loading were prepared by grinding a 1:9 w/w mixture of the corresponding two components.

2.2. Techniques

The BET surface area and porosity of catalysts were determined from nitrogen physisorption measured on a Micromeritics ASAP 2010 instrument at −196 °C. Before measurement, the samples were evacuated at 250 °C for 2 h. Powder X-ray diffraction (XRD) patterns of catalysts were recorded on a PANalytical Xpert diffractometer with CuKα radiation (λ = 1.542 Å). XRD patterns were attributed using the JCPDS database. ICP-AES elemental analysis was carried out on a Spectro Ciros optical emission spectrometer. Thermo Flash EA 1112 series analyzer was used to determine carbon content in spent catalysts by combustion chemical analysis.

STEM imaging and EDX analysis of catalysts was carried out on an aberration-corrected JEOL JEM 2100FCs instrument operated at 200 kV, equipped with an EDAX Octane T Optima 60 windowless silicon drift detector. For STEM analysis, the samples were prepared by scooping up the powder catalyst by a TEM grid (holey carbon film on 300 Ni mesh, Agar Scientific) followed by shaking to remove excess material from the grid.

Pt dispersion in the catalysts was measured by hydrogen chemisorption at room temperature in a flow system on a Micromeritics TPD/TPR 2900 instrument using the hydrogen-oxygen titration pulse method described previously [14,15]. The Pt dispersion, D, defined as the Pt fraction at the surface, $D = Pt_s/Pt_{total}$, was calculated assuming the stoichiometry of H_2 adsorption: $Pt_sO + 1.5H_2 \rightarrow Pt_sH + H_2O$ [31,32]. The average diameter of metal particles, d, was obtained from the empirical equation d (nm) = 0.9/D [32]. For some PtAu/CsPW catalysts, the metal particle size was also estimated by XRD using the Scherrer equation, with line broadening assessed as the full width at half maximum intensity (FWHM).

2.3. Catalyst testing

Hydrodeoxygenation of 3-pentanone was carried out in the gas phase in flowing H_2. The catalysts were tested under atmospheric pressure in a Pyrex fixed-bed down-flow microreactor (9 mm internal diameter) fitted with an on-line gas chromatograph (Varian Star 3400 CX instrument with a 30 m × 0.25 mm HP INNOWAX capillary column and a flame ionization detector). The temperature in the reactor was controlled by a Eurotherm controller (±0.5 °C) using a thermocouple placed at the top of the catalyst bed. The ketone was fed by passing H_2 flow controlled by a Brooks mass flow controller through a stainless steel saturator, which held 3-pentanone at 0 °C (ice bath) to maintain the chosen reactant partial pressure of 1.0 kPa (1.0 mol% concentration of 3-pentanone in H_2 flow), unless stated otherwise. The downstream gas lines and valves were heated to 150 °C to prevent substrate and product condensation. The gas feed entered the reactor at the top at a flow rate of 20 mL min^{-1}. The reactor was packed with 0.20 g catalyst powder of 45–180 μm particle size. Typically, the reaction was carried out at a space time W/F = 400 g h mol^{-1}, where W is the catalyst weight (in grams) and F is the inlet molar flow rate

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