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Aqueous-phase reforming of alcohols with three carbon atoms on carbon-supported Pt

Lidia I. Godina[a], Anton V. Tokarev[a], Irina L. Simakova[b,c], Päivi Mäki-Arvela[a], Ewelina Kortesmäki[a], Jan Gläsel[d], Leif Kronberg[a], Bastian Etzold[d], Dmitry Yu. Murzin[a,*]

[a] Åbo Akademi University, Turku/Åbo, 20500, Finland
[b] Boreskov Institute of Catalysis, pr. Lavrentieva 5, Novosibirsk, 630090, Russia
[c] Novosibirsk State University, Pirogova Str. 2, Novosibirsk, 630090, Russia
[d] Ernst-Berl-Institut für Technische und Makromolekulare Chemie, Technische Universität Darmstadt, Darmstadt, Germany

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ABSTRACT

Aqueous-phase reforming of propanol-1, propane-1,2-diol and glycerol was performed at 498 K and 29.7 bar in a continuous reactor with platinum supported on a polymer-derived carbon, as a catalyst. The number of hydroxyl groups of the reactant influenced the product distribution. An unexpectedly long stabilization period − more than 150 h of time-on-stream − was found to be an important feature of the catalyst.

1. Introduction

Low-temperature conversion of biomass-based feedstock to different energy carriers appears to be a promising technology [1]. Aqueous-phase reforming (APR) is a single stage process, which allows the formation of H_2 or alkanes directly from aqueous solutions of various organic compounds, such as alcohols, polyols, sugars [2], bio-oil [3,4], cellulose [5,6] and different types of lignocellulosic biomass [7–9]. APR proceeds through a complex reaction network, which results in only H_2 and CO_2 in an ideal situation. However, in practice the product distribution is much more diverse. Not only valuable hydrogen and CO_2, but also alkanes in the gas phase and different intermediates in the liquid phase are typically formed as a result of APR. However, an appropriate choice of the catalyst can shift the reaction pathways to the formation of either hydrogen or alkanes [10,11]. While carbon supports might give lower yield compared to metal oxides [12], they possess extraordinary hydrothermal stability compared to the last ones [13]. For instance, metal-free γ-alumina can be transformed relatively fast into boehmite in liquid water at 473 K. Even if such transformation is retarded in the presence of metal particles, it causes catalyst deactivation, probably due to blocking specific surface hydroxyl groups which act as initial hydration sites [14].

Carbon materials in general are very attractive as catalyst supports due to their tunable chemical and textural surface properties. One of the most serious drawbacks of classical activated carbon-based catalysts is the nature of fine powders or granules of poor mechanical strength always encompassed by fines. This leads to high pressure drops in continuous or tedious filtration in batch operation. Contrary to natural precursors with large variability, which are widely employed for synthesis of activated carbon, polymers are well-defined precursors with constantly high quality. As the polymer can be provided in different shapes like fibers, foams or spheres, corresponding structured and shaped porous carbons can be synthesized. Especially spherical shaped carbons have received a growing attention due to excellent fluid dynamic properties and high abrasion resistance to, leading to practically dust-free handling [15–18]. This is of particular interest in continuous operation such as aqueous phase reforming requiring a low pressure drop. The spherical shape and particulate character improve the handling properties during reactor (un-)loading and catalyst preparation. Taking into account the high surface area and large pore volume polymer based spherical activated carbons (PBSAC) are already widely employed in gas- and liquid-phase sorption processes [15–17,19–22]. Very recently PBSAC was introduced as a support for noble metals and was employed in hydrogenation reactions [23].

Previously [24], carbon composite material Sibunit was used as a support for platinum catalysts active in APR of xylitol. This material is produced by the pyrolitic carbon deposition on a granulated carbon black [25]. A subsequent activation stage with steam at 973–1123 K is needed to remove a part of carbon by gasification leading to a sponge-

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[*] Corresponding author.
E-mail address: dmurzin@abo.fi (D.Y. Murzin).

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like system including meso- and macropores.

In the current work PBSAC supported platinum catalyst was employed for aqueous phase reforming of alcohols bearing three carbon atoms. Aqueous-phase reforming of commercial and crude glycerol on carbon-supported Pt catalysts was extensively described in the literature [12,26–44]. At the same time, just a few references can be found for propanol-1 [45,46] and 1,2-propanediol [47] APR. Propanol-1 was converted on Pt/Al_2O_3 [45] *per se* and promoted with ZnO [46], demonstrating that addition of ZnO enhanced hydrogen production. 1,2-propanediol conversion was studied only on Pt/Al_2O_3 together with butane-1,4-diol [47]. However, this process has been already shown to be depended on the support type [48], making it difficult to compare directly the data for propanol and diol with the literature.

In the current study PBSAC supported Pt catalyst was chosen for elucidation of its activity in APR of propanol-1, propane-1,2-diol and glycerol.

2. Experimental

2.1. Catalyst preparation and characterization

The PBSAC support TV1518 derived from a polystyrene-divinylbenzene copolymer was obtained from Blücher GmbH. The spherical polymer particles (d_p = 110–360 μm) were additionally sulfonated to further enhance thermal stability, and were then subjected to carbonization and activation processes. The catalyst was finally prepared from this pristine support via ion exchange according to a method described in the literature [49]. The carbon support TV1518 was oxidized with 50 wt.% sulfuric acid at 363 K for 2.5 h, intensively washed with deionized water, Thereafter the platinum precursor hexachloroplatinic acid (CPA) was deposited from an aqueous solution through electrostatic adsorption. Oxidation step with sulphuric acid was introduced in order to obtain good platinum dispersion [49]. For 1 g of catalyst with a nominal loading of 0.5 wt.% the appropriate amount of CPA was dissolved in 1.1 mL 1 M HCl and 5.9 mL H_2O. The sulfuric acid treated TV1518 was quickly added to the suspension and slowly stirred at ambient temperature for 24 h. The impregnated material was collected by filtration, rinsed with 40 mL H_2O per gram of catalyst and finally dried at 393 K under vacuum. The subsequent reduction was carried out inside the APR reactor prior the experiment at 523 K for 2 h in pure hydrogen.

The catalyst was characterized by means of temperature-programmed reduction (TPR), CO-chemisorption, temperature-programmed oxidation (TPO), temperature-programmed desorption (TPD), inductively coupled plasma analysis (ICP), nitrogen physisorption, transmission electron microscopy (TEM), X-ray fluorescence (XRF).

TPR analysis was performed by means of the AutoChem 2900 instrument. The catalyst sample (0.1 g) was placed in a U-shaped quartz tube and heated from room temperature to 835 K at a rate of 5 K/min. The reduction was performed in 1% H_2 (Ar).

The platinum content was determined with inductively coupled plasma optical emission spectrometry (Ciros CCD, Spectro Analytical Instruments). The sample was prepared by dissolution of platinum with a solution of hydrofluoric acid, nitric acid, and hydrochloric acid at a ratio of 2:2:1 by volume.

Transmission electron microscopy (TEM) was performed using a JEM-2010 microscope (JEOL, Japan) with a lattice resolution of 0.14 nm at an accelerating voltage of 200 kV. Before TEM measurements the samples of catalysts were dispersed in isopropanol and dropped on a copper grid coated with a carbon film. To estimate the value of a mean diameter more than 250 particles were counted. The mean diameter (d_m) of particles was calculated using the following equation: $d_m = \sum_i (x_i d_i)/\sum_i x_i$, where x_i is the number of particles with diameter d_i.

The local elemental analysis was performed with energy-dispersive X-ray spectroscopy using a Phoenix spectrometer (EDAX, USA) equipped with a Si(Li) detector giving the energy resolution not worse than 130 eV. To determine the size dependence of the metal particle composition, EDX line scan data were collected from the particles that lie on the support away from the other particles with the probe diameter about 20 nm. Quantitative EDX measurements were carried out e.g. using Pd Lα line, which is not overlapping with the other X-ray emission lines.

CO-chemisorption was used for evaluation of Pt dispersion and metal particles size. Analysis was performed by means of CO pulse chemisorption apparatus (Micromeritics, AutoChem 2900). The catalyst was reduced prior to CO-titration during 2 h at 523 K. Hydrogen was removed from the surface, and the titration was conducted by CO pulses (10 vol.% CO in He) at 298 K. The Pt to CO stoichiometry was assumed to be 1/1.

The textural properties of both fresh and used catalyst were determined using low-temperature nitrogen physisorption at 77 K (Quadrasorb SI, Quantachrome). Prior to measurements, the samples were degassed in vacuum at 523 K for at least 12 h. The specific surface area and the total pore volume were calculated according to the BET method and to the Gurvich rule, respectively.

TPD and TPO analysis was performed via a NETZSCH STA 409 PC instrument. Fresh and used samples (25 mg) were placed in alumina crucible and heated up to 1273 K (heating rate 5 K/min) in nitrogen or air flow (20 ml/min)

2.2. APR experiments

Experiments were conducted in a continuous reactor, described previously [50]. A stainless-steel tube (520 × 6.4 mm) was located in a furnace and connected to gas inlet and HPLC pump. The tube was filled sequentially with a bed of sand, followed by 1 g of catalyst located in the middle of reactor, and another bed of sand. Nitrogen (1% He) and aqueous solutions of alcohols (mono- and polyols) were co-fed in a down-flow mode. Gas- and liquid-phase reaction products were analyzed by means of HPLC and micro-GC respectively. The liquid samples were frozen just after sampling. The experimental set-up is shown in Fig. 1. The mass balance closure for this set-up is typically around 90% slightly depending on the substrate.

The catalyst was reduced in-situ at 523.5 K under an excess of hydrogen (flow 40 ml/min) during 2 h prior the tests. The catalyst was heated up to the final temperature at a heating rate of 5 K/min, maintained for 2 h and slowly cooled down to 498 K. Hydrogen was flushed out with nitrogen flow (24 ml/min), and the reactor was pressurized to 29.8 bar.

Propanol-1, propane-1,2-diol and glycerol were consequently tested on the same catalyst loading. Aqueous solutions of alcohols (5 wt.%) were fed with different flow rates (0.1–2.0 mL/min) in a trickle-bed mode. Nitrogen with 1% He was used as a carrier gas in a co-current down-flow (20 ml/min). Scheme of catalytic experiments and flow rates is shown in Fig. 2. Solution of propanol-1 was tested during the first 75 h of time-on-stream (TOS), and was replaced directly to the diol solution for the next 75 h TOS. Regeneration was applied before feeding of glycerol solution during 150 h TOS. Pt catalyst was shown [51] to be successfully regenerated via flushing with acetone, water, and repetitive reduction procedure. In addition, the final catalytic activity was compared with the initial one by feeding of propanol-1 just after glycerol.

2.2.1. GC analysis

Gas-phase products were analyzed online by means of a micro-GC (Agilent Micro-GC 3000A) equipped with four columns: Plot U, OV-1, Alumina and Molsieve.