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Platinum on carbonaceous supports for glycerol hydrogenolysis: Support effect

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ABSTRACT

Metal vapor synthesis (MVS) technique was applied to generate Pt-nanoparticles of different size (<1.3 nm and 2.5 nm) deposited onto carbonaceous supports, mainly characterized by a different surface area. The supported catalysts were employed in the glycerol hydrogenolysis reaction carried out under basic reaction conditions at 433 and 453 K to obtain 1,2-propanediol as the main liquid product. Comparison of the composition of the liquid- and gas-phase products obtained by the different catalysts showed a clear dependence of aqueous-phase reforming, water–gas shift reaction activity as well as 1,2-propanediol chemoselectivity on the degree of Pt-sintering occurring on different carbon supports. High-resolution transmission electron microscopic and X-ray powder diffraction studies carried out on as-synthesized and recovered heterogeneous catalysts provided clear evidences that a high surface area carbon support, such as Ketjen Black EC-600JD, notably retards nanoparticle aggregation.

1. Introduction

The hydrogenolysis (*i.e.*, dehydration and successive hydrogenation) of glycerol, which is the major by-product of biodiesel production, brings about the formation of the value-added diols 1,2-propanediol (1,2-PD) [1–7] and 1,3-propanediol (1,3-PD) [8,9], which are mainly applied in the synthesis of biodegradable polymers, functional fluids, foods, cosmetics, and fragrances [10]. Glycerol (GLY) hydrogenolysis generally needs harsh catalytic conditions (*i.e.*, 400–500 K, basic reaction conditions and a dihydrogen pressure of 210–4500 psi) to proceed [10,11]. The activity of metal supported catalysts for glycerol hydrogenolysis follows the order Ru ≈ Cu ≈ Ni > Pt > Pd [11]. The main issue of glycerol hydrogenolysis reactions is related to the selective breaking of C–C or C–O bonds of the triol. In this respect, Pt shows generally much lower C–C hydrogenolysis activity compared to Ru, being hence a suitable candidate for the base-mediated chemoselective hydrogenolysis of GLY to 1,2-PD and lactate [5–7]. Along with the hydrogenolysis activity, aqueous-phase reforming (APR) is also observed, which is a structure sensitive process (*i.e.*, selectivity depends on metal particle size) [12–17]. Tomishige discussed a related nanoparticle (NP) size-sensitivity for the Ru-/C-mediated GLY hydrogenolysis reaction to give 1,2-PD as main product (*i.e.*, smaller particles were less selective for the 1,2-PD production) [4]. Directly connected to the selectivity problem is the stabilization of Pt-NPs in the course of the catalytic hydrogenolysis reaction. In this respect, the application of bimetallic Pt-Ru-NPs [7] and particle modification by additional ligands [18] did not really improve the performance of Pt-based catalysts. On the other hand, the nature of the support used notably influences the NPs' growth, since it behaves as a macroligand which interacts with the NPs' surface by its functional groups. Herein, we systematically study the effect of the support surface area on the sintering of Pt-NPs during glycerol hydrogenolysis reaction. To this purpose, we chose three graphite-type carbon supports, which differ mainly in surface area and atomic oxygen content (*i.e.*, Ketjen Black EC-600JD (C^K) (1396 m^2/g, 6.2%) [19], Vulcan XC-72 (C^V) (254 m^2/g, 5.4%) [19], and few layer graphene (C^G) (55 m^2/g, 3.9%) [20]. Pt-NPs of controlled size (<1.3 nm and 2.5 nm, respectively) were deposited on the different carbon supports by means of metal vapor synthesis (MVS) technique [21].

2. Experimental

2.1. Materials

GLY and NaOH were purchased from Aldrich and used as received. Mesitylene and *n*-pentane were purified by conventional

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methods, distilled, and stored under argon. C^K and C^V were purchased from Cabot Corp. USA, while C^G was prepared as reported in the literature [20]. Water was bidistilled.

2.2. Catalyst preparation

The Pt-NPs supported onto C^K, C^V, and C^G were synthesized by the MVS technique as follows: Platinum vapors generated at 1.45×10^{-6} psi by resistive heating of a tungsten wire surface coated with electrodeposited platinum (ca. 102.0 mg) were co-condensed with either mesitylene or *n*-pentane (60.0 mL) in a glass reactor at 77 K. The reactor chamber was heated to the melting point of the solid matrix, and the resulting brown solution (55.0 mL) was kept under argon atmosphere in a Schlenk tube at 195 K. The Pt-content of the obtained Pt-solvated metal atoms (SMAs) was determined by ICP-OES (1.4 mg/mL for Pt/mesitylene and 0.6 mg/mL for Pt/*n*-pentane). The SMAs (33.0 mg of Pt, 24.0 mL of Pt/mesitylene, or 55.0 mL of Pt/*n*-pentane) were added to a dispersion of the support (1.10 g) in either mesitylene or *n*-pentane (20.0 mL). The resulting suspension was warmed up to 298 K under stirring for 12 h. Afterward the solvent was removed by vacuum and the obtained solids $Pt@C^K/C^V/C^G$ were washed with *n*-pentane and dried under reduced pressure. All isolated samples contained 3.0 wt.% of Pt as determined by ICP-OES analysis.

2.3. Catalyst characterization

Transmission electron microscopy (TEM) analysis of the supported Pt-NPs was carried out with a ZEISS LIBRA 200FE High-resolution Transmission Electron Microscope (HRTEM), equipped with a FEG source operating at 200 kV, in column second-generation omega filter for energy selective spectroscopy (EELS) and imaging (ESI), HAADF-STEM facility, EDS probe for chemical analysis, integrated tomographic HW and SW. The samples of the supported catalysts were ultrasonically dispersed in isopropanol and a drop of the suspension was deposited on a holey-carbon film supported on a copper TEM grid of 300 mesh. Histograms of the particle size distribution were obtained by counting at least 500 particles. The mean particle diameter (d_m) was calculated using the formula $d_m = \sum d_i n_i / \sum n_i$, where n_i is the number of particles with diameter d_i. Powder X-ray diffraction (PXRD) spectra were acquired at room temperature with a PANalytical X'PERT PRO powder diffractometer, employing Cu Kα radiation ($\lambda = 1.5418$ Å), and a parabolic MPD-mirror. The spectra were acquired in the 2Θ range from 5.0° to 100.0°, applying a step size of 0.0263° and a counting time of 70.9 s.

ICP-OES analyses of the supported catalysts were carried out with an iCAP 6200 Duo upgrade, Thermofisher instrument. A sample (1.0 mL) of Pt-SMA solution was heated over a heating plate in a porcelain crucible in the presence of aqua regia (2.0 mL) for six times, dissolving the solid residue in 0.5 M aqueous HCl. The limit of detection calculated for platinum was 2 ppb.

The BET-specific surface area of selected Pt-containing samples was determined by nitrogen adsorption at 77 K using a Micromeritics ASAP 2020 analyzer.

The metal dispersion and particle size of $Pt_a@C^K$, $Pt_b@C^K$, $Pt_a@C^V$, and $Pt_b@C^V$ was determined with the latter apparatus by dihydrogen chemisorption at 308 K in the pressure range between 0.09 and 9.7 psi. The sample was pretreated by a H_2 flow for 1.5 h at T_{red} of 423 and 473 K, followed by evacuation at $T_{evacuation} = (T_{red} + 10\ K)$ for 10 h. After cooling the sample to 308 K, it was again evacuated for 2 h and then analyzed at 308 K. The metal surface area was determined from the total amount of adsorbed H_2 at 308 K and then extrapolated to zero pressure, assuming a Pt/H stoichiometry equal to unity. The amount of chemisorbed gas on the sample surface was determined after subtracting the physisorbed contribution.

2.4. Catalytic hydrogenolysis reaction

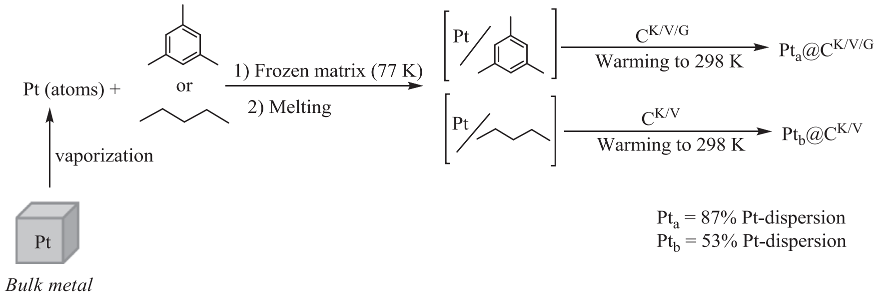
Supported Pt catalysts $Pt_a@C^{K/V/G}$ (100.0 mg, 0.01538 mmol of Pt, *a* corresponds to a 87% Pt dispersion; 0.01338 mmol $Pt_{surface}$) and $Pt_b@C^{K/V}$ (164.0 mg, 0.02522 mmol of Pt, *b* corresponds to a 53% Pt dispersion; 0.01338 mmol $Pt_{surface}$) were introduced into a stainless steel autoclave, which was then sealed and evacuated. Afterward a deaerated solution of GLY (17.046 mmol) (*i.e.*, GLY to $Pt_{(surface)}$ molar ratio of 1274) and NaOH (40.0 mmol) in water (50.0 mL) was introduced into the autoclave by suction at room temperature. The autoclave was then charged with dihydrogen (600 psi) at 303 K and heated to the desired reaction temperature under agitation (1000 rpm). After the desired reaction time, the autoclave was cooled to room temperature and the gaseous reaction products were analyzed with a QIC Series Mass Spectrometer (Hiden Analytical). The residual gas pressure was then released, the autoclave opened, and the liquid phase neutralized with sulfuric acid (0.1 M) and afterward analyzed by high pressure liquid chromatography (HPLC) (*i.e.*, Shimadzu-UFLC apparatus, equipped with a RID detector and a Alltech OA-1000 organic acid column of 300 mm (length) and a 6.5 mm (i.d.); 0.01 N H_2SO_4 was used as eluent combined with a eluent flow rate of 0.4 mL/min at 338 K.

Supported catalysts were recovered by filtration, washed with water (3 × 10.0 mL) and acetone (2 × 10.0 mL), and then dried at room temperature.

Recovered $Pt_a@C^K$ and $Pt_a@C^V$ was used for recycling experiments carried out at 433 K.

The GLY conversion (%), the amount of gas-phase products (%), the chemoselectivity of the liquid products (%), and TOF values were determined as follows:

GLY conversion $(\%) = [\mathrm{mol}(GLY_{initial}) - \mathrm{mol}(GLY_{unreacted})] / \mathrm{mol}(GLY_{initial}) \times 100$.



Scheme 1. Catalysts' synthesis by MVS technique.