

Chemoselective Hydrogenolysis of Glycerol Catalyzed by Platinum on Carbonaceous Supports

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ABSTRACT

Highly dispersed Pt-nanoparticles supported onto carbonaceous materials, which are characterized by their surface area, were employed to catalyze the hydrogenolysis of glycerol in water. The surface area of the support proved to steer the aggregation process of the nanoparticles with time, consequently influencing the catalyst performance in terms of glycerol conversion, reforming activity and chemoselectivity versus 1,2-propandiol, which was the main liquid product. The support with the highest surface area showed the best control on the nanoparticles' aggregation.

Keywords: platinum, glycerol, hydrogenolysis, metal vapor synthesis, carbonaceous support

INTRODUCTION

The hydrogenolysis of C-C and C-O bonds in polyols generally occurs under basic conditions in the presence of dihydrogen (210-4500 psi) at temperatures from 400 to 500 K by means of supported metal catalysts (i.e. Ru, Pd, Pt, Ni and Cu) [1]. The main issue of hydrogenolysis is to selectively break selected C-C and/or C-O bonds, producing hence more valuable polyols or diols. Diols such as ethylene glycol (EG), 1,2-propandiol (1,2-PD), and 1,3-propandiol (1,3-PD) are mainly applied in the synthesis of biodegradable polymers, functional fluids, foods, cosmetic flavors, and fragrances [2]. The hydrogenolysis of glycerol, which brings about the formation of 1,2-PD [3-5] and 1,3-PD [6-9] as major compounds, has received notable attention due to the low cost of glycerol (GLY), which is the by-product of an increasing biodiesel production. The activity of supported metal catalysts for the hydrogenolysis of a 80% GLY solution at 470 K and 225 psi decreases in the order (Ru, Cu, Ni) > Pt > Pd [3]. Pt shows generally much lower C-C hydrogenolysis activity compared to Ru and is thus a valuable candidate for the base-mediated chemoselective hydrogenolysis of glycerol to 1,2-PD and lactate (LA) [10-11], whereas acid mediated Pt-based catalysts yield mainly 1,3-PD [9].

The chemoselective product formation as well as the stabilization of the heterogeneous catalyst against NPs' sintering are important issues in the heterogeneous glycerol hydrogenolysis reaction conducted under harsh reaction conditions (i.e. reaction temperature \geq 473 K). Consequently, a good stability of the support material is crucial for an efficient catalytic process. In this context, carbonaceous supports such as activated carbon and carbon nanotubes (CNT) were shown to be stable even under harsh reaction conditions encountered in aqueous phase reforming processes of biomasses [12-19].

RESULTS AND DISCUSSION

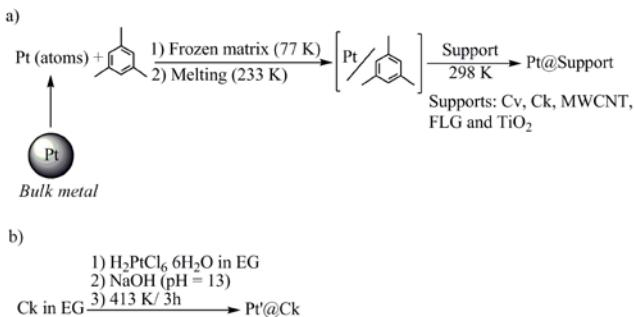
We supported well-defined Pt-NPs, obtained by metal vapor synthesis (MVS) [20] (Scheme 1a), onto different carbonaceous supports such as Vulcan XC-72 (Cv), Ketjen Black EC-600JD (Ck), multi-walled carbon nanotubes (MWCNT), few layer graphene (FLG) and for comparison reason also on TiO₂. The morphological properties of all supports used herein are summarized in Table 1.

Support	Surface area (m ² /g)	Pore Volume (mL/100g)	Atomic oxygen (%) (XPS)
Cv [21]	254	174	5.4
Ck [21]	1400	480-510	6.2
MWCNT [22]	225	-	1.1
FLG [23]	55	-	3.9
TiO ₂ (P25) [24]	56	25	-

Table 1: Morphological properties of the supports used.

The formation of mesitylene stabilized Pt-nanoclusters which can then be supported very easily by adding the support of choice, makes MVS a very attractive synthesis procedure for supported Pt-NPs, ensuring: (i) comparable Pt-NPs' dimensions on each support and (ii) the presence of only Pt(0) on the support. In fact, the synthesis of metal-NPs based on the chemical reduction of oxidized metal precursors suffers from partial metal reduction (i.e. the degree of metal ion reduction is generally strongly depending on the experimental condition chosen such as reduction medium and reaction temperature [25]). An alternative synthesis procedure based on the reduction of

$\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ under basic conditions ($\text{pH} = 13$) in the presence of Ck and EG gave $\text{Pt}'@\text{Ck}$ (Scheme 1b).



Scheme 1: Synthesis procedures for supported Pt-NPs.

HRTEM-images acquired for all supported Pt catalysts, synthesized by MVS procedure, showed a NPs' diameter of 1.5 nm, regardless of the support used. Conversely, Pt-NPs synthesized by a typical chemical reduction (Scheme 1b) showed NPs of 5.4 nm in size. Accordingly, only the XRPD spectrum of $\text{Pt}'@\text{Ck}$ (Figure 1, trace c) showed the characteristic Bragg reflections of cubic Pt ($\text{Fm}\bar{3}\text{m}$) (Figure 1).

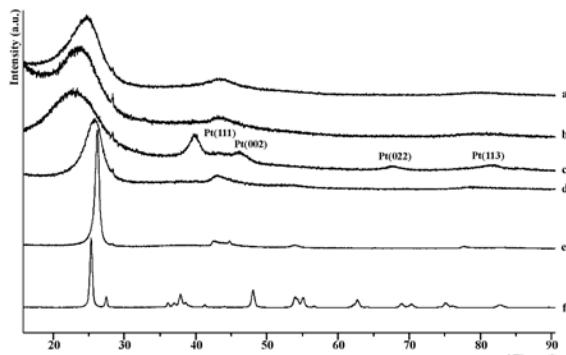
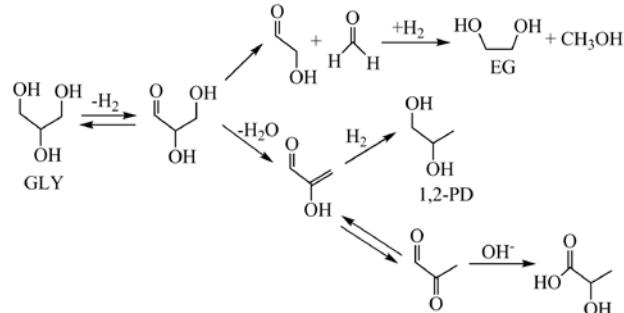


Figure 1: XRPD spectra of: (a) $\text{Pt}@Cv$, (b) $\text{Pt}@Ck$, (c) $\text{Pt}'@\text{Ck}$, (d) $\text{Pt}@CNT$, (e) $\text{Pt}@FLG$ and (f) $\text{Pt}@TiO_2$.

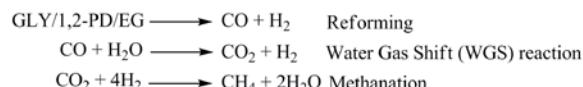
The supported Pt-NPs were then applied in the hydrogenolysis reaction of glycerol carried out in water and in the presence of NaOH (0.8M) and dihydrogen pressure (600 psi at 303 K) at 453 K. Liquid and gaseous reaction products were formed under these catalytic conditions (Scheme 2). The main liquid hydrogenolysis product was 1,2-PD, regardless of the support used (Table 2), while EG and MeOH, obtained by a base-assisted retro-aldol reaction [26] and LA, yielded as minor products (Table 2). LA was obtained as the solely liquid product when the catalytic reactions were carried out in the presence of base but in the absence of dihydrogen (Table 2, entry 3). In case of $\text{Pt}@TiO_2$ formate (FA) (ca 2-3%), instead of LA, was obtained as minor product. The gaseous reaction phase consisted mainly of excess dihydrogen, CO, CO_2 ($\text{CO}:\text{CO}_2$ 9:1 molar ratio) and methane (traces) (Scheme 2b). From a comparison of the catalysts' performance under identical experimental conditions (Table 2) it can be inferred that

$\text{Pt}@Ck$ is the most active catalyst in terms of glycerol conversion and chemoselectivity as far as the formation of 1,2-PD is concerned (Table 2, entry 5 vs entries 1, 9 and 11) outperforming not only $\text{Pt}@TiO_2$ (entry 5 vs 13) but also $\text{Pt}'@\text{Ck}$ (entry 5 vs 7).

a) Liquid phase products



b) Gas phase products



Scheme 2: Liquid and gas phase products formed under glycerol hydrogenolysis reaction conditions.

Entry ^a	Catalyst	Conv (%) ^b	C-deficit (%) ^c	1,2-PD (%) ^d	EG (%) ^d	LA (%) ^d
1	$\text{Pt}@Cv$	79	27	55	6	4
2 ^e	$\text{Pt}@Cv$	94	45	47	6	-
3 ^f	$\text{Pt}@Cv$	100	54	-	-	47
4 ^g	$\text{Pt}@Cv$	53	22	53	2	4
5	$\text{Pt}@Ck$	82	27	60	4	4
6 ^g	$\text{Pt}@Ck$	57	14	73	7	-
7	$\text{Pt}'@\text{Ck}$	76	23	54	11	5
8 ^g	$\text{Pt}'@\text{Ck}$	58	19	52	13	2
9	$\text{Pt}@CNT$	42	21	48	1	5
10 ^h	$\text{Pt}@CNT$	61	29	44	2	7
11	$\text{Pt}@FLG$	49	33	21	trace	12
12 ^h	$\text{Pt}@FLG$	50	21	36	2	21
13 ⁱ	$\text{Pt}@TiO_2$	66	33	46	2	-
14 ^{h,i}	$\text{Pt}@TiO_2$	72	36	46	2	-

^aCatalytic conditions: Pt (3 wt%, 0.01538 mmol), H_2O (50 mL), glycerol (17.046 mmol), NaOH (40.0 mmol) T (453 K), $p(\text{H}_2)$ (600 psi at 303 K), t (4h). ^bConversion (%): $[\text{mol}(\text{gly}_{\text{initial}})-\text{mol}(\text{gly}_{\text{unreacted}})-\text{mol}(\text{products})]/\text{mol}(\text{gly}_{\text{initial}}) \times 100$. ^cCarbon deficit (%): $[\text{mol}(\text{products})-\text{mol}(\text{gly}_{\text{unreacted}})]/\text{mol}(\text{gly}_{\text{initial}}) \times 100$. ^dChemoselctivity (%): $[\text{mol}(\text{product})]/[\text{mol}(\text{gly}_{\text{initial}})-\text{mol}(\text{gly}_{\text{unreacted}})] \times 100$. ^eWithout base. ^fWithout $p(\text{H}_2)$. ^gT (433 K). ^h(8h) ⁱFA formed: entry 13 (2%) and entry 14 (3%).

Table 2: Catalytic glycerol hydrogenolysis by Pt@supports.

$\text{Pt}@FLG$ proved to be the less efficient catalyst in terms of substrate conversion, stability with time and chemoselectivity for 1,2-PD (Table 2, entry 11 vs 12).

The outstanding performance of $\text{Pt}@Ck$ is obvious by decreasing the hydrogenolysis reaction temperature from 453 to 433 K, gaining a chemoselectivity for 1,2-PD of 73% (Table 2, entry 6).

HRTEM-analysis carried out on recovered catalysts (i.e. after catalysis lasting 4h at 453 K) showed for Pt@Ck (Figure 2b) and Pt@TiO₂ (Figure 2e) the lowest NP aggregation, whereas Pt@Cv (Figure 2a), Pt@CNT (Figure 2c) and Pt@FLG (Figure 2d) experienced a significant increase in particle size. It should be mentioned at this stage that Pt@FLG represented the worst case as far as particle aggregation is concerned, showing worm-like Pt-NP aggregates (Figure 2d).

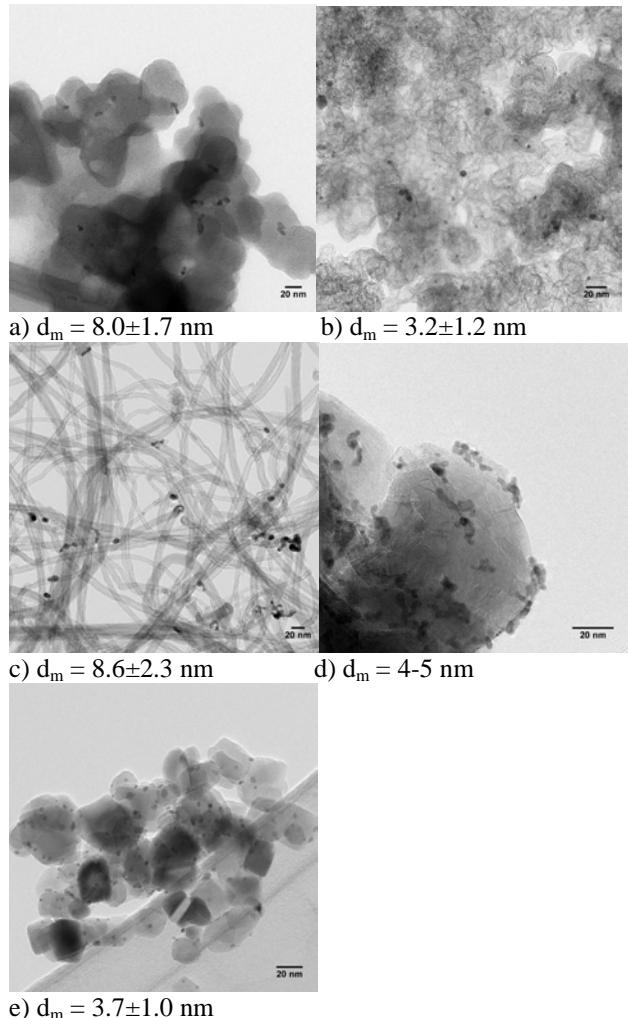


Figure 2: HRTEM-images aquired for recovered Pt-NP-based catalysts: (a) Pt@Cv, (b) Pt@Ck, (c) Pt@CNT, (d) Pt@FLG and (e) Pt@TiO₂.

CONCLUSIONS

The synthesis of small Pt-NPs (1-1.5 nm) by means of MVS followed by supporting them onto Ck which is the carbon support with the highest surface area used in this study gave a valuable heterogeneous Pt-based catalyst which proved to be suitable for glycerol hydrogenolysis even at 433 K, yielding 1,2-PD with a chemoselectivity of 73%. Upon decreasing the carbon surface area from 1400 to 55 m²/g, as in the case of FLG, the Pt-NPs' aggregation

increased dramatically under real catalytic conditions influencing negatively the catalytic activity and chemoselectivity versus 1,2-PD.

EXPERIMENTAL SECTION

Materials. H₂PtCl₆·6H₂O, EG, GLY and NaOH were purchased from Aldrich and used as received. Mesitylene was purified by conventional methods, distilled and stored under argon. Vulcan XC-72, Ketjen Black EC-600JD were purchased from Cabot Corp. USA. MWCNT [22] and FLG [23] were synthesized as reported in the literature.

Synthesis of Pt@Support by MVS. Platinum vapors generated at 10⁻⁴ mbar by resistive heating of a tungsten wire surface coated with electrodeposited platinum (102 mg) were co-condensed with mesitylene (60 mL) in a glass reactor at 77 K. The reactor chamber was heated to the melting point of the solid matrix (233 K) and the resulting yellow-brown solution (55 mL) was kept under argon atmosphere in a Schlenk tube at 233 K. The platinum content of the mesitylene solvated platinum solution was determined by ICP-OES (1.4 mg/mL). The Pt/mesitylene solution (25.0 mL, 35.0 mg Pt) was added to a dispersion of the support (1.10 g) in mesitylene (20 mL). The resulting suspension was stirred for 12h at room temperature. Afterwards mesitylene was removed by vacuum and the light brown solid, containing Pt (3 wt%) was washed with n-pentane and dried under reduced pressure.

Synthesis of Pt@Ck. Ground Ketjen Black (3.0 g) was suspended in EG (126 mL) and treated with ultrasound for half an hour. Afterwards the suspension was deareated by a flow of nitrogen and mechanically stirred, followed by the slow addition of a solution of H₂PtCl₆ (270 mg) in EG. Afterwards NaOH (2.5 g) dissolved in EG (23 mL) and water (8 mL) was added slowly to the latter suspension at room temperature under nitrogen. Once the addition was completed (pH = 13) the suspension was refluxed at 413 K for three hours under nitrogen. Then the reaction mixture was allowed to cool to room temperature followed by its filtration in air atmosphere. The isolated support was successively washed with water until pH neutrality was reached and dried under vacuum at 303 K. Yield: 5.95 g (Pt 1.1 wt%).

Catalytic hydrogenolysis reactions. Supported Pt catalysts (0.01538 mmol of Pt) was introduced into a stainless steel autoclave, which was successively sealed and evacuated. Afterwards a deareated solution of glycerol (17.046 mmol) and NaOH (40.0 mol) in water (50.0 mL) was introduced into the autoclave by suction at room temperature. The autoclave was then successively charged with dihydrogen (600 psi) at 303 K, heated at the desired reaction temperature under then stirred (1000 rpm). After the chosen reaction time, the autoclave was cooled to 283 K and the gaseous reaction products were analyzed by means of an online mass spectrometer. The residual gas pressure was then released, the autoclave opened, the liquid phase

neutralized with sulphuric acid (0.1M) and analyzed by high pressure liquid chromatography (HPLC). The supported catalyst was recovered by filtration, washed several time with water and acetone and then dried at room temperature.

Characterization of supported catalysts.

Transmission electron microscopic analyses of the heterogeneous Pt-based catalysts were carried out with a ZEISS LIBRA 200FE High Resolution Transmission Electron Microscope (HRTEM), equipped with a FEG source operating at 200kV. Powders of the supported catalysts were ultrasonically dispersed in isopropyl alcohol 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 300 particles. Powder X-ray diffraction (PXRD) spectra were acquired at room temperature with a PANalytical X'PERT PRO powder diffractometer, employing $\text{Cu}_{\text{K}\alpha}$ radiation ($\lambda = 1.5418 \text{ \AA}$) 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 was carried out with an iCAP 6200 Duo upgrade, Thermo Fisher instrument.

Analysis of the reaction products. The gaseous reaction products stemming from catalytic reforming process were analyzed with a QIC Series Mass Spectrometer (Hiden Analytical), while the aqueous reaction solutions were analyzed by HPLC (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.); 0.01N H_2SO_4 was used as eluent applying a flow rate of 0.8mL/min at 308 K or 0.4mL/min at 338 K.

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