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Base-free aerobic oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid over Pt/C catalysts synthesized by pulse alternating current technique

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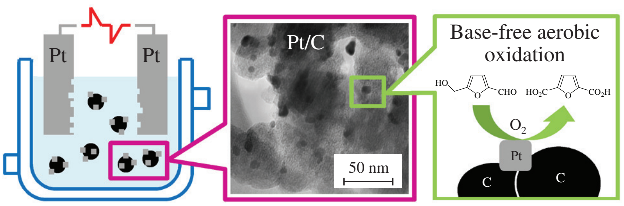
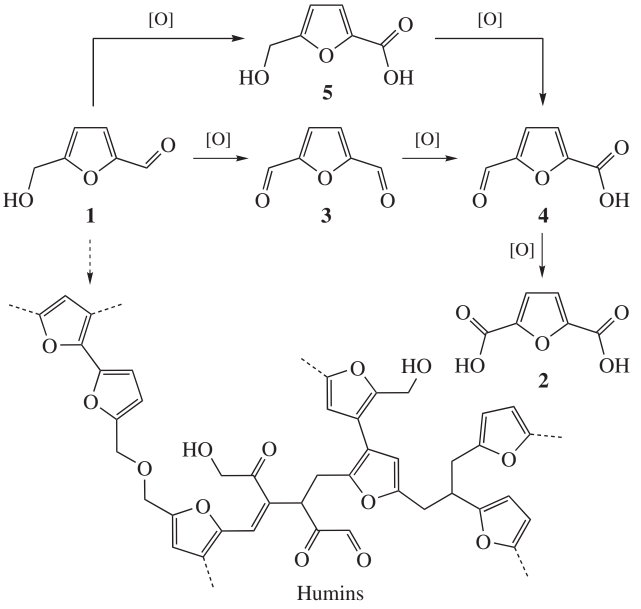
The Pt/C catalysts with various Pt content (5–30 wt%) synthesized *via* electrochemical pulse alternating current technique have been evaluated for the base-free aerobic oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid. The higher Pt content in the catalyst (30 wt%) provides the product yield up to 65% upon performing the process in concentrated (~0.1 M) aqueous solutions of the substrate.



5-Hydroxymethylfurfural **1** and its derivatives, such as 2,5-furandicarboxylic acid **2** and 2,5-diformylfuran **3** are regarded as platform chemicals for synthesis of various valuable compounds.[1–8] Diacid **2** is one of the most promising bio-based monomers, which can replace oil-based terephthalic and isophthalic acids for production of polymers like polyethylene terephthalate in future.[1,8–10] Diacid **2** is prepared by the oxidation of substrate **1** with the formation of various intermediates and by-products depending on the reaction conditions (Scheme 1).[1,9,11] Heterogeneously catalyzed oxidations of compound **1** with air or molecular oxygen are considered to be most promising for industrial implementation.[1] High activity and selectivity have been found for precious-metal based catalysts.[9] Platinum-based catalysts on different supports in alkaline aqueous solutions enables oxidation of hydroxy aldehyde **1** into diacid **2** in up to ~100% yields.[1,9] However, oxidation in alkaline solutions leads to large quantities of mineral wastes at the product isolation, which requires acidification to separate free acid, and this increases the risk of reactor corrosion.[9] Therefore, the aerobic oxidation of substrate **1** in the absence of base (base-free oxidation) seems environmentally more friendly and suitable for large-scale industrial applications.[12] The main drawback of base-free oxidation processes[12–15] typically consists in necessity for the use of diluted (up to 10^{-2} M) solutions of compound **1** to minimize by-product (mainly humines) formation and to prevent catalyst deactivation. In addition, catalysts with low Pt loading (⩽5 wt%) require prolonged time for oxidation (12–24 h) under base-free conditions.[12–15] Despite high yields of diacid **2**, all of these methods do not provide high overall process efficiency from industrial point of view.



Scheme 1

In recent years, a new environment-friendly and cheap method for the preparation of heterogeneous platinum catalysts *via* electrochemical dispersion of metal platinum under pulse current electrolysis was developed.[16–18] As distinct from many conventional ‘chemical’ methods, the electrochemical dispersion technique allows one to tune Pt loadings in a wide range providing narrow Pt nanoparticles size distribution (8–10 nm).[16–18] Catalysts Pt/C obtained *via* electrochemical dispersion revealed enhanced stability combined with good activity for complete oxidation of simple organic substances in fuel cells.[17,18] Nevertheless, potential of these catalysts for oxidative synthesis of valuable organic compounds is still unexplored.

In the current study, we investigated possibilities of base-free oxidation **1** → **2** with molecular O_2 in concentrated (0.1 M) aqueous solutions using Pt/C catalysts with enhanced Pt content (up to 30 wt%) obtained *via* electrochemical dispersion of platinum metal. To the best of our knowledge, this is the first example of application of Pt/C catalyst obtained by such a technique in organic synthesis.

The Pt/C (C is Vulcan XC-72) catalysts were prepared by electrochemical dispersion of Pt electrodes under pulse alternating current, as was described previously.[16] The platinum loadings in the catalysts were 5, 15 and 30 wt%. These catalysts are hereafter denoted as Pt/C-5, Pt/C-15 and Pt/C-30, respectively. The average Pt particle size along the [111] direction (D_{111}) calculated using the Scherrer equation from XRD data[†] (Figure S1, Online Supplementary Materials) was 9±1 nm. According to the TEM images of Pt/C samples (Figure S2), platinum nanoparticles were uniformly distributed over the surface of carbon support.

Oxidation of substrate **1** was studied at 105 °C in a batch-type autoclave. In catalytic experiments, 0.1 M aqueous solution of **1**, initial molar ratio of **1**/Pt = 20 : 1, oxygen pressure of 0.25 MPa were applied.[‡] The reaction mixture was analyzed by high-performance liquid chromatography (HPLC).[§]

According to HPLC analyses, the oxidation of hydroxy aldehyde **1** proceeds sequentially through the partially oxidized intermediates, **3** and **4** (see Scheme 1), in agreement with the published data for analogous base-free aerobic oxidations over carbon supported Pt catalysts.[12,14,15] The product yield curves are typical of continuous processes (Figures 1 and S5). Higher Pt contents (15 and 30 wt%) in the studied catalysts provided higher oxidation rates (see Figure 1). Thus, with Pt/C-5 catalyst within 6 h nothing of product **2** was detected, whereas Pt/C-15 and Pt/C-30 catalysts provided the 30 and 63% yields, respectively (Figures 1 and S5). Prolongation of the reaction time from 6 to 10 h enhanced the product yield substantially (up to 66%) for Pt/C-15 catalyst and only slightly (up to 65%) for Pt/C-30 catalyst. However, prolongation of the synthesis to 10 h significantly dropped the selectivity (see Figure 1), apparently owing to decomposition of intermediate compounds and polymerization of substrate **1** into humins.[6] Note that in preparative experiments with the prolonged reaction time (10 h) the yields of diacid **2** were lower because substantial amounts of by-products complicated its separation and purification.

Remarkably, the Pt/C-5 catalyst with the low Pt content (5 wt%) furnished very low (~0%) selectivity of the process and promoted loss of substrate **1** due to formation of unidentified by-products (see Figure 1). This may be caused by adverse catalytic activity of activated carbon support.[19] Thus, it was revealed that activated carbon (Vulcan XC-72 without Pt) promoted decomposition of compound **1** (Table 1, entries 4–6). In these experiments, loss of the latter owing to simple physical adsorption was excluded by preliminary saturation of activated carbon in large excess of 0.1 M solution of substrate **1**. Since initial **1**/Pt molar ratio was the same in all catalytic experiments, use of the catalyst with low Pt content (5 wt%) may be regarded as administration of enhanced

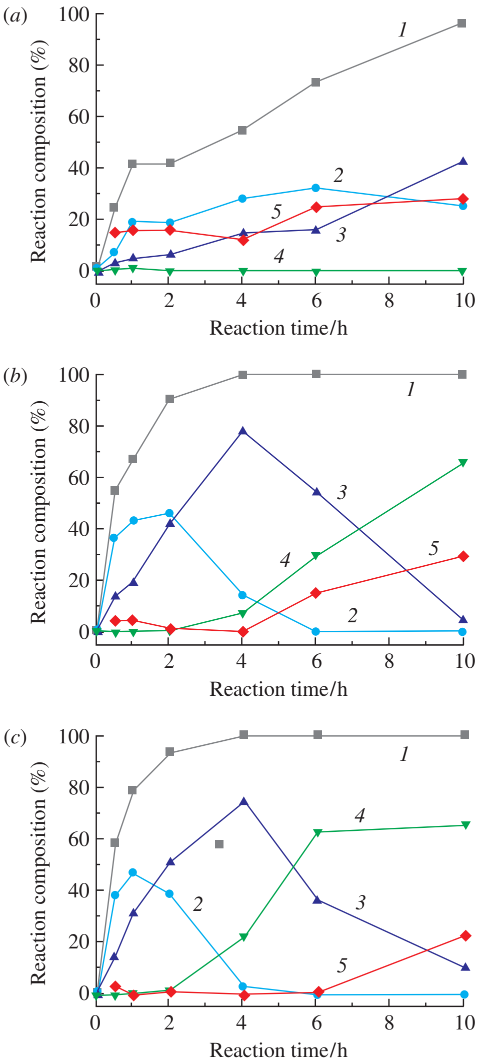


Figure 1 Kinetic curves for catalytic oxidation of compound **1** at 105 °C and 0.25 MPa on (*a*) Pt/C-5, (*b*) Pt/C-15, and (*c*) Pt/C-30. (*1*) Conversion of **1**, and (*2*)–(*5*) yields of **3**, **4**, **2** and unidentified products, including humins, respectively.

Table 1 Effect of carbon content in the Pt/C catalyst on the oxidation of **1**.[a]

Entry	Catalyst	Catalyst components/mg		Conversion of **1** (%)	Yield of **2** (%)	UIP[b] (%)
		Pt	C			
1	Pt/C-5	5	95.0	74	0	25
2	Pt/C-15	5	28.0	100	30	15
3	Pt/C-30	5	11.7	100	63	1
4	Vulcan XC-72	0	95.0	18	0	18
5	Vulcan XC-72	0	28.0	12	0	12
6	Vulcan XC-72	0	11.7	12	0	12

[a] Reaction conditions: 0.1 M aqueous solution of **1** (5 ml), 0.25 MPa O_2, 105 °C, 6 h. [b] UIP denotes unidentified products, including humins.

[†] The XRD studies and crystallite size determination were performed with an ARL X'TRA powder diffractometer, Thermo Scientific (CuKα target, $\lambda = 1.5418$ Å). XRD data were collected in the 2θ range of 5–80° using step scan mode with a step size of 0.03° and step scan rate 2.25 deg min^{-1}.

[‡] All oxidation experiments were conducted in a batch-type glass-lined stainless-steel autoclave (250 ml) equipped with a thermo-controller, a pressure gauge and a magnetic stirrer using 0.1 M aqueous solutions of substrate **1** (5 ml). The initial **1**/Pt molar ratio of 20 : 1 was used in all experiments. The air was removed from the reactor by flushing oxygen before catalytic run. Then, the reactor was pressurized with oxygen to 0.25 MPa and heated at 105 °C in a thermostat for appropriate time.

[§] For HPLC analysis, the reactor was rapidly cooled to room temperature in water bath, the pressure was reduced to atmospheric, and the reaction mixture was made alkaline by adding a certain amount of sodium bicarbonate. Then the catalyst was separated by centrifugation. The composition of the reaction medium was determined by HPLC using an Agilent 1260 Infinity LC system equipped with a Discovery Zr-Carbon column (150 mm × 4.6 mm). The mobile phase was tetrahydrofuran and aqueous solution of phosphoric acid (0.025 M) with the volume ratio of 40 : 60 at a flow rate of 0.9 ml min^{-1}, column temperature 60 °C, and detection wavelength of 265 nm. The contents of components **1**–**5** were determined using interpolation from calibration curves prepared by the using pure authentic substances. ^{1}H and ^{13}C NMR spectra of diacid **2** are presented in Figures S3, S4.

[¶] For isolation of diacid **2** after the catalytic run with the use of Pt/C-30 catalyst at 0.25 MPa within 6 h, the reactor was rapidly cooled to room temperature in water bath and decompressed, and the mixture was diluted with water (5 ml). The resulted suspension was heated up to 80–85 °C, the catalyst was separated by hot filtration and washed with a small volume (~3 ml) of hot water. The filtrate obtained was combined with washings and evaporated at reduced pressure to a volume of ~1.5 ml, then cooled to 5 °C. The white solid precipitate was collected by centrifugation and recrystallized once from water to give pure 2,5-furandicarboxylic acid **2** (41 mg, 52% yield). The physical and spectral characteristics of the product obtained were identical with those described previously.[13]

carbon loading into the reaction mixtures causing higher loss of compound **1** due to decomposition (see Table 1, entry 1). Mechanism of this decomposition catalyzed by carbon surface is not clear. Probably, adsorption of substrate **1** on activated carbon promotes its polymerization to humins since its higher concentration on carbon surface allows a hydrogen-bonding network to be formed between sorbate molecules (*cf.* ref. 6).

In general, higher Pt content in Pt/C catalysts provides higher oxidation rate and higher selectivity for base-free oxidation **1** → **2** in 0.1 M aqueous solutions. According to the obtained results, use of Pt/C-30 catalyst at 0.25 MPa within 6 h would be preferable. Under these conditions, diacid **2** was obtained in 52% isolated yield.¶

In conclusion, we have demonstrated that Pt/C catalysts with enhanced Pt content (15–30 wt%) provide selective base-free aerobic oxidation of concentrated (0.1 M) aqueous solutions of 5-hydroxymethylfurfural **1** to give 2,5-furandicarboxylic acid **2** in up to 65% yields. To the best of our knowledge, the present results represent the first example of application of heterogeneous Pt/C catalyst obtained by pulse alternating current technique in organic synthesis. More detailed studies are anticipated in the near future to evaluate various catalyst supports effect and to optimize oxidation parameters for better yields of product **2**.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.07.031.

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