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Title: Aerobic Oxidation of Xylose to Xylaric acid in Water over Pt Catalysts

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## Aerobic Oxidation of Xylose to Xylaric acid in Water over Pt Catalysts Sunitha Sadula and Basudeb Saha\* Catalysis Center for Energy Innovation and Department of Chemical and Biomolecular

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#### Abstract

Energy-efficient catalytic conversion of biomass intermediates to functional chemicals can enable bio-products viable. Herein, we report an efficient and low temperature aerobic oxidation of xylose to xylaric acid, a promising bio-based chemical for the production of glutaric acid, over commercial catalysts in water. Among several heterogeneous catalysts investigated, Pt/C exhibits the best activity. Systematic variation of reaction parameters in the pH range of 2.5 to 10 suggests that the reaction is fast at higher temperatures but high C-C scission of intermediate C<sub>5</sub>oxidized products to low carbon carboxylic acids undermines xylaric acid selectivity. The C-C cleavage is also high in basic solution. The oxidation at neutral pH and 60 °C achieves the highest xylaric acid yield (64%). O<sub>2</sub> pressure and Pt-amount have significant influence on the reactivity. Decarboxylation of short chain carboxylic acids results in formation of CO<sub>2</sub>, causing some carbon loss; however such decarboxylation is slow in the presence of xylose. The catalyst retained comparable activity, in terms of product selectivity, after five cycles with no sign of Pt leaching.

#### Introduction

Platform chemicals are building blocks for many chemical end products, polymers, medicine, household and industrial consumable goods, building materials and others. Currently, most building block chemicals are obtained from conventional carbon sources, and cause over

10,000 million metric tons of carbon emissions as per 2010 report.<sup>[1]</sup> Bio-based platform chemicals are widely accepted as promising feedstock or end products to improve future energy security, minimize conventional carbon utilization, and reduce greenhouse gas emissions. Glutaric acid (GA) is one such platform chemical,<sup>[2]</sup> which has applications in fine chemicals, agricultural products, medicine and architecture<sup>[3]</sup>. GA is an essential ingredient for polyvinyl chloride (PVC), polyester, polyamide, resin, synthetic rubber and more.<sup>[4]</sup> Currently, GA is obtained as a byproduct from adipic acid (AA) production process in which petroleum-based KA oil (a mixture of cyclohexanone and cyclohexanol) is used as the starting material.<sup>[5]</sup> <sup>[6]</sup> For example, DuPont process extracts 2% GA from its AA process.<sup>[6]</sup> Currently, GA production and supply are constrained by the production scale of AA and its market demand. Thus, a standalone GA manufacturing process is desirable.



**Scheme 1:** Schematic illustration for xylose conversation to glutaric acid (GA). HDO = hydrodeoxygenation.

Xylose oxidized xylaric acid could be a potential building block for standalone production of GA (Scheme 1). The catalytic oxidation of biomass intermediates to renewable diacids, e.g., 2,5-furandicarboxylic acid (FDCA)<sup>[7, 8]</sup> and glucaric acid<sup>[9-11]</sup> has been reported by us and others. These diacids have been commercialized by Avantium, BASF, Rennovia, Rivertop Renewable, BioAmber and others because of their strong market demand.

Similar to FDCA and glucaric acid, xylaric acid has also been identified as one of the top ten value added chemicals.<sup>[2]</sup> In addition, its precursor, xylose, can be easily extracted from lignocellulosic biomass. However, the research and commercialization activities on xylose oxidation to xylaric acid are very limited. About half a century ago, xylose oxidation with nitric acid reported 44% xylaric acid yield.<sup>[12]</sup> Highly exothermic reaction conditions and NO<sub>x</sub> gas release are some drawbacks in the nitric acid mediated oxidation. Recently, oxygen has been used as a co-oxidant with nitric acid for xylose oxidation.<sup>[13]</sup> Venema et al.<sup>[14]</sup> reported aerobic oxidation of xylose using a Pt catalyst at low xylose loading (2.5 wt%) and a constant pH of 9. Rennovia Inc. used a Pt/silica catalyst (4 wt% Pt) to achieve 29% xylaric acid at 90 °C and 5 bar oxygen for 8 h.<sup>[15]</sup> The later reaction was conducted on a micro-liter scale in a 96 wellreactor system which was not reproduced on a reasonable laboratory scale. In addition, the effects of reaction temperature, O<sub>2</sub> pressure, reaction time and pH on the oxidation of xylose and product selectivity were not studied.

In contrast to poor yield of xylaric acid, xylose oxidation to xylonic acid, an intermediate oxidation product with one carboxylic acid group (Scheme S1; *vide infra*), is more selective. For example, Pruesse et al. reported 99% selectivity of xylonic acid at 78% conversion of xylose with a Au catalyst<sup>[16]</sup> under basic pH (pH 9). High selectivity of xylonic acid has also been reported in aerobic oxidation of xylose with metallic Cu<sup>[17]</sup> and chlorine.<sup>[18]</sup> Electrocatalytic oxidation of xylose with Pt and Au electrodes formed xylonic acid and xylitol in alkaline solutions.<sup>[19]</sup>

Building on our prior study of efficient glucose oxidation to glucaric acid in water,<sup>[9]</sup> herein we report the results of xylose oxidation with activated carbon, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> supported Pt, Pd, Rh and Cu catalysts in acidic, basic and neutral solutions. The Pt/C catalyst exhibits the

highest selectivity to xylaric acid yield (64%). Xylonic acid oxidation is slower than xylose oxidation. Several low carbon carboxylic acids are formed via C–C bond scission of  $C_5$  carboxylic acids and the C–C scission depends on the temperature,  $O_2$  pressure, Pt loading and pH.

#### **Experimental Section**

**Materials**. Pt/C (5 wt% Pt), Pt/Al<sub>2</sub>O<sub>3</sub> (5 wt% Pt), Rh/C (5 wt% Rh), Pd/C (5 wt% Pd) and Cu/C (5 wt% Cu) were purchased from Sigma-Aldrich. Pt/SiO<sub>2</sub> (5 wt% Pt) was purchased from Strem Chemicals. All catalysts were used as purchased. Xylose (>99% purity) was purchased from Sigma-Aldrich. Standard samples (lithum xylonate, oxalic acid, tartaric acid, glyceric acid, glycolic acid, lactic acid) for HPLC method development and calibration were purchased from Sigma-Aldrich and were used as received. Xylaric acid disodium salt was purchased from Omicron Biochemicals. DI water was used for preparation of all solutions.

**Catalysts characterization**. Pulse CO chemisorption was performed on an Altamira AM-200ip instrument. Before CO chemisorption, the sample was treated with He at 120 °C and then cooled down to 30 °C. Pulses of CO in a He carrier gas were injected at 30 °C. The signal was monitored by using a thermal conductivity detector (TCD). Surface areas of the catalysts were calculated from N<sub>2</sub> physisorption data, measured at –196 °C on a Micromeritics 3Flex Surface Characterization Analyzer, using the Brunauer–Emmett–Teller (BET) equation. Barrett–Joyner– Halenda (BJH) desorption was used to estimate pore volumes and pore sizes. Before N<sub>2</sub> physisorption, the samples were degassed under vacuum at 80 °C overnight.

**Oxidation reaction**. Aerobic oxidation of xylose or other substrates were carried out in a 100 mL Parr reactor (model number 4793), equipped with a thermocouple for measuring the actual temperature of the reaction mixture, pressure gauge, rupture disk and pressure relieve valve. In

typical experiments, the reactor was loaded with 20 mL of an aqueous solution of 10 wt% xylose (2 g; 13.3 mmol) and calculated amount of catalyst. After adding a magnetic bar to the reactor, it was sealed, pressurized with oxygen (grade 4.4), purged three times and then pressurized to the desired pressure. The pressurized reactor was placed in a band heater and heated to desired temperature at the heating rate of 10 °C/ min. The solution was stirred at a constant rate of 800 rpm using the magnetic bar. Upon reaction for a set time, the reactor was cooled down in an ice bath and depressurized by releasing the relieve valve. Aqueous 5M  $H_2SO_4$  and 2M NaOH solutions were used to adjust the initial pH of the solutions. Unless otherwise mentioned, initial reaction rates for xylose and xylonic acid oxidation were calculated at about 15% conversion.

The following equations were used for calculations of conversion, selectivity and yield.

Conversion (%) = 
$$\frac{Moles \ of \ carbon \ converted}{Moles \ of \ carbon \ in \ initial \ feed} \times 100$$
  
Selectivity (%) =  $\frac{Moles \ of \ carbon \ product}{Moles \ of \ carbon \ converted} \times 100$   
Yield (%) =  $\frac{Moles \ of \ carbon \ product}{Moles \ of \ carbon \ in \ initial \ feed} \times 100$ 

Carbon balance given for each reaction is the sum of carbon moles of products detected by HPLC and carbon moles of unconverted xylose.

**Product analysis.** The product solutions were filtered and diluted 10-fold in DI water for analysis on a HPLC (Waters model e2695) equipped with an Agilent Hi-Plex H column and a refractive index (RI) detector (Waters 2414) as well as a photodiode array (PDA) detector (Waters 2998). The column compartment temperature was set to 75 °C. An aqueous solution of 8.5 mM  $H_2SO_4$  was used as a mobile phase at a flow rate of 0.1 mL/min. Organic acid and unknown peaks (e.g. keto-xylaric acid) were identified using a LC-MS (Agilent 6120). Quantification of xylose, xylaric acid, xylonic acid and other C-C cleaved organic acids was

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based on their respective pre-calibrated plots of peak areas vs. concentrations using standard samples. Xylaric acid and tartaric acid peaks were not well separated in the chromatogram collected using the PDA detector. Thus, these two peaks were deconvoluted (Figure S1) using origin software. Similarly xylose and xylonic acid peaks were not well separated in the chromatogram collected using the RI detector. These two peaks were also deconvoluted to obtain their accurate peak areas. At high xylose conversion, xylonic acid peak of the chromatogram collected using the PDA detector was well separated and distinguished, and hence this peak area was subtracted from the total xylose and xylonic acid peak area of the chromatogram collected using the RI detector to obtain unconverted xylose. The accuracy of this method was validated by injecting mixtures of known concentrations of xylose and xylonic acid standards. Ketoxylaric acid was not quantified because of lack of an authentic commercial standard sample to develop a calibration plot. The product solutions were also analyzed using a Wavelength Dispersive X-ray Fluorescence (WDXRF) Spectrometer (Rigaku Supermini200) and a pH meter (Fisher Scientific accumet Basic AB15) to measure metals leaching and acidity of the solutions during oxidation.

#### **Results and discussion**

Initially, we screened several heterogeneous catalysts containing different metals and supports to evaluate their catalytic performance for xylose oxidation (Figure 1). Two blank experiments were also performed; one without any catalyst and another with activated carbon support (without any metal loading). These experiments were conducted at low temperature and  $O_2$  pressure (60 °C and 2 bar  $O_2$ ) to slow down the reaction, especially for Pt catalysts, so the initial rates can be calculated at low xylose conversion. Figure 1 shows Pt/C is the most effective

(initial rate = 21.4 mmol g<sup>-1</sup> h<sup>-1</sup>). The effectiveness of the catalysts, in terms of initial rates, decreases in the order of  $Pt/C > Pt/Al_2O_3$  (12.4)  $> Pt/SiO_2$  (7.1) > Rh/C (2.5) > Pd/C (1.5). Ru/C and Cu/C are ineffective. Turn of frequencies (TOFs) of Pt/C, Pt/Al\_2O\_3 and Pt/SiO\_2 are compared in Figure S2. Xylose oxidation with a Cu catalyst was also ineffective in a prior report.<sup>[17]</sup> Because of high activity of the Pt/C catalyst, it was chosen for further investigation.



**Figure 1**. Comparison of initial rates of xylose oxidation over different heterogeneous catalysts. Reaction conditions: 10 wt% xylose, 60 °C, 2 bar  $O_2$  and xylose/metal (mol/mol) = 54. Initial rates were calculated at 15% xylose conversion.

The oxidation with the Pt/C catalyst at 14 bar O<sub>2</sub> and 80 °C is fast in the beginning, achieving 81% xylonic acid selectivity at 76% xylose conversion within 30 min (Table S1 and Figure 2a and Figure S3). Xylonic acid is then slowly oxidized to xylaric acid (Scheme S1), similar to glucose oxidation to glucaric acid.<sup>[9]</sup> Other products (OP) such as oxalic, tartaric, glycolic and glyceric acids are also formed as the reaction progressed. The stack plots of HPLC chromatograms in Figure S1 show a decrease in xylonic acid peak intensity with an increase in peak intensity of xylaric acid and OP. Similar C-C scission of glucose oxidized products to low

carbon carboxylic acids has been reported.<sup>[9, 11]</sup> Selectivity of xylaric acid, xylonic acid and OP reached 40%, 29% and 14%, respectively, in 10 h (Table S1). Tartaric (7%) and glycolic (6%) acids are the major short chain carboxylic acids, consistent with a prior report by Venema et al.<sup>[14]</sup> The aldehyde group oxidation of xylose to xylonic acid is faster than the alcoholic group oxidation of xylonic acid to xylaric acid. Similar observation has been reported for glucose and 5-hydroxymethylfurfural (HMF) oxidation.<sup>[7, 9, 20, 21]</sup> The reaction for a prolonged time (15 h) achieves higher xylaric acid selectivity (50%); however, the C-C scission leading to formation of OP (22%) also enhanced. Total carbon balance is within 92-71% (Table S1). Unquantified keto-xylaric acid and small fractions of other products undetected by HPLC could account for carbon mass loss. Figure 2b shows a decrease in pH of the solution with time due to formation of xylaric acid, which is a little stronger acid (pKa = 2.79) than xylonic acid (pKa = 3.39).<sup>[22, 23]</sup>



**Figure 2**. Xylose oxidation profile over Pt/C in water as a function of reaction time: (a) conversion of xylose and selectivity of oxidation products. Carbon balance is the sum of carbon moles of products detected by HPLC and carbon moles of unconverted xylose. Other products (OP) are oxalic acid, tartaric acid, glycolic acid and glyceric acid (Table S1). The results for first 3 h of reaction are given in Figure S3. (b) pH profile of the solution during progression of

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oxidation. Reaction conditions: 10 wt% xylose, 20 mL  $H_2O$ , 0.96 g Pt/C catalyst (xylose/Pt molar ratio 54), 14 bar  $O_2$ , 80 °C, initial pH 6.8.

The effect of pH. To investigate the effect of pH on xylose oxidation, we varied initial pH of the solution from 2.5 to 10. The reaction time at each pH was also varied from 1 h to 15 h. The results in Figure 3 (Table S2) show xylose conversions in acidic (pH 2.5) and basic (pH 10) solutions are slightly higher (>95%) than that in neutral solution (pH 6.8) for reaction time of 1 h, while the conversions are comparable when the reactions were carried out for a longer time. Xylonic and xylaric acids selectivity at pH 6.8 and 10 are slightly better than that at pH 2.5 (Table S2). For the reaction time of 15 h, xylaric acid selectivity at pH 6.8 is better than those in acidic and basic solutions. The selectivity of OP increases from acidic to basic pH, suggesting the C-C scission is favored as the pH value of the solution increased. The carbon loss is higher in acidic solution than those in neutral and basic solutions (Table S2), which is likely due to the formation of other oxidation products in acidic medium or acid catalyzed oligomerization of carboxylic species, which are undetected by HPLC and HPLC-MS and consistent with our prior observation.<sup>[9]</sup> A pH drop from 10 to 2.5 occurs within 1 h due to the formation of acidic carboxylic acid species (Figure S4a). Similarly, pH of a reaction solution of initial pH of 2.5 drops to 2.0 within the same reaction time scale. (Figure S4b)



Xylose Conversion Xylonic acid Xylaric acid Tartaric acid Glycolic acid Oxalic acid Glyceric acid

**Figure 3**. The effect of initial pH on xylose conversion and product selectivity; (a) pH 2.5, (b) pH 6.8 and (c) pH 10. Reaction conditions: 10 wt% xylose, 20 mL H<sub>2</sub>O, 0.96 g Pt/C catalyst (xylose/Pt molar ratio = 54), 14 bar O<sub>2</sub>, 80 °C, initial pH of the solution was adjusted by adding 5 M H<sub>2</sub>SO<sub>4</sub> and 2 M NaOH. Detailed results are given in Table S1.

A control experiment of pure xylonic acid oxidation gives keto-xylaric, glycolic, glyceric oxalic and tartaric acids, besides xylaric acid. Formation of such low carbon products via retroaldol C-C scission has been reported.<sup>[9, 14, 20, 24, 25]</sup> Keto-xylaric acid is likely formed via isomerization of xyluronic acid, which is an intermediate oxidation product of xylaric acid Accepted Manuscr

(Scheme S1). A prior report showed tartronic acid was also formed along with tartaric, glycolic and oxalic acids from xylonic acid in basic solution (pH 9),<sup>[14]</sup> which we have not observed.

Glycolic and glyceric acids could also be formed from oxidation of C-C cleaved products (glycolaldehyde and glyceraldehydes) of xylose (Scheme 2). Small amount of oxalic acid is likely formed from oxidation of glycolic acid.<sup>[20]</sup> Tartaric acid is the second major oxidation product of xylose after xylaric and xylonic acids, which is also obtained from oxidation of pure xylonic acid. We believe xylose oxidized xylonic acid isomerizes to xyluronic acid, which then decarboxylates to tartaraldehyde and carbon dioxide. Tartaraldehyde is then oxidized to tartaric acid. We observed carbon dioxide formation during oxidation of xylose, pure xylonic acid and other short chain carboxylic acids (tartaric, glycolic and oxalic acids) which makes this argument convincing (Table S3). Carbon dioxide also accounts for low carbon balance in detected oxidized products (Figure S5). At low concentrations of tartaric or glycolic acids that were formed during oxidation of xylose alone, they are quantitatively converted to CO<sub>2</sub>. However, when xylose and glycolic acid or tartaric acid mixture was used as substrate, there are unconverted glycolic or tartaric acid in the solution, suggesting decarboxylation of tartaric acid or glycolic acid could be slow because of surface coverage by xylaric acid or xylonic acid. Prior studies on decarboxylation of glycerol over platinum and cobalt catalysts,<sup>[20, 25-27]</sup> or complete conversion oxalic acid to carbon dioxide on a platinum catalyst<sup>[28]</sup> agree with our observation. On the basis of above discussion, we propose a plausible reaction pathway in Scheme 2.



**Scheme 2:** Proposed reaction pathways for xylose oxidation to observed products. Blue color represents observed products.

The effects of  $O_2$  pressure, reaction temperature and Pt concentration. The effects of  $O_2$  pressure, reaction temperature, and Pt concentrations were studied on xylose oxidation. The reaction time was varied from 1 h to 15 h at three different  $O_2$  pressures (2, 6 and 14 bar). Xylose conversion at 2 bar  $O_2$  is lower than those of 6 bar and 14 bar (Figure 4a). The conversions are comparable at 6 and 14 bars, with a slight variation along the reaction time. Xylaric acid selectivity at 14 bar  $O_2$  is better than that at 6 bar  $O_2$  throughout the reaction time while the selectivity is significantly lower at 2 bar  $O_2$  (Figure 4b), which could be due to slow oxidation of

xylonic acid and hence its accumulation in the solution. The selectivity of OP increases with increasing  $O_2$  pressure, indicating higher  $O_2$  pressure promotes C-C cleavage.



**Figure 4.** The effect of O<sub>2</sub> pressure on xylose oxidation: (a) xylose conversion and (b) selectivity of xylaric acid and OP. XA and OP stand for xylaric acid and other products (oxalic acid, tartaric acid, glyceric acid and glycolic acids). Reaction conditions: 10 wt% xylose, 20 mL H<sub>2</sub>O, 0.96 g Pt/C catalyst (xylose/Pt molar ratio 54), 80 °C and initial pH 6.8.

Next we varied reaction temperature from 60 °C to 100 °C at a fixed O<sub>2</sub> pressure of 6 bar and xylose to Pt molar ratio of 54. The reaction at 60 °C is slow in the beginning (Figure 5a). The reactions at other three temperatures (80 °C, 90 °C and 100 °C) have a slight difference in xylose conversion up to 4 h. Xylonic acid formation is fast in the temperature range of 80 °C – 100 °C, however its subsequent oxidation to xylaric acid is facile at higher temperatures, resulting in lower selectivity of xylonic acid 90 °C and 100 °C (Figure 5b). Xylonic acid oxidation is significantly slow at 60 °C, which attributes to very slow formation of xylaric acid at this temperature in comparison with higher temperatures (Figure 5c). Xylaric acid formation curves follow similar trend at 80 °C – 100 °C; however, its selectivity decreased as temperature increased, owing to C-C cleavage to low carbon acids at higher temperatures, consistent with the

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results in Figure 5d showing higher selectivity of OP at higher temperatures. In contrast, xylaric acid selectivity at 60 °C increased exponentially with the reaction time due to formation of least amount of OP (<2%). When compared with our prior report of glucose oxidation with the Pt/C catalyst,<sup>[9]</sup> xylose oxidation achieves higher xylaric acid selectivity at lower temperature and  $O_2$  pressure, which is likely due to the following reasons: (1) faster xylose oxidation than glucose, as reported previously<sup>[29]</sup>, and (2) low C-C cleavage at lower temperature and  $O_2$  pressure.



**Figure 5**. Xylose oxidation profiles at 60 °C, 80 °C, 90 °C and 100 °C; (a) xylose conversion, (b) xylonic acid selectivity, (c) xylaric acid selectivity and (d) other product selectivity. Other products are oxalic acid, tartaric acid, glyceric acid and glycolic acids. Reaction conditions: 10 wt% xylose, 20 mL H<sub>2</sub>O, 0.96 g Pt/C catalyst (xylose/Pt molar ratio 54), 6 bar O<sub>2</sub> and initial pH 6.8.

The dependence of xylose oxidation on the xylose/Pt molar ratio in the range of 27 to 106 was studied at 60 °C and 6 bar  $O_2$  for 10 h (Table 1). The results show a decrease in xylaric acid selectivity from 43% to 20% as the Pt amount decreased (xylose/Pt ratio increased from 27 to 54) while xylonic acid selectivity decreased from 31% to 53% at quantitative xylose conversion. Slow oxidation of xylonic acid at xylose/Pt ratio of 54 results in its high accumulation of xylonic acid. Upon further decreasing the Pt loading (increasing xylose/Pt molar ratio to 116), only 10% xylaric acid selectivity is observed at 83% xylose conversion. Noteworthy, xylonic acid selectivity in the later reaction is comparable to the reaction carried out at xylose/Pt molar ratio of 54, indicating xylonic acid oxidation products (other than OP), which are undetected by HPLC, might be the reason for lower xylaric acid selectivity at the ratio of 116. Carbon balance at xylose/Pt ratio of 54 and 116 are lower than that at xylose/Pt ratio of 27, which confirms formation of other undetected oxidation products.

Table 1. Effect of Platinum	concentration	on xylose oxidation	over Pt/C catalyst.

-	Entry	Xylose/Pt	Conversion	Selectivity (%)			Carbon
		(mol/mol)	(%)	Xylonic	Xylaric	<b>OP</b> <sup>a</sup>	balance
_				acid	acid		(%)
	1	27	99	31	43	3	88
	2	54	99	53	20	0.1	73
	3	116	83	47	10	0	74

<sup>a</sup> Other products include tartaric acid and oxalic acid. Reaction conditions: 5 wt% xylose in entry 1, 10 wt% xylose in entry 2, 20 wt% xylose in entry 3, 20 mL H<sub>2</sub>O, 0.96 g Pt/C, 60 °C, 6 bar O<sub>2</sub>, initial pH 6.8 and 10 h reaction time.

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**Mechanism of xylose oxidation.** It has been observed that xylose conversion to xylaric acid occurs via rapid oxidation of the aldehyde group of xylose and much slower oxidation of the – CH<sub>2</sub>OH group of xyloinc acid. Mechanistic investigation of xylose oxidation is very limited. The mechanism of HMF oxidation, which has similar functional groups (–OH, –CHO) as xylose, to FDCA has been reported in basic and base-free solutions.<sup>[30-32], [33-35]</sup> In basic solution, the oxidation of the aldehyde group of HMF occurs by rapid and reversible hydration to a geminal diol, followed by a hydrogen transfer to the metal surface, thus forming a carboxylic acid, 2-hydroxymethyl-5-furancarboxylic acid (HMFC). The –CH<sub>2</sub>OH group of HMFC is then oxidized via (oxidative) dehydrogenation to aldehyde, followed by similar hydration and hydrogen transfer of the aldehyde to carboxylic acid, FDCA. The Pt-catalyzed oxidation of HMF in base-free condition also followed similar mechanism through active participation of water.<sup>[35, 36]</sup> Xylose with similar functional groups (-OH, -CHO) as HMF is expected to follow the similar oxidation mechanism of HMF (Scheme S2).

To rationalize slow gluconic oxidation in our prior study, which showed similar oxidation behavior as xylose and xylonic acid, we have estimated the free energy of adsorption of various oxidized species of glucose.<sup>[9]</sup> The calculation suggested that the C=O group interacts more strongly than the alcoholic group; thus glucaric acid adsorbed more strongly than open chain glucose and gluconic acid. Similarly, xylaric acid, adsorbed strongly on the surface than xylsoe and xylonic acid, could block the active sites as it is formed and hence slow the reaction down. We propose that the oxidation of xyloinc acid is slow due to the (oxidative) dehydrogenation of – CH<sub>2</sub>OH to –CHO is slow. This dehydrogenation step is not necessary for xylose oxidation to xyloinc acid. **Recyclability of Pt/C.** To check the stability of Pt/C, we reused the catalyst for 5 cycles. After each cycle, the catalyst was recovered by filtration, washed thoroughly with water, dried and reused for the next cycle. The results in Figure 6 show the catalyst retained comparable activity, in terms of product selectivity, in the 5<sup>th</sup> cycle. CO uptake and surface properties (pore volume and pre size) of the catalyst after the 5<sup>th</sup> cycle are comparable to the fresh catalyst (Figure S6). WDXRF of product solutions did not show any presence of Pt, indicating no Pt leaching during oxidation.<sup>[9]</sup> To further understand the structural changes, we have carried out XRD analysis of the catalyst before and after the reaction. The characteristic diffraction peaks of Pt [111], [200], [220], [311] at 20 values of 39.9, 46.5, 67.8 and 81.2° respectively are present in the recovered catalyst after the 5<sup>th</sup> cycle (Figure S7).



**Figure 6**. Recycling studies of the Pt/C catalyst for xylose oxidation. Reaction conditions: 10 wt% xylose, 20 mL H<sub>2</sub>O, 0.96 g Pt/C catalyst (xylose/Pt molar ratio 54), 6 bar O<sub>2</sub>, 60 °C and 20 h, initial pH 6.8.

#### Conclusions

We studied aerobic oxidation of xylose to xylaric acid using activated carbon, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> supported Pt, Pd, Rh and Cu catalysts in acidic, basic and neutral solutions. The Pt/C catalyst is the most effective of these in terms of initial rate as well as xylaric acid selectivity. Xylose oxidation to xylonic acid is fast while xylonic acid oxidation is slow due to the (oxidative) dehydrogenation of the  $-CH_2OH$  group to -CHO is slow. The reaction in base-free water achieves the best xylaric acid selectivity. Higher temperatures, higher O<sub>2</sub> pressure and higher pH cause C-C cleavage of C<sub>5</sub> species to short chain carboxylic acids, resulting in lower xylaric acid selectivity. A maximum of 64% xylaric acid selectivity at quantitative conversion of xylose is achieved at an initial pH of 6.8, 60 °C, 6 bar O<sub>2</sub> and xylose/Pt molar ratio of 54. A plausible reaction pathway is proposed based on the product distribution. The catalyst is stable with comparable performance in the 5<sup>th</sup> cycle.

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