High Structure Sensitivity of Vapor-Phase Furfural Decarbonylation/Hydrogenation Reaction Network as a Function of Size and Shape of Pt Nanoparticles

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Supporting Information

ABSTRACT: Vapor-phase transformations of furfural in H2 over a series of Pt nanoparticles (NPs) with various particle sizes (1.5–7.1 nm size range) and shapes (rounded, cubes, octahedra) encapsulated in poly(vinylpyrrolidone) (PVP) and dispersed on MCF-17 mesoporous silica were investigated at ambient pressure in the 443–513 K temperature range. Furan and furfuryl alcohol (FFA) were two primary products as a result of furfural decarbonylation and hydrogenation reactions, respectively. Under conditions of the study both reactions exhibited structure sensitivity evidenced by changes in product selectivities, turnover rates (TORs), and apparent activation energies ($E_A$'s) with Pt particle size and shape. For instance, upon an increase in Pt particle size from 1.5 to 7.1 nm, the selectivity toward FFA increases from 1% to 66%, the TOR of FFA production increases from $1 \times 10^{-3}$ s$^{-1}$ to $7.6 \times 10^{-2}$ s$^{-1}$, and $E_A$ decreases from 104 kJ mol$^{-1}$ to 15 kJ mol$^{-1}$ (9.3 kPa furfural, 93 kPa H$_2$, 473 K). Conversely, under the same experimental conditions the decarbonylation reaction path is enhanced over smaller nanoparticles. The smallest NPs (1.5 nm) produced the highest selectivity (96%) and highest TOR values ($8.8 \times 10^{-2}$ s$^{-1}$) toward furan formation. The $E_A$ values for decarbonylation ($\sim 62$ kJ mol$^{-1}$) was Pt particle size independent. Furan was further converted to propylene via a decarbonylation reaction, but also to dihydrofuran, tetrahydrofuran, and $n$-butanol in secondary reactions. Furfuryl alcohol was converted to mostly to 2-methylfuran.

KEYWORDS: Pt nanoparticles, Pt/SiO$_2$ catalyst, structure sensitivity, furfural, decarbonylation, hydrogenation

Achieving the highest possible performance in catalytic reaction processing only becomes possible when the catalyst’s structure is tuned to and sustained at its optimal state under reaction conditions. This is especially important for a class of heterogeneous catalytic reactions that are commonly referred to as structure-sensitive; that is, their reaction kinetics are influenced by the active metal’s particle size and/or morphology. Previous studies have demonstrated that many industrially significant reactions including ammonia synthesis, hydrocarbon reforming, Fischer–Tropsch synthesis, and catalytic combustion are structurally sensitive. More recently, the advances in the synthetic chemistry of well-defined transition metal nanoparticles have provided the tools to study structural sensitivity, and subsequent structure sensitivity was found for many of the selective hydrogenation reactions of heteroatom containing hydrocarbons. In this Letter, we examine the selective chemistry of furfural over the size-dependent series of PVP-capped Pt nanoparticle (NP) catalysts.

Here we report that Pt NPs of sizes less than 2 nm are highly selective toward decarbonylation of furfural’s carbonyl group, while Pt NPs larger than 2 nm predominately produce furfuryl alcohol. Furfural was selected as the reactant because of the recent interest in sustainable production of liquid fuels and fine chemicals from nonpetroleum derived feedstock (such as biomass).

Furfural is an aromatic compound produced primarily from the dehydration of C$_5$ sugars and is a major component of bio-oils. Different transition metals show different catalytic activity with respect to transformations of its highly reactive carbonyl group. For instance, Cu is highly selective for hydrogenation of the furfural to furfuryl alcohol. On the other hand, Pd is an...

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efficient catalyst for decarbonylation of furfural to furan.\textsuperscript{11–13} Ni and Pt, depending on conditions, can promote both reactions to a different extent.\textsuperscript{8,15} At high temperatures (550–600 K), the decarbonylation reaction dominates, while at lower temperatures the hydrogenation activity becomes significant, which leads to the formation of furfuryl alcohol.

**Experimental Section. Materials.** Hexachloroplatinate acid, H$_2$PtCl$_6$·6H$_2$O (99.9% pure on metals basis), Pt-(acetylacetonate)$_2$ (97%), PVP (M$_w$ = 29 000 g/mol), Pluronic P123 (M$_w$ = 5800, EO$_{20}$PO$_{70}$EO$_{20}$, EO = ethylene oxide, PO = propylene oxide), tetraethoxysilane (TEOS, 98%) and all other chemicals used in material synthesis (all of high purity) were purchased from Sigma-Aldrich. The liquid furfural (ACS purity, 99%, Sigma-Aldrich) was purified by vacuum distillation. The H$_2$, N$_2$, He, and ethylene gas (all high purity, >99.995%) used in reaction studies were supplied by PraxAir. The H$_2$ and N$_2$ gases used in furfural reaction kinetic studies were additionally purified by passing through molecular sieve traps (S-trap, Supelco).

**Material Synthesis.** The PVP capped Pt NPs in the size range 1.5–7.1 nm were synthesized by alcohol reduction methods. The approach for synthesis of the 1.5, 2.6, 3.6, and 7.1 nm particle sizes is described in literature.\textsuperscript{16} The methods for preparing 1.9 and 5.0 nm sizes were developed in house. The shape of all Pt NPs used in the study can be characterized as rounded (polyhedral) based on TEM characterization. The details of synthesis method for each of the sizes of Pt NPs in the 1.5–7.1 nm size range are provided in the Supporting Information, and TEM images are shown in Figure S1. MCF-17 mesoporous silica was synthesized according to a method reported in the literature and described in the Supporting Information.\textsuperscript{7,18}

The MCF-17 supported catalysts were prepared by mixing the mesoporous silica powder with colloidal solutions of Pt NPs in ethanol, then subjecting the mixture to sonification for 3 h at room temperature in a commercial ultrasonic cleaner (1510R-MT, 70 W, Branson). After immobilization of the NPs in the support, the resulting precipitate was separated by centrifugation (550 × 9.8 m/s$^2$, 20 min). The samples prepared using PVP were thoroughly washed with ethanol to ensure removal of excess polymer at this stage. The resulting catalysts were dried in air at 373 K overnight before use.

**Material Characterization.** The sizes of the Pt NPs were analyzed using a Hitachi H-7650 transmission electron microscope (TEM) operated at 120 kV. High resolution (HR) and annular dark field (ADF) TEM images were obtained using a Jeol 2100 LaB$_6$ microscope and a Jeol 2100-F microscope, both operating at 200 kV, respectively. The average TEM-projected Pt particle sizes and the size distribution histograms were determined from TEM images by counting 300 particles. Figure 1 shows the particle size distribution histograms, the mean sizes, and standard deviations of the size-dependent series of Pt NPs. TEM and HRTEM pictures (Figures 1 and S1) indicate nanocrystalline Pt nanoparticles with polyhedral shapes (i.e., spherical). The total Pt loadings were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Perkin-Elmer optical emission spectrometer (Optima 7000 DV). The instrument was calibrated using a platinum standard (Fluka, TraceCERT 1000 mg L$^{-1}$). The total specific surface area of MCF-17 support was determined via N$_2$ (UHP grade, 99.9999%, PraxAir) physisorption at 77 K using an Autosorb-1 (Quantachrome) analyzer.

**Catalytic Activity Measurements.** Activities of the Pt/MCF-17 series catalysts in the vapor-phase furfural/H$_2$ reaction were evaluated in a tubular fixed catalyst bed reactor at ambient pressure. The 1/4” diameter stainless steel reactor was mounted vertically, which allowed for the downflow operation. A 0.300 g load of catalyst/diluant mixture, corresponding to a 8.5 cm catalyst bed height, was placed in the middle of the reactor tube, delimited by a layer of purified glass wool and a layer of purified alumina granulate at each end. Prior to mixing, both catalyst sample and diluant (pure MCF-17) were pellettized to obtain 160–250 μm size granulates. The amount of catalyst in the catalyst/diluant mixture was varied from 0.050 to 0.300 g to achieve a similar furfural conversion (3% ± 1% at 473 K, 9.3 kPa furfural, 93 kPa H$_2$, 1300 h$^{-1}$ GHSV), which is required for selectivity comparison. The “freshly” loaded catalyst was pretreated under an ambient pressure flow of a H$_2$ (10 sccm) and N$_2$ (10 sccm) gas mixture at 533 K for 2 h. The heating/cooling rate during the pretreatment was limited to 1 K min$^{-1}$. After the pretreatment, the reactor was cooled down to 443 K under the same gas flow. Each kinetic measurement was repeated two or more times for any given catalyst material to establish the uncertainly in the measurements. For the selectivities and TOR comparison measurements a constant 0.4 mL h$^{-1}$ flow (at 293 K) of liquid purified furfural was continually injected using a syringe pump (Kent Scientific) equipped with a Hamilton syringe (Gastight) into the preheating reactor head which was maintained at 423 K. In the preheating zone, furfural evaporated and mixed with 20 sccm flow of H$_2$, resulting in a two-component gas flow with a furfural:H$_2$ ratio of 1:10 entering the reactor at near ambient pressure. A Baratron type (890B, MKS Instruments) capacitance pressure manometer was used to monitor the reactor inlet pressure. The reaction products were sampled in the vapor phase at the reactor outlet and analyzed via an in-line gas chromatograph (GC). After passing through a GC sampling loop, the reactor outlet flow was then directed to a hydrocarbon scrubber which was vented at ambient pressure. All flow lines between the reactor outlet and the scrubber were heated to 433
K to maintain the flow components in the vapor phase. The quantitative analysis of the flow composition was performed using a Hewlett-Packard (5890 Series II) GC which was equipped with a 10 m dimethylpolysiloxane (HP-1, Hewlett-Packard) capillary column and a flame ionization detector (FID). The characteristic retention times and FID response factors for the individual compounds were established via prior calibrations. A PC based GC ChemStation software (Hewlett-Packard) was used for automation of the GC sampling, data collection, and post-run processing.

The reaction sequence included conditioning of a “fresh” catalyst sample under reactant stream (9.3 kPa furfural, 93 kPa H2, 1300 h−1 GHSV) at 443 K for 1 h and an Arrhenius dependence measurement, which was performed as an increasing temperature sequence measured in the 443–513 K temperature range with 5 and 10 K temperature increments and a 2 h hold time at each temperature point. Additionally, for the 3.6 nm sample the partial pressure dependence measurements were performed at 453, 473, and 493 K by varying the furfural flow rate in the 0.2–1.2 mL h−1 range and H2 flow rate in the 10–60 sccm range. During the measurements no detectable catalyst deactivation was observed, suggesting that the deactivation rates were very low. The product selectivity was calculated as:

\[
\text{selectivity}(\%) = \frac{\text{mol product formed}}{\text{mol furfural consumed}} \times 100\%
\]

Ethylene hydrogenation activities were determined using the setup and under reaction conditions that have been described elsewhere.4,5 The number of Pt surface sites per unit weight of catalyst (Pt sites mg−1) were determined using the known TOR of 11 molecules of ethylene (surface Pt site)−1 s−1 at 293 K, 13.3 kPa H2, and 1.33 kPa C2H4.4,5 The detailed description of the ethylene hydrogenation study protocol and results of catalyst characterization (Table S1) are presented in the Supporting Information. The TOR values for furan and FFA production were calculated by taking a ratio of the molecular production rate measured per unit weight of catalyst (molecules mg−1 Pt site s−1) for each individual compound and the number of active surface Pt sites per unit weight of catalyst determined during the ethylene hydrogenation measurements.

Results and Discussion. Reaction chemistry of furfural, when catalyzed by supported heterogeneous Pt catalysts, is complex and leads to formation of multiple primary and secondary reaction products. Nevertheless, during the vapor phase catalysis in the 443–513 K temperature range (experimental conditions of the study) the four reaction products: furan, furfuryl alcohol, 2-methylfuran, and propylene (furan ring cracking) measured in the 443–513 K temperature range as a function of Pt NP size. These data are also summarized in Table 1 for the 3.6 nm Pt NPs. Additional data on the product selectivity dependencies on Pt NPs shapes and the Arrhenius plots for different particle sizes are shown in the Supporting Information in Figures S2 and S3, respectively. Figure 3 shows steady-state product selectivities to furan and furfuryl alcohol products measured at a single temperature of 473 K multiple times to determine the standard deviation of selectivity value as a function of the Pt NP size. The two primary reactions in the furfural reaction network over Pt NP catalysts are very sensitive to both Pt particle size and shape. The polyhedral Pt particles below 2 nm in size produce predominantly furan, while the polyhedral Pt particles above 3 nm produced predominantly furfuryl alcohol. The highest selectivity to furfuryl alcohol is achieved over 6.8 nm Pt NPs with octahedral morphology, while similarly sized 6.8 nm Pt NPs with cube morphology show a substantially lower selectivity to the product. The product selectivities to formation of 2-methylfuran and propylene appear to be structure-insensitive, as there were no clear correlations between the selectivity values and the Pt NP size and/or shape. The primary catalytic reactions leading to formation of furan and furfuryl alcohol dominate the reaction network, as combined product selectivities to these two compounds are in excess of 90% in the 443–513 K temperature range. The formation of furfuryl alcohol is favored in the lower side of the temperature range, while the formation of furan becomes dominant in the higher side of the temperature range. This temperature dependence is likely to be due to the thermodynamic limitation.

Scheme 1. Essential Reactions Network in Furfural Transformations over Pt, Including Two Primary Reactions: (1) Furfural Decarbonylation and (2) Carbonyl Group Hydrogenation, and Two Secondary Reactions: (3) Furan Ring Cracking/Decarbonylation, and (4) –OH Group Hydrogenolysis Reaction Pathways**

*The combined selectivity to the products shown exceeds 95% under conditions studied. Indeed, only trace amounts of dihydrofuran, tetrahydrofuran, tetrahydrofurfuryl alcohol, 2-methyltetrahydrofuran, and other similar compounds were detected during the measurements. Another possible catalytic route for a secondary reaction—an aldol condensation of furfuryl alcohol with furfural is also a minor route on the Pt/MCF-17 catalysts, with the measured selectivity to aldol condensation product being less than 1% under conditions studied.

Figure 2 shows steady-state product selectivities of vapor phase furfural transformations to furan, furfuryl alcohol, 2-methylfuran, and propylene (furan ring cracking) measured in the 443–513 K temperature range as a function of Pt NP size. The remaining volume of reaction products constitutes by the trace amounts of 2,3-dihydrofuran (DHF), tetrahydrofuran (THF), n-butanol, 2-methyltetrahydrofuran, 1-pentanol, 2-pentanol, tetrahydrofurfuryl alcohol, 1,2-pentadiol, 1,5-pentadiol, and furfural aldol condensation products.
of the decarbonylation/hydrogenation reaction network, as the endothermic decarbonylation reaction becomes more favorable at higher temperatures, opposing the exothermic hydrogenation reaction, which becomes more favorable at lower temperatures.

Figure 4 shows the apparent activation energies measured for formation of furan, furfuryl alcohol, and total conversion of furfural as a function of size for polyhedrally shaped Pt NPs. The apparent $E_A$ for furan formation is on the order of 60 kJ mol$^{-1}$ and is Pt NP size independent, while the apparent $E_A$ of furfuryl alcohol formation is highest (107 kJ mol$^{-1}$) for very small Pt NPs (1.5 nm) but drops rapidly as particle size increases to 1.9 nm (32 kJ mol$^{-1}$) and to 5 nm (12 kJ mol$^{-1}$).

Table 1. Conversion and Product Selectivities of the Furfural Reaction over 3.6 nm Pt/MCF-17 Catalyst

<table>
<thead>
<tr>
<th>temp. (K)</th>
<th>conv. (%)</th>
<th>W/F g$_{cat}$/mol (h)</th>
<th>selectivity (%)</th>
<th>furan</th>
<th>DHF</th>
<th>Pr</th>
<th>FFA</th>
<th>2-MF</th>
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<td>453</td>
<td>1.2</td>
<td>41.4</td>
<td>28</td>
<td>0.7</td>
<td>0.6</td>
<td>68</td>
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<td></td>
<td>0.8</td>
<td>20.7</td>
<td>24</td>
<td>0.7</td>
<td>0.8</td>
<td>72</td>
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<tr>
<td></td>
<td>0.5</td>
<td>13.8</td>
<td>22</td>
<td>1.0</td>
<td>0.7</td>
<td>74</td>
<td>1.8</td>
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</tr>
<tr>
<td>473</td>
<td>1.8</td>
<td>41.4</td>
<td>34</td>
<td>0.7</td>
<td>0.7</td>
<td>63</td>
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<tr>
<td></td>
<td>1.1</td>
<td>20.7</td>
<td>31</td>
<td>0.9</td>
<td>0.8</td>
<td>66</td>
<td>1.3</td>
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<tr>
<td></td>
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<td>31</td>
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<tr>
<td>493</td>
<td>3.1</td>
<td>41.4</td>
<td>30</td>
<td>1.0</td>
<td>0.8</td>
<td>67</td>
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<tr>
<td></td>
<td>1.9</td>
<td>20.7</td>
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<td>66</td>
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<td></td>
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<td>1.1</td>
<td>0.8</td>
<td>65</td>
<td>1.4</td>
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</tr>
</tbody>
</table>

Figure 3. Steady-state product selectivities to furan (blue) and furfuryl alcohol (red) versus TEM-projected Pt particle sizes measured at 473 K under 1300 h$^{-1}$ of GHSP flow of reactant mixture containing 9.3 kPa furfural and 93 kPa H$_2$. 

Figure 2. Steady-state product selectivities to (a) furan, (b) furfuryl alcohol, (c) 2-methylfuran, and (d) furan ring cracking products measured in the 443–513 K temperature range under 1300 h$^{-1}$ of GHSP flow of reactants mixture containing 9.3 kPa furfural and 93 kPa H$_2$. 

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The decarbonylation and hydrogenation reaction paths as a function of Pt NPs size. Decarbonylation of furfural to furan is clearly a structure sensitive reaction as the TOR values decrease more than a factor of 12 upon increasing the Pt particle size from 1.5 to 2.6 nm, followed by a moderate increase in the TOR values upon further increase of Pt particle size from 2.6 to 7.1 nm. The "U"-shaped dependence of TOR on Pt NP size can be explained by a presence of two different types of catalytically active surface sites. The first site is highly active and available only on the small particles (below 2 nm), while the second site is less active and becomes available only as a Pt particle size increases above 2.5 nm. Alternatively, this behavior could be related to the electronic effects of a single catalytic site as a function of Pt NPs size. Indeed, the very small Pt NPs could be electron-deficient, and this deficiency could substantially facilitate the rate of catalytic turnover, compared to the activity of the same site on "more" metallic larger size Pt NPs. The furfural's carbonyl group hydrogenation is also structure-sensitive, evident by more than 40-fold increase in TOR values upon increasing the Pt particle size from 1.5 to 5 nm and also by the change of the apparent activation energy.

**Conclusion.** Vapor phase furfural hydrogenation studies were performed on a series of silica supported monodisperse Pt NP catalysts. It was found that the product selectivity was highly dependent on the size and shape of the NP catalysts. Small particles were found to give predominantly furan as a product, via decarbonylation, while larger sized particles yielded both furan and furfuryl alcohol, the carbonyl hydrogenation product. Octahedral particles were found to be selective to furfuryl alcohol, while cube shaped particles produced an equal amount of furan and furfuryl alcohol. The differences in selectivity have been attributed to the presence of two different catalytically active sites which change in ratio with NP size and shape.

**ASSOCIATED CONTENT**

**Supporting Information**

Nanoparticle synthesis, catalysis preparation, characterization, and ethylene hydrogenation studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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