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Selective Hydrogenation of 2-Methylfuran and 2,5-Dimethylfuran over Atomic Layer Deposited Pt Catalysts on Multi-Walled Carbon Nanotube and Alumina Supports

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2-Methylfuran and 2,5-dimethylfuran were hydrogenated in the vapor phase to corresponding tetrahydrofurans, linear 2-ketones and alcohols over Pt nanoparticles supported on multi-walled carbon nanotubes (MWCNTs) and alumina by atomic layer deposition. The hydrogenation behavior of sub-nm Pt deposited on alumina was influenced by the support acidity. As compared to a commercial Pt/C catalyst, the Pt/MWCNT catalyst contained similarly sized Pt nanoparticles that displayed a broader size distribution and significantly more *n*-alkanes than oxygenates during hydrogenation of these alkyl-substituted furans.

2-Methylfuran (2MF) and 2,5-dimethylfuran (DMF) are important biomass-derived intermediates in the fine chemical processing, which are mainly used for the synthesis of crysanthemate pesticides, perfume intermediates and chloroquinine lateral chains in pharmaceutical intermediates.^[1] Upgrading these substituted furans to valuable chemicals often involves hydrogenation of the aromatic furan ring and its opening via hydrogenolysis, which typically result in mixtures of substituted tetrahydrofurans (THFs), ketones and alcohols.^[2] Although highly selective hydrogenation of 5-hydroxymethyl furfural to DMF and furfural to 2-MF has been reported,^[3] further improving the selectivity of DMF and 2-MF hydrogenation and hydrogenolysis reactions is crucial for producing desired products in high yield. Moreover, while many studies reported Pt (and Pd) to be highly promising catalysts for these reactions,^[4] the current understanding of the molecular structure-reactivity relationships for supported Pt catalysts for 2-MF and DMF hydrogenation reactions is still rather limited.

Highly dispersed carbon-supported Pt nanoparticle used as catalysts in selective hydrogenation reactions have been traditionally prepared by liquid-phase processing.^[4] Although these methods can produce very small Pt nanoparticles, they lack the ability to precisely control their size distributions, which has significant implications for their catalytic properties. On the other hand, atomic layer deposition (ALD) has emerged in recent years as a promising novel method of growing very small Pt and other noble metal nanoparticles with improved size control layer by layer via alternating exposure of the catalytic support to trimethyl(methylcyclopentadienyl) platinum {Me3(MeCp)Pt} and O₂.^[5] This study probes the nanostructures, surface characteristics and catalytic behaviors of Pt ALD catalysts grown on multi-walled carbon nanotubes^[6] and alumina and compares these characteristics with those of a commercial Pt/C catalyst obtained by conventional liquid-phase processing.

The bright-field TEM images of the Pt ALD catalysts (Figure 1) revealed the presence small Pt nanoparticles supported on MWCNTs, whereas only few Pt nanoparticles could be discerned in the alumina supported catalysts due to lower contrast difference between Pt and alumina, smaller Pt loadings and smaller Pt particle sizes in this catalyst. Therefore, HAADF-SEM imaging was employed to characterize these catalysts due to higher Z-contrast differences in this method.



Figure 1. Bright-field TEM images of (left) Pt ALD/MWCNT and (right) Pt ALD/Al_2O_3.

HAADF-STEM imaging of the ALD and commercial Pt catalysts (Figure 2) revealed significant differences in the size and shape of Pt nanoparticles in these catalysts that were evaluated with the help of ImageJ software.^[7]



Figure 2. HAADF-STEM images and particle size distributions of (top) Pt/C (BASF), (center) Pt ALD/MWCNT, and (bottom) Pt ALD/Al_2O_3 (average particles size; 2.39, 2.23 and 0.97 nm, respectively).

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Visual observation revealed a significantly broader size distribution of Pt nanoparticles in the commercial Pt/C catalyst as compared to the Pt ALD/MWCNT, which displayed greater particle size uniformity. The Pt ALD/Al₂O₃ catalyst showed the presence of significantly smaller Pt particles than in the other two catalysts due to lower Pt loading and stronger Pt-support interactions in this catalyst. However, these differences were not apparent when the average Pt particle size was evaluated by the ImageJ software, e.g., 2.32±1.50 nm for Pt ALD/MWCNT vs. 2.39±1.22 nm for Pt/C (BASF) shown in Figure 2. It should be noted that ImageJ overestimated the average size of Pt nanoparticles in the commercial Pt/C catalyst due to reduced contrast differences for the small Pt nanoparticles (ca. 1 nm and smaller) present in this catalyst. In the case of the Pt ALD/Al₂O₃ catalyst, ImageJ was unable to recognize smaller Pt nanoparticles present in this catalyst due to reduced contrast differences with alumina. Therefore, the Pt particle sizes were measured manually from STEM images, which also overestimated the average particle size (0.97±0.37 nm) in this catalyst (Figure 2).

The HAADF-STEM images were further examined in order to gain insights into the structure of small Pt nanoparticles in these catalysts. While Pt particles smaller than ~2 nm were not ordered, only few ~2.3 nm Pt particles present in the Pt/C catalyst (BASF) were oriented appropriately to show the presence of atomic planes (Figure 1Sa). The contrast profile analysis in the direction normal to these planes indicated regular d-spacings of 2.27±0.03 Å that agreed well with d(111) = 2.27 Å in the bulk Pt structure. Although significant Pt lattice contraction (5-10%) has been reported for very small Pt nanoparticles (<2 nm),^[8] it is expected to be negligible for larger Pt particles, such as the ~2.3 nm particle shown in Figure 1Sa. The Pt ALD/MWCNT catalyst showed the presence of similarly sized hexagonal Pt particles showing regular arrays of Pt atomic columns (Figures 1Sb and c) as well as Pt nanoparticles displaying a series of the (111) planes (Figure 1Sd) and (100) planes (Figure 1Se). The distances between the nearestneighbor atomic columns in Figures 1Sb and c were determined by the contrast profile analysis indicating that these particles possessed essentially the bulk structure of Pt viewed along the [110] crystallographic direction. The high-resolution STEM images of the Pt ALD/Al2O3 catalyst were also examined, but revealed no atomic level details due to the presence of smaller Pt nanoparticles in this catalyst and reduced elemental contrast between Pt and the alumina support material.

The surface sites present in these catalysts were further probed by the temperature-programmed desorption/reaction of CO (Figures 2S-4S). The TPD spectra shown in Figure 2S indicated simultaneous evolution of CO and CO₂ that peaked at ca. 360K for the 0.47 wt. % Pt ALD/Al₂O₃ catalyst. The observation of CO₂ in this temperature range suggested the occurrence of the water-gas shift (WGS) reaction with the participation of surface hydroxyls present on the alumina surface. However, H₂ formed in this reaction was adsorbed strongly on the Pt surface at these temperatures (>450K). The second, smaller peak of CO₂ was also observed at ca. 530K, which was not accompanied by CO desorption suggesting that the Boudouard reaction may be responsible for its formation at higher temperatures.^[9] A similar reaction behavior during CO TPD was reported recently by Gould et al.^[9] for Pt ALD catalysts supported on alumina.

The CO desorption/reaction spectra of the two carbonsupported Pt catalysts (Figures 3S and 4S) exhibited complex behavior that was dominated by CO desorption from and reactions on the carbon-based surfaces. Both catalysts exhibited two CO desorption peaks centered at ca. 350 and 660K. According to Marchon et al.^[10] and Li et al.^[11], these peaks are likely due to desorption of CO from weakly bound surface species, such as carbonyl and/or cyclic ethers present on the surface of polycrystalline carbon and carbon nanotubes, respectively. Some CO₂ was also observed during CO TPD from the 5 wt. % Pt/C catalyst (BASF) with peaks at ca. 360, 430 and 680K. The lowest temperature peak at 360K corresponded to a similar feature observed for the 0.47 wt. % Pt ALD/Al₂O₃ catalyst suggesting that the WGS reaction may be responsible for its formation, whereas the CO₂ evolution at higher temperatures agreed well with CO2 peaks observed during CO TPD from polycrystalline graphite by Marchon et al.^[10] Marchon et al.^[10] observed CO₂ desorption at 443 and 673K and explained it by thermal decarboxylation of lactone groups in the surface of polycrystalline graphite, whereas Li et al.^[11] assigned the high temperature CO₂ peak (693K) to decomposition of carboxylic anhydrides. On the other hand, the Pt ALD/MWCNT catalyst exhibited two distinct CO₂ loss features, i.e., a peak at ca. 390K likely associated with the WGS reaction, and a shallow peak at 460K with a long tail extending to ca. 550K suggesting that the MWCNTs in this catalyst contained significantly fewer surface defects and of a different kind, such as carboxylates,^[11] as compared to the carbon support in the commercial Pt/C catalyst.

CO TPD spectra also revealed evolution of hydrogen from these supported Pt catalysts. The majority of this hydrogen was chemisorbed by the Pt nanoparticles during their reduction in hydrogen. The two carbon-supported catalysts displayed a low temperature peak at ca. 420K, which was assigned to hydrogen chemisorbed at Pt atoms located in bulk-like lattice sites.[12] However, the largest H₂ peaks were observed at ca. 600 and 680K for the 5 wt. % Pt/C (BASF) and 5.48 wt. % Pt ALD/MWCNT catalysts, respectively. The peaks above 673K were previously assigned to hydrogen strongly bonded to defect sites in Pt nanoparticles or ultradispersed Pt nanoparticles.^[12] Some other H₂ evolution features were also observed in the TPD spectra of these two catalysts at 500-720K suggesting marked differences in relative abundance of these ultradispersed Pt nanoparticles. The 0.47 wt. % Pt ALD/Al₂O₃ catalyst displayed the highest concentration of hydrogen desorbed at high temperature, followed by the 5 wt. % Pt/C (BASF) and 5.48 wt. % Pt ALD/MWCNT catalysts, respectively. Moreover, the 0.47 wt. % Pt ALD/Al_2O_3 catalyst desorbed hydrogen at the lowest temperature (580K) followed by the commercial 5 wt. %Pt/C (600K) and 5.48 wt. % Pt ALD/MWCNT catalysts (660K). Similar differences in H₂ desorption behavior were recently reported by Li et al.^[11] for supported Pt and Pt-Ru catalysts used in selective hydrogenation of phenylacetylene, where the highest

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reactivity was observed for the Pt/CNT catalyst that displayed the lowest H_2 desorption temperature. Therefore, hydrogen desorption behavior of supported Pt catalysts is expected to have important consequences for their reactivity in other selective hydrogenation reactions, such as those of 2-MF and 2,5-DMF, which is discussed below.

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The surface acidity of these catalysts was probed by ammonia TPD, which is an established method of determining the acid characteristics of heterogeneous catalysts due to the small size, stability, and strong basicity (pKa = 9.2) of the ammonia molecule.^[13] The types of surface acid sites distinguished by the temperature ranges of ammonia desorption are typically categorized as weak (423-573K), moderate (573-723K), and strong (723-923K). The ammonia TPD profiles of the three catalysts investigated in this study are shown in Figures 5S-7S. It can be seen from Figure 5S that the 0.47 wt. % Pt ALD/Al₂O₃ catalyst is distinguished from both the 5 wt. % Pt/C (BASF) and 5.48 wt. % Pt ALD/MWCNT catalysts (Figures 6S and 7S, respectively) by the presence of moderately strong acid sites. The 5 wt. % Pt/C (BASF) and 5.48 wt. % Pt ALD/MWCNT catalysts displayed similar acidity characteristics, with the Pt ALD/MWCNT having considerably less weak surface acidity.



Figure 3. 2,5-DMF hydrogenation ($H_2/2$,5-DMF = 10, GHSV = 2,500 h⁻¹) over (a) 5.48 wt. % Pt ALD catalyst supported on MWCNTs and (b) commercial 5 wt. % Pt/C catalyst.

The results of 2,5-DMF and 2-MF hydrogenation over atomic layer deposited Pt catalysts on MWCNT and alumina supports



Figure 4. 2-MF hydrogenation (H₂/2-MF = 10, GHSV = 2,500 h⁻¹) over (a) 5.48 wt. % Pt ALD catalyst supported on MWCNTs and (b) commercial 5 wt. % Pt/C catalyst.

are shown in Figures 3-5, where these catalysts are compared to the commercial 5 wt. % Pt catalyst supported on carbon (BASF). As expected, these results indicated that 2,5-DMF is more reactive than 2-MF due its greater activation by the two methyl group substituents on the furan ring. 2,5-DMF was completely converted over both the Pt ALD/MWCNT and commercial catalysts over the entire temperature range investigated (353-573K) and H₂/2,5-DMF ratios of 3 and 10. However, the Pt ALD/MWCNT catalyst was much more active in deep 2,5-DMF hydrogenation to hexane over the entire temperature range investigated than the commercial 5 wt. % Pt/C catalyst, while the latter catalyst exhibited a yield of 2hexanol (ca. 80 mol. %) at low temperatures (Figure 3). We believe that the presence of moderately strong acid sites in the Pt ALD/MWCNT catalyst (Figure 5S) may be responsible for the observed deep 2,5-DMF hydrogenation to hexane over this catalyst. The yield of 2-hexanol over the commercial catalyst declined at higher temperatures, which was accompanied by the concomitant rise of 2-hexanone yield because the formation of the latter molecule becomes more thermodynamically favorable at elevated temperatures.

Both the Pt ALD/MWCNT and commercial catalyst exhibited similar behavior in 2-MF hydrogenation, while the Pt ALD/Al₂O₃ catalyst was slightly less active below 473K (Figure 4). Both catalysts resulted in a ca. 80 mol. % yield of 2-pentanone at

573K and 100 % 2-MF conversion, the balance being a mixture of butane and some pentane.



Figure 5. Hydrogenation of substituted furans over 0.47 wt. % Pt ALD catalyst supported on alumina: (a) H₂/2,5-DMF = 3, (b) H₂/2,5-DMF = 10, and (c) H₂/2-MF = 10. GHSV = $2,500 \text{ h}^{-1}$.

The 0.47 wt. % Pt ALD catalyst supported on alumina was highly active in 2,5-DMF hydrogenation over the entire temperature range investigated (100 % conversion). Under relatively H₂-lean conditions (H₂/2,5-DMF = 3) this catalyst

exhibited ca. 50 mol. % yield of 2-hexanone and 40 mol. % yield of 2,5-DMTHF at 393K, which rapidly declined with temperature, whereas the yield of hexane reached 100 mol. % at 473-523K and then decreased above 523K to 70 mol. % yield likely due to occurrence of cracking reactions (Figure 5b). No 2-hexanol was

detected over this catalyst over the entire temperature range investigated at $H_2/2$,5-DMF = 3. Under H_2 -rich conditions $(H_2/2,5-DMF = 10)$, the yield of of 2-hexanone reached ca. 60 mol. % at 393K, while 2,5-DMTHF was present in trace amounts. Some 2-hexanol (ca. 10 mol. %) was also detected at low temperatures (423K). However, these products disappeared when the reaction temperature reached 473K, which was accompanied by a rapid rise in hexane formation (100 mol. %). The yield of hexane declined above 523K due to hexane cracking, but the extent of cracking was less at $H_2/2,5$ -DMF = 10 as compared to $H_2/2,5$ -DMF = 3: ca. 15 mol. % vs. 30 mol. % at 573K. It is interesting to observe the absence of cracking reactions over the Pt ALD/MWCNT catalyst, which suggests the role of moderately strong acidity of the alumina support (Figure 5S) in these reactions. The role of alumina support acidity was also manifested in the case of 2-MF hydrogenation (Figure 5c), where its conversion remained relatively constant at ca. 40 mol. % at 353-473K and declined to ca. 20 mol. % at 548K probably due to surface coking with carbonaceous deposits. This catalyst also displayed a complex distribution of furan ring hydrogenation and C-O bond hydrogenolysis products suggesting a generally greater role played by the acidic alumina support during 2-MF hydrogenation over the 0.47 wt. % Pt ALD/alumina catalyst.

We attempted to explain the catalytic behavior of the Pt ALD and commercial Pt/C catalysts on the basis of their structural differences. The Pt ALD/Al₂O₃ catalyst was considerably less selective to oxygenates during 2,5-DMF hydrogenation than the commercial Pt/C and Pt ALD/MWCNT catalysts producing instead n-hexane in a 100 mol. % yield. The significantly smaller Pt nanoparticle size in the Pt ALD/Al₂O₃ catalyst coupled with a high concentration of relatively low-temperature H₂ desorption sites (580K) probably contributed to greater activity and resulting deep hydrogenation behavior of this catalyst towards 2,5-DMF. On the other hand, these surface sites apparently possessed insufficient activity towards 2-MF, as its conversion did not exceed 50 mol. % over the entire temperature range investigated. The lower catalytic activity of the Pt ALD/Al₂O₃ catalyst in 2-MF hydrogenation coupled with the surface acidity of the alumina support contributed to a complex product distribution observed for this catalyst.

The Pt ALD/MWCNT catalyst displayed a similar catalytic activity during 2,5-DMF hydrogenation as compared to the commercial Pt/C catalyst but lower selectivity to oxygenates and higher selectivity to *n*-hexane, most likely due to the presence of defect sites in Pt nanoparticles or ultradispersed Pt nanoparticles manifested in high desorption temperature of H₂ (680K). On the other hand, this ALD catalyst displayed very similar catalytic behavior to that of the commercial Pt/C catalyst during 2-MF hydrogenation.

Experimental Section

Experimental details are available in the Supporting Information.

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Entry for the Table of Contents

Layout 1:

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2-MFand 2,5-DMF were hydrogenated over nanoparticulate Pt catalyst supported on multi-walled carbon nanotubes by atomic layer deposition (ALD). ALD resulted in a broader Pt nanoparticle dispersion and significantly more nalkanes than oxygenates as compared to commercial Pt/C catalyst.



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Title

Selective Hydrogenation of 2-Methylfuran and 2,5-Dimethylfuran over Atomic Layer Deposited Pt Catalysts on Multi-Walled Carbon Nanotube and Alumina Supports