

Deuterium-Labeling Study of the Hydrogenation of 2-Methylfuran and 2,5-Dimethylfuran over Carbon-Supported Noble Metal Catalysts

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2-Methylfuran and 2,5-dimethylfuran were deuterated over Pd and Pt catalysts at 90–220 °C. Furan ring saturation over a Pd/C catalyst occurred at low reaction temperatures, which led to deuterated THFs, followed by progressive D exchange in the THF ring at higher temperatures. Finally, H/D exchange occurred in the methyl groups on the THF ring. Cleavage of the C–O bond also occurred over a Pd/C catalyst at elevated temperatures, which resulted in deuterated ketones, for which all H atoms were exchanged for D. Alcohols were produced over a Pt/C catalyst at low temperatures because they are more stable than the corresponding ketones. D replaced H on all carbon atoms of the furan ring and saturated the O and C atoms of the broken C–O bond in both deuterated 2-pentanol and 2-hexanol. At low temperatures (90–105 °C), all H atoms in the deuterated alcohols were exchanged for D except for the last two hydrogen atoms on the methyl groups.

The catalytic transformations of biomass into fuels and value-added chemicals have received considerable attention in the past decade as green alternatives to the petrochemical processes. From an environmental standpoint, such processes based on renewable feedstocks result in lower carbon dioxide emissions, which contribute to global warming.^[1] For instance, substituted furans and their derivatives are important chemical intermediates derived from biomass that can be hydrogenated into a variety of specialty chemicals, solvents, and alternative fuels.^[2] In particular, two hemicellulose- and cellulose-derived molecules, 2-methylfuran and 2,5-dimethylfuran, have highly promising physical and chemical properties for applications as alternative fuels.^[3] They possess energy densities of 31.2 and 32.9 MJ kg⁻¹, respectively, which are approximately 40% greater than the energy density of ethanol; furthermore, they possess high research octane numbers of 103 and 101, respectively.^[4]

Further upgrading of these substituted furans to valuable chemicals involves hydrogenation of the aromatic furan ring and its opening by hydrogenolysis, which typically result in mixtures of substituted tetrahydrofurans (THFs), ketones, and alcohols.^[5] Although the highly selective hydrogenation of 5-hydroxymethylfurfural to 2,5-dimethylfuran and furfural to 2-methylfuran has been reported,^[6] improving the selectivity of the 2,5-dimethylfuran and 2-methylfuran hydrogenation and hydrogenolysis reactions is crucial for producing the desired products in high yields. Moreover, whereas many studies report Pt and Pd to be highly promising catalysts for these reactions,^[7] the current understanding of the hydrogenation pathways of 2-methylfuran and 2,5-dimethylfuran are still rather limited.

In this study, the hydrogenation pathways of 2-methylfuran and 2,5-dimethylfuran over two carbon-supported Pt and Pd catalysts were investigated by using D₂- and D-labeled products analyzed by GC–MS by employing chemical ionization. Deuterium labeling is frequently used in the chemical sciences to elucidate reaction pathways,^[8] whereas MS can distinguish deuterated diastereomers by means of rearrangements involving five- and six-membered cyclic transition states.^[9] Moreover, chemical ionization used in MS largely preserves the parent molecular ions and, therefore, is particularly promising for the identification of D-labeled molecules in complex product mixtures.^[10]

THFs, alcohols, and ketones were observed over Pt/C and Pd/C catalysts under different reaction conditions (Tables 1 and 2). The main differences in the catalytic behavior between the Pd and Pt catalysts were observed at low temperatures. The hydrogenation of 2-methylfuran and 2,5-dimethylfuran over the Pd/C catalyst at low reaction temperatures resulted in ring saturation and formation of THFs, whereas linear alcohols were

Table 1. Product yields during the hydrogenation of 2,5-dimethylfuran.^[a]

Catalyst	Temperature [°C]	Yield [mol %]			
		2,5-dimethyltetrahydrofuran	2-hexanone	2-hexanol	others
Pt/C	95	82.3	9	8.7	0
	105	50.1	35.5	14.4	0
	130	37.1	43.8	19.1	0
	220	13.5	70.2	2.1	14.2
Pd/C	95	100	0	0	0
	125	100	0	0	0
	150	98.6	0	0	1.4
	220	41.3	45	0	13.8

[a] The conversion of 2,5-dimethylfuran was 100% in all cases.

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Table 2. Product yields during the hydrogenation of 2-methylfuran.^[a]

Catalyst	Temperature [°C]	Yield [mol%]			
		2-methyltetrahydrofuran	2-pentanone	2-pentanol	others
Pt/C	90	7.8	7	78.6	6.7
	100	7.1	10.2	73.6	9.1
	150	3.9	15.2	67.5	13.4
	200	0	72.6	7	20.4
Pd/C	95	97.3	2.7	0	0
	120	75.6	23.2	0	1.2
	150	61.2	37.2	0	1.6
	200	17.4	78.2	0	4.4

[a] The conversion of 2-methylfuran was 100% in all cases.

produced over the Pt/C catalyst. However, the product distributions over these two catalysts were similar above 150 °C. Therefore, owing to these similarities, the deuteration of 2-methylfuran and 2,5-dimethylfuran over the Pt/C catalyst was not investigated in this study at elevated temperatures.

Figure 1 shows the mass distribution of deuterated dimethyltetrahydrofurans (DMTHFs) obtained over the Pd/C catalyst at different reaction temperatures. The mass charge ratios of deuterated 2,5-dimethylfuran varied from $m/z=97$ to 113 corresponding to some residual 2,5-dimethylfuran ($m/z=97$) to fully deuterated $[D_{12}]$ -2,5-dimethyltetrahydrofuran ($m/z=113$).

Some residual 2,5-dimethylfuran was observed at 90 °C, whereas the highest value of $m/z=106$ in a deuterated product indicated that the original furan ring was saturated with D and also underwent partial H/D exchange (6 D) without C–O bond cleavage. Populations in the $m/z=106$ –109 range dramatically increased at 120 °C, whereas the abundance of $m/z < 104$ species decreased. Ratios in the $m/z=106$ –109 range correspond to complete H exchange for D in a furan ring as well as partial D exchange in one methyl group.

At 200 °C, the concentrations of the DMTHF species with a fully deuterated THF ring ($m/z < 107$) decreased, whereas those of DMTHF for which both methyl group substituents underwent complete D exchange ($m/z > 108$) increased up to $m/z=113$. These results indicate that 2,5-dimethylfuran ring saturation with D occurs at low temperature, followed at higher temperatures by gradual H/D exchange involving the

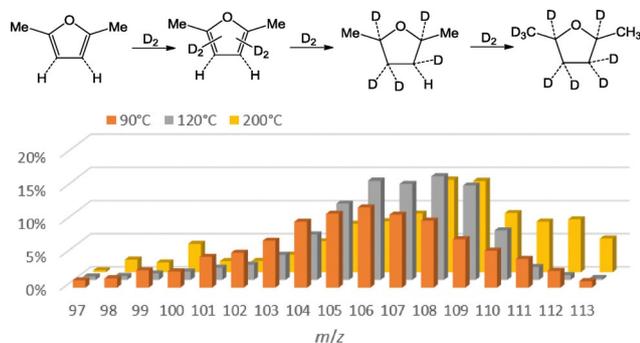


Figure 1. Relative abundances of deuterated DMTHF species over Pd/C catalyst.

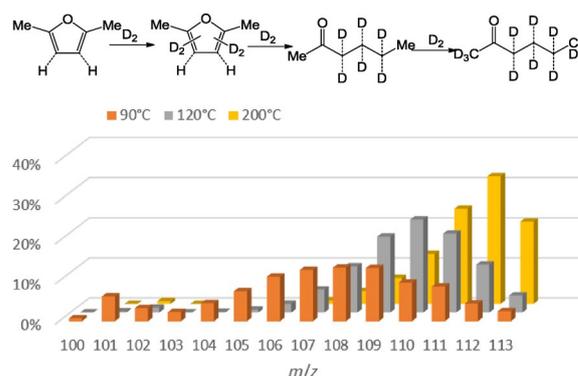


Figure 2. Relative abundances of deuterated 2-hexanone species over Pd/C catalyst.

original H atoms on the DMTHF ring. Finally, at even higher temperatures, H atoms of the two methyl groups are gradually exchanged for D until the DMTHF is completely deuterated.

Figure 2 shows the relative abundance of various deuterated 2-hexanone species observed over the Pd/C catalyst. Most 2-hexanone species formed at 90 °C possess ratios between $m/z=104$ and 112. The peak at $m/z=104$ corresponds to 2-hexanone with 3 H atoms exchanged for D, whereas the highest abundance was observed for $m/z=108$, which corresponds to 7 H atoms exchanged for D.

As reported in our previous study, the hydrogenation of 2,5-dimethylfuran to 2,5-dimethyltetrahydrofuran at low temperature occurs over the Pd/C catalyst with high selectivity.^[11]

The results of the present D-labeling study further indicate that ring saturation and H/D exchange occur first followed by C–O bond hydrogenolysis. Moreover, according to an earlier study,^[12] only alkylfurans with unprotected α -carbon atoms exhibit appreciable H/D exchange activity, which indicates that some H could be exchanged for D early on, and this is in agreement with our findings at the low reaction temperature. At a reaction temperature of 120 °C, populations shift up to $m/z=107$ –112, whereas populations in the $m/z=104$ –106 range decrease in abundance. The highest abundance for $m/z=110$ corresponds to 9 D atoms in 2-hexanone. We assume that in this species H is fully replaced by D in the original furan ring as well as one methyl group. As the reaction temperature is increased further to 200 °C, the extent of H/D exchange increases such that all H atoms in 2-hexanone are replaced by D.

2-Hexanol was also observed over Pt/C at low reaction temperature (90 °C) owing to its greater stability at this temperature relative to that of 2-hexanone.^[11] As shown in Figure 3, the relative abundances peak at $m/z=108$, which corresponds to the presence of 5 D atoms in 2-hexanol. It is interesting to compare the D content in 2-hexanol formed at a low temperature over the Pt/C catalyst (Figure 3) with that in 2-hexanone formed at higher temperature over the Pd/C catalyst (Figure 2). The presence of 5 D atoms in 2-hexanol suggests that C–O bond hydrogenolysis in 2,5-dimethyltetrahydrofuran occurs before any significant H/D exchange in the DMTHF ring. On the other hand, the presence of 7 D atoms in 2-hexanone formed over the Pd/C catalyst indicates complete H/D on C2–

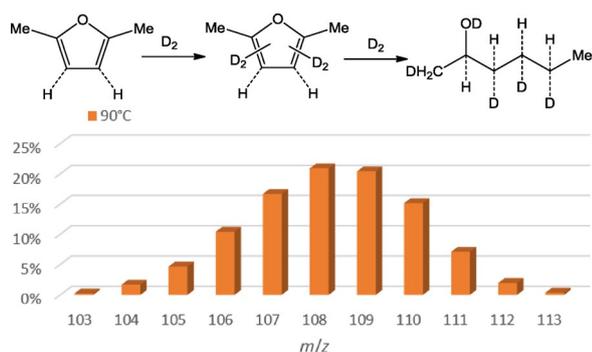


Figure 3. Relative abundances of deuterated 2-hexanol species at 90 °C over Pt/C catalyst.

C5 of the original 2,5-dimethylfuran ring and even some H/D exchange involving the methyl substituents.

The saturation of 2-methylfuran with deuterium over the Pd/C catalyst shows essentially the same trends as that of 2,5-dimethylfuran. Figure 4 shows the m/z distribution of deuterated 2-methyltetrahydrofuran species at three reaction temperatures. The highest abundance observed at $m/z=89-90$ corresponds to exchange of three to four hydrogen atoms for deuterium at 95 °C. This deuterium content is indicative of saturation of the original furan ring with deuterium without further H/D exchange in the 2-methyltetrahydrofuran ring.

The maximum peak of $m/z=95$ corresponds to complete replacement of all hydrogen atoms in the 2-methyltetrahydrofuran ring by deuterium. As the reaction temperature is increased further to 130 °C, the highest abundances are observed for species with $m/z > 96$, which indicates that almost all H atoms, except the last remaining one to two, are exchanged for deuterium.

Figure 5 shows the relative abundances of deuterated 2-pentanone species formed at 120 and 220 °C over the Pd/C catalyst, whereas the hydrogenation of 2-methylfuran at 95 °C produces only deuterated 2-methyltetrahydrofuran.

At 130 °C, the abundance of species gradually increases from $m/z=89$ to 92, which corresponds to 2-pentanone with two to five hydrogen atoms replaced by deuterium. The presence of 2-pentanone with fewer than 4 D atoms suggests the presence

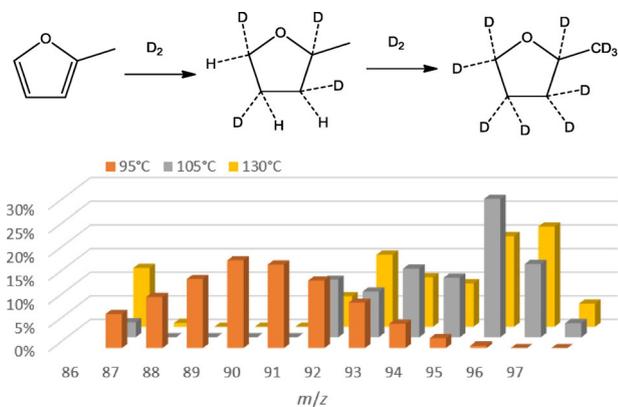


Figure 4. Relative abundances of deuterated 2-methyltetrahydrofuran species over Pd/C catalyst.

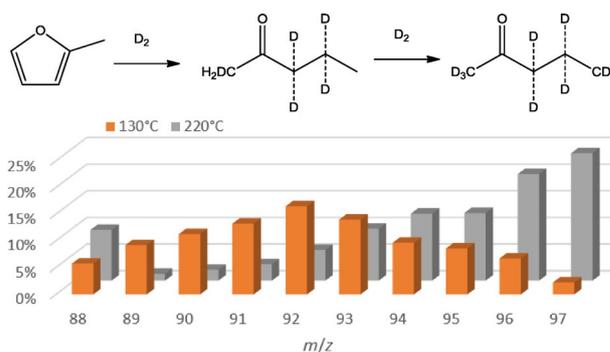


Figure 5. Relative abundances of deuterated 2-pentanone species at 130 and 220 °C over Pd/C catalyst.

of a pool of H atoms on the Pd surface, which is capable of contributing hydrogen atoms to intermediates in the hydrogenation of 2-methylfuran. The m/z population gradually decreases at $m/z > 93$, which corresponds to almost all H atoms in 2-pentanone exchanged for D, except for the H atoms in the original methyl group on the 2-methylfuran ring. As the reaction temperature is increased to 220 °C, the species with $m/z=94-97$ become the most abundant, and this is indicative of the predominance of deeply and even fully deuterium-exchanged species ($m/z=97$).

2-Pentanol was also produced over the Pt/C catalyst at 95 and 105 °C. As shown in Figure 6, the most abundant species at 95 °C for this product is at $m/z=94$, which corresponds to 5 H atoms exchanged for D, and this is the same extent of D exchange as that observed for deuterated 2-hexanol. This observation suggests that the hydrogenolysis pathways of 2-methylfuran and 2,5-dimethylfuran leading to linear alcohols at low temperatures are also similar. As the reaction temperature is increased to 105 °C, the maximum population peak of the product is shifted to $m/z=97$, for which 9 H atoms are exchanged for D except the last three in the methyl group.

In summary, the Pt and Pd catalysts showed significant differences in their hydrogenation behavior at low temperature, for which C–O bond hydrogenolysis leading to linear alcohols occurred over the Pt catalyst after double bond saturation but before any significant H/D exchange. Deuterated ketones were obtained over the Pt catalyst at high temperatures owing to

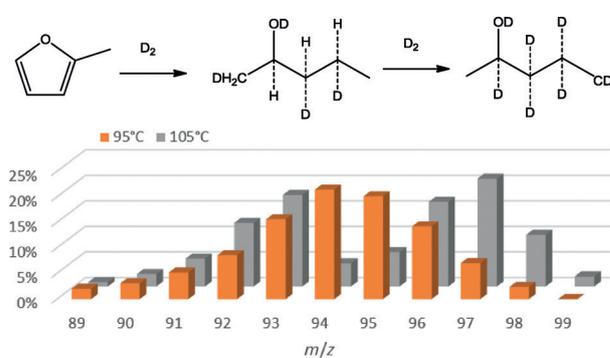


Figure 6. Relative abundances of deuterated 2-pentanol species at low reaction temperatures over Pt/C catalyst.

their greater thermodynamic stability relative to that of alcohols. On the other hand, the Pd catalyst showed double-bond saturation behavior followed by progressive H/D exchange in the tetrahydrofuran species at low temperatures, which underwent C–O bond cleavage and isomerization to the corresponding ketones at high temperatures. Recent studies have shed some light onto the nature of these transformation steps on Pt and Pd surfaces. Thus, Kliewer et al.^[13] investigated the hydrogenation of furan over Pt by using sum frequency generation vibrational spectroscopy (SFGVS). They observed that the planar furan ring lay flat on all Pt surfaces investigated, whereas both THF and butanol (as butoxy) product species were bound through the O atom in an upright geometry. Aliaga et al.^[14] further investigated the hydrogenation of 2-methylfuran and 2,5-dimethylfuran at 20–120 °C over 7 nm cubic Pt nanoparticles that resulted in linear alcohols as the dominant hydrogenation products under these low-temperature conditions. SFGVS further indicated that these alkylfurans lay flat on the Pt surface, whereas the corresponding THFs and alcohol species were adsorbed in an upright position through the O atoms. Significantly less cracking was observed for 2-methylfuran and 2,5-dimethylfuran relative to that observed for furan, which was explained by the electronic and steric hindrance effects introduced by the extra methyl groups in these two species, which force the aromatic rings away from the Pt surface.

On the other hand, Wang et al.^[15] recently studied the hydrogenation of furan on Pd(111) by DFT and found the flat furan ring to be bound to three surface Pd atoms through four H atoms. The number of surface bonds decreased with hydrogenation, which resulted in bent cyclic intermediates that weakly interacted with the Pd surface. A singly hydrogenated intermediate, HF, was indicated as a reactive intermediate toward both hydrogenation and ring opening. The partial pressure of hydrogen was suggested as a critical factor in controlling the selectivity toward ring opening versus further hydrogenation to DHF and THF. Given that the forward and backward reactions are generally fast and thermodynamics are dominant at high temperatures, 1-butanol becomes a major product with increasing temperature. At low temperatures, ring opening is slow, which makes THF the major product. These theoretical results appear to be in agreement with the experimental results of Horiuchi and Medlin,^[16] who investigated the adsorption and hydrogenation behavior of 2,3- and 2,5-dihydrofuran on Pd(111). At temperatures below approximately 330 °C, 2,3-dihydrofuran was hydrogenated to THF, whereas 2,5-dihydrofuran underwent dehydrogenation to furan. Both species underwent ring opening above approximately 400 °C.

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