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Molybdenum Carbide as a Highly Selective Deoxygenation Catalyst for Converting Furfural to 2-Methylfuran

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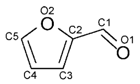
Selectively cleaving the C=O bond outside the furan ring of furfural is crucial for converting this important biomass-derived molecule to value-added fuels such as 2-methylfuran. In this work, a combination of density functional theory (DFT) calculations, surface science studies, and reactor evaluation identified molybdenum carbide (Mo_2C) as a highly selective deoxygenation catalyst for converting furfural to 2-methylfuran. These results indicate the potential application of Mo_2C as an efficient catalyst for the selective deoxygenation of biomass-derived oxygenates including furanics and aromatics.

Biomass upgrading is a promising alternative in order to meet recent energy and environment challenges.[1–3] Several furanic molecules have been introduced as platform chemicals in biomass conversion.[4] These furanic molecules can be produced by hydrolyzing and dehydrating cellulose and hemicellulose, which comprise more than 55 wt% of the components of raw biomass.[1] Furfural (Scheme 1) is one of the most important biomass-derived furanic molecules, as described in previous reports.[5,6] Furfuryl alcohol, which can be obtained by selectively hydrogenating the C1=O1 bond of furfural,[7–10] is a desirable compound for producing resins.[11] Another desirable compound is 2-methylfuran, from the selective cleavage of the C1=O1 bond, which has a high energy density, a high blending research octane number (RON), and has been shown to be a promising fuel additive for gasoline in a recent 90 000 km road test.[6]



Scheme 1. Molecular structure of furfural.

The conversion of furfural to 2-methylfuran requires selective deoxygenation of the C1=O1 bond while leaving the furan ring intact. Copper- [12] and nickel-based[13,14] catalysts have been reported as active towards the conversion of furfural into 2-methylfuran. However, the copper chromite catalyst required for making 2-methylfuran is toxic while the yield of 2-methylfuran on monometallic nickel catalysts is less than 15%. Resasco et al. reported that adding iron into Ni/SiO_2 could improve the yield of 2-methylfuran.[14] This was achieved, however, at relatively high temperature (ca. 523 K). Other common deoxygenation catalysts include precious metals such as ruthenium,[15] rhodium,[16] palladium,[17] rhenium,[18] and cobalt or nickel molybdenum (CoMo, NiMo) sulfide catalysts.[19] The precious-metal catalysts suffer from low selectivity due to undesirable side reactions involving C–C bond cleavage and also from the limited abundance of precious metals, which might become a cost issue for large-scale applications for biomass conversion. On the other hand, the CoMo and NiMo sulfide catalysts require high operating temperatures and additional separation units because of the possible leaching of sulfur.[20]

Molybdenum carbide (Mo_2C) is emerging as a hydrodeoxygenation (HDO) catalyst. It has been demonstrated to possess high activity towards HDO and high C–O scission selectivity compared to C–C scission in the study of small oxygenates such as ethanol[21] and propanal.[22] A recent report suggested that Mo_2C is more stable compared to tungsten carbide (W_2C) in the HDO of guaiacol.[20] However, the fundamental reason behind the selective HDO activity of Mo_2C is not well understood. Because different oxygen-containing functional groups usually coexist in biomass molecules, furfural, which contains carbon–oxygen bonds both outside and inside the furan ring, should be an excellent probe molecule for studying the selective HDO activity of Mo_2C for biomass molecules.

In this work we report the unique HDO properties of Mo_2C for selectively cleaving the C=O bond outside the furan ring of furfural, while leaving the C–O bond inside the ring intact. Density functional theory (DFT) calculations predict that furfural adsorbs onto the Mo_2C surface in a configuration that favors selective cleavage of the C1=O1 bond while leaving the furan ring intact. This favorable bonding configuration was confirmed by using surface vibrational spectroscopy over a well-characterized Mo_2C surface, and the production of 2-methylfuran was detected by temperature programmed desorption (TPD) experiments. Finally, the promising results on model surfaces were extended to flow reactor evaluation on porous Mo_2C catalysts, confirming the production of 2-methylfuran with high selectivity at relatively low temperatures.

DFT calculations of binding energies of furfural and several related molecules, including furan, 2-methylfuran, and furfuryl alcohol, were performed on a close-packed $Mo_2C(0001)$ surface. A DFT calculation of furfural on a typical precious-metal

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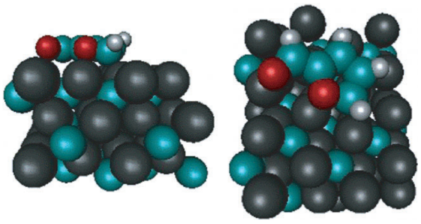
Table 1. Binding energies (BEs) and bond lengths (*d*) of furfural and its derivatives on Mo_2C and Pt(111) as calculated by DFT.

Sample	BE on Mo_2C [eV]	BE on Pt(111) [eV]	d(M–O1)[a] [Å]	d(C1–O1)[b] [Å]
furan	1.17	0.89	–	–
2-methylfuran	1.60	0.76	–	–
furfural	3.54	0.66	2.03	1.35 (1.23[c])
furfural on Pt(111)	–	–	2.20	1.31 (1.23[c])
furfuryl alcohol	1.14	–	2.43	1.47 (1.44[c])

[a] Distance between O1 and the closest metal atom. [b] Distance between C1 and O1 atoms. [c] In parentheses: distance between C1 and O1 atoms for each molecule in the gas phase.

surface, Pt(111), was also performed for comparison. The results are summarized in Table 1. The optimized adsorption configuration of furfural on Mo_2C is shown in Scheme 2.



Scheme 2. Optimized configuration of furfural on Mo_2C.

For furfural, the binding configuration through the C1=O1 bond is more favorable on both Mo_2C and Pt(111). The binding energy of furfural on Mo_2C is much larger than that on Pt(111), revealing a much stronger interaction between Mo_2C and the C1=O1 bond. In addition, the distance between O1 and the metal atom is much shorter on Mo_2C than that on Pt(111), while the distance between C1 and O1 is elongated to a larger degree on Mo_2C than that on Pt(111), consistent with Mo_2C having a stronger interaction with the C1=O1 bond. In contrast, furan and 2-methylfuran adsorb onto Mo_2C through the furan ring with significantly lower binding energies as compared to that of furfural (3.54 eV), confirming a stronger interaction between the C1=O1 bond and the Mo_2C surface. Furfuryl alcohol adsorbs onto Mo_2C mainly through the oxygen atom of the hydroxyl group with a binding energy of 1.14 eV.

The strong interaction between the C1=O1 bond of furfural and the Mo_2C surface predicted by DFT calculations was confirmed by high-resolution electron energy loss spectroscopy (HREELS) measurements. The vibrational-mode assignments of furfural are provided in Table S1 of the Supporting Information. As shown in Figure 1 a, the peak associated with $\tilde{\nu}$(C=O) at 1644 cm^{-1} is shifted to 1596 cm^{-1} at 200 K and nearly disappears at 300 K, indicating that the C1=O1 bond is weakened, most likely through a η^2(C,O) di–σ bonding configuration on Mo_2C, as reported on other surfaces.[23–25] As shown in Table S1, the DFT-generated frequencies match well with the experimentally observed frequencies of chemisorbed furfural, supporting that furfural adsorbs onto Mo_2C through a η^2(C,O) di–σ bonding configuration.

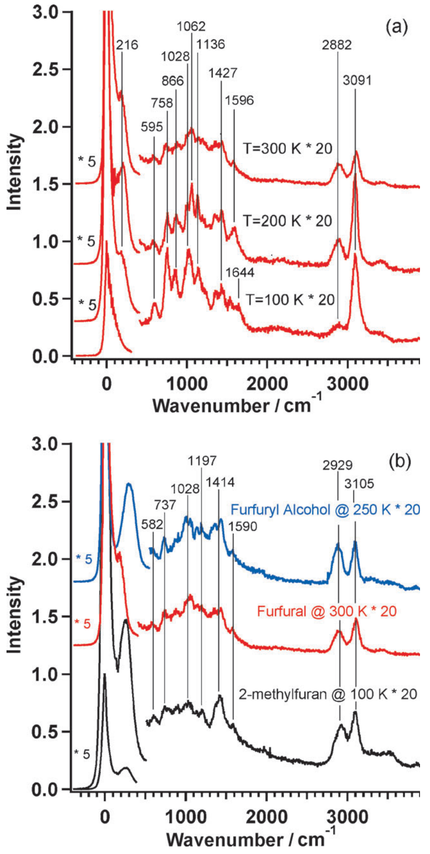


Figure 1. HREELS of (a) furfural (red), and (b) 2-methylfuran (black) and furfuryl alcohol (blue) adsorbed onto Mo_2C after annealing the surface to various temperatures.

The HREELS of furfuryl alcohol and 2-methylfuran on Mo_2C are compared (Figure 1 b) to identify possible reaction intermediates. For the spectrum of furfural at 300 K, the peak positions were almost identical to those observed for adsorbed 2-methylfuran, suggesting that a methylfuran-like intermediate was produced after the reaction of furfural with Mo_2C at 300 K. A similar methylfuran-like intermediate was also formed from the reaction of furfuryl alcohol at 250 K. This was confirmed by the TPD results (Figure 2) after exposing furfural (red spectrum)

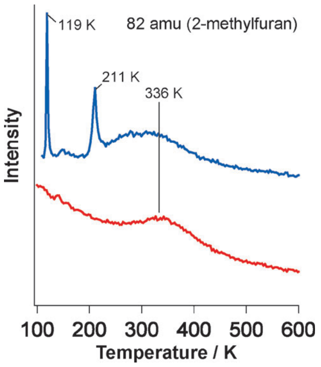


Figure 2. TPD spectra of 2-methylfuran desorption from the reaction of furfural (red) and furfuryl alcohol (blue) on Mo_2C. The sharp peaks at 119 K and 211 K for the TPD spectrum of furfuryl alcohol are from the cracking pattern of molecular desorption of furfuryl alcohol.

and furfuryl alcohol (blue spectrum) onto the Mo_2C surface, which showed that 2-methylfuran was produced from the reaction of both molecules.

The direct production of 2-methylfuran from furfural in ultrahigh vacuum (UHV) has not been reported. UHV studies of furfural on a Pd(111) surface identified furan as the major product.[26] The temperature range for producing 2-methylfuran from furfural (between 300 K and 400 K) is consistent with the HREELS results (Figure 1 a), in which the methylfuran-like intermediate was produced at 300 K. In addition, Figure 2 shows that the 2-methylfuran desorption peak is similar between the reaction of furfural and furfuryl alcohol, suggesting a similar intermediate leading to the formation of 2-methylfuran.

Results from model surfaces suggest that Mo_2C should be an efficient catalyst for selectively deoxygenating furfural to make 2-methylfuran due to the strong interaction between the C1=O1 bond of furfural and the Mo_2C surface. In order to verify the promising results from model surfaces, porous Mo_2C catalysts were synthesized and tested for their catalytic performance towards furfural HDO in a flow reactor. Consistent with results from model surfaces, 2-methylfuran was found to be the dominant product, with selectivity at around 60% at all time-on-stream as shown in Figure 3 a. The high 2-methylfuran selectivity at relatively low reaction temperature (around 423 K) distinguishes the Mo_2C catalysts from nickel-based catalysts mentioned in the introductory paragraphs. The second major product were C_{10}^{+} heavier compounds, with selectivity close to 30%. The selectivity towards furfuryl alcohol was less than 7%, consistent with TPD results showing that Mo_2C could also selectively break the branched C–O bond of furfuryl alcohol to make 2-methylfuran. Finally, the selectivity to furan, the product of C–C bond cleavage from furfural, was found to be less than 1%, suggesting that Mo_2C can selectively break the C1=O1 bond without C–C bond scission.

Although it has excellent performance in selectivity, the as-synthesized Mo_2C catalyst was not stable, as indicated by the deactivation of either furfural conversion (Figure 3 b) or 2-methylfuran site time yield (2 MF STY) (Figure 3 c) over the first few hours on stream. Although the rate of deactivation gradually decreased as the reaction proceeded, the deactivation continued even after 20 h on stream. However, the catalysts could be fully regenerated after deactivation via treatment in pure H_2 ($1.67\ cm^3 s^{-1}$) at 750 K for 1 h. A comparable catalytic performance was obtained after the first and second regeneration cycle, as shown in Figure 3. Also, the reaction was inferred to be catalytic because the area under the 2 MF STY curve (Figure 3 c) corresponded to ca. 22 mol of 2-methylfuran per mol of catalytic site (measured by CO uptake at 423 K).

More importantly, the deactivation of the catalyst was considered to be due to the furfural feed. As shown in Figure 4, HDO reactions of anisole (containing aromatic groups) and propanal (containing aldehyde groups) on the same Mo_2C catalyst were stable for 18 h and 5 h, respectively. Polymerization of furanic molecules, one of the important reasons for catalyst deactivation for the catalytic reaction of furanic molecules as reported in previous literature,[27] could ultimately encapsulate the catalyst and cause deactivation. Future efforts should focus on identifying reaction conditions and feed compositions that could potentially reduce the polymerization of these molecules.

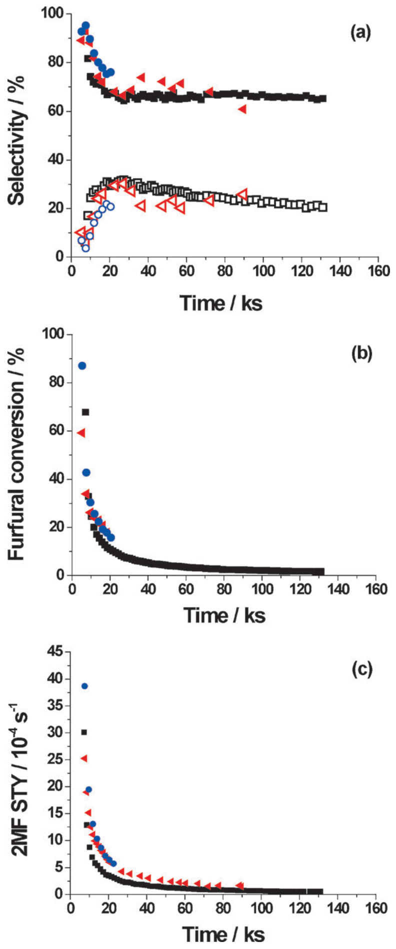


Figure 3. (a) Product selectivity for the reaction of furfural (solid symbols for 2-methylfuran, open symbols for heavier compounds; the selectivity of furfuryl alcohol (less than 7% at all time-on-stream) is not shown for clarity). (b) Conversion of furfural, and (c) 2-methylfuran site-time-yield (2 MF STY, normalized by the amount of irreversible chemisorbed CO on the Mo_2C at 423 K) vs. time on stream for the fresh Mo_2C catalyst (■) and the same catalyst after the first (△) and second (●) regeneration cycle. Experimental conditions: 423 K, atmospheric pressure.

In conclusion, a combination of density functional theory (DFT) calculations, surface science experiments, and flow reactor evaluation reveals that Mo_2C is a highly selective hydrodeoxygenation (HDO) catalyst for producing 2-methylfuran from furfural. DFT calculations and high-resolution electron energy loss spectroscopy (HREELS) experiments indicate that a strong interaction between Mo_2C and the C1=O1 bond is responsible for the high selectivity. Catalyst deactivation is likely due to the polymerization of the furfural feed. These results suggest the possibility of using Mo_2C as a promising HDO catalyst to upgrade other furanic molecules from cellulose and oxygen-containing aromatics from lignin.

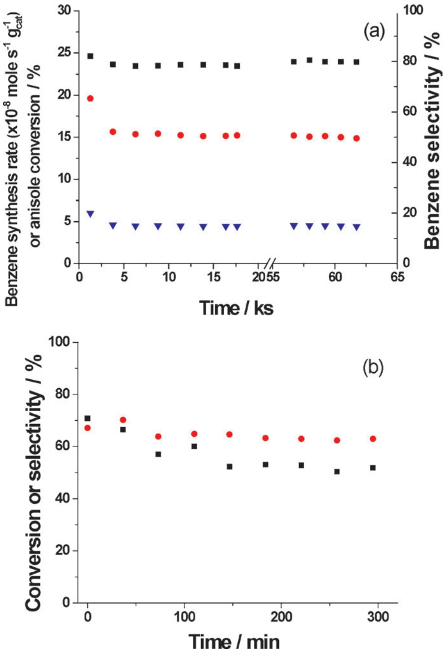


Figure 4. (a) ■ Benzene selectivity, ● anisole conversion, and ▼ benzene synthesis rate vs. time on stream for the reaction of anisole on Mo_2C, experimental condition: 420 K, atmospheric pressure. (b) ■ Propanal conversion and ● propylene selectivity vs. time on stream for the reaction of propanal on Mo_2C. Experimental conditions: 573 K, atmospheric pressure.[22]

Experimental Section

Details about calculation and experimental procedures are provided in the Supporting Information. Briefly, DFT calculations were performed using the Vienna ab initio Simulation Package (VASP).[28] The Mo_2C surface was approximated by a 4×4 unit cell, mixing three layers of metal and three layers of carbon. For all calculations, the top two layers were allowed to relax. Experimentally, the Mo_2C surface was prepared by ethylene decomposition into the interstitial sites of Mo(110). The procedure was repeated several times until a 0.4~0.6 atomic ratio of C/Mo was reached. The porous Mo_2C catalysts were synthesized by a temperature-programmed reaction method based on a prior report.[22]

The gas phase HDO of furfural was carried out in a flow quartz reactor (10 mm inner diameter) at atmospheric pressure housed within a three-zone split tube furnace (Series 3210, Applied Test System) using 0.64 g Mo_2C catalyst of 40~80 mesh size. The reaction temperature was 423 K. The typical pressure drop caused by the catalyst bed was less than 5 kPa. Prior to the reaction, the catalyst was treated in H_2 (Minneapolis Oxygen, 99.999 %) with a total flow rate of 1.67 $cm^3 s^{-1}$ at 750 K for 1 h (with a ramping rate of 0.185 $K s^{-1}$ from room temperature). Subsequently, the reactor temperature was cooled to 423 K and the gas flow was switched from pure H_2 to the reaction mixture (1.67 $cm^3 s^{-1}$) consisting of 0.24/2.50/bal vol % of furfural (Sigma, 99 % ACS reagent), CH_4 (Matheson, 99.97 %), and H_2 (Minneapolis Oxygen, 99.999 %) in which CH_4 was used as an internal standard. The catalyst was regenerated by heating from 423 K (reaction temperature) to 750 K in a flow of H_2 (1.67 $cm^3 s^{-1}$) and holding at 750 K for 1 h before cooling to 423 K for the next reaction.

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Keywords: biomass · carbides · density functional theory calculations · deoxygenations · molybdenum carbide

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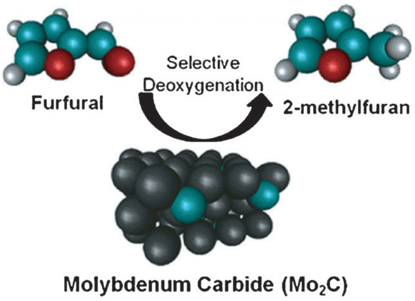

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