

Mechanistic Investigation of the Hydrodeoxygenation of Furfural to 2-methylfuran over Ru/C Using Isotopic Labeling Techniques

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Introduction

Fundamental understanding regarding the role of the surface mediated reaction mechanism in biomass upgrading to fuels and chemicals is key to the rational design of catalysts. Hydrodeoxygenation (HDO) of oxygenated furanics, e.g., furfural and 5-hydroxymethylfurfural, to reduced furanics, e.g., 2-methylfuran (2-MF) and 2,5-dimethylfuran, is an important step in the upgrade of cellulose/hemicellulose-based biomass to fuels and chemicals [1]. Previous studies show that a mildly oxidized Ru/C catalyst performs furfural HDO toward 2-MF using catalytic transfer hydrogenation (CTH) using 2-propanol (IPA) as a hydrogen source [2, 3]. However, the role of the catalyst in HDO remains unclear.

Furfural HDO consists of 2 key steps: (1) the hydrogenation of furfural to furfuryl alcohol (FA), and (2) hydrogenolysis of FA to 2-MF. We hypothesize that the hydrogenation step can happen either via metal-mediated hydrogenation via surface adsorbed H-atoms from the dehydrogenation of IPA or via Lewis acid-mediated hydrogenation, where a hydrogen atom is transferred in one, concerted step from IPA in a Meerwein-Ponndorf-Verley type mechanism. Furthermore, we suspect that the hydrogenolysis step occurs either via direct hydrogenolysis, where a surface adsorbed hydrogen directly cleaves the C-O bond in FA, or via ring activation, where a hydrogen atom is first added to the ring before removal of oxygen.

Materials and Methods

All reactions were conducted in liquid-phase in a 100 mL stainless steel Parr reactor at 140 °C. After reaction, products were analyzed in both GC (Agilent 7890A) and GCMS (Shimadzu QP2010 Plus).

Results and Discussion

Mass fragmentation pattern analysis indicates that the hydrogenolysis step from FA to 2-MF proceeds at least in part via a ring activated mechanism. By using 2-propanol- d_8 (IPA- d_8) as a source of hydrogen (or deuterium) ring activation (Figure 1B) can be distinguished from direct hydrogenolysis (Figure 1A) via additional D incorporation in the 2-MF formed. In direct hydrogenolysis, the C-O bond is cleaved, and a D is subsequently added, which will yield a 2-MF molecule with 1 additional atomic mass unit. Ring activation, in contrast occurs with an additional step, where a D is first added to the C₃ position in 2-MF before C-O bond scission. This additional D is observed in the 2-MF mass spectrum after reaction (Figure 1C).

Kinetic studies further reveal that C-H bond scission rather than C-O bond scission is rate limiting, since a substantial kinetic isotope effect (KIE) was calculated using IPA versus IPA- d_8 . Kinetic data of FA hydrogenolysis were collected from 0 to 4 h, which shows that the only products are 2-methylfuran and (2-isopropoxy-2-methyl)furan (the ether formed from IPA and FA). By assuming elementary kinetics (Figure 2A), relative rate constants and subsequently

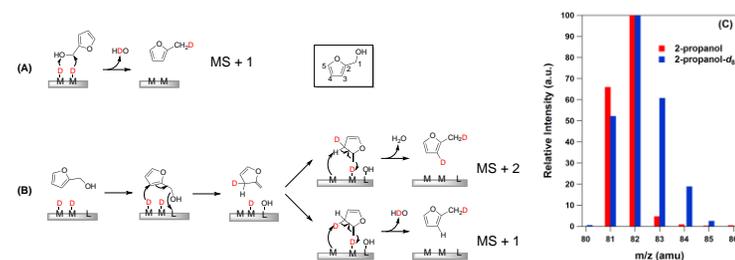


Figure 1. Schematic of the hydrogenolysis pathway to 2-MF from FA via direct hydrogenolysis (A), and ring activation (B), as well as the mass spectrum from both IPA and IPA- d_8 (C).

the KIE can be approximated using nonlinear least squares, showing that the hydrogenolysis step shows a significant KIE value of 1.6 (Figure 2B, blue lines), whereas ether formation does not (Figure 2B, red lines), where the estimated KIE is 1.0. This agrees with our findings that C-H bond scission is rate determining in the HDO pathway toward 2-MF.

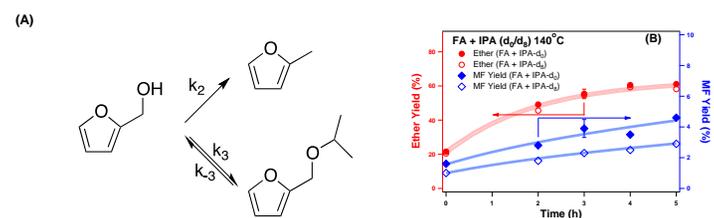


Figure 2. Reaction scheme used in the model (A), and the key resulting kinetics (B) in both experiments (markers) and the model (lines).

Significance

This fundamental work provides a molecular understanding of the hydrogenation and hydrogenolysis steps in the HDO of furfural to 2-MF. To this end, the importance of the co-existence of both metal and Lewis acid sites on the Ru/RuO_x/C catalyst is revealed, giving rise to a detailed explanation of the catalyst's enhanced performance in using CTH via IPA. Kinetic studies supplement our findings, demonstrating that C-H, rather than C-O, bond scission is rate limiting. By studying bifunctional materials and understanding the role of active sites, the rational design of such active materials may be facilitated for other catalytic processes.

References

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