Design of multistage reactor systems for the production of high carbon number hydrocarbon fuels from furans by distributing multifunctional catalysts

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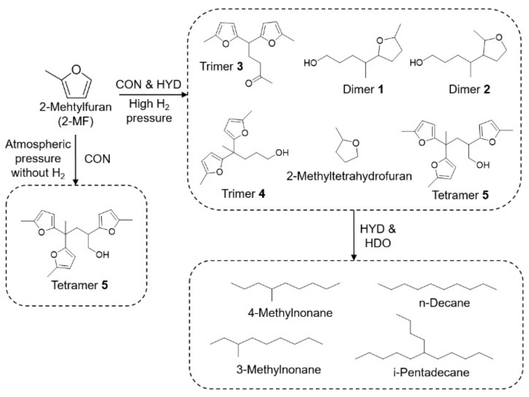
Introduction

- ✓ Furfural and its derivatives are byproducts of lignocellulose saccharification.
- ✓ Furfural is a poison of sugar fermentation, which must be removed for the purification of sugars, such as glucose and xylose.
- ✓ For the removal and valorization of furfural, the production of high carbon number hydrocarbon fuels, usually replacement of petroleum-based diesel and aviation fuels, from furfural and its derivatives has been suggested in literature.

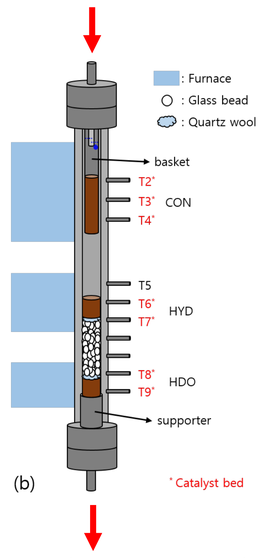
  (References: A. Corma, et al., *Angew. Chem. Int. Ed.*, 2011, **50**, 2375-2378.)



- ✓ The production of high carbon number hydrocarbon fuels can be achieved by **(i) condensation of furan compounds and (ii) hydrogenation/hydrodeoxygenation of furan condensates**.
- ✓ Goal of this study: **(i) one-pot selective production of high carbon number hydrocarbon fuels from furfural derivative. (ii) understanding the effects of catalysts on the reaction networks of furan-to-hydrocarbon fuels.**

Reaction method

Reactant (2-methylfuran)



Product (i-Pentadeane)

- ✓ Three catalyst beds were filled with the same catalysts including Ru/WZr, Ni/WZr, and Pd/WZr. (WZr = tungstate-zirconia)
- ✓ Each catalyst bed were operated at different reaction temperature to activate the different reaction including condensation (1st step), hydrogenation (2nd step), and hydrodeoxygenation (3rd step).
- ✓ The product compositions depending on the catalysts used were studied to understand the effects of catalysts on the product selectivity.

Reaction results depending on the catalysts

Three-step process results

Entry	Catalyst	WHSV (h^{-1})	Catalyst bed temperature (°C)[b]	Liquid yield (%) / oil yield (%) / diesel fraction oil yield (%)[c, d,e,f]	O/C ratio (atom/atom)[c, g]	H/C ratio (atom/atom)[c, g]
	Reactant (2-MF)				0.2683	1.2
A1	Step 1: 3 wt% Ru/WZr	0.33	93-103	84.3 / 67.5 / 54.4	0.0089	2.1
	Step 2: 3 wt% Ru/WZr	1.00	160-178			
	Step 3: 3 wt% Ru/WZr	1.00	250-260			
A2	Step 1: 20 wt% Ni/WZr	0.36	81-108	76.5 / 62.2 / 50.5	0.0096	2.2
	Step 2: 20 wt% Ni/WZr	1.09	162-177			
	Step 3: 20 wt% Ni/WZr	1.09	246-259			
A3	Step 1: 3 wt% Pd/WZr	0.38	86-107	84.9 / 68.8 / 45.1	0.0096	2.2
	Step 2: 3 wt% Pd/WZr	1.13	162-177			
	Step 3: 3 wt% Pd/WZr	1.13	248-259			

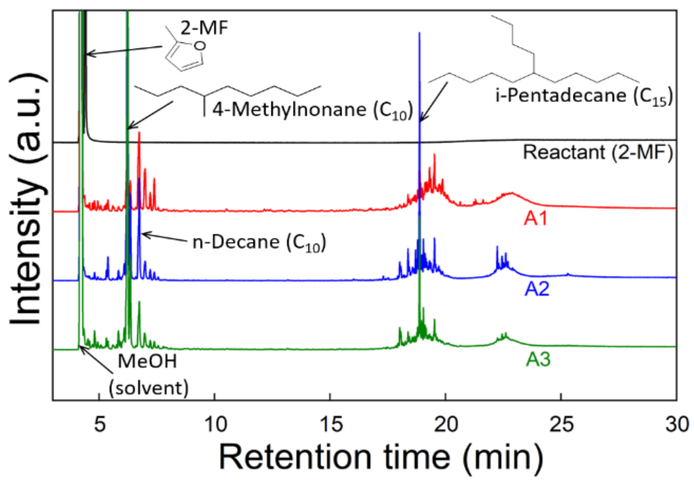
[a]Step 1: condensation, step 2: hydrogenation, step 3: hydrodeoxygenation. All products were biphasic mixtures. [b]Temperature range measured in the catalyst bed is listed. [c]Products were obtained at 3-9 h of time-on-stream. [d]Liquid yield (%) = (Mass of liquid product out)/(Mass of 2-MF reactant in) × 100. [e]Oil yield (%) = (Mass of oil product out)/(Mass of 2-MF reactant in) × 100. [f]SimDist-GC results of oil product were used to measure diesel fraction ranged at 160-340 °C. [g]Elemental analysis results of oil products were used.

Product composition measured by SimDist-GC

Entry	Product composition (wt%)		
	C5 (48-55 ℃)	C10 (160-170 ℃)	C15 (240-265 ℃)
A1	10	22	25
A2	14	50	18
A3	25	35	17

- ✓ Preferred formation of C5 deoxygenated hydrocarbons: Pd/WZr
- ✓ Preferred formation of C10 deoxygenated hydrcarbons: Ni/WZr
- ✓ Preferred formation of C15 deoxygenated hydrocarbons: Ru/WZr

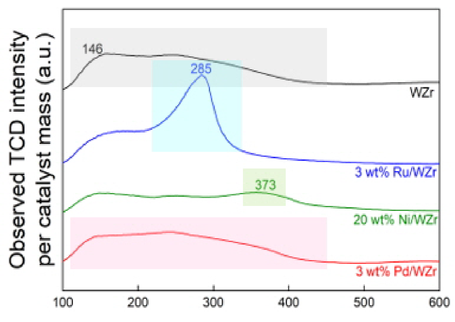
Selectivity was manipulated by the selection of catalysts



Characterization of catalysts

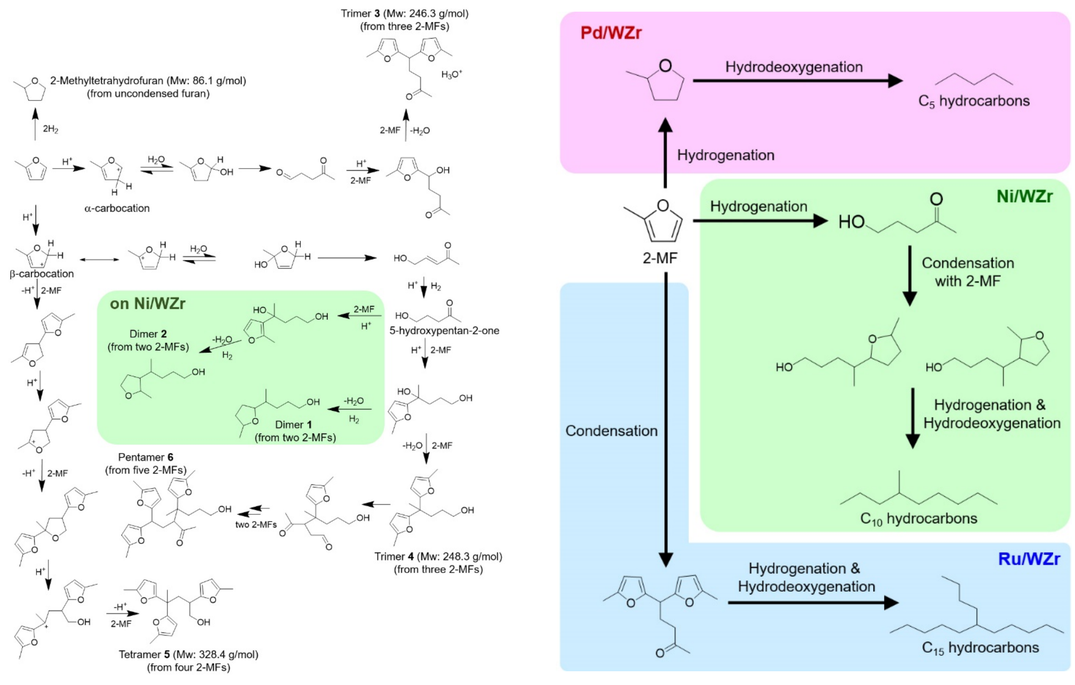
Catalyst characterization by NH_3 TPD, N_2 physisorption, and CO chemisorption.

Catalyst	Acid density (μmol/g catalyst)	BET surface area (m^2/g)	BJH peak pore width (nm)	[CO]/ [Metal] (mol/mol)
WZr	117 (4.8)	57	7.7	-
3 wt% Ru/WZr	135 (4.1), 239 (6.5)	52	7.9	0.233
20 wt% Ni/WZr	n.a. (n.a.)	55	8.3	0.011
3 wt% Pd/WZr	117 (4.7), 395 (8.3), 302 (8.7)	41	7.8	0.024



- ✓ High acidity and high metal surface area of Ru/WZr were observed.
- ✓ Reaction selectivity should be adjusted by the acidity and hydrogenation activity of catalysts.

Characterization of catalysts



- ✓ Reaction network depending on the catalysts was investigated based on the GC-MS/FID and NMR measurement of reaction products/intermediates.

Conclusion

- ✓ WZr-supported metals, comprising composites of Ni, Pd, and Ru nanoparticles and WZr powder, were used for three different catalysis reactions: acid-catalyzed condensation, metal-catalyzed hydrogenation, and metal-acid-catalyzed hydrodeoxygenation.
- ✓ The preferred production of C_5, C_{10}, and C_{15} hydrocarbons from 2-MF on Pd, Ni, and Ru/WZr, respectively, could provide a useful means of modifying the applications of xylose-derived fuels.

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