

Catalytic Conversion of Carbohydrates to Mono-Functional Hydrocarbons Followed by Catalytic C-C Coupling

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Introduction

We have demonstrated the conversion of aqueous sugar and polyol solutions over a PtRe/C catalyst into a mixture of mono-functional hydrocarbons containing alcohols, ketones, carboxylic acids and heterocyclic compounds in the C₄-C₆ range, whereby ~80% of the oxygen content of the carbohydrate feed is removed in a single reaction step [1]. We have also studied a carbohydrate deoxygenation process, whereby the carbohydrate is first dehydrated over acid sites and the resulting alkene is saturated via co-fed hydrogen over metal sites to yield alkanes [2]. In our current work, the required hydrogen is supplied via *in-situ* aqueous-phase reforming [3] of a fraction of the carbohydrate feed, and the deoxygenation reactions result in a mixture of oxygenates, in contrast to only alkanes. Over 40% of this carbohydrate-derived organic mixture consists of ketones and secondary alcohols that can undergo aldol condensation / hydrogenation at 623 K over a bi-functional Pd/CeZrO_x catalyst under H₂ to form singly-branched C₈-C₁₂ ketones that are precursors for diesel and jet fuels. Additionally, we have shown that C₄-C₆ carboxylic acids can be converted with nearly 100% yield into C₇ to C₁₁ ketones via ketonization over CeZrO_x. In the present contribution, we probe C-C coupling mechanisms over Pd/CeZrO_x and CeZrO_x catalysts by studying the effects of temperature, space velocity and pressure on the conversion of representative model compounds such as 2-hexanone and n-butanol.

Materials and Methods

The conversions of 60 wt% sorbitol and 40 wt% glucose solutions over PtRe/C catalysts to mixtures of mono-functional hydrocarbons are described in detail elsewhere [1]. A mixed oxide CeZrO_x catalyst was prepared by co-precipitation, as described in detail elsewhere [4]. Condensation reaction studies were carried out in a down-flow fixed bed reactor, loaded with 2 g of catalyst. Hydrogen was co-fed with the 2-hexanone reagent in a 4:1 molar ratio at 5 bar total pressure. Space-velocity studies were conducted at 2 and 0.5 hr⁻¹ for a temperature of 623 K. Temperature studies were conducted at 573-623 K for a WHSV of 2 hr⁻¹.

Results and Discussion

Yields of various classes of mono-functional hydrocarbons resulting from the conversion of 60 wt% sorbitol are summarized in figure 1a, and the product carbon chain length distribution resulting from the ketonization and subsequent aldol condensation of a glucose-derived organic feed is shown in figure 1b. The results of 2-hexanone conversion over Pd/CeZrO_x and CeZrO_x are summarized in table 1. These data show that the presence of Pd increases 2-hexanone conversion and selectivity to the primary condensation product (a C₁₂ ketone). The role of Pd is to hydrogenate and thereby stabilize the unsaturated aldol adduct formed during aldol condensation. The formation of C₉ and C₁₈ species was also observed, and these species included linear nonanones and 1,3,5-tributyl benzene (resulting from

aromatization). The yields of C₉ and C₁₈ products increased with decreasing space velocities for all sets of conditions specified in Table 1, thus suggesting that these species are secondary products. The apparent activation energies towards the production of C₁₂, C₁₈, and C₉ species over Pd/CeZrO_x with H₂ co-feed are equal to 15, 28 and 140 kJ/mol, respectively. The similarity of the activation energies for C₁₂ and C₁₈ formation suggests that these species are formed through similar bond-making processes. The considerably higher activation energy of C₉ formation suggests that a C-C bond breaking process is involved. The addition of 10 mol % n-butanol to the 2-hexanone feed results in a reversible 70% decline in 2-hexanone self-condensation activity, and 100% cross condensation of the primary alcohol with 2-hexanone.

Significance

Understanding of C-C coupling mechanisms over Pd/CeZrO_x will aid in the development of an integrated process for the upgrading of biomass derived compounds into C₆+ fuel components.

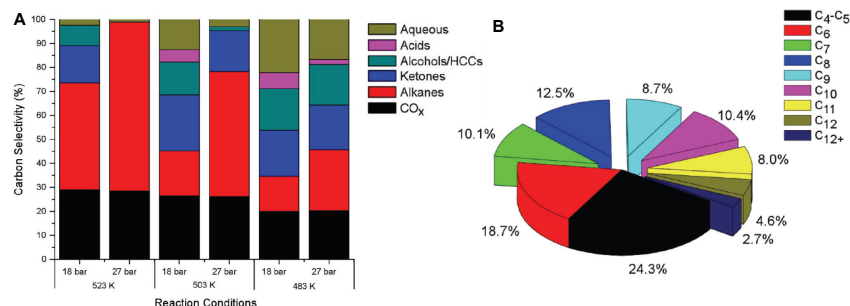


Figure 1. (A) Carbon selectivities for the conversion of sorbitol over PtRe/C (HCCs denotes heterocyclic compounds) and (B) product distributions for ketonization followed by aldol condensation of glucose-derived organic feed.

Catalyst	WHSV (hr ⁻¹)	Conversion (%)	Selectivity (%)		
			C ₉	C ₁₂	C ₁₈
Pd/CeZrO _x	0.5	78	15	81	4
Pd/CeZrO _x	2	62	6	92	2
CeZrO _x	0.5	36	23	51	26
CeZrO _x	2	19	11	69	20

Table 1. Conversions and selectivities of 2-hexanone conversion over PdCeZrO_x and CeZrO_x catalysts as a function of space-velocity at 623 K

References

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