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Catalytic Conversion of Furan to Gasoline-Range Aliphatic Hydrocarbons via Ring Opening and Decarbonylation Reactions Catalyzed by Pt/γ-Al_2O_3

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Abstract Conversion of furan in the presence of H_2 catalyzed by Pt/γ-Al_2O_3 at 573 K and 1.4 bar leads to the formation of alkanes and alkenes, some in the gasoline-range, including C_7 hydrocarbons, butenes, propene, and propane.

Keywords Biomass conversion · Processes and reactions · Furan conversion · Hydrocarbons from furan

1 Introduction

The goal of converting biomass to fuels has motivated extensive recent research on the catalytic reactions of whole cellulosic biomass and of sugars formed by deconstruction of biomass. Furan is an important product in the catalytic fast pyrolysis of cellulose [1] and in the catalytic conversion of sugars [2, 3] and sugar-derived products such as furfural [4, 5]. Furfural is an important product in the conversion of cellulose-derived sugars catalyzed by solids in aqueous slurries [6]. Our goal was to go beyond this work to consider catalytic reactions of furan and test it as a potential intermediate in biofuels synthesis.

Conversion of furan catalyzed by a solid acid, HZSM-5, leads to benzofuran and polycyclic aromatics [4]. Furan can also be converted into light aliphatics (C_2–C_6) and aromatics in a fast pyrolysis process with HZSM-5 catalyst at temperatures ranging from 673 to 873 K [7]. Furan was proposed as an intermediate in the conversion of furfural to butane with various silica-supported metal catalysts [5].

We now report the first observation of furan conversion to C_7 gasoline-range aliphatic hydrocarbons.

2 Experimental

Reactions catalyzed by Pt/γ-Al_2O_3 (205966-100G, Sigma-Aldrich, 1 wt% Pt, surface area 206 m^2 g^{-1}, platinum dispersion 0.25) or HY zeolite [CBV 720, Zeolyst, Si/Al = 15.0 (atomic)] powders were carried out in a once-through packed-bed flow reactor under the following conditions, with furan (Sigma-Aldrich, 99 %) vaporized at 305 K into a flowing gas stream: temperature, 573 K; pressure, 1.4 bar; catalyst mass, 50.2–200.8 mg; gas feed (30 % H_2, 70 % N_2) flow rate, 3.0×10^{-3} mol min^{-1}; furan flow rate, 1.65×10^{-3} mol min^{-1}. Product streams were analyzed periodically by gas chromatography and gas chromatography/mass spectrometry. The reaction system, analytical instrumentation, and data analyzes have been reported [8].

3 Results

Product analyses (Table 1) show that benzofuran was the only significant product in the conversion of furan in the absence of H_2 when the catalyst was HY zeolite; this acid-catalyzed dehydration is well known [4, 7]. But when the catalyst was platinum supported on the acidic γ-Al_2O_3 and H_2 was co-fed, other products were formed (Table 1); the unexpected result is the formation of C_7 aliphatics.

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Table 1 Products formed in the conversion of furan catalyzed by HY zeolite and by Pt/γ-Al_2O_3 at 573 K and 1.4 bar; gas feed flow rate, 3.0×10^{-3} mol min^{-1}; furan flow rate, 1.65×10^{-3} mol min^{-1}; catalyst mass, 10.0–200.8 mg

Catalyst	Product(s)	Reaction class
HY zeolite	Benzofuran	Condensation
Pt/γ-Al_2O_3	Propane	Hydrogenolysis, decarbonylation
	Propene	Hydrogenolysis, decarbonylation
	Carbon monoxide	Hydrogenolysis, decarbonylation
	Butenes	Hydrogenation, dehydration
	2,3-Dihydrofuran	Hydrogenation
	Butanal	
	Tetrahydrofuran	Hydrogenation
	1-Butanol	Hydrogenolysis
	2-*n*-Butylfuran	Alkylation
	Heptanes	Sequence of reactions
	Heptenes	Sequence of reactions

Table 2 Furan conversion and product yields at various space velocities in reaction catalyzed by Pt/γ-Al_2O_3 at 573 K and 1.4 bar; gas feed flow rate, 3.0×10^{-3} mol min^{-1}; furan molar flow rate, 1.65×10^{-3} mol min^{-1}

Product	[a]Product yield $\times 10^3$ at [b]*WHSV* = 33.6	Product yield $\times 10^3$ at [b]*WHSV* = 135	Product yield $\times 10^3$ at [b]*WHSV* = 674
Propane	83	34	12
Propylene	100	17	19
Carbon monoxide	41	17	7.0
2,3-Dihydrofuran	0.074	0.20	0.52
Butanal	1.2	1.3	1.4
Tetrahydrofuran	1.0	0.87	0.67
C_7 aliphatics	1.3	0.49	0.21

[a] Product yield in units of (mol of product)/(mol of reactant fed)

[b] WHSV in units of (g of reactant)/(g of catalyst × h)

The yields of the major products propene, propane, and CO in the conversion of furan catalyzed by Pt/γ-Al_2O_3 increased with increasing inverse space velocity. The formation of propane and propene, explained by a sequence of hydrogenation, hydrogenolysis, and decarbonylation reactions, is consistent with the observations reported [9, 10], characterizing reaction with a sulfided Ni–Mo/Al_2O_3 catalyst. The formation of 2,3-DHF and THF is explained by furan hydrogenation, a reaction known to be catalyzed by metals [11–13]. The formation of butanol and butanal is explained by ring opening reactions with and without H_2, respectively. Butenes are formed by butanol dehydration [9] (Table 2).

4 Discussion

C_7 hydrocarbons are possibly formed by reaction of C_3 and C_4 aliphatics (e.g., protonation of butene and subsequent reaction with propene to form heptene by donation the proton back to the support). C_7 hydrocarbons can also be formed by reaction of an aldehyde (e.g., butanal) with an alkene (e.g., propene); this reaction can lead to the formation of alcohols (e.g., heptanols), which can be dehydrated to form alkenes (e.g., heptenes). We observed heptenes, but expect that they were rapidly hydrogenated on the metal function of the catalyst to form heptanes, which we also observed.

5 Conclusions

We have observed the conversion of furan to produce not just C_3–C_4 aliphatics and C_4 oxygenates but also—surprisingly—C_7 aliphatics when the catalyst was Pt/γ-Al_2O_3 used in the presence of H_2. Both the metal function and H_2 were necessary for C–O bond breaking and oxygen removal leading to aliphatic hydrocarbons including C_7's. The combination of these products in a one-step conversion of furan might be useful for the production of gasoline from cellulosic biomass via oxygen-containing compounds such as furfural (an intermediate in the aqueous-phase processing of cellulosic sugars). Thus, our results demonstrate a pathway for the production of gasoline from biomass.

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