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Investigating hydrogenation and decarbonylation in vapor-phase furfural hydrotreating over Ni/SiO₂ catalysts: Propylene production



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ABSTRACT

Furfural can be mass-produced from lignocellulose biomass and can be a platform chemical for producing valuable chemicals. In this study, we examine Ni/SiO₂ catalysts for the conversion of furfural under a hydrogen atmosphere. The reactivity and the product selectivity are governed by the reaction temperature and the Ni particle size. A catalyst pretreatment by including calcination prior to hydrogen reduction leads to Ni/SiO₂–CR with large Ni particles (~ 15 nm) and a high selectivity to furfuryl alcohol (FA) at below 200 °C. The Ni/SiO₂–R is hydrogen-pretreated without a prior calcination and it contains small Ni particles (~ 5 nm) and exhibits relatively high selectivity to furan. The turnover frequency (TOF) of furfural conversion is 239 and 408 h⁻¹, respectively, on Ni/SiO₂-CR and Ni/SiO₂-R at 175 °C, when the former shows 100% selectivity to FA and the latter exhibits a selectivity of around 38% and 62%, to FA and furan, respectively. Moreover, the furan can be reacted to produce propylene and CO by the Ni catalysts at above 200 °C and Ni/SiO₂-R exhibits a higher activity than Ni/SiO₂-CR. The results suggest that the furfural hydrotreating reaction over Ni catalysts is structure sensitive and a proper design of catalyst and operating temperature can provide a full furfural utilization, either to FA (a biofuel), or to furan and propylene (as chemical feedstock).

1. Introduction

Biomass can be processed through the so-called bio-refinery processes to sustainably produce valuable chemicals and fuels. Bio-refinery involves the breakdown of high-molecular-weight to platform chemicals and the uses of which to produce chemicals and fuels. In addition to biogas, bio-oil, and bio-char harvest by cracking via pyrolysis or hydrothermal methods, procedures like depolymerization and hydrodeoxygenation are indispensable in biomass utilization [1–3]. Both sugar platform and syngas platform are considered as viable approaches for producing bio fuels and chemicals [4,5]. The sugar platform uses furfural and hydroxymethyl furfural (HMF) from 5-carbon and 6-carbon sugar units as the platform chemicals, while the syngas platform refers to conversions of syngas from biomass gasification. The sugar platform is theoretically more efficient than the syngas platform because it does not require breaking all of the C—C bonds; therefore, the conversions of furfural and HMF to valuable chemicals have attracted great interests [6, 7].

Furfural was first mass-produced from oat hulls by Quaker Oats Company in 1922 [8], and furfural has become a precursor [9] for furfuryl alcohol (FA), solvents, pharmaceuticals, chemical intermediates, flavors & fragrance, herbicides, and pesticides, etc. One type of furfural processing is its reaction with hydrogen wherein hydrogenation, decarbonylation, ring opening (hydrogenolysis) and combinations of these can occur [9,10]. These results are somewhat similar to the hydrotreating process in oil refinery for reducing aromatics (via hydrogenation and hydrogenolysis) and heteroatoms (e.g., oxygen, sulfur, nitrogen). Product selectivity from such furfural hydrotreating is important, and catalyst plays a determining role.

Many catalysts, mainly Group IB and VIII metal catalysts, have been tested for furfural hydrotreating. The early works of Wilson et al. [11, 12] show that product selectivity depends on both the type of catalysts

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and the reaction conditions (temperature, concentration, solvent, and extent of reaction). In general, Group IB catalysts (such as Cu) catalyze hydrogenation of the aldehyde group of furfural to produce furfuryl alcohol (FA) selectively and then to methylfuran (MF) [13]. The group VIII catalysts can produce FA or THFA selectively under mild conditions, and many studies have been carried out in liquid phase. Gong et al. [14] used Ni supported on N-doped active carbon achieving 100% selectivity to THFA and concluded a synergistic effect of Ni sites and suitable N doping content to the catalytic performance. Tayler et al. [15] used Pt catalysts on different supports and concluded that polar solvents and support acidity could influentially lead to high FA selectivity.

At elevated temperatures, decarbonylation (e.g., of furfural to furan), hydrodeoxygenation (e.g., of FA to MF), ring opening (e.g., of furfural to butanal), and hydrogenation (e.g., of furan ring and aldehyde group) can occur simultaneously, especially when using Group VIII catalysts. Lee et al. [16] used high throughput method to examine the initial activity of aqueous-phase hydrogenation over different Group VIII catalysts and found that Ni and Pt were the two having ring-opening catalytic activity. Sitthisa and Resasco [17] reported that vapor-phase furfural hydrotreating over Ni catalysts leads to FA, furan, and ring-open products (C4s, including butanol and butane). Nakagawa et al. [18] examined gas-phase furfural hydrotreating at 130 °C over Ni/SiO2 and found FA and tetrahydrofurfuryl alcohol (THFA) as the major products. They mentioned that furfural hydrogenation to FA was not specifically influenced by changes in Ni particle size but FA hydrogenation to THFA was influenced. No other study mentioned about such particle size dependent reaction characteristics during furfural hydrotreating over Ni catalysts. In contrast, the ring-opening product was mainly propylene over Pt catalysts [19], instead of C4s frequently noted over Ni catalysts. Furthermore, Pushkarev et al. [20] clearly demonstrated that the reaction products from furfural hydrotreating over Pt catalysts depended on Pt particle size; smaller Pt particles preferred decarbonylation to form furan while large Pt particles led to more FA formation from aldehyde hydrogenation. Thus, it would be interesting to examine the furfural hydrotreating of Ni catalysts with different metal particle size.

Nickel catalysts are relatively inexpensive and have been used in different industrial catalytic processes. In this study, we examined Ni/ SiO₂ catalysts for vapor-phase furfural hydrotreating attempting to understand how the reaction products can be controlled. In particular, whether the reaction is governed by metal particle size, i.e., a structure sensitive reaction where the specific activity and the product selectivity can be altered by varying surface sites (edge, step or terrace), is studied. The results indicate that furfural hydrotreating over Ni/SiO₂ is indeed dependent on metal particle size. In addition, the decarbonylation products include propylene, which has not been reported over Ni catalysts by flow reactor system although propylene was found to desorb from furfural over Ni(111) surface by temperature-programmed desorption (TPD) and density functional theory (DFT) calculation [21]. The sequential decarbonylation of furfural to furan and to propylene is a molecular efficient reaction route as that CO would be the only byproduct.

2. Experimental

2.1. Catalyst preparation

Supported 5 wt% Ni/SiO₂ catalysts were prepared by an incipientwetness impregnation of Ni nitrate (Aldrich, 98%) aqueous solution on a SiO₂ support (Davison 952, 300 m²/g, 80~120 mesh, used after calcination at 550 °C). After impregnation, catalysts were put at room temperature, 12 h for the equilibrium of capillarity, and then dried to 120 °C, 12 h, is denoted Ni/SiO₂. The catalyst calcined in air at 400 °C, 4 h, is denoted as Ni/SiO₂-C. The catalyst with/without calcination was reduced under 10% H₂ in N₂ at 350 °C, 1 h, and is denoted by a suffix R as Ni/SiO₂-R and Ni/SiO₂-CR.

2.2. Catalyst characterization

Temperature-programmed reduction (TPR) analysis was performed at 5 °C/min using 10% H₂ in nitrogen and a TCD detector; the H₂O formed during TPR was trapped by a molecular sieve column installed prior to the detector. The catalyst was typically purged by He at 50 °C till TCD became stable and then switched to H₂/N₂ flow and the temperature was ramped. The Ni content was analyzed by inductively coupled plasma-atomic emission spectrometer (ICP-AES, JY 2000). The Ni size (calculated with Scherrer equation) and the structure were examined by X-ray diffraction (XRD) analysis using a synchrotron radiation source (Beamline #1C, National Synchrotron Radiation Research Center, Hsinchu, Taiwan). The electron storage ring was operated at 1.5 GeV with a beam current of 100-200 mA. The XRD patterns were recorded and processed to be consistent with using a wavelength of 1.5418 Å (the energy of Cu K_{α 1}) and at a scan rate of 10° min⁻¹ with steps of 0.05° from 10 to 90°. The metal (Ni) dispersion was calculated by assuming a H_{ad} / M_S ratio of 1, based on H₂ chemisorption from dual-isotherm analysis at room temperature using the BELSORP-max instrument. Thermogravimetric analysis (TGA, Perkin-Elmer, Diamond TG/DTA) was performed to study catalyst coking after furfural hydrotreating, in dry air flow (25 mL/min) from 30 to 800 °C at a heating rate of 10 °C/min. Transmission Electron Microscopy (TEM) analysis was performed using a Philips Tecnai F30 FEI-TEM at an acceleration voltage of 200 kV. The catalyst powders were sprayed on resin gel and a 100-nm thin slice was cut after the resin is set using FIB (Focused Ion Beam) for TEM measurement.

2.3. Catalytic reaction tests

Furfural (Acros, 99%) was distilled at 60 °C under vacuum to become clear liquid before feeding to the reactor. Reaction tests were performed in a quartz-tube packed-bed reactor (7 mm, I.D.) at atmospheric pressure using a home-made reaction system. The catalyst was reduced in line with 80 vol% H_2/N_2 (50 mL/min) at 350 °C for 1 h. Furfural was fed by a syringe pump and carried by H_2 /He flows into the reactor at $P_{Furfural} = 8$ kPa, $P_{H2} = 80$ kPa and a WHSV (weight hourly space velocity, furfural mass flow rate divided by cat. weight) of $5 \sim 25 \text{ h}^{-1}$. Both He and H₂ were of 99.995% purity and were flown through moisture and oxygen trap columns before entering the system. The reaction was carried out in a stepwise temperature-ascending-descending mode from 175 to 300 °C, wherein the steady reactions under isothermal conditions were reported. The reactor effluent was analyzed using gas chromatography with TCD detector and two columns (5% Bentone34 + 5% Dinonyl Phthalate on Chromosorb W-HP and Porapak-T) via a 10-port valve. The mass balance of the effluent was analyzed and typically within \pm 10% of the feed except when the temperature approached 300 °C. The steadystate performance was observed typically after from 30 to 90 min onstream and the average performance during that period, typically with a \pm 5% error, is used for data analysis. Turnover frequency was calculated based on the observed kinetic rate and the metal (Ni) surface measured by H_2 chemisorption assuming $H_{ad}/Ni_s = 1$.

3. Results and discussion

3.1. Catalyst characterization

The as-prepared catalyst was pretreated in two ways; one was calcined prior to hydrogen reduction (Ni/SiO₂-CR) and the other was directly reduced with hydrogen (Ni/SiO₂-R). The calcined catalyst after reduction can result in larger Ni particles than that without calcination [22]. Both the Ni/SiO₂ and the Ni/SiO₂-C catalysts were examined using TPR analysis as shown in Fig. 1. The former showed the characteristics of Ni nitrate reduction (including nitrate decomposition signal) while the latter indicated the reduction of NiO. NiO phase is typically reduced by H₂ at 300–400 °C in TPR and its dispersion (particle size) can



Fig. 1. TPR traces of as-prepared Ni/SiO_2 and that after calcination, Ni/SiO_2-C. Thin solid lines represent TPR after the samples were reduced at 350 $^\circ C$ by H_2 for.1 h.

influence the reduction temperature [23]. The remnant low intensity TPR signal after 400 °C suggests a possible presence of a small amount of difficultly reduced Ni species, for which Ni-silicate is one possible explanation [22,23].

XRD results in Fig. 2 show that Ni/SiO₂-C contained NiO crystal phase which was not found in the as-prepared Ni/SiO₂. After hydrogen reduction (at 350 °C), both samples contained metallic Ni crystal structure. The Ni particle size calculated with Scherrer equation is 5.3 and 14.9 nm, respectively, for Ni/SiO₂-R and Ni/SiO₂-CR, in consistent with the previous report [22] that a calcination before reduction lead to an increased Ni particle size. The Ni/SiO₂-CR catalyst showed a small shoulder peak near 43°, possibly due to the presence of remnant unreduced NiO phase or reoxidation of nanoparticles by air during ex situ XRD measurement. The texture properties of the prepared catalysts are listed in Table 1. The Ni dispersion (Table 1) calculated based on H₂ chemisorption analysis is 8.4% and 21.4%, respectively, for Ni/SiO₂-CR and Ni/SiO₂-R. With a generally accepted correlation of dispersion $\sim 1/d_{\rm Ni}$ (nm), this corresponds to 11.9 nm and 4.7 nm, respectively, for the two catalysts which are consistent with that analyzed from XRD.

3.2. Furfural hydrotreating



The observed products from furfural hydrotreating are divided into 4

Fig. 2. XRD pattern of Ni/SiO₂ and Ni/SiO₂-R for before and after $\rm H_2$ reduction at 350 $^\circ C$ using synchrotron light source.

Table 1	
Texture properties of the prepa	red catalysts.

Catalyst	BET SA	Ni ^a	D ^b _{Ni}	d ^c _{Ni}	d ^d _{Ni}
	(m²/g)	(wt%)	(%)	(nm)	(nm)
SiO ₂	297	0	-	-	-
Ni/SiO ₂ -R	222	4.9	21.4	4.7	5.3
Ni/SiO ₂ -CR	267	4.9	8.4	11.9	14.9

a. Ni content from ICP-AES results.

b. The dispersion (%) is calculated with (H2 chemisorption)/(theoretical H2 consumption*reduction degree)*100%.

c. The Ni particle size calculated from chemisorption data using dNi =1/DNi. d. The particle size calculated by Scherrer equation based on XRD Ni(111) peak width.

groups to simplify the discussion, based on their possible routes of formation shown in Scheme 1. Group A products indicate the hydrogenation of aldehyde side chain to the formation of FA and methyl furan (MF). Group B contains furan and tetrahydrofuran (THF), resulting from decarbonylation of furfural with/without ring hydrogenation. Group C refers to the decarbonylation of Group B products with propylene as the main observed species. Group D refers to the ring opening products that include butanal, butanol, and butane (summed up as C4 products). The observed products of this study with selectivity are listed in Tables 2 and 3. The consistent amount of CO byproduct and decarbonylation products were observed corresponding to Scheme 1, Tables 2, and 3 in our study.

Fig. 3 shows the results of furfural hydrotreating over the Ni/SiO₂ catalysts. The unreduced catalysts and the SiO₂ support showed negligible activity. Ni/SiO₂-R and Ni/SiO₂-CR exhibited different activity and product selectivity. Ni/SiO₂-R resulted in a higher furfural conversion than Ni/SiO₂-CR at each reaction temperature. At 175 °C, Ni/SiO₂-R had 85% furfural conversion with 41% selectivity of Group A (mainly FA) and 59% selectivity of Group B (mainly furan); Ni/SiO₂-CR had 29% furfural conversion with 100% selectivity of Group A (FA). The Ni/SiO₂-R was more active than Ni/SiO₂-CR; the different product selectivity will be examined and discussed later.

In the ascending-temperature sequence, both Ni/SiO₂-R and Ni/SiO₂-CR showed a similar temperature-driven product shift toward less products of Group A. Up to 225 °C, Ni/SiO₂-R had an increasing furfural conversion to 100%, a decreasing selectivity of Group A to 10%, an increasing selectivity of Group B to 79%, and an appearing selectivity of Group C (propylene) to 9%. The Ni/SiO₂-CR had an increasing furfural conversion to 70%, a decreasing selectivity of Group A to 50%, and an increasing selectivity of Group B to 48%. This indicates that



Scheme 1. Possible reaction routes of furfural hydrotreating over Ni/SiO₂ catalysts leading to the observed products and their grouping.

Table 2Furfural hydrotreating of Ni/SiO2-R.

		Selectivity ((%)					
Temperature (°C)	Conversion (%)	A		В		С	D	
		FA	MF	FR	THF	PP	BAL	BOL
175	84.6	39.0	1.8	59.2	0.0	0.0	0.0	0.0
200	97.9	6.8	4.4	72.9	2.2	9.2	1.1	3.4
225	100.0	6.5	3.5	78.4	0.7	9.0	0.7	1.2
250	100.0	0.0	0.3	73.2	0.5	23.6	2.4	0.0
275	100.0	0.0	0.0	70.5	0.5	25.4	3.3	0.3
300	74.5	0.0	0.0	70.6	0.7	26.5	2.2	0.0
250	25.9	0.0	0.0	85.1	0.0	14.9	0.0	0.0
200	18.4	0.0	0.0	100.0	0.0	0.0	0.0	0.0

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Furfural hydrotreating of Ni/SiO₂-CR.

		Selectivity (%)						
Temperature (°C)	Conversion (%)	A			В		С	D	
		FA	MF	FR		THF	PP	BAL	BOL
175	28.8	100.0	0.0	0.0		0.0	0.0	0.0	0.0
200	49.7	87.0	5.7	0.0		1.6	4.1	1.6	0.0
225	70.2	50.0	0.0	47.6		0.7	0.0	1.6	0.0
250	90.9	7.8	3.5	66.5		2.8	14.1	5.3	0.0
275	90.0	2.4	2.3	69.2		2.3	18.2	5.6	0.0
300	13.9	0.0	0.0	100.0		0.0	0.0	0.0	0.0
250	7.6	0.0	0.0	100.0		0.0	0.0	0.0	0.0
200	0.0	-	-	-		-	-	-	-

FA: furfuryl alcohol.

MF: methylfuran.

FR: furan (typically observed with a concurrent CO formation at 1:1 M ratio).

THF: tetrahydrofuran.

PP: propylene (typically observed with a concurrent CO formation at 1:1 M ratio).

BAL: butanal.

BOL: butanol.

decarbonylation (Group B and Group C products) was preferentially promoted over hydrogenation (Group A) by the ascending temperature.

At 275 °C, 100% furfural conversion was achieved over Ni/SiO₂-R; the selectivity of Group B dropped while the selectivity of Group C gained with a simultaneous small gain in the selectivity of Group D. The Group A was no more present at this temperature. Similar shifts in product selectivity were also found with Ni/SiO₂-CR. The results showed that the decarbonylation (to Group B and C) became the dominant reaction at 275 °C. The C-balance data (in Fig. 8) indicates that carbonaceous deposit (coking) became obvious at above 275 °C which caused deactivation and changes in product selectivity. At 300 °C and the subsequent descending sequence, both catalysts showed a deactivation in furfural conversion; the decay was more dramatic over Ni/SiO₂-CR than Ni/SiO₂-R. Moreover, the catalysts produced only decarbonylation products (Groups B and C), no hydrogenation product, during the subsequent descending sequence. It suggests that the sites for hydrogenation.

3.3. Furan hydrotreating

Furan and propylene, the decarbonylation products of furfural, were found over our Ni/SiO₂ catalysts. The formation of propylene from furfural hydrotreating was reported over Pt catalysts [20,24] but it was not previously reported over Ni catalysts. One report [21] indicates that propylene desorbed from Ni(111) surface at around 30 °C during furfural TPD. To confirm the sequential decarbonylation and hydrogenation pathway over Ni catalysts, we performed furan hydrotreating over the Ni catalysts and the results are shown in Fig. 4. The observed products with selectivity are listed in Tables 4 and 5.

In the temperature-ascending sequence, both Ni/SiO2-R and Ni/

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SiO₂-CR showed a similar temperature-driven product shift; THF (from ring hydrogenation) was the major product at low temperatures and propylene (from decarbonylation) with correspondingly produced CO were the only products at high temperatures. There was no ring opening product (Group D product mentioned earlier). Therefore, we proposed in Scheme 1 that Group D products were from the furfural's ring opening, not from furan, over the Ni catalysts. Ni/SiO₂-R showed higher furan conversions than Ni/SiO₂-CR but the trends of product selectivity shift with temperature were nearly the same. That the product contained only THF at low temperature was consistent with that observed during furfural hydrotreating, i.e., the Ni catalysts preferentially catalyzed hydrogenation at low temperatures. Similarly, the propylene product at high temperature indicates that Ni catalysts preferentially catalyze decarbonylation at high temperatures. During the descending sequence after 300 °C, both catalysts showed deactivation; Ni/SiO₂-CR exhibited more severe deactivation than Ni/SiO2-R and its hydrogenation activity was more subject to deactivation than decarbonylation, similar with furfural hydrotreating.

3.4. Reaction route

Fig. 5 shows the influence of space time on furfural hydrotreating over Ni/SiO₂-R and Ni/SiO₂-CR at 175 °C. The linear relation at short contact time (WHSV⁻¹ \leq 0.1 h) in Fig. 5a was used to calculate the turnover frequency (TOF) based on the slope, corresponding to kinetic rate, and the surface metal fraction from hydrogen chemisorption. The calculated furfural TOFs are 408 and 236 h⁻¹, respectively, for Ni/SiO₂-R and Ni/SiO₂-CR at 175 °C. Fig. 5b shows that the furfural hydrotreating product selectivity to FA and furan remained constant at around 38% and 62%, respectively, over Ni/SiO₂-R at 175 °C when space time



Fig. 3. (a) Furfural conversion of Ni/SiO₂-R, Ni/SiO₂-CR, and SiO₂ catalysts and the product selectivity over (b) Ni/SiO₂-R and (c) Ni/SiO₂-CR during furfural hydrotreating tests. Reaction conditions: WHSV of 5 h⁻¹; P_{Furfural} = 8 kPa, P_{H2} = 80 kPa, balance with Helium at 1 bar; temperature ascending sequence from 175 to 300 °C and then descending from 300 to 200 °C. The presented data were the average of 1.5 h onstream time at isothermal conditions with a typical error of \pm 5%. The products of Group A to D are depicted in Scheme 1.





Fig. 4. (a) Furan hydrotreating conversion of Ni/SiO₂-R and Ni/SiO₂-CR ; (b) is product selectivity of Ni/SiO₂-R and Ni/SiO₂-CR. Reaction conditions: WHSV of 5 h⁻¹; P_{Furan} = 8 kPa, P_{H2} = 80 kPa, balance with Helium at 1 bar; temperature sequence of ascending from 175 to 300 °C and then descending from 300 to 200 °C. The presented data were the average of 1.5 h onstream time at isothermal conditions with a typical error of \pm 5%.

Table	4
Furan	hydrotreating of Ni/SiO ₂ -R.

Temperature (°C)	Conversion	Selectivity (%	Selectivity (%)		
	(%)	THF	PP		
175	31.5	100.0	0.0		
200	46.6	98.7	1.3		
225	54.1	64.9	35.1		
250	77.6	20.4	79.6		
275	95.0	0.0	100.0		
300	99.3	0.0	100.0		
250	45.9	34.6	65.4		
200	40.6	100	0		

was varied. This suggests that the two products were formed from parallel reaction pathways, not from a sequential pathway. The results confirm that furan formation is from the decarbonylation of furfural but not from the hydrogenolysis (side chain cleavage) of FA. The selectivity to FA over Ni/SiO₂-CR at 175 °C was 100% in the range of furfural conversion observed, which was higher than that of Ni/SiO₂-R at the

Table 5

Furan hydrotreating of Ni/SiO₂-CR.

Temperature (°C)	Conversion	Selectivity (%	Selectivity (%)		
	(%)	THF	РР		
175	50.2	100.0	0.0		
200	47.2	100.0	0.0		
225	51.8	51.6	48.4		
250	46.9	18.8	81.2		
275	53.4	0.0	100.0		
300	58.4	0.0	100.0		
250	8.5	0.0	100.0		
200	0	-	-		

THF: tetrahydrofuran.

PP: propylene (typically observed with a concurrent CO formation at 1:1 M ratio).



Fig. 5. Influence of space time on furfural hydrotreating over Ni/SiO₂ catalysts at 175 °C: (a) the furfural conversion vs. $WHSV^{-1}$ and (b) the product selectivity vs. furfural conversion.

same levels of furfural conversion. The TOF toward furan formation over Ni/SiO₂-R at 175 °C is estimated as 253 h⁻¹ (408 h⁻¹ × 62%, equivalent to 7 × 10⁻² s⁻¹), similar to that over Pt nanoparticles of 1.5 nm size (8.8 × 10⁻² s⁻¹ at 473 K, 9.3 kPa furfural, 93 kPa H₂) [20]. The TOF toward furfuryl alcohol formation over Ni/SiO₂-R at 175 °C is 155 h⁻¹, less than the 236 h⁻¹ observed over Ni/SiO₂-CR. This indicates that the selectivity to side chain aldehyde hydrogenation is favorable over the larger Ni particles of Ni/SiO₂-CR and the furfural hydrotreating reaction over Ni catalysts is a structure-sensitive reaction. We also examined the effect of space velocity on furan hydrotreating, and the results are shown in

Fig. S1. However, the THF was the only product observed in the tests at 175 °C. The results indicate that at this temperature, the hydrogenation is the dominant reaction pathway and Ni/SiO₂-CR had a higher hydrogenation activity than Ni/SiO₂-R under the conditions of this study.

3.5. Coking analysis

The catalysts after hydrotreating tests were analyzed by TGA and the weight loss attributable to carbonaceous residue are shown in Fig. 6 and Table 6. Although not active, SiO₂ contained carbonaceous deposit after reaction test. This indicates that adsorbed furfural formed residue over SiO2 under the reaction conditions. Ni/SiO2-CR showed a lower amount of carbonaceous residue (weight basis) than Ni/SiO₂-R and the furan hydrotreating reaction resulted in less residue than furfural hydrotreating. Derivative thermogravimetry (DTG) was also examined to identify different types of carbonaceous residue (Fig. S2). Either the type or the amount of carbonaceous residue can be correlated to the extent of deactivation noticed in Fig. 3a. ICP analysis indicated that the Ni content in the spent catalysts was almost the same as that before reaction. XRD of spent catalysts indicates the presence of Ni₃C carbide phase (PDF#06-0697), whose formation can be caused by carbon deposition on Ni [25, 26]. The spent Ni/SiO₂-R had a higher TGA weight loss (Fig. 6) and a more obvious Ni₃C diffraction peak (Fig. 7) than the spent Ni/SiO₂-CR. Carbonaceous deposit monitored by carbon balance at reactor effluent (Fig. 8) indicates that carbonaceous deposit formed starting from 275 °C and became significant at 300 °C. The results suggest that the furfural hydrotreating over Ni/SiO2 should not go above 250 °C to avoid carbonaceous deposit and deactivation.

3.6. Morphology

The TEM images of reduced and spent catalysts are shown in Fig. 9. The results indicate that Ni/SiO₂-R contains Ni particles mostly in the range from 3 to 8 nm while Ni/SiO₂-CR contains Ni particles mostly larger than 10 nm. This is consistent with the particle size analysis from XRD. The spent catalysts show similar particles as the corresponding reduced catalysts, with no observable fibrous coke. The high-resolution images of selected Ni particles in Ni/SiO₂-R and Ni/SiO₂-CR are shown in Fig. 9(e) and (f), wherein the revealedp-spacing of 0.206 and 0.204 nm, respectively, corresponds to that of Ni (111). The difference in the exposed facets between smaller particle in Ni/SiO₂-R and larger particle in Ni/SiO₂-CR are not significant. According to TEM results, the different product selectivity between the two catalysts may be related to the exposed terrace dimension.



Fig. 6. Thermogravimetric analysis of Ni/SiO₂ before and after furfural/furan hydrotreating reaction.

Table 6

Comparison Ni wt% before and after reaction and the carbon lost wt%.

Catalyst	Ni fresh (%)	Ni used (%)	wt. Loss (%)	Carbon Species
Ni/SiO ₂ -R-Furfural Ni/SiO ₂ -CR- Furfural	4.9 4.9	4.8 4.8	8 4.3	330, 360 °C 330, 360 °C
SiO ₂ -Furfural	-	-	2.4	400 °C
Ni/SiO2-R-Furan	4.9	4.9	1.6	260 °C
Ni/SiO2-CR-Furan	4.9	4.9	0.8	310 °C



Fig. 7. XRD pattern of Ni/SiO₂-R and Ni/SiO₂-CR after furfural hydrotreating using synchrotron light source.



Fig. 8. The carbonaceous deposits were monitored by carbon balance at the reactor effluent (typically with \pm 5% error) during furfural hydrotreating. The reaction could maintain nearly steady state at an on-stream time range of 0.5 to 2.5 h.

3.7. Discussion

That propylene can be produced through sequential decarbonylation of furfural has not been reported over Ni catalysts to the best of our knowledge. We confirm the sequential decarbonylation to propylene via the tests of furan hydrotreating. The two Ni/SiO₂ catalysts examined in this study indicate that both the reaction rate and the product selectivity of vapor-phase furfural hydrotreating change with Ni particle size, indicating a structure-sensitive reaction. From thermodynamic minimum surface energy consideration (Wulff construction), truncated octahedral is the most stable model of nanoparticles of fcc metals. According to the model, the metal dispersion, D (number of surface atoms / total number of atoms), can be approximated by D = 1/d, where d represents the particle size in nm. This leads to a Ni dispersion of 0.2 and 0.067, respectively, for 5 nm and 15 nm size Ni particle. Furthermore, the theoretical fraction of terrace, edge, and corner sites can be calculated according to truncated octahedral model [27]. Accordingly, the fraction of terrace (facet) sites is around 0.8 and 0.92, respectively, over 5 nm and 15 nm Ni particle, while the fraction of edge/corner sites is 0.2 and 0.08, respectively. This results in a calculated ratio of the number edge/corner sites over the two sizes of Ni particle as 0.2*0.2 / 0.067*0.08 = 7.5. This strongly indicates that the Ni/SiO₂-R catalyst contains more than seven times of edge/corner sites comparing to the Ni/SiO₂-CR.

The reaction of furfural + H₂ \leftrightarrow FA is exothermic, with $\Delta H^{\circ} = -61$ kJ/mol based on the enthalpy of formation of gas at standard conditions listed in National Institute of Standards and Technology (NIST) website. Sitthisa et al. [28] reported an equilibrium constant of 4.56, 2.98, and 2.01, respectively, at 230, 270, and 290 °C. From that and an assumption of ideal gas, we calculated the equilibrium conversion of furfural to FA as near 100% at 230–290 °C under the feed conditions of this study. This indicates that the reaction is not thermodynamically limited under the conditions of this study. We showed that this reaction is favored over Ni/SiO₂-CR at lower temperature but it is kinetically suppressed with a lower selectivity over Ni/SiO₂-R (having smaller Ni particles). To the best of our knowledge, this has not been reported for Ni catalysts, although similar observation was reported over Pt [20] and Pd [29,30] catalysts.

Pushkarev et al. [20] reported that both Pt particle size and shape caused significant influences on the product selectivity of furfural hydrotreating; for Pt/SiO₂ in the range of 443–513 K, the dominant product was furan over polyhedral Pt of < 2 nm while furfuryl alcohol was preferred over larger Pt nanoparticles. Cai et al. [31] performed DFT calculations and showed consistent conclusions in that the furfural decarbonylation can be promoted by decreasing particle size and by increasing temperature. They showed that terrace sites would favor hydrogenation and corner sites would favor decarbonylation. Our results showed a similar trend in having more furan production over smaller Ni particles. Based on thermodynamic minimum surface energy model of fcc nanoparticles, more than 7 times of edge/corner sites can be presented over the Ni/SiO₂-R compared to the Ni/SiO₂-CR. This suggests that the corner/step sites of Ni favor the furfural decarbonylation while terrace sites favor side chain hydrogenation.

Sitthisa and Resasco [17] reported that Pd/SiO₂ showed approximately 1:1 yield of furan and furfuryl alcohol at 210 °C but furan became the dominant product at higher temperature. Recent results showed that selective modification of Pd surface sites can result in a significant shift in product selectivity, indicating a structure sensitivity furfural hydrotreating reaction. Pang et al. [29] reported that Pd/Al₂O₃ catalysts had high furan selectivity at 190 °C and a modification with octadecanethiol self-assembled monolayers significantly suppressed the furan formation rate resulting in a shift in product selectivity toward furfuryl alcohol. Zhang et al. [30] reported that Pd/Al₂O₃ catalysts had high furfuryl alcohol selectivity at 190 °C and showed that a modification by ALD (atomic layer deposition) led to increased furan selectivity. Both studies proposed that step sites of Pd/Al₂O₃ are active for furfural side chain hydrogenation and terrace sites are active for furfural decarbonylation. This is in contradiction to the results of Pt [20] and Ni catalysts (this study) wherein small metal particles favor decarbonylation. The exact reason of such discrepancy is not known but it is suspected that the adsorption configuration of furfural may be influenced by the presence of long-chain alkane thiols and/or acidic sites of support [29]. Nevertheless, these results also demonstrated the structure sensitivity of furfural hydrotreating.

We did not observe THFA (tetrahydro furfuryl alcohol) or THMF (tetrahydro methyl furan) in our reaction products. This may be caused by the influence of H_2 /furfural feed ratio, reaction temperature and



Fig. 9. TEM image of (a)Ni/SiO₂-R and (b) Ni/SiO₂-CR (hydrogen reduction); (d) Ni/SiO₂-R-rxn and (d)Ni/SiO₂-CR-rxn (after furfural hydrotreating); HR-TEM images indicate the Ni (111) lattice of (e) Ni/SiO₂-R and (f) Ni/SiO₂-CR.

maybe space velocity. Nakagawa et al. [18] studied Ni/SiO₂ catalyst under a high H₂/furfural ratio and a low space time (H₂/furfural = 36/1, 0.884 g_{cat}h/mol_{furfural}) and THFA was the major product with a selectivity of 94% and 77%, respectively, at 140 °C and 170 °C. Sitthisa and Resasco [17] examined Ni/SiO₂ under H₂/furfural = 25/1 and a space time of 9.6 g_{cat}h/mol_{furfural} at 210 °C and recorded the product selectivity of furan (32%), FA (31%) and THFA (5%). These results indicate that the selectivity to FA and THFA decrease when reaction temperature is increased and when H₂/furfural ratio is decreased. In our study, the reaction conditions were under low H₂/furfural (10/1) and high space time (19.4 g_{cat} h / mol_{furfural}) at temperatures from 175 to 300 °C. This may be the reason why we did not observed THFA and THMF. This also suggests that the reaction product from furfural hydrotreating can be tuned by adjusting operating conditions.

4. Conclusions

The product distribution of furfural hydrotreating is governed by both the Ni particle size of Ni/SiO₂ and the reaction temperature. Over Ni/SiO₂, a hydrogenation route (to furfuryl alcohol) is preferred at <

200 °C and a decarbonylation route (to furan and propylene) becomes dominant at > 200 °C under the conditions of this study. The Ni/SiO₂-CR with ca. 15 nm particle size exhibits a high hydrogenation activity at low temperature. The Ni/SiO₂-R with ca. 5 nm particle size exhibits a high selectivity to furan at low temperature, and the decarbonylation of furan to propylene becomes obvious at around 250 °C. These results illustrate the structure sensitivity of the furfural hydrotreating over Ni catalysts, suggesting that the terrace sites preferentially catalyze side chain hydrogenation and the edge or step sites catalyze decarbonylation. The Ni/ SiO₂-CR can selectively produce FA at 175 °C and it is applicable for this purpose. With Ni/SiO₂-R, furan and propylene can be produced at above 200 °C via sequential decarbonylation with CO as the byproduct, demonstrating a high molecular efficiency furfural utilization to produce CO, propylene, and furan. This can be an attractive furfural hydrotreating route for bio-refinery, as a viable alternative to replace propylene production from petroleum.

CRediT authorship contribution statement

Szu-Hua Chen: Formal analysis, Investigation, Data curation. Ya-Chun Tseng: Formal analysis, Investigation, Data curation. Sheng-Chiang Yang: Conceptualization, Methodology, Writing - review & editing. Shawn D. Lin: Conceptualization, Methodology, Writing - review & editing, Funding acquisition.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcata.2021.118020.

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