

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/283621486>

# Efficient Preparation of Liquid Fuel 2,5-Dimethylfuran from Biomass-Derived 5-Hydroxymethylfurfural over Ru–NaY Catalyst

ARTICLE in ACS SUSTAINABLE CHEMISTRY & ENGINEERING · OCTOBER 2015

Impact Factor: 4.64 · DOI: 10.1021/acssuschemeng.5b00857

---

READS

27

3 AUTHORS, INCLUDING:



Atul S. Nagpure

CSIR - National Chemical Laboratory, Pune

5 PUBLICATIONS 5 CITATIONS

SEE PROFILE



Nishita Satyendra Lucas

CSIR - National Chemical Laboratory, Pune

11 PUBLICATIONS 61 CITATIONS

SEE PROFILE

# Efficient Preparation of Liquid Fuel 2,5-Dimethylfuran from Biomass-Derived 5-Hydroxymethylfurfural over Ru–NaY Catalyst

Atul S. Nagpure, Nishita Lucas, and Satyanarayana V. Chilukuri\*

Catalysis & Inorganic Chemistry Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, India

**S** Supporting Information

**ABSTRACT:** An efficient catalytic process for the selective conversion of biomass-derived 5-hydroxymethylfurfural (HMF) to high quality liquid fuel 2,5-dimethylfuran (DMF) was achieved over Ru nanoparticles dispersed on NaY zeolite. The structural and morphological features of the catalysts were studied by using various physicochemical characterization techniques. HMF conversion of 100 mol % with 78 mol % DMF yield was achieved using 2 wt % Ru–NaY catalyst in a short duration of the reaction. This catalyst displayed excellent recyclability without any loss in activity when it was used for five times. The study clearly showed that well-dispersed Ru nanoparticles are highly active and selective for the conversion of HMF to DMF. The reaction pathway for the conversion of HMF to DMF was explored by monitoring the reaction intermediates at different stages and intervals of the reaction.



**KEYWORDS:** Biomass, Biofuels, Hydrogenolysis, 2,5-Dimethylfuran, Ru–NaY

## INTRODUCTION

Heavy dependence on fossil fuels like petroleum and coal for the production of chemicals and fuels is alarming, as it is not sustainable in the long run. Therefore, the synthesis of renewable fuels and valuable chemicals from biomass has become imperative to replace petroleum based fossil fuels.<sup>1–4</sup> Hydrogenolysis of biomass components offers an excellent prospect for the future biorefinery concept, as biomass-derived substrates contain good amount of oxygen.<sup>5,6</sup> In that context, the hydrogenolysis of biomass-derived 5-hydroxymethylfurfural (HMF) to 2,5-dimethylfuran (DMF) is an important reaction in the up-gradation of biomass-derived platform compounds for obtaining biofuels. DMF is known as one of the potential transportation liquid fuel. Compared to the bioethanol, DMF has a high research octane number (RON = 119), superior energy density (30 kJ cm<sup>−3</sup>), and ideal boiling point (92–94 °C).<sup>7</sup> Further, DMF consumes only one-third of the energy in the evaporation stage, it is immiscible with water, and easier to blend with gasoline compared to ethanol.<sup>7,8</sup> The DMF has been successfully tested as biofuel in a single cylinder spray guided direct-injection spark-ignition engine.<sup>9</sup> The performance of DMF was satisfactory against gasoline. These excellent characteristics make DMF a more ideal and promising biomass-derived liquid biofuel. Moreover, DMF is also a renewable source for the synthesis of *p*-xylene via Diels–Alder reaction.<sup>10–12</sup>

Several research groups have studied the hydrogenolysis of HMF to DMF over various supported metal catalysts. Román-Leshkov et al. used bimetallic CuRu/C catalyst, that gave 100% HMF conversion with 71% DMF yield after 10 h in 1-butanol at 220 °C and 6.8 bar H<sub>2</sub> pressure.<sup>7</sup> On the other hand, Raines

et al. reported the hydrogenolysis of crude HMF obtained from the corn stover and achieved 49% DMF yield under similar reaction conditions.<sup>13</sup> Bell et al. achieved 15% DMF yield and 47% HMF conversion using Pd/C catalyst in ionic liquid under H<sub>2</sub> pressure of 62 bar.<sup>14</sup> The lower yield of DMF was attributed to the low solubility of H<sub>2</sub> in ionic liquids and as a consequence high H<sub>2</sub> pressure was required in this process. Rauchfuss et al. proposed a milder reaction pathway for the production of DMF yield up to 95% in 15 h, using Pd/C as catalyst and formic acid as the hydrogen donor.<sup>15</sup> To get high yield of DMF, simultaneous use of formic acid and H<sub>2</sub>SO<sub>4</sub> is necessary. However, both the acids are highly corrosive and environment unfriendly. Zhang et al. reported 60.3% DMF yield in 1-butanol at 260 °C by using Ru/C catalyst.<sup>16</sup> Zu et al. obtained 93.4% DMF yield over Ru/Co<sub>3</sub>O<sub>4</sub> catalyst in tetrahydrofuran (THF) after 24 h reaction.<sup>17</sup> Gallo et al. studied the HMF hydrogenolysis over RuSn/C catalyst to get 46% DMF yield.<sup>18</sup> Chatterjee et al. reported the use of Pd/C catalyst in supercritical CO<sub>2</sub> to get high yield of DMF.<sup>19</sup> But, this process involved the use of high pressure CO<sub>2</sub> and H<sub>2</sub>. Wang et al. achieved very good yield of DMF (98%) by using bimetallic PtCo nanoparticles supported on hollow carbon spheres.<sup>20</sup> Recently, we have reported the hydrogenolysis of HMF over Ru supported on hydrotalcite-derived mixed metal oxide catalyst and achieved 58% DMF yield.<sup>21</sup>

Riisager et al. adopted a new approach for the hydrogenation of HMF by catalytic transfer hydrogenation (CTH) over Cu–

**Received:** August 11, 2015

**Revised:** October 7, 2015

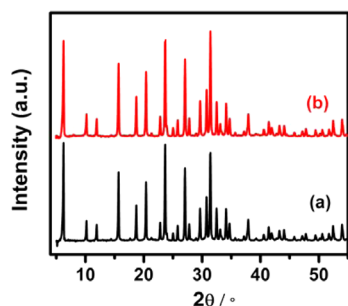
**Published:** October 12, 2015

doped porous metal oxide catalyst.<sup>22</sup> They used methanol as the reaction medium as well as hydrogen donor, achieving up to 48% DMF yield with 100% HMF conversion at 260 °C. Vlachos et al. achieved 81% DMF yield by employing Ru/C as catalyst and 2-propanol as hydrogen donor at 190 °C for 6 h.<sup>23</sup> However, when the recovered Ru/C catalyst was used in second cycle, significant drop in activity was observed (13% DMF yield with 47% HMF conversion). The catalyst deactivation observed just after its first use was attributed to the blockage of active Ru sites as a result of the deposition of high molecular weight byproducts. Morikawa et al. studied the CTH of HMF using cyclohexane to get 60% DMF yield over Pd/C and AlCl<sub>3</sub> catalysts.<sup>24</sup> However, most of these reported processes do not offer good space time DMF yield and have other drawbacks such as high metal content of the catalyst, high H<sub>2</sub> pressure and recyclability issues. Therefore, there is a need to develop an economically viable and environmental friendly process for the selective conversion of HMF to DMF.

Ru based catalysts are known for their superior activity in the production of alkanes from polyols.<sup>25,26</sup> The Ru–NaY catalyst has been known as an active catalyst for the hydrogenation of cinnamaldehyde,<sup>27</sup> hydrogenation of benzene,<sup>28</sup> CO methanation,<sup>29</sup> hydrogenation of nitriles,<sup>30</sup> and so on. Herein, we have reported the effectiveness of Ru–NaY catalyst for the selective hydrogenolysis of biomass-derived HMF to DMF in the presence of THF solvent (which can be prepared from biomass-derived furfural). The Ru–NaY catalyst gave high yield of DMF (78 mol %) in a short duration (1 h) as well as displayed an excellent reusability in the conversion of HMF to DMF. Our results demonstrate that the Ru–NaY catalysts have significant potential for further development of a biomass-derived HMF to DMF process for the production of renewable liquid fuels.

## RESULTS AND DISCUSSION

**Structural Characteristics of the Catalysts.** Figure 1 shows the X-ray diffraction (XRD) profiles of as synthesized 2



**Figure 1.** XRD profiles of (a) NaY zeolite and (b) 2 wt %Ru–NaY catalyst.

wt %Ru–NaY catalyst and its parent NaY zeolite (CBV-100, Si/Al ratio = 2.5). The similarity in diffraction pattern of both the samples shows that NaY zeolite has retained its crystalline structure after Ru exchange.<sup>28</sup> Moreover, XRD peaks corresponding to Ru were not observed, demonstrating that the Ru nanoparticles are highly dispersed on NaY zeolite support. The BET surface areas of NaY and 2 wt %Ru–NaY were found to be 886 and 851 m<sup>2</sup>/g, respectively (Table 1), showing negligible change on exchange of Ru. The above investigations further demonstrate that no change in crystallinity or porosity occurred due to ion-exchange process. Structural characteristics and chemical compositions of the other supported metal catalysts used in this study are given in the Supporting Information (Table S1). The morphologies of the NaY zeolite and Ru-containing NaY catalysts were investigated by scanning electron microscopy (SEM), and the results are given in the Supporting Information (Figure S1). The SEM micrographs demonstrate that the morphology of Ru-containing catalysts did not undergo any change with respect to the parent NaY zeolite.

The Ru metal dispersion and metal surface area of 2 wt % Ru–NaY catalyst were investigated by H<sub>2</sub> chemisorption using freshly reduced sample. The Ru dispersion and metal surface areas were 53.2% and 3.86 m<sup>2</sup>/g, respectively (Table 1). The high Ru metal dispersion confirms the homogeneous distribution of Ru nanoparticles on NaY support with an average Ru crystallite size of 2.5 nm. The Ru nanoparticles sizes as well as their distribution were also investigated using transmission electron microscopy (TEM) and the results are depicted in Figure 2. The micrograph of 2 wt %Ru–NaY shows that Ru nanoparticle sizes are in the 1–5 nm range and are well-dispersed over NaY support. The calculated average Ru nanoparticle sizes were in 2.7 nm range, which is in accordance with the H<sub>2</sub> chemisorption result. Because average Ru nanoparticle size (2.5 nm) is larger than pore size of NaY zeolite, most of the Ru may be present on the external surface. However, it is to be noted that NaY zeolite used for this study has small crystallite size (45–60 nm), its nearly 30% external surface area is available for Ru dispersion. Temperature-programmed reduction (TPR) in H<sub>2</sub> was used to study the reducibility of the Ru supported on NaY zeolite and the results are given in the Supporting Information (Figure S2). TPR profile of 2 wt %Ru–NaY catalyst composed of only one H<sub>2</sub> consumption peak in the 70–150 °C temperature range, which may be attributed to the reduction of RuO<sub>x</sub> species.<sup>31</sup> The X-ray photoelectron spectroscopy (XPS) spectrum of Ru 3d in 2 wt %Ru–NaY catalyst is given in the Supporting Information (Figure S3). The peaks centered at 280.2 and 284.3 eV were assigned to metallic Ru (Ru<sup>0</sup>), corresponding to Ru<sup>0</sup> 3d<sub>5/2</sub> and Ru<sup>0</sup> 3d<sub>3/2</sub>, respectively.<sup>32</sup> Whereas, the peaks at 281.5 and 285.9 eV are attributed to the Ru in the +4 oxidation state (RuO<sub>2</sub>), hence assigned to Ru<sup>4+</sup> 3d<sub>5/2</sub> and Ru<sup>4+</sup> 3d<sub>3/2</sub>, respectively.<sup>32</sup> On

**Table 1.** Textural Properties and Ru Metal Characteristics of the Catalysts

samples	BET surface area (m <sup>2</sup> /g)	total pore volume <sup>a</sup> (cm <sup>3</sup> /g)	Ru content <sup>b</sup> (wt %)	Ru metal dispersion <sup>c</sup> (%)	average Ru crystallite size <sup>c</sup> (nm)	Ru metal surface area <sup>c</sup> (m <sup>2</sup> /g)
NaY	886	0.35				
1 wt %Ru–NaY	861	0.34	0.97	47.4	2.8	1.72
2 wt %Ru–NaY	851	0.34	1.98	53.2	2.5	3.86
3 wt %Ru–NaY	827	0.33	2.95	19.3	6.9	2.11

<sup>a</sup>Total pore volume at  $P/P_0 = 0.899$ . <sup>b</sup>Estimated by ICP-OES. <sup>c</sup>Determined by H<sub>2</sub> chemisorption.

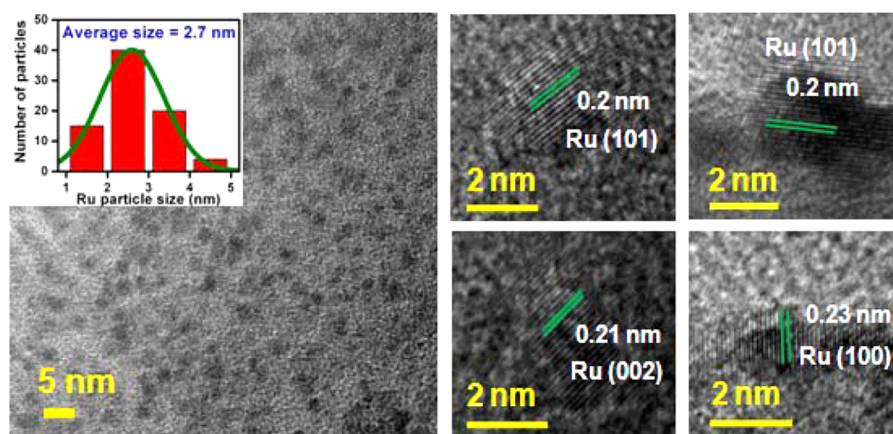


Figure 2. TEM micrograph and Ru particle size distribution of 2 wt %Ru-NaY catalyst.

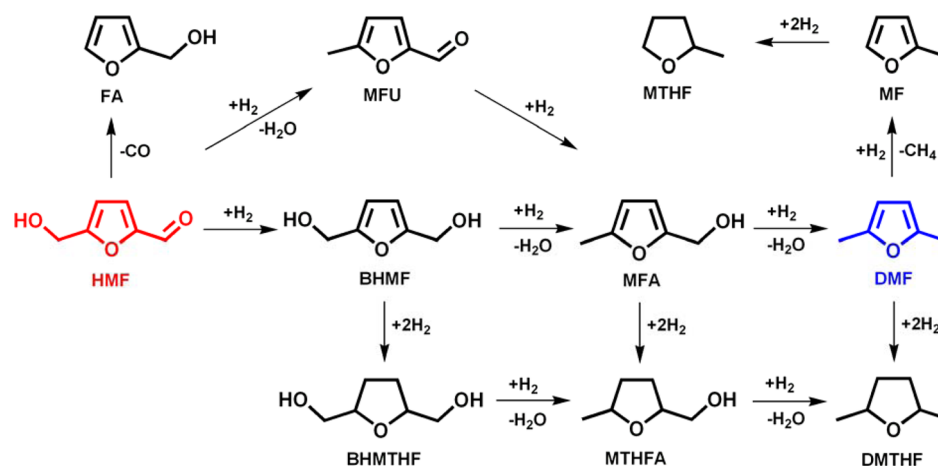
Table 2. Product Distribution During HMF Hydrogenolysis over Different Supported Metal Catalysts<sup>a</sup>

entry	catalyst	HMF conv. (mol %)	product yields (mol %)					TOF <sup>c</sup> (h <sup>-1</sup> )
			BHMF	MFA	DMF	DMTHF	others <sup>b</sup>	
1	2 wt%Pt-NaY	100	7.8	14.0	30.4	4.0	43.8 (5.1)	60.8
2	2 wt%Pd-NaY	100	15.6	19.0	49.3	1.1	15.0 (2.4)	98.6
3	2 wt%Rh-NaY	92.0	11.5	12.8	40.1	10.7	16.9 (3.4)	80.2
4	2 wt%Ru-NaY	100	0	0	78.0	11.8	10.2 (1.2)	156.0
5	2 wt%Au-NaY	65.6	25.5	5.5	8.2	0	26.4 (3.7)	16.4
6	5 wt%Ni-NaY	35.5	6.4	5.2	2.6	0	21.3 (2.4)	5.2
7	5 wt%Cu-NaY	30.1	5.5	1.5	3.2	0	19.9 (5.6)	6.4
8	2 wt %Ru-HY <sup>d</sup>	85.5	2.5	2.2	40.5	3.0	37.3 (8.5)	81.0
9	NaY	20.2	0	0	0	0	20.2 (20.2)	0
10	none	6.3	0	0	0	0	6.3 (6.3)	0

<sup>a</sup>Reaction conditions: molar ratio of HMF to metal (200); temperature (220 °C); H<sub>2</sub> pressure (15 bar); solvent (THF, 25 mL); reaction time (1 h).

<sup>b</sup>Includes furfuryl alcohol (FA), 5-methyl furfural (MFU), 2-methylfuran (MF), 2,5-bis(hydroxymethyl)tetrahydrofuran (BHMTF), 5-methyl tetrahydrofurfuryl alcohol (MTHFA), hexanediol, and some unidentified products (values in brackets). <sup>c</sup>TOF = turnover frequency (moles of DMF produced per mole of metal per hour). <sup>d</sup>2 wt %Ru-HY (acidity =2.43 mmol/g), ≈25 mol % of polyols was obtained with 2 wt %Ru-HY catalyst.

Scheme 1. Reaction Network for the Hydrogenolysis of HMF to DMF over 2 wt %Ru-NaY



the basis of the XPS results, the relative percentage of Ru metal and Ru oxide were 76 and 24%, respectively. The single peak at 284.5 eV is assigned to C 1s originating from the carbon contamination of the sample surface.

**Catalytic Activity in the Hydrogenolysis of HMF to DMF.** Hydrogenolysis of HMF over Different Supported Metal Catalysts. The hydrogenolysis of HMF was investigated using Pt, Pd, Rh, Ru, Au, Ni, and Cu catalysts supported on

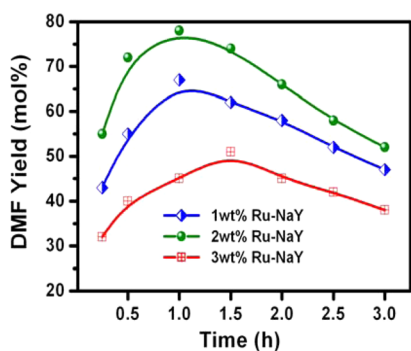
NaY zeolite. The HMF conversions and product yields are summarized in the Table 2 (Figure S4 and Table S2 in the Supporting Information). Under the reaction conditions studied (temperature = 220 °C, reaction time = 1 h, and H<sub>2</sub> pressure = 15 bar), mainly four products were observed: DMF, 2,5-dimethyltetrahydrofuran (DMTHF), 2,5-bis-(hydroxymethyl)furan (BHMF), and 5-methyl furfuryl alcohol (MFA). Pathways for the formation of these products are given



in Scheme 1. The HMF conversion was in the range of 30.1 to 100 mol % and reactivity followed the order  $\text{Cu} < \text{Ni} < \text{Au} < \text{Rh} < \text{Pd} = \text{Pt} = \text{Ru}$  (Table 2). Though 100 mol % HMF conversion was seen for Pt–NaY and Pd–NaY catalysts, the DMF yields were low at 30.4 and 49.3 mol % respectively, when compared to their Ru counterpart (Table 2, entry 1 and 2). Similarly, with Rh–NaY, Au–NaY, Ni–NaY, and Cu–NaY catalysts, poor catalytic activity as well as poor DMF selectivity's were observed, leading to 40.1, 8.2, 2.6, and 3.2 mol % DMF yields at 92, 65.6, 35.5, and 30.1 mol % HMF conversion, respectively (Table 2, entry 3, 5, 6, and 7). It is gratifying to note that excellent DMF yield of 78 mol % with 100 mol % HMF conversion was achieved with 2 wt %Ru–NaY catalyst (Table 2, entry 4). These findings are in good agreement with the literature, which generally reports that the Ru based catalysts are highly selective for the conversion of HMF to DMF.<sup>33</sup>

When the hydrogenolysis reaction was carried out over Ru supported on proton exchanged HY zeolite, HMF conversion as well as the product distributions changed significantly (Table 2, entry 8). The HMF conversion has dropped to 85.5 mol % on this catalyst, giving only 40.5 mol % DMF yield and the most of the HMF was converted to polyols ( $\approx 25$  mol %). The Brønsted acid sites of HY zeolite in 2 wt %Ru–HY catalyst (acidity = 2.43 mmol/g, Figure S5) may be responsible for the enhancement in side reactions, e.g., ring opening through breakage of furanic C–O bond, which is normally catalyzed by Brønsted acid sites.<sup>34–37</sup> On the other hand, Lewis acid sites of 2 wt %Ru–NaY catalyst (acidity = 1.12 mmol/g, Figure S5) are expected to increase deoxygenation ability of the catalyst and thus help to improve the DMF yield. Recently, Fu et al. reported synergy between hydrogenating Ni sites and deoxygenating Lewis acid sites, in nickel–tungsten carbide catalysts, for obtaining very high yield of DMF from HMF.<sup>38</sup>

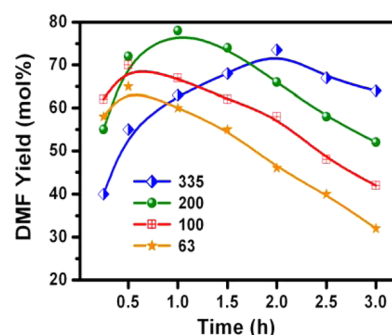
To optimize the Ru content of the catalyst, catalysts with different wt % of Ru supported on NaY zeolite were prepared and evaluated for HMF hydrogenolysis (Figure 3). Because all



**Figure 3.** Effect of Ru content of the catalyst on DMF yields. Reaction conditions: molar ratio of HMF to Ru (200); temperature (220 °C);  $\text{H}_2$  pressure (15 bar); solvent (THF, 25 mL).

NaY supported Ru catalysts gave 100% HMF conversion within half an hour of the reaction, only DMF yield as a function of reaction time is compared. Catalyst with 2 wt %Ru (2 wt %Ru–NaY) showed the highest activity giving 78 mol % DMF yield within 1 h of the reaction time. However, under similar reaction conditions DMF yields were only 67 and 45 mol % over 1 and 3 wt %Ru–NaY catalysts, respectively. More importantly, significant increase in the yields of ring hydrogenated products such as DMTHF and 2,5-bis(hydroxymethyl)tetrahydrofuran

(BHMTHF) were observed over 3 wt %Ru–NaY catalyst. This could be attributed to larger Ru crystallite size (6.9 nm) over this catalyst.<sup>21</sup> On the otherhand, the main byproduct was MTHFA over 1 wt %Ru–NaY catalyst, as a result of hydrogenation of MFA. The superior activity exhibited by 2 wt %Ru–NaY in terms of DMF yield could be attributed to its smaller Ru crystallite size (2.5 nm) and higher Ru metal surface area (3.86  $\text{m}^2/\text{g}$ ). The smaller Ru crystallite size suppresses the ring hydrogenation, thus leading to better DMF yield.<sup>21</sup> Further, the effect of HMF/Ru molar ratio on DMF yields with 2 wt %Ru–NaY catalyst was also studied, and the results are given in Figure 4 (Table S3). At a higher HMF to Ru

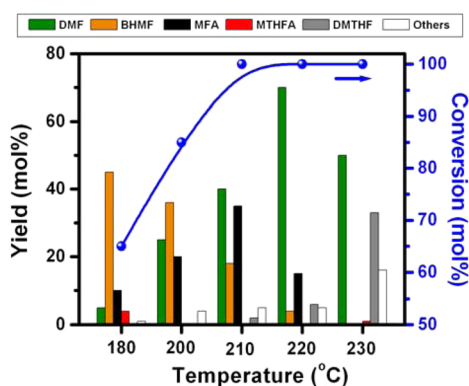


**Figure 4.** Effect of HMF to Ru molar ratio on DMF yields over 2 wt % Ru–NaY catalyst. Reaction conditions: temperature (220 °C);  $\text{H}_2$  pressure (15 bar); solvent (THF, 25 mL).

ratio (335), even prolonging the reaction beyond a point did not improve the DMF yield. This is due to the consecutive reaction of DMF to give DMTHF. A lower HMF to Ru molar ratio (63 and 100) was also not beneficial to get high yield of DMF, as higher Ru led to consecutive hydrogenation of DMF giving unwanted byproducts such as DMTHF, 2-methylfuran (MF), and 2-methyltetrahydrofuran (MTHF). The HMF/Ru molar ratio of 200 was found to be optimum to achieve high yield (78 mol %) of DMF within 1 h of reaction time. Therefore, to attain maximum yield of DMF, optimum HMF/Ru molar ratio and reaction time are essential.

To ascertain the desirability of Ru in the catalyst, HMF hydrogenolysis was carried out in its absence, using only NaY zeolite, it converted only 20.2 mol % of HMF, but hardly yielded any DMF in the product (Table 2, entry 9). Whereas, blank experiment in the absence of a catalyst did not show any activity for DMF formation (Table 2, entry 10). It is important to note that the complete hydrogenolysis of HMF to DMF was mainly catalyzed by Ru nanoparticles. Because high yield of DMF at high HMF conversion was achieved, it was decided to carry out further investigations using 2 wt %Ru–NaY catalyst.

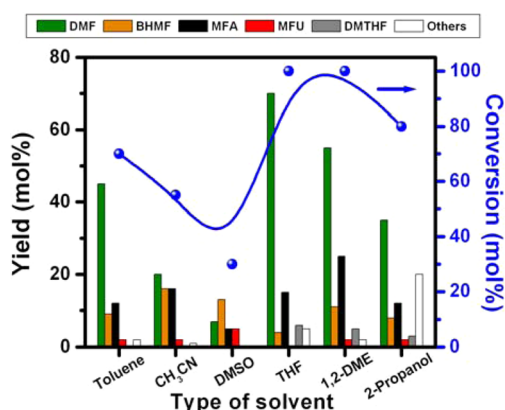
**Effect of Reaction Temperature.** The influence of reaction temperature on the HMF conversion and product yields was studied by varying the temperature in the 180–230 °C range over 2 wt %Ru–NaY catalyst at 10 bar  $\text{H}_2$  pressure (Figure 5). When the reaction was performed at 180 °C, the HMF conversion was low (65.5 mol %), which increased at higher temperatures to reach a maximum of 100 mol % at 210 °C. At lower temperature (180 °C), the main product was BHMf (45 mol %) and the yield of DMF was considerably low (5 mol %).<sup>21</sup> However, the DMF yield improved substantially with increasing reaction temperature, which reached 69.5 mol % at 220 °C. But, when the reaction temperature was further increased to 230 °C, the yield of DMF dropped (50.1 mol %)



**Figure 5.** Effect of reaction temperature on HMF conversion and product yields. Reaction conditions: molar ratio of HMF to Ru (200);  $H_2$  pressure (10 bar); solvent (THF, 25 mL); reaction time (1 h).

and the ring hydrogenation of DMF became prominent,<sup>21,22</sup> yielding 33.2 mol % of DMTHF. These results demonstrate that the low temperatures (180 and 200 °C) are not suitable to achieve good yield of DMF, while high temperature (230 °C) assisted the consecutive hydrogenation of DMF leading to high DMTHF yield. Therefore, 220 °C was found to be the optimum temperature for selective conversion of HMF to DMF.

**Effect of Solvent.** The influence of solvent in the liquid-phase hydrogenolysis of HMF to DMF was investigated over 2 wt %Ru–NaY catalyst at 220 °C and at 10 bar  $H_2$  pressure (Figure 6). Solvents of different chemical nature, such as

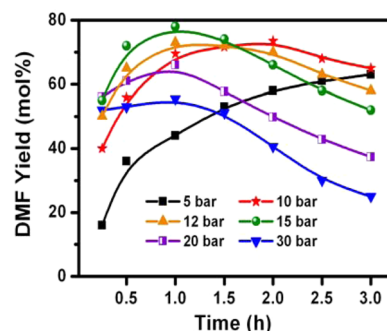


**Figure 6.** Effect of solvent on HMF conversion and product yields. Reaction conditions: molar ratio of HMF to Ru (200); temperature (220 °C); solvent (25 mL);  $H_2$  pressure (10 bar); reaction time (1 h).

nonpolar (toluene), aprotic polar (THF, 1,2-dimethoxyethane (1,2-DME), dimethyl sulfoxide (DMSO) and acetonitrile ( $CH_3CN$ )) and protic (2-propanol) solvents were used to investigate the effect of solvent on HMF hydrogenolysis. The results shown in Figure 6 clearly show that the catalytic activity is profoundly solvent dependent, which follows the order THF > 1,2-DME > toluene > 2-propanol >  $CH_3CN$  > DMSO. Lower activity seen for DMSO,  $CH_3CN$ , and toluene solvents could be explained on the basis of the competitive adsorption between the solvent and the reactant molecules on the active catalytic sites. Solvents containing nitrogen ( $CH_3CN$ ) or sulfur (DMSO) are known to deactivate the Ru based catalysts, as a result of interaction of lone pair of electrons on nitrogen/sulfur with the empty d orbitals of Ru metal.<sup>39</sup> Strong adsorption of

DMSO and  $CH_3CN$  would completely block Ru active sites for HMF adsorption, thus inhibiting HMF hydrogenolysis. When toluene was used as solvent, hydrogenated compounds of toluene were observed in the product mixture under the reaction conditions studied.<sup>21,40</sup> This shows that toluene and HMF compete for the same active sites, which leads to the lower availability of active sites for HMF adsorption, thus suppressing HMF hydrogenolysis rate. On the other hand, formation of undesirable condensed products (ethers and acetals,  $\approx 16$  mol %) were observed with 2-propanol as the solvent, which may be facilitated by the residual acidity of 2 wt %Ru–NaY catalyst.<sup>41</sup> This brings down the concentration of HMF in the solution, leading to reduced rate of HMF hydrogenolysis. The highest activity was observed in THF solvent giving 69.5 mol % yield of DMF at 100 mol % HMF conversion.

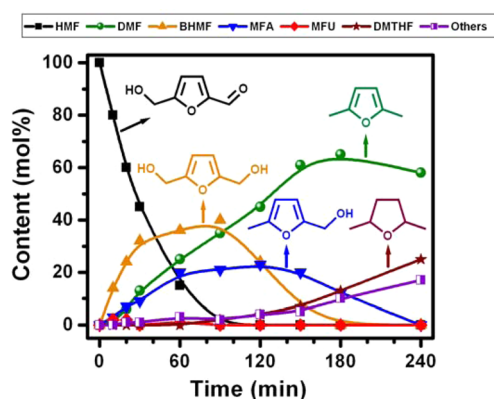
**Influence of  $H_2$  Pressure.** The effect of  $H_2$  pressure on the DMF yield was studied over 2 wt %Ru–NaY catalyst by varying the pressure in the range of 5–30 bar at 220 °C (Figure 7).



**Figure 7.** Effect of  $H_2$  pressure on DMF yield as a function of reaction time. Reaction conditions: molar ratio of HMF to Ru (200); temperature (220 °C); solvent (THF, 25 mL).

When the reaction was carried out at low pressure (5 bar), intermediate products such as BHMF and MFA formed in major quantities, which are converted to DMF on prolonging the reaction time.<sup>21</sup> When  $H_2$  pressure is further increased (10 and 12 bar), the DMF yield reaches maximum after certain reaction time, but decreased thereafter on continuation of the reaction for further duration. The highest yield of the targeted DMF (78 mol %) was obtained at 15 bar  $H_2$  pressure within 1 h of reaction time. The decrease in DMF yield is due to its ring hydrogenation, a consecutive reaction, leading to the formation of DMTHF. Hence, increasing the  $H_2$  pressure to 20 and 30 bar, the DMF yield was adversely affected. At higher  $H_2$  pressure, DMF yield suppressed mostly due to the formation of DMTHF in significant amounts.<sup>17,21</sup> Moreover, the concentration of other undesirable byproducts such as MTHFA, BHMTF, and hexanediol also increased at higher  $H_2$  pressure.<sup>21</sup> Hence, an optimum  $H_2$  pressure of 15 bar was chosen to obtain high yield of DMF.

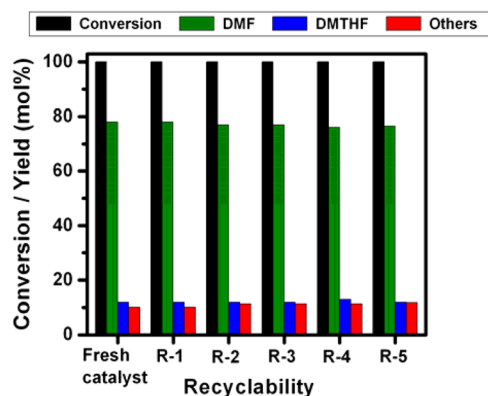
**Proposed Reaction Pathway for DMF from HMF.** To understand the reaction path in the hydrogenolysis of HMF to DMF, the reaction was carried out at 200 °C under 10 bar  $H_2$  pressure using 2 wt %Ru–NaY catalyst. The reaction intermediates formed during the course of the reaction were determined by GC–MS and using authentic standards. Figure 8 shows the variations in the concentration of reactant (HMF) and different products formed during the course of reaction. Under the reaction conditions used, a very short reaction time



**Figure 8.** Effect of reaction time on HMF conversion and product yields on 2 wt %Ru–NaY. Reaction conditions: molar ratio of HMF to Ru (200); temperature (200 °C); solvent (THF, 25 mL); H<sub>2</sub> pressure (10 bar).

(10 min) provided low HMF conversion (20 mol %), which gradually increased to 100 mol % as the time progressed to 90 min, and the product distributions changed in a complex manner with progress of the reaction. The BHMF yield reached maximum at 40 mol % after 90 min and then decreased with increasing time. A similar profile was also observed for MFA to that of BHMF, passing through the maxima at 120 min. The yield of DMF increased continuously up to certain reaction time, increasing to a maximum, which then decreased with increasing reaction time. The yield of 5-methyl furfural (MFU) was very low (<2 mol %) over the entire duration of the reaction. The low yield of MFU may be due to the fact that its formation is not rapid enough.<sup>21</sup> On the basis of the results discussed above and the reported literature,<sup>19,21,23</sup> we hypothesize that the reaction proceeds through the hydrogenation of –CHO in HMF, followed by the hydrogenolysis of the –OH functionalities in BHMF to give DMF via MFA (Scheme 1). In a consecutive step, DMF was hydrogenated to DMTHF along with the formation of other byproducts such as MF, MTHF, and 2-hexanol, on prolonging the reaction time.

**Recyclability Study.** The recyclability study of the 2 wt % Ru–NaY catalyst was carried out by repeating the HMF hydrogenolysis reaction with the same catalyst (Figure 9). The catalyst recyclability studies were carried out as follows. After



**Figure 9.** Recyclability experiments with 2 wt %Ru–NaY catalyst in the hydrogenolysis of HMF to DMF. Reaction conditions: molar ratio of HMF to Ru (200); solvent (THF, 25 mL); temperature (220 °C); H<sub>2</sub> pressure (15 bar); reaction time (1 h).

the first run, the content of the reactor was transferred to a centrifuge tube. The liquid phase was decanted, analyzed by GC-FID and the catalyst was washed three times with 20 mL of THF. After centrifugation, the liquid phase was discarded and the catalyst was dried at 100 °C for 6 h and was reused directly with fresh HMF for the hydrogenolysis reaction. This procedure was repeated for four more times. The results in Figure 9 clearly show that the catalytic performance remains same even after being reused for five times. These results indicate good stability of the catalyst. Chemical analysis using ICP-OES also showed no leaching of Ru after each recycle. Moreover, the amount of Ru in the catalyst after five cycles was found to be same as that of the starting catalyst.

## CONCLUSIONS

Transition metal exchanged NaY catalysts, including Ru–NaY catalysts, were synthesized via a simple ion exchange method and used for the selective hydrogenolysis of biomass-derived HMF to DMF. Ruthenium based catalysts were found to be superior compared to other transition metal catalysts supported on NaY. On the basis of the results of investigations, a plausible reaction pathway for the conversion of HMF to DMF was proposed. The experimental results clearly show that DMF is formed through the hydrogenolysis of –OH groups in BHMF followed by MFA. Under optimized reaction conditions, a maximum DMF yield of 78 mol % could be achieved within 1 h of reaction over 2 wt %Ru–NaY catalyst. The catalyst can be reused for five times without loss in activity. This study shows that Ru–NaY catalyst, due to its high activity and excellent recyclability, has tremendous potential for the conversion of biomass oxygenates to biofuels.

## EXPERIMENTAL SECTION

**Chemicals.** All the chemicals were reagent grade and used without further purification. HMF (99%), DMF (99%), DMTHF (99%), MF (99%), MTHF (99%), RuCl<sub>3</sub>·3H<sub>2</sub>O, and THF (98%) were sourced from Sigma-Aldrich. MFU (99%), PdCl<sub>2</sub>·2H<sub>2</sub>O, H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, RhCl<sub>3</sub>·3H<sub>2</sub>O, HAuCl<sub>4</sub>·3H<sub>2</sub>O, CuCl<sub>2</sub>·2H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O, *n*-decane, and AgNO<sub>3</sub> were purchased from Alfa Aesar. NaY zeolite (CBV-100, Si/Al ratio = 2.5) and NH<sub>4</sub>Y zeolite (CBV-500, Si/Al ratio = 2.6) were obtained from Zeolyst International, USA. Toluene, 2-propanol, CH<sub>3</sub>CN, DMSO, NaBH<sub>4</sub>, and 1,2-DME were obtained from Loba chemicals, Mumbai.

**Preparation of Catalysts.** Ru supported on NaY zeolite catalyst was prepared by ion exchange method. In a typical synthesis, 1.96 g of NaY zeolite was dispersed in 40 mL of deionized water in a 100 mL round-bottomed flask. To this was added 8 mL of RuCl<sub>3</sub> solution (Ru content 5 mg/mL, for 2 wt %Ru–NaY), and the resulting slurry was stirred for 3 h at 80 °C. The mixture was then cooled, filtered, and washed until no chloride ions were detected (confirmed by AgNO<sub>3</sub> test). The remnant was dried in a hot air oven at 100 °C for 10 h. Subsequently, NaBH<sub>4</sub> (Ru/NaBH<sub>4</sub> = 1:4 mol mol<sup>−1</sup>) in ethanol was added with continuous stirring at room temperature for 2 h to get Ru in its metallic state. The sample was filtered, washed thrice with 50 mL of deionized water, and dried at 100 °C for 10 h. A similar procedure was adopted for the preparation of 1 wt %Ru–NaY, 3 wt %Ru–NaY, 2 wt %Pt–NaY, 2 wt %Rh–NaY, 2 wt %Pd–NaY, 2 wt %Au–NaY, 5 wt %Ni–NaY, and 5 wt %Cu–NaY catalysts. Ru supported on acidic HY (2 wt %Ru–HY catalyst) was prepared by ion exchange of NH<sub>4</sub>Y zeolite with RuCl<sub>3</sub> at 80 °C for 3 h. The sample was then cooled, filtered, washed with deionized water, and dried in an oven at 100 °C for 10 h. This crystalline material was subsequently calcined in air at 300 °C and reduced using NaBH<sub>4</sub>.

**Characterization Techniques.** The XRD patterns of all the samples were obtained using a PANalytical X'pert Pro dual goniometer operating at 30 mA and 40 kV. The spectra were scanned using Cu Kα



( $\lambda = 1.5406 \text{ \AA}$ ) radiation using a Ni filter. Data was recorded in  $2\theta$  range of  $5\text{--}90^\circ$  with  $0.02^\circ$  step size using a flat holder in Bragg–Brentano geometry. The BET surface areas of the samples were examined by  $\text{N}_2$ -sorption isotherms at  $-196^\circ\text{C}$  (Quantachrome Autosorb IQ). Ru metal dispersion was studied by  $\text{H}_2$ -chemisorption (Quantachrome Autosorb IQ). Prior to chemisorption at  $40^\circ\text{C}$ , the catalyst was reduced *in situ* in  $\text{H}_2$  flow at  $250^\circ\text{C}$ . The amount of metal present in the samples was estimated by ICP-OES (Spectro Arcos, FHS-12). The SEM images of the samples were recorded using JEOL-JSM-5200 to study the morphology. The samples were prepared by dispersing them ultrasonically in 2-propanol, transferring them on to a sample holder, and subsequently dried and gold coated before SEM analysis. To collect TEM images of the catalysts, an FEI Technai TF-30 instrument operating at  $300 \text{ kV}$  was used. The samples for TEM analysis were prepared by placing a droplet of diluted suspension of sample in 2-propanol onto a carbon-coated copper grid (mesh 200) that was evaporated at room temperature. XPS measurements were carried out using a VG Microtech Multilab ESCA 3000 with  $\text{Mg K}\alpha$  radiation ( $h\nu = 1253.6 \text{ eV}$ ). The base pressure in analyzing chamber was maintained at  $3\text{--}6 \times 10^{-10} \text{ mbar}$ . The peak corresponding to carbon 1s at  $284.5 \text{ eV}$  was taken as reference in estimating the binding energy values of various elements in the catalyst. The TPR studies were carried out on a Micromeritics Autochem-2920 instrument in the temperature range  $50\text{--}600^\circ\text{C}$  using  $5\% \text{ H}_2$  in He as the probe gas at a heating rate of  $5^\circ\text{C}/\text{min}$ . Before the TPR study, the catalyst was pretreated at  $300^\circ\text{C}$  for 1 h using  $5\% \text{ O}_2$  in He gas mixture. The consumption of  $\text{H}_2$  in the TPR study was measured quantitatively by a thermal conductivity detector (TCD) instrument, which was calibrated before the TPR study. The acidity of the samples was determined by temperature-programmed desorption (TPD) of  $\text{NH}_3$  using a Micromeritics Autochem-2920 instrument. Before TPD run, the sample was activated at  $400^\circ\text{C}$  in He flow ( $40 \text{ mL}/\text{min}$ ) for 1 h. Subsequently, the temperature was brought down to  $80^\circ\text{C}$  and  $\text{NH}_3$  was sorbed by exposing the sample to a stream of  $10\% \text{ NH}_3$  in He ( $30 \text{ mL}/\text{min}$ ) for 0.5 h. Then the temperature was increased to  $100^\circ\text{C}$  and physisorbed  $\text{NH}_3$  was removed by flushing with He for 1 h. Desorption of  $\text{NH}_3$  was carried out in He flow ( $40 \text{ mL}/\text{min}$ ) by increasing the temperature from  $100$  to  $800^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ . The amount of  $\text{NH}_3$  desorbed was monitored using TCD.

**Evaluation of Catalysts.** All the reactions were carried out using a  $100 \text{ mL}$  parr autoclave (SS316). In a typical experiment, the reactor was charged with  $1 \text{ mmol}$  ( $126 \text{ mg}$ ) of HMF, solvent ( $25 \text{ mL}$ ), *n*-decane ( $0.2 \text{ g}$ , internal standard), and desired quantity of freshly reduced catalyst. The contents were mixed thoroughly and the reactor was sealed, purged 2–3 times with  $\text{H}_2$  gas, and filled with the same gas to the required  $\text{H}_2$  pressure. Subsequently, the reaction vessel was heated under stirring ( $800 \text{ rpm}$ ) to the desired temperature. Liquid samples were withdrawn periodically during the reaction and analyzed by GC (Agilent 7890A) equipped with a flame ionization detector (FID) instrument having a CP Sil 8 CB capillary column ( $30 \text{ m}$  length,  $0.25 \text{ mm}$  diameter). Product identification was done using authentic standards and GC–MS (Varian, Saturn 2200). The FID sensitivity of BHMF and MFA was assumed to be equal to that for HMF and MFU, respectively.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acssuschemeng.5b00857](https://doi.org/10.1021/acssuschemeng.5b00857).

Structural characteristics and chemical composition of various catalysts, SEM images,  $\text{H}_2$ -TPR, XPS spectra,  $\text{NH}_3$ -TPD, yields of other products on different catalysts, effect of reaction time on HMF conversion and DMF selectivity, and influence of time on DMF yield on different catalysts (PDF).

## ■ AUTHOR INFORMATION

### Corresponding Author

\*Satyanarayana V. Chilukuri. E-mail: [sv.chilukuri@ncl.res.in](mailto:sv.chilukuri@ncl.res.in). Tel.: +91-20-25902019. Fax: +91-20-25902633.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

Atul S. Nagpure and Nishita Lucas acknowledge Council of Scientific and Industrial Research (CSIR), New Delhi, for providing senior research fellowships. Authors also acknowledge financial support from CSIR Network project CSC-0122.

## ■ REFERENCES

- (1) Huber, G. W.; Iborra, S.; Corma, A. Synthesis of transportation fuels from biomass: Chemistry, catalysts and engineering. *Chem. Rev.* **2006**, *106*, 4044–4098.
- (2) Corma, A.; Iborra, S.; Velty, A. Chemical Routes for the Transformation of Biomass into Chemicals. *Chem. Rev.* **2007**, *107*, 2411–2502.
- (3) Chheda, J. N.; Huber, G. W.; Dumesic, J. A. Liquid-phase catalytic processing of biomass-derived oxygenated hydrocarbons to fuels and chemicals. *Angew. Chem., Int. Ed.* **2007**, *46*, 7164–7183.
- (4) Shimizu, K.; Satsuma, A. Toward a rational control of solid acid catalysis for green synthesis and biomass conversion. *Energy Environ. Sci.* **2011**, *4*, 3140–3153.
- (5) Kunkes, E. L.; Simonetti, D. A.; West, R. M.; Serrano-Ruiz, J. C.; Gärtner, C. A.; Dumesic, J. A. Catalytic conversion of biomass to monofunctional hydrocarbons and targeted liquid fuel classes. *Science* **2008**, *322*, 417–421.
- (6) Ragauskas, A. J.; Williams, C. K.; Davison, B. H.; Britovsek, G.; Cairney, J.; Eckert, C. A.; Frederick, W. J., Jr.; Hallett, J. P.; Leak, D. J.; Liotta, C. L.; Mielenz, J. R.; Murphy, R.; Templer, R.; Tschaplinski, T. The path forward for biofuels and biomaterials. *Science* **2006**, *311*, 484–489.
- (7) Román-Leshkov, Y.; Barrett, C. J.; Liu, Z. Y.; Dumesic, J. A. Production of dimethylfuran for liquid fuels from biomass-derived carbohydrates. *Nature* **2007**, *447*, 982–985.
- (8) Kazi, F. K.; Patel, A. D.; Serrano-Ruiz, J. C.; Dumesic, J. A.; Anex, R. P. Techno-economic analysis of dimethylfuran (DMF) and hydroxymethylfurfural (HMF) production from pure fructose in catalytic processes. *Chem. Eng. J.* **2011**, *169*, 329–338.
- (9) Wang, C.; Xu, H.; Daniel, R.; Ghafourian, A.; Herreros, J. M.; Shuai, S.; Ma, X. Combustion characteristics and emissions of 2-methylfuran compared to 2,5-dimethylfuran, gasoline and ethanol in a DISI engine. *Fuel* **2013**, *103*, 200–211.
- (10) Williams, C. L.; Chang, C. C.; Do, P.; Nikbin, N.; Caratzoulas, S.; Vlachos, D. G.; Lobo, R. F.; Fan, W.; Dauenhauer, P. J. Cycloaddition of biomass-derived furans for catalytic production of renewable p-xylene. *ACS Catal.* **2012**, *2*, 935–939.
- (11) Wang, D.; Osmundsen, C. M.; Taarning, E.; Dumesic, J. A. Selective production of aromatics from alkylfurans over solid acid catalysts. *ChemCatChem* **2013**, *5*, 2044–2050.
- (12) Chang, C. C.; Green, S. K.; Williams, C. L.; Dauenhauer, P. J.; Fan, W. Ultra-selective cycloaddition of dimethylfuran for renewable p-xylene with H-BEA. *Green Chem.* **2014**, *16*, 585–588.
- (13) Binder, J. B.; Raines, R. T. Simple chemical transformation of lignocellulosic biomass into furans for fuels and chemicals. *J. Am. Chem. Soc.* **2009**, *131*, 1979–1985.
- (14) Chidambaram, M.; Bell, A. T. A two-step approach for the catalytic conversion of glucose to 2,5-dimethylfuran in ionic liquids. *Green Chem.* **2010**, *12*, 1253–1262.
- (15) Thananathanachon, T.; Rauchfuss, T. B. Efficient production of the liquid fuel 2,5-dimethylfuran from fructose using formic acid as a reagent. *Angew. Chem., Int. Ed.* **2010**, *49*, 6616–6618.



- (16) Zhang, J.; Lin, L.; Liu, S. Efficient Production of Furan Derivatives from a Sugar Mixture by Catalytic Process. *Energy Fuels* **2012**, *26*, 4560–4567.
- (17) Zu, Y. H.; Yang, P. P.; Wang, J. J.; Liu, X. H.; Ren, J. W.; Lu, G. Z.; Wang, Y. Q. Efficient production of the liquid fuel 2,5-dimethylfuran from 5-hydroxymethylfurfural over Ru/Co<sub>3</sub>O<sub>4</sub> catalyst. *Appl. Catal., B* **2014**, *146*, 244–248.
- (18) Gallo, J. M. R.; Alonso, D. M.; Mellmer, M. A.; Dumesic, J. A. Production and upgrading of 5-hydroxymethylfurfural using heterogeneous catalysts and biomass-derived solvents. *Green Chem.* **2013**, *15*, 85–90.
- (19) Chatterjee, M.; Ishizaka, T.; Kawanami, H. Hydrogenation of 5-hydroxymethylfurfural in supercritical carbon dioxide/water: A tunable approach to dimethylfuran selectivity. *Green Chem.* **2014**, *16*, 1543–1551.
- (20) Wang, G. H.; Hilgert, J.; Richter, F. H.; Wang, F.; Bongard, H. J.; Spliethoff, B.; Weidenthaler, C.; Schuth, F. Platinum-cobalt bimetallic nanoparticles in hollow carbon nanospheres for hydrogenolysis of 5-hydroxymethylfurfural. *Nat. Mater.* **2014**, *13*, 293–300.
- (21) Nagpure, A. S.; Venugopal, A. K.; Lucas, N.; Manikandan, M.; Thirumalaiswamy, R.; Chilukuri, S. Renewable fuels from biomass-derived compounds: Ru-containing hydrotalcites as catalysts for conversion of HMF to 2,5-dimethylfuran. *Catal. Sci. Technol.* **2015**, *5*, 1463–1472.
- (22) Hansen, T. S.; Barta, K.; Anastas, P. T.; Ford, P. C.; Riisager, A. One-pot reduction of 5-hydroxymethylfurfural via hydrogen transfer from supercritical methanol. *Green Chem.* **2012**, *14*, 2457–2461.
- (23) Jae, J.; Zheng, W.; Lobo, R. F.; Vlachos, D. G. Production of dimethylfuran from hydroxymethylfurfural through catalytic transfer hydrogenation with ruthenium supported on carbon. *ChemSusChem* **2013**, *6*, 1158–1162.
- (24) Morikawa, S. Reduction of 5-hydroxymethylfurfural. *Noguchi Kenkyusho Jiho* **1980**, *23*, 39–44.
- (25) Chen, L.; Zhu, Y.; Zheng, H.; Zhang, C.; Zhang, B.; Li, Y. Aqueous-phase hydrodeoxygenation of carboxylic acids to alcohols or alkanes over supported Ru catalysts. *J. Mol. Catal. A: Chem.* **2011**, *351*, 217–227.
- (26) Miyazawa, T.; Koso, S.; Kunimori, K.; Tomishige, K. Development of a Ru/C catalyst for glycerol hydrogenolysis in combination with an ion-exchange resin. *Appl. Catal., A* **2007**, *318*, 244–251.
- (27) Hajek, J.; Kumar, N.; Maki-Arvela, P.; Salmi, T.; Murzin, D. Y. Selective hydrogenation of cinnamaldehyde over Ru/NaY zeolite. *J. Mol. Catal. A: Chem.* **2004**, *217*, 145–154.
- (28) Zahmakiran, M.; Kodaira, T.; Ozkar, S. Ruthenium(0) nanoclusters stabilized by zeolite framework as superb catalyst for the hydrogenation of neat benzene under mild conditions: Additional studies including cation site occupancy, catalytic activity, lifetime, reusability and poisoning. *Appl. Catal., B* **2010**, *96*, 533–540.
- (29) Abdel-Mageed, A. M.; Eckle, S.; Anfang, H. G.; Behm, R. J. Selective CO methanation in CO<sub>2</sub>-rich H<sub>2</sub> atmospheres over a Ru/zeolite catalyst: The influence of catalyst calcination. *J. Catal.* **2013**, *298*, 148–160.
- (30) Huang, Y.; Adeeva, V.; Sachtler, W. M. H. Stability of supported transition metal catalysts in the hydrogenation of nitriles. *Appl. Catal., A* **2000**, *196*, 73–85.
- (31) McCarthy, T. J.; Marques, C. M. P.; Trevino, H.; Sachtler, W. M. H. Suppressed hydrogen chemisorption of zeolite encaged metal clusters: discrimination between theoretical models on the basis of Ru/NaY. *Catal. Lett.* **1997**, *43*, 11–18.
- (32) Chakroune, N.; Viau, G.; Ammar, S.; Poul, L.; Veautier, D.; Chehimi, M. M.; Mangeney, C.; Villain, F.; Fievet, F. Acetate- and thiol-capped monodisperse ruthenium Nanoparticles: XPS, XAS and HRTEM Studies. *Langmuir* **2005**, *21*, 6788–6796.
- (33) Hu, L.; Tang, X.; Xu, J. X.; Wu, Z.; Lin, L.; Liu, S. J. Selective transformation of 5-hydroxymethylfurfural into the liquid fuel 2,5-dimethylfuran over carbon-supported ruthenium. *Ind. Eng. Chem. Res.* **2014**, *53*, 3056–3064.
- (34) Nikbin, N.; Caratzoulas, S.; Vlachos, D. G. On the Brønsted acid-catalyzed homogeneous hydrolysis of furans. *ChemSusChem* **2013**, *6*, 2066–2068.
- (35) Bui, L.; Luo, H.; Gunther, W. R.; Roman-Leshkov, Y. Domino reaction catalyzed by zeolites with Brønsted and Lewis acid sites for the production of  $\gamma$ -valerolactone from furfural. *Angew. Chem., Int. Ed.* **2013**, *52*, 8022–8025.
- (36) Nishimura, S.; Ikeda, N.; Ebitani, K. Selective hydrogenation of biomass-derived 5-hydroxymethylfurfural (HMF) to 2,5-dimethylfuran (DMF) under atmospheric hydrogen pressure over carbon supported PdAu bimetallic catalyst. *Catal. Today* **2014**, *232*, 89–98.
- (37) Tuteja, J.; Choudhary, H.; Nishimura, S.; Ebitani, K. Direct synthesis of 1,6-hexanediol from HMF over a heterogeneous Pd/ZrP catalyst using formic acid as hydrogen source. *ChemSusChem* **2014**, *7*, 96–100.
- (38) Huang, Y. B.; Chen, M. Y.; Yan, L.; Guo, Q. X.; Fu, Y. Nickel-tungsten carbide catalysts for the production of 2,5-dimethylfuran from biomass-derived molecules. *ChemSusChem* **2014**, *7*, 1068–1072.
- (39) Takagi, H.; Isoda, T.; Kusakabe, K.; Morooka, S. Effects of solvents on the hydrogenation of mono-aromatic compounds using noble-metal catalysts. *Energy Fuels* **1999**, *13*, 1191–1196.
- (40) Fang, M.; Machalaba, N.; Sanchez-Delgado, R. A. Hydrogenation of arenes and N-heteroaromatic compounds over ruthenium nanoparticles on poly(4-vinylpyridine): a versatile catalyst operating by a substrate-dependent dual site mechanism. *Dalton Trans.* **2011**, *40*, 10621–10632.
- (41) Hajek, J.; Kumar, N.; Maki-Arvela, P.; Salmi, T.; Murzin, D. Y.; Paseka, I.; Heikkilä, T.; Laine, E.; Laukkanen, P.; Vayrynen, J. Ruthenium-modified MCM-41 mesoporous molecular sieve and Y zeolite catalysts for selective hydrogenation of cinnamaldehyde. *Appl. Catal., A* **2003**, *251*, 385–396.