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Renewable fuels from biomass-derived compounds: Ru containing hydrotalcites as catalysts for 2,5-dimethylfuran from HMF

Atul S. Nagpure, Ashok Kumar Venugopal, Nishita Lucas, Marimuthu Manikandan, Raja Thirumalaiswamy* and Satyanarayana Chilukuri*

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Production of transportation fuels from renewable biomass is hugely important considering the current ecological concerns over CO₂ built up in the atmosphere. Ruthenium containing hydrotalcite (HT) catalysts were applied for the selective hydrogenolysis of biomass-derived 5-hydroxymethylfurfural (HMF) to 2,5-dimethylfuran (DMF). Structural and morphological features of the catalysts were examined using various physico-chemical characterization techniques. Influence of various reaction parameters, such as reaction temperature, solvent and Ru content of the catalyst etc., were investigated with respect to HMF conversion and DMF yield. The study clearly shows that well dispersed Ru nanoparticles are highly active and selective in the conversion of HMF to DMF. A catalyst containing only 0.56 wt% Ru converted 100 mol% of HMF to yield 58 mol% of DMF. This catalyst was found to be recyclable as the activity was retained even after five cycles of reaction. 2-Propanol was found to be good solvent as it helped to improve DMF yield due to transfer hydrogenation. Based on the investigations, a reaction pathway for HMF to DMF was proposed for the present Ru based catalyst system.

1. Introduction

At present, there is an alarmingly heavy dependence on fossil fuels, which is not sustainable. Moreover, their indiscriminate use is leading to ecological problems. Hence, utilization of biomass to produce renewable fuels and valuable chemical intermediates is gaining increasing attention.¹⁻⁴ Hydrogenolysis is an important process in the biomass refinement, as biomass-derived materials have high oxygen content.^{5,6} 5-Hydroxymethylfurfural (HMF), an important platform chemical, that can be synthesized from hexoses, has been identified as a key player in the bio-based renaissance. It can be converted to levulinic acid, ethyl levulinate, γ -valerolactone and the highly promising transportation fuel additive 2,5-dimethylfuran (DMF).⁷⁻¹² The DMF is particularly attractive due to its superior energy density (30 kJcm⁻³), high research octane number (RON=119) and ideal boiling point (92-94 °C).⁸ Further, DMF is immiscible with water and also easier to blend with gasoline compared to ethanol. Biomass derived DMF has been tested as a biofuel in a single-cylinder gasoline direct-injection research engine.¹³ The performance of DMF was satisfactory against gasoline in terms of ignition, emission and combustion characteristics. These attributes bode very well for the use of DMF as an alternative fuel for transportation.

There were several recent reports on the conversion of biomass to DMF. Dumesic and co-workers utilized a two step process to convert fructose to DMF.⁸ The first step involved the dehydration of fructose to HMF using HCl in a biphasic solvent system, followed by vapor phase hydrogenolysis of HMF to DMF, using a Cu-Ru/C catalyst. Thananathanachon and Rauchfuss showed a milder pathway for the production of DMF using formic acid as a reagent and Pd/C as catalyst.¹⁴ Formic acid functioned as a hydrogen donor during the second step, which also assists in the deoxygenation of HMF to DMF. To get high yield of DMF, formic acid and H₂SO₄ have to be used simultaneously. But, both the acids are not environment friendly. Chidambaram and Bell used Pd/C as a catalyst in ionic liquids to convert 47 mol% of HMF, to yield 15 mol% DMF.¹⁵ A potential drawback of this method is the low solubility of H₂ in ionic liquids. As a result, high pressure of H₂ (62 bar) has to be used, making the process highly energy intensive.

Hansen et al. reported catalytic transfer hydrogenation (CTH) of HMF over Cu-containing mixed metal oxides using supercritical methanol that yielded 48 mol% DMF.¹⁶ Gallo et al. studied the hydrogenolysis of HMF in the presence of lactones using a RuSn/C catalyst to get DMF yields up to 46 mol%.¹⁷ Yang and Sen reported the conversion of biomass-derived carbohydrates to 2,5-dimethyltetrahydrofuran (DMTHF), an alternate fuel that can be obtained on further hydrogenation of DMF, using homogeneous RhCl₃ and RuCl₃ catalysts.^{18,19} The same research group has also reported the synthesis of 5-methyl furfural (MF) from fructose using heterogeneous Pd/C as

Catalysis Division, CSIR- National Chemical Laboratory,
Dr. Homi Bhabha Road, Pune-411008, India,
Tel.: +91-20-25902019; Fax: +91-20-25902633.

E-mail: sv.chilukuri@ncl.res.in (Dr. Satyanarayana Chilukuri)
t.raja@ncl.res.in (Dr. T. Raja)

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catalyst.²⁰ Morikawa et al. studied the CTH of HMF using cyclohexane over AlCl₃ and Pd/C catalysts for a DMF yield of 60 mol%.²¹ These CTH routes, however, have several disadvantages including that of using mineral acids as co-catalysts to enhance hydrogenation activity.^{14,22,23}

Recently, it was suggested that the use of catalysts with high amount of precious metal is not conducive to the overall process economics for the production of liquid transportation fuels from biomass-derived compounds.²⁴ Commercial application of the HMF to DMF process will be feasible only by developing a strategy that minimizes the precious metal content of the catalyst. The Ru based catalysts are known for their effectiveness in the hydrogenolysis of polyols to alkanes.^{25,26} Hence, in the present report we have demonstrated for the first time, the efficiency of Ru doped hydrotalcite (HT) catalyst with very low (0.56 wt%) Ru content for the hydrogenolysis of HMF to DMF. This catalyst showed high catalytic activity and DMF selectivity, in addition excellent re-usability for the conversion of HMF to DMF. Effect of various reaction parameters was also investigated on the performance of the catalyst by variation of solvent, reaction temperature, H₂ pressure and the Ru metal content in the catalyst. These Ru based HT catalysts have significant potential for further development and are expected to pave the way for realising the goal of renewable liquid fuels from biomass.

2. Results and discussion

2.1. Structural and morphological characteristics of the catalysts

Structural, textural and morphological characteristics of the as synthesized Ru doped HT samples (RH-1, RH-2 and RH-3) along with corresponding HT precursor were investigated. Fig. 1a shows XRD profiles of as synthesized samples, that have characteristic peaks belonging to pure HT ($d_{(003)} = 7.65 \text{ \AA}$). No extraneous peaks belonging to other phases (JCPDS. No. 70-2151) were seen. These results show that Ru may be present in the brucite-like lattice of HT, as no peaks corresponding to any of ruthenium or its oxide phases were seen. The intensities of reflections, pertaining to layered structure decreased with increasing Ru content of the sample. The XRD pattern of calcined-reduced Ru doped HT derived catalysts (RH-1, RH-2 and RH-3) are given in Fig. 1b, which also includes the spectra of Ru impregnated sample (RH-imp). The RH-imp has Ru content similar to that of RH-1. The reflections belonging to periclase phase of Mg(Al)O (JCPDS. No. 4-829) were seen predominantly. In addition to mixed metal oxide phase, metallic Ru peaks were also present in the case of higher Ru containing catalysts (RH-3). The BET surface areas of calcined HT (HT_{cal}) and calcined-reduced Ru containing catalysts are given in Table 1. Surface areas of HT_{cal}, RH-1, RH-2, RH-3 and RH-imp were 210, 194, 180, 142 and 185 m²/g, respectively. The surface area decreased with increasing Ru content of the sample, when compared to HT_{cal}. The decrease in surface area may either be attributed to the poor crystallinity, as reflected in lower XRD intensities (Fig. 1) or due to the blockage of pores by segregated Ru-oxide phases of the sample.²⁷

The morphologies of the HT and Ru doped HT precursors were investigated by SEM. Some of their representative images are shown in Fig. 2. The micrographs demonstrate flower-like

morphology²⁸ of parent HT, which has not changed even after Ru incorporation. Dispersion of Ru in the Ru-containing catalysts was investigated by H₂ chemisorption. The Ru metal dispersion, average crystallite size and metal surface areas are included in Table 1. The metal dispersions were: RH-1, 47.6%; RH-2, 33.1%; RH-3, 10.3% and RH-imp, 32.4%. Good Ru dispersion in RH-1 catalyst (47.6%) confirms homogeneous distribution of Ru on the metal oxide support with average Ru crystallite size of 2.8 nm. The Ru particle sizes as well as its distribution were also investigated by TEM. These results are shown in Fig. 3. Micrographs of RH-1 shows that Ru nanoparticles are in the 2-6 nm range, dispersed over the HT derived metal oxide support. The average particle size of Ru was 3.1 nm, calculated through surface area averaged TEM particle size by assuming that the Ru particles are hemispherical in shape, with the flat side on the support. These values for the three catalysts, RH-1, RH-2 and RH-3, are in close agreement with the values obtained from H₂ chemisorption (Table 1; Table S1, ESI†).

Temperature programmed reduction (TPR) studies helped to understand the reducibility of the Ru supported on mixed oxides. TPR profiles (Fig. 4) comprised of two H₂ consumption peaks. The first reduction peak is in the range of 120-190 °C, while the second is in 200-330 °C range. These peaks must be due to different interactions of RuO_x species with the support.²⁹ The low temperature peak is probably due to the weak interaction of Ru with the support, while the high temperature peak may be due to stronger interaction of Ru with the support. In case of RH-1, the intensity of the low temperature peak was weak. But, its intensity enhanced with increasing Ru content, implying that loosely bound Ru concentration increased. There is also a shift of high temperature peak towards low temperature at high Ru content, particularly in the case of impregnated catalyst. In case of RH-imp sample, both low and high temperature peaks have merged.

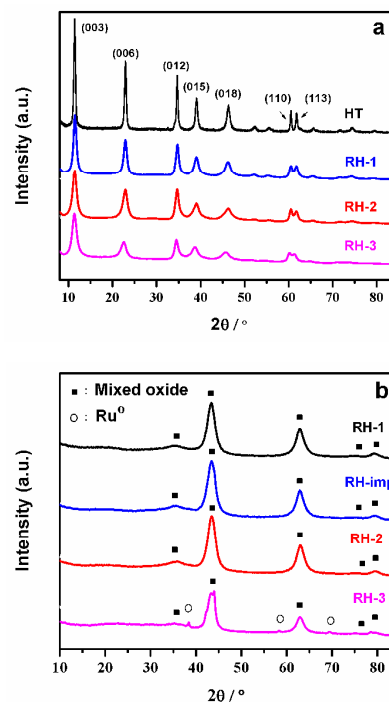
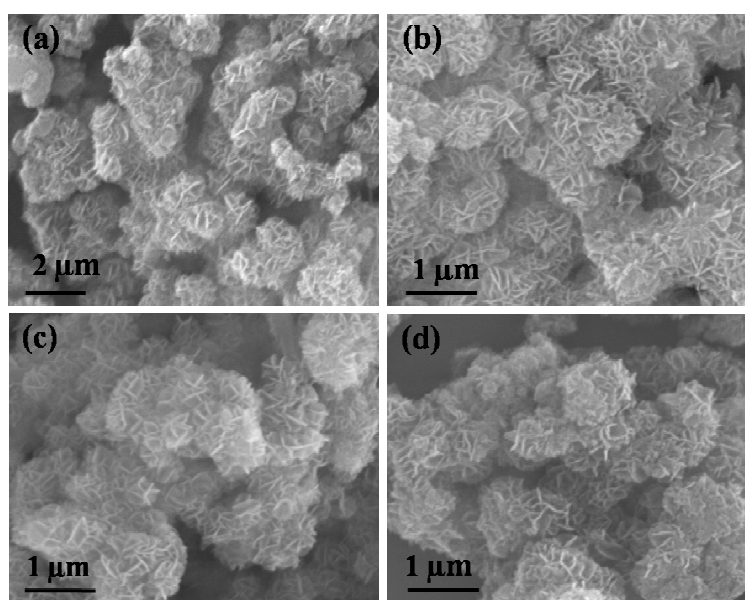
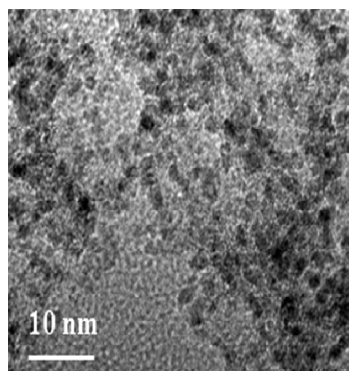
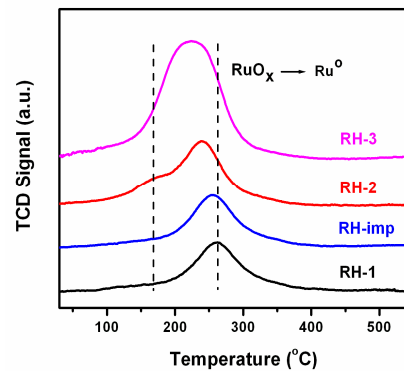
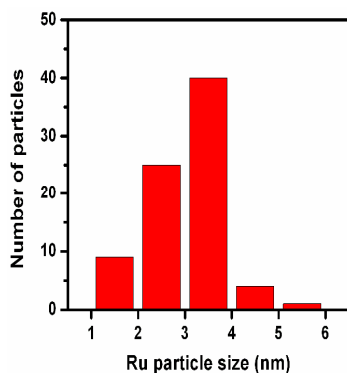


Fig. 1 X-ray diffractograms of (a) as synthesized precursors and (b) calcined-reduced catalysts.

Table 1 Chemical composition and structural characteristics of the catalysts.

| Catalyst ^a | Synthesis composition Mg:Al:Ru | Ru content (wt%) ^b | BET surface area (m ² /g) ^c | Ru metal dispersion (%) ^d | Average Ru crystallite size (nm) ^d | Average Ru particle size (nm) ^e | Ru metal surface area (m ² /g) ^d |
|-----------------------|--------------------------------|-------------------------------|---|--------------------------------------|---|--|--|
| HT _{cat} | 3:1:0 | 0 | 210 | --- | --- | --- | --- |
| RH-1 | 3:0.97:0.03 | 0.56 | 194 | 47.6 | 2.8 | 3.1 | 0.97 |
| RH-2 | 3:0.94:0.06 | 1.0 | 180 | 33.1 | 4.0 | 4.3 | 1.20 |
| RH-3 | 3:0.90:0.10 | 1.7 | 142 | 10.3 | 12.9 | 14.0 | 0.56 |
| RH-imp ^f | 3:0.97:0.03 | 0.58 | 185 | 32.4 | 4.1 | --- | 1.18 |

^a Catalyst precursors prepared by co-precipitation. ^b Estimated by ICP-OES. ^c Calcined-reduced samples. ^d Determined by H₂ chemisorption. The catalysts were calcined at 450 °C and reduced at 350 °C for metal dispersion studies. ^e Calculated based on surface area averaged TEM particle size, ^f Prepared by dry-impregnation method.

**Fig. 2** SEM images of as synthesized (a) HT, (b) RH-1, (c) RH-2 and (d) RH-3 catalyst.**Fig. 3** TEM micrograph and Ru particle size distribution on RH-1 catalyst.**Fig. 4** TPR profiles of various Ru catalysts.

2.2. Catalytic activity in hydrogenolysis of HMF to DMF

2.2.1. Effect of reaction temperature

The influence of reaction temperature on HMF conversion and DMF yield over RH-1 catalyst were systematically investigated by varying the reaction temperature in 180-230 °C temperature range. The HMF conversions and DMF yields are shown in Fig. 5 and Fig. 6, respectively. It can be clearly seen (Fig. 5) that the temperature played an important role with regard to HMF conversion, as it has increased on raising the reaction temperature. In addition, HMF conversion also increased with reaction time. After 4 h of reaction, HMF conversion increased from 70 to 100 mol%, on raising the reaction temperature from 180 to 210 °C. On the other hand, complete conversion of HMF could be seen within 2 h of the reaction, when the reaction was carried out in the 220-230 °C temperature range. Moreover, the reaction temperature has a profound influence on DMF yield, as may be seen in Fig. 6. The DMF yield increased continuously as a function of reaction time, when the reaction temperature was raised from 180 to 210 °C, indicating that intermediates like 2,5-bis(hydroxymethyl)furan (BHMF), 5-methyl furfuryl alcohol (MFA) and MF that formed during the course of the reaction were converted to DMF with increasing reaction temperature as well as with reaction time.^{8,15} On further increasing the reaction temperature to 220 °C, a high DMF yield of 58 mol% could be reached after 4 h of reaction time. But, the DMF yield has fallen on further increasing the reaction time (Fig. 6 and entry 3, Table 3). This fall in DMF yield could be attributed to its ring hydrogenation leading to the formation of DMTHF. The DMF yield decreased continuously at higher reaction temperature (230 °C), which clearly implies that the ring hydrogenation is predominant at higher reaction temperatures (entry 4, 5 and 6, Table 3), leading to the formation of DMTHF as a principal product.¹⁶ Thus, 220 °C seems to be optimum temperature to get good yield of DMF after 4 h of reaction with this catalyst.

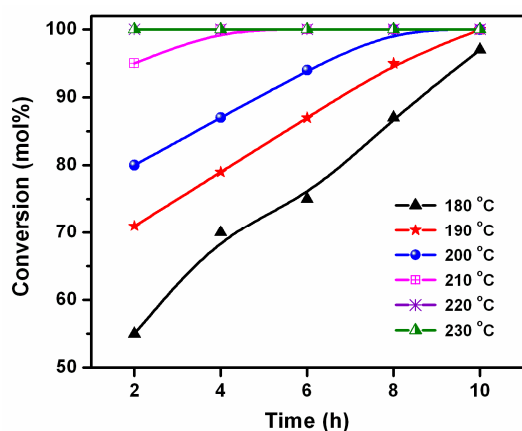


Fig. 5 Effect of reaction temperature on HMF conversion as a function of reaction time. Reaction conditions: HMF (1 mmol, 126 mg); catalyst (RH-1, 50 mg); H₂ pressure (10 bar); solvent (2-propanol, 25 mL); stirring speed (500 rpm).

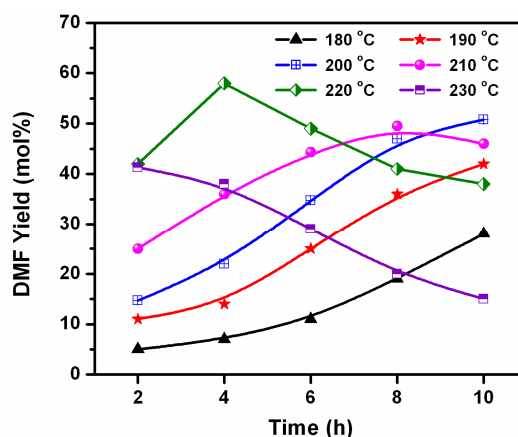


Fig. 6 Effect of reaction temperature on DMF yield as a function of reaction time. Reaction conditions: HMF (1 mmol, 126 mg); catalyst (RH-1, 50 mg); H₂ pressure (10 bar); solvent (2-propanol, 25 mL); stirring speed (500 rpm).

2.2.2. Effect of solvent

Effect of solvent on the catalytic activity in the liquid-phase hydrogenolysis of HMF to DMF was investigated over RH-1 catalyst at 220 °C and at 7 bar H₂ pressure. Solvents of different chemical nature, such as protic (2-propanol), aprotic polar (tetrahydrofuran (THF) and 1,2-dimethoxyethane (1,2-DME)) and non-polar (toluene) solvents were used to investigate the influence on hydrogenolysis activity and DMF selectivity. The results given in Fig. 7 clearly show that the RH-1 activity is heavily solvent dependent. It can be seen that the catalytic activity follows the order; 2-propanol > THF ≈ 1,2-DME > toluene. The lower HMF hydrogenolysis activity in toluene could be explained on the basis of competitive adsorption between reactant and solvent on the active catalytic sites. Moreover, with toluene as a solvent, hydrogenated compounds of toluene were observed under the reaction conditions studied. Competitive adsorption between toluene and HMF on the active catalytic results in reduced availability of active sites for the HMF. As a result, hydrogenolysis activity of HMF drops down. Toluene adsorption strength is controlled by the degree of overlap of the carbon π molecular orbitals with the d bands of Ru metal.³⁰

To understand the reason behind the superior activity in presence of 2-propanol, experimental runs were carried out in the absence of H₂ at 220 °C under 5 bar N₂ pressure over RH-1, RH-2, RH-3 and RH-imp catalysts (Fig. S1, ESI†). Catalyst RH-1 exhibited superior activity in terms of CTH, compared to other catalysts probably due to the smaller Ru crystallite size. The results of the CTH experiments, using RH-1 in the absence of H₂, with different solvents is given in Fig. 8. About 14 mol% DMF yield was seen after 5 h of reaction with 2-propanol as solvent. Acetone was detected as one of the product in this experiment, implying hydrogen transfer from 2-propanol. However, the 2-propanol consumed for the purpose of CTH was low (<1 mol%), as it was used as solvent at high solvent to substrate molar ratio (>300). No CTH was seen when THF or 1,2-DME were used as solvents under similar conditions. These results strongly suggest that in 2-propanol, HMF is hydrogenated on RH-1 catalyst via an

additional reduction mechanism involving hydrogen transfer from 2-propanol to HMF in the presence of Ru metal catalyst.³⁰ Thus, HMF is getting hydrogenated by molecular H₂ as well as by hydrogen transfer from 2-propanol over the catalyst (Fig. S2, ESI[†]). However, the rate of HMF hydrogenation using molecular H₂ is comparatively much higher than that of CTH (difference in DMF yield in Fig. 7 and Fig. 8). To understand this aspect further, effect of temperature, effect of Ru content and effect of H₂ pressure were investigated with THF as solvent, which is not expected to be reactive in the given conditions. These results are given in supporting information (Fig. S3, Fig. S4 and Fig. S5, ESI[†]). Unlike 2-propanol, variation of any of the reaction

parameter did not lead to change in DMF yield, clearly demonstrating the advantage of 2-propanol as solvent. In view of higher apparent catalytic activity and superior DMF yield, 2-propanol was chosen as the solvent for further investigations. It is well known that there are differences between heterogeneous catalytic hydrogenation using hydrogen donor molecules as the source of hydrogen and hydrogenation using molecular H₂.³¹ The CTH reaction could occur through direct hydride transfer from 2-propanol to HMF. Further investigations are required to delineate the mechanism for hydrogenolysis using 2-propanol as the hydrogen source.

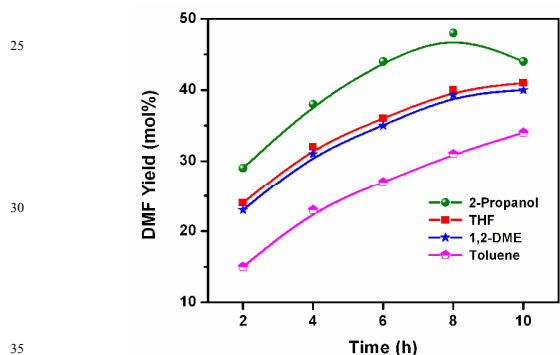


Fig. 7 Effect of solvent on DMF yield as a function of reaction time. Reaction conditions: HMF (1 mmol, 126 mg); catalyst (RH-1, 50 mg); temperature (220 °C); solvent (25 mL); H₂ pressure (7 bar); stirring speed (500 rpm).

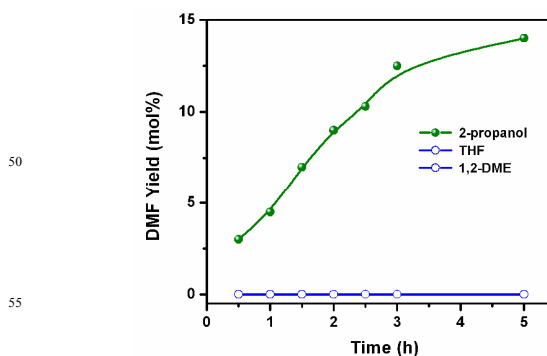
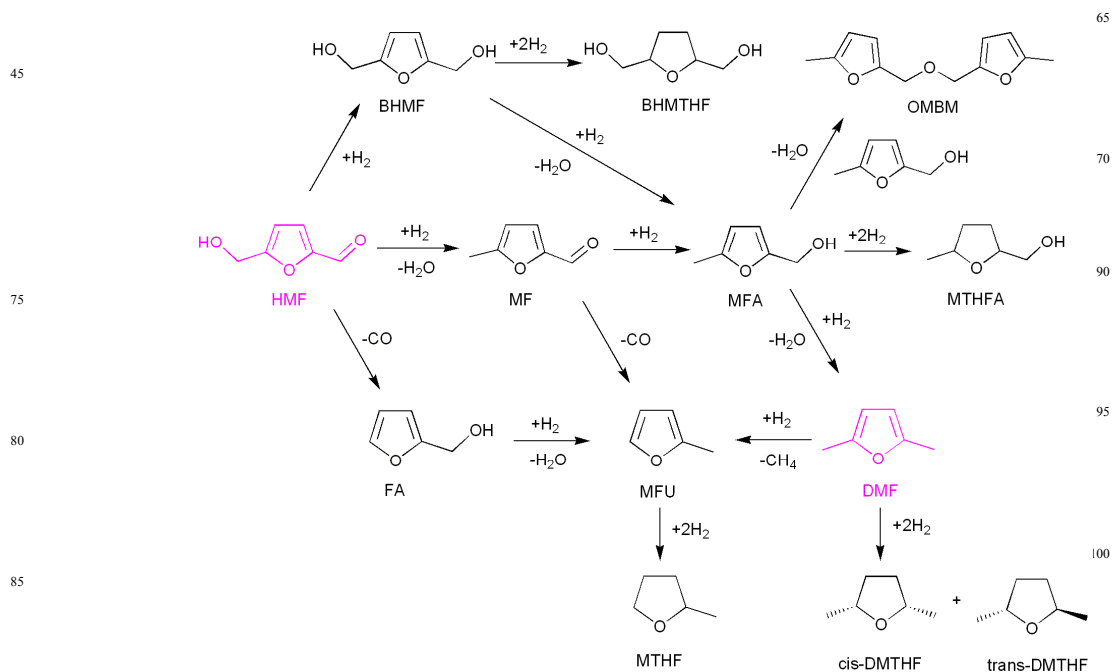


Fig. 8 CTH of HMF as a function of reaction time over RH-1 catalyst. Reaction conditions: HMF (1 mmol, 126 mg); catalyst (50 mg); temperature (220 °C); solvent (25 mL); N₂ pressure (5 bar); stirring speed (500 rpm).



Scheme 1 Reaction network of the hydrogenolysis of HMF to DMF over RH-1 catalyst.

Compounds: 5-hydroxymethylfurfural (HMF); 2,5-bis(hydroxymethyl)furan (BHMTHF); 5-methyl furfural (MF); 5-methyl furfuryl alcohol (MFA); furfuryl alcohol (FA); 2,5-bis(hydroxymethyl)tetrahydrofuran (BHMTHF); 5-methyltetrahydrofurfuryl alcohol (MTHFA); 5,5'-(oxybis(methylene))bis(2-methylfuran) (OMBM); 2,5-dimethylfuran (DMF); cis-2,5-dimethyltetrahydrofuran (cis-DMTHF); 2-methylfuran (MFU); trans-2,5-dimethyltetrahydrofuran (trans-DMTHF); 2-methyltetrahydrofuran (MTHF).

Table 2 Product distributions during HMF hydrogenolysis over different catalysts.^a

| Entry | Catalyst | HMF conv. (mol%) | Yield (mol%) | | | | | | | | TOF (h ⁻¹) ^c |
|-------|-------------------|------------------|--------------|-------|------|-----|----|--------|-----|---------------------|-------------------------------------|
| | | | DMF | DMTHF | BHMF | MFA | MF | BHMTHF | MFU | Others ^b | |
| 1 | RH-1 | 100 | 58 | 6 | 5 | 8 | 4 | 2 | 3 | 14 (3) | 52.3 |
| 2 | RH-2 | 100 | 48 | 10 | 8 | 11 | 5 | 6 | 1 | 11 (4) | 24.4 |
| 3 | RH-3 | 92 | 35 | 9 | 8 | 8 | 4 | 15 | 2 | 11 (7) | 10.4 |
| 4 | RH-imp | 100 | 45 | 8 | 7 | 12 | 4 | 7 | 2 | 15 (4) | 39.0 |
| 5 | HT _{cal} | 32 | <1 | 0 | 1 | 1 | 0 | 0 | 0 | 29 (29) | -- |
| 6 | none | 8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 8 (8) | -- |

^a Reaction conditions: HMF (1 mmol, 126 mg); catalyst (50 mg); temperature (220 °C); H₂ pressure (10 bar); solvent (2-propanol, 25 mL); reaction time (4 h); stirring speed (500 rpm). ^b It includes 5-methyltetrahydrofurfuryl alcohol (MTHFA), furfuryl alcohol (FA), 5,5'-(oxybis(methylene))bis(2-methylfuran) (OMBM), 2,5-bis(hydroxymethyl)tetrahydrofuran (BHMTHF) and other unidentified products (condensation products, value in the bracket corresponding to the unidentified products). ^c TOF = Turnover frequency (moles of DMF produced per mole of Ru).

2.2.3. Effect of Ru metal content of catalysts

To optimise the Ru content of the catalyst, a series of catalysts with different wt% of Ru were prepared and evaluated for HMF hydrogenolysis. The HMF conversions and product yields are summarized in Table 2 (Fig. S2, ESI[†]). Catalyst RH-1 has shown the highest activity in terms of HMF hydrogenolysis, yielding 58 mol% DMF at 100 mol% HMF conversion (entry 1, Table 2). However, under similar reaction conditions, DMF yields were only 48, 35 and 45 mol% over RH-2, RH-3 and RH-imp catalysts, respectively. When Ru content was low (RH-1 with 0.56 wt% Ru), smaller yield of hydrogenated products of BHMF and DMF were observed, that led to high yield of DMF. On the other hand, over high Ru containing catalysts (RH-2 and RH-3) significant increase in the yields of ring hydrogenated products such as 2,5-bis(hydroxymethyl)tetrahydrofuran (BHMTHF) and DMTHF were observed. This could be a result of larger Ru crystallite size in these catalysts (Table 1). However, the metal surface areas of RH-2 and RH-imp were higher than RH-1 (Table 1). Even then, RH-1 was found to be superior, as the smaller crystallite size (2.8 nm) suppresses ring hydrogenation thus leading to better DMF yield over RH-1. This is a welcome result, as low Ru containing hydrotalcite catalyst (RH-1) can achieve high DMF yield (58 mol%), which may be helpful for economic production of transportation fuels from biomass.

To ascertain the desirability of Ru in the catalyst, HMF hydrogenolysis was carried out in its absence, using only HT_{cal}, which gave <1 mol% DMF yield (entry 5, Table 2). Blank experiments with HMF in 2-propanol, in the absence of catalyst, showed no activity for DMF formation (entry 6, Table 2). But, minor amounts of by-products, probably as a result of HMF polymerization and condensation reactions were observed in the absence of catalyst.

2.2.4. Effect of H₂ pressure

The influence of H₂ pressure on the HMF hydrogenolysis was studied by varying the pressure in the range of 1-13 bar. Results of these experiments are given in Fig. 9. When the reaction was

carried out in the low pressure range (1 to 7 bar), the intermediate products such as BHMF, MFA and MF formed in significant quantities, showing that the hydrogenolysis was incomplete. As a result, only 48 mol% DMF yield was obtained even after 8 h of reaction under 7 bar H₂ pressure. On increasing the H₂ pressure to 10 bar, the DMF yield reached maximum (58 mol%) over RH-1 catalyst within 4 h of reaction. But, the DMF yield decreased on continuation of the reaction for further duration (Fig. 9 and entry 3, Table 3). Similarly, increasing the H₂ pressure further to 13 bar has an adverse affect on DMF yield, mostly due to increased rate of consecutive ring hydrogenation of DMF, leading to the DMTHF formation in significant quantities (entry 8, 9 and 10, Table 3). Moreover, the concentration of other unwanted by-products such BHMTHF and 5-methyltetrahydro-furfuryl alcohol (MTHFA) increased at higher pressure (13 bar). These results clearly show that at higher H₂ pressures, ring hydrogenation is predominant reaction leading to the lower yield of DMF (Table 3). Hence, 10 bar of H₂ pressure was found to be optimum, which was used for further investigations.

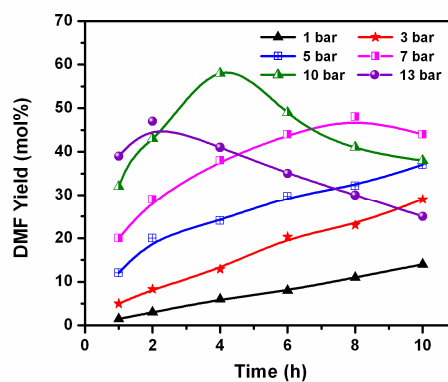


Fig. 9 Effect of H₂ pressure on DMF yield as a function of reaction time. Reaction conditions: HMF (1 mmol, 126 mg); catalyst (RH-1, 50 mg); temperature (220 °C); solvent (2-propanol, 25 mL); stirring speed (500 rpm).

2.2.5. Effect of catalyst content

Amount of catalyst used in the reaction is an important parameter that needs to be optimized to get high DMF yield. Experiments were conducted by varying the amount of RH-1 catalyst from 15 to 70 mg at 220 °C, while maintaining the same substrate content (Fig. 10). These experiments showed that the DMF yield increased initially with catalyst content. When catalyst was 15 mg, the DMF yield reached maximum of 40 mol% after 12 h of reaction, which declined on further increasing the reaction time. When 30 mg of catalyst was used, DMF yield reached to 46 mol% in slightly shorter duration (10 h) of reaction time. With 50 mg of catalyst, the maximum DMF yield of 58 mol% was accomplished only in 4 h reaction time, but it decreased when the reaction was continued further, mostly due to ring hydrogenation of DMF. However, when the catalyst content was further increased to 70 mg, a much lower DMF yield of 44 mol% was achieved, which reduced with further increasing time on stream. These results show that with increased duration of reaction even at low catalyst content, the DMF undergoes consecutive hydrogenation leading to DMTHF formation. At higher catalyst contents, more active sites are available, which drive the formation of side products such as MFU and MTHF in addition to hydrogenated products MTHFA and DMTHF, leading to lower DMF yield. Hence, optimization of catalytic sites and reaction time are essential to obtain maximum DMF yield. Based on these studies, 50 mg of catalyst was found to be optimum under the given reaction conditions.

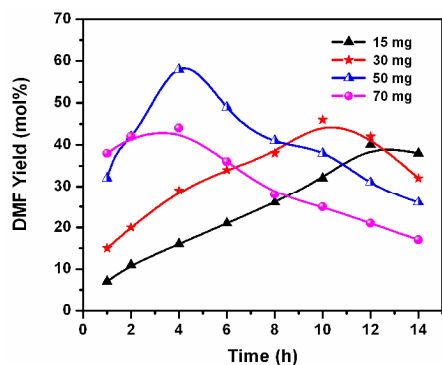


Fig. 10 Effect of catalyst content on DMF yield as a function of reaction time over RH-1 catalyst.

Reaction conditions: HMF (1 mmol, 126 mg); temperature (220 °C); H₂ pressure (10 bar); solvent (2-propanol, 25 mL); stirring speed (500 rpm).

2.2.6. Proposed reaction pathway

To understand the reaction network of HMF hydrogenolysis to DMF, studies were carried out at lower temperature (180 °C) while monitoring the products as a function of time using RH-1 catalyst. The results are shown in Fig. 11. When the reaction time was increased from 1 to 10 h, the conversion of HMF increased from 40 to 97 mol% and the concentration of products changed in a complex manner. The yield of DMF increased continuously with reaction time, while the yield of BHMF reached plateau at 38 mol% after 5 h and then decreased with increasing reaction time. The MFA yield also showed a similar trend like that of BHMF, passing through the maximum at 4 h. Though MF, DMTHF and MFU were also observed in the product, their yields were low during the entire duration of the reaction. The low yield of MF may be attributed to the fact that it does not form fast enough. Based on these results, a reaction network of HMF hydrogenolysis to DMF is proposed (Scheme 1).

DMTHF and MFU were also observed in the product, their yields were low during the entire duration of the reaction. The low yield of MF may be attributed to the fact that it does not form fast enough. Based on these results, a reaction network of HMF hydrogenolysis to DMF is proposed (Scheme 1).

To validate the proposed reaction sequence in scheme 1, hydrogenolysis experiments were conducted with MF as the starting substrate. The results (Fig. 12) demonstrate that MF has been quite reactive. Within 3 h of reaction time, this intermediate was converted principally to MFA and DMF. With the increasing reaction time, the yield of MFA decreased but DMF yield increased. The results of this experiment show that the rate of MF hydrogenation to MFA is fast, with subsequent hydrogenolysis of MFA to DMF being very rapid. Low yield of DMTHF and MFU were also observed, whose concentration increased with time followed by the formation of DMF.

The cis- and trans-DMTHF isomers have different physical properties, e.g. boiling points, which can be distinguished and quantified by GC-FID. Our experiments show that the formation of cis-DMTHF is favoured over the trans-DMTHF, with a cis:trans molar ratio of \approx 6.5:1 under the given experimental conditions (Table 3). This may be explained in terms of steric crowding. During the course of reduction reaction, addition of the second hydrogen molecule takes place to the same face as the first would result in less steric hindrance, whereas hydrogen molecule may be sterically crowded by the methyl group restricting the formation of trans-DMTHF (Scheme 2).

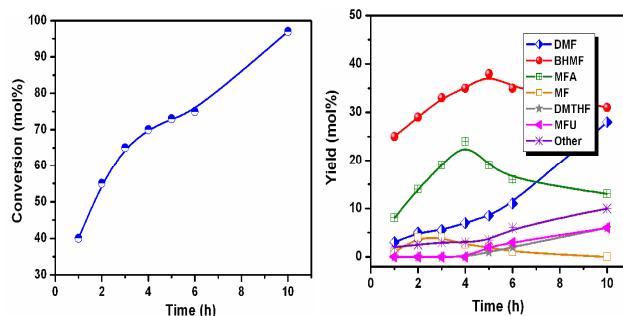


Fig. 11 Conversion of HMF and product yields as a function of time at 180 °C. Left: Conversion of HMF. Right: Yields of various products.

Reaction conditions: HMF (1 mmol, 126 mg); catalyst (RH-1, 50 mg); H₂ pressure (10 bar); solvent (2-propanol, 25 mL); stirring speed (500 rpm).

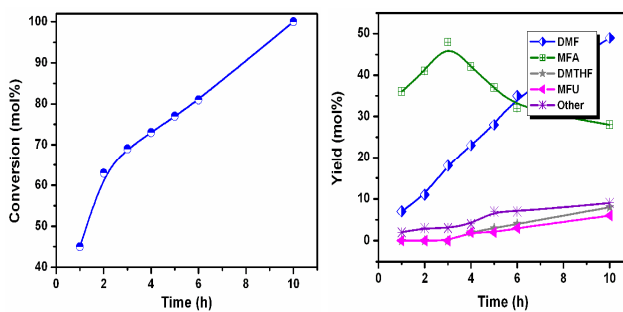


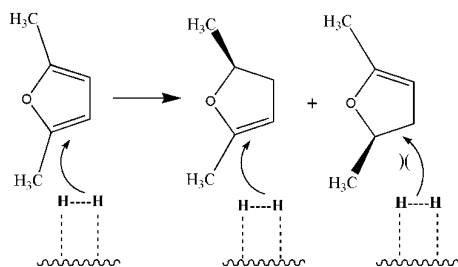
Fig. 12 Conversion of MF and product yields as a function of time at 180 °C. Left: Conversion of MF. Right: Yields of various products.

Reaction conditions: MF (1 mmol, 110 mg); catalyst (RH-1, 50 mg); H₂ pressure (10 bar); solvent (2-propanol, 25 mL); stirring speed (500 rpm).

Table 3 Effect of reaction temperature and hydrogen pressure on DMTHF yield.^a

| Entry | Time (h) | Temp (°C) | DMF yield (mol%) | DMTHF yield (mol%) | cis : trans ratio of DMTHF |
|-----------------|----------|-----------|------------------|--------------------|----------------------------|
| 1 | 4 | 210 | 36 | 3 | 6.3 |
| 2 | 4 | 220 | 58 | 6 | 6.2 |
| 3 | 6 | 220 | 49 | 15 | 6.7 |
| 4 | 4 | 230 | 38 | 17 | 6.6 |
| 5 | 6 | 230 | 29 | 26 | 6.4 |
| 6 | 8 | 230 | 20 | 32 | 6.5 |
| 7 ^b | 4 | 220 | 38 | 2 | 6.1 |
| 8 ^c | 2 | 220 | 47 | 7 | 6.8 |
| 9 ^c | 4 | 220 | 41 | 12 | 6.6 |
| 10 ^c | 6 | 220 | 35 | 21 | 6.6 |
| 11 ^d | 4 | 220 | 30 | 19 | 6.7 |

^a Reaction conditions: HMF (1 mmol, 126 mg); catalyst (RH-1, 50 mg); H₂ pressure (10 bar); solvent (2-propanol, 25 mL); stirring speed (500 rpm). ^b H₂ pressure (7 bar). ^c H₂ pressure (13 bar). ^d H₂ pressure (16 bar).



Scheme 2 Mechanism for the preferential formation of cis-DMTHF isomer over the trans-DMTHF isomer from DMF over RH-1 catalyst.

2.2.7. Recyclability of the catalyst

Catalyst recyclability is of great importance in order to apply the best found catalytic system and convert it into an industrial process. The recyclability of the RH-1 catalyst was evaluated by repeating the reaction with the same catalyst at least five times without any regeneration/activation (Fig. 13 and Fig. S7, ESI†). The results show that the catalyst remains active even after five cycles, though minor drop in DMF yield was observed probably due to blockage of some catalytic sites. However, on regeneration by calcination-reduction steps, 100% activity was restored. These results indicate good stability of the catalyst. Product mixture at the end of each recycle was analyzed by ICP-OES, for the presence of any Ru due to leaching out of the catalyst. No such leaching was observed. Moreover, the concentration of Ru in the catalyst was similar to that of starting catalyst even after five cycles.

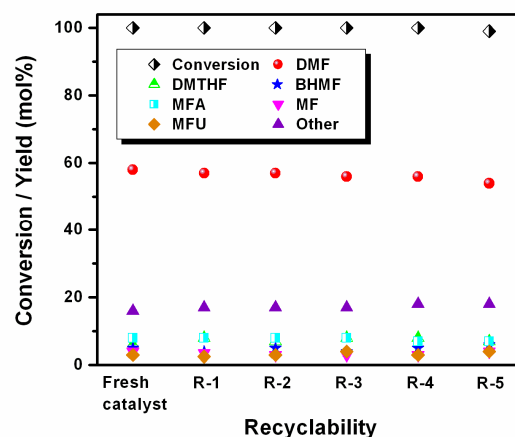


Fig. 13 The recyclability experiments of RH-1 catalyst in HMF hydrogenolysis. Reaction conditions: Solvent (2-propanol, 25 mL); molar ratio of HMF to Ru of 360; temperature (220 °C); H₂ pressure (10 bar); reaction time (4 h); stirring speed (500 rpm).

3. Conclusions

The present investigations demonstrate that highly dispersed Ru containing mixed metal oxide catalysts can be obtained by the calcination of hydrotalcite-like precursors, which were obtained through co-precipitation. As a result, even low Ru metal (0.56 wt%) containing catalysts were highly active in the conversion of HMF to DMF. The possible reaction pathway to DMF from HMF was explored by using the intermediate compound MF as starting material. Analysis of intermediate products at different stages of reaction showed that DMF is formed via BHMf followed by MFA. Under optimized reaction conditions; a maximum DMF yield of 58 mol% was achieved at 220 °C, at 10 bar H₂ pressure with 2-propanol as the solvent. The catalyst can be recycled without any significant loss in activity. Higher DMF yields were seen with 2-propanol as the solvent, as a result of hydrogen transfer from 2-propanol to the HMF on Ru metal. This study clearly shows that Ru containing mixed metal oxide derived catalysts have excellent potential for the conversion of biomass oxygenates to biofuels.

4. Experimental section

4.1. Chemicals

All the chemicals were reagent grade and used without further purifications. HMF (99%), DMF (99%), DMTHF (99%), MFU (99%), MTHF (99%) and THF (98%) were procured from Sigma Aldrich. MF (99%) and Ru(NO)(NO₃)₃ were purchased from Alfa Aesar, while Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, toluene, 2-propanol and 1,2-dimethoxyethane were purchased from Loba chemicals, India.

4.2. Preparation of Catalysts

Ruthenium doped HT catalyst precursors were prepared by coprecipitation method at a constant pH of 9.5-10. In a typical synthesis, an aqueous solution containing Mg(NO₃)₂·6H₂O (0.25 mol), Al(NO₃)₃·9H₂O (0.25 mol) and Ru(NO)(NO₃)₃ (1.5 wt%,

Ru content 15 mg/mL) was prepared in 50 mL double distilled deionized water. This solution was added drop wise to a second solution containing Na₂CO₃ (0.125 M) in 50 mL double distilled deionized water under vigorous stirring at 30 °C. The pH of the mixture was maintained constant while adding aqueous 0.25 M NaOH. The precipitate formed was filtered, washed thoroughly and dried at 100 °C for 10 h. Subsequently, it was calcined in air at 450 °C for 4 h followed by reduction in H₂ stream (30 mL/min) at 350 °C for 3 h. These samples with different Ru contents were designated as RH-1, RH-2 and RH-3. A similar procedure was adopted for the preparation of Mg-Al HT sample with Mg/Al mole ratio 3 without using Ru(NO)(NO₃)₃ solution. The Ru impregnated catalyst (RH-imp) was prepared by pore filling dry-impregnation method. For this, an aqueous solution of Ru(NO)(NO₃)₃ was added drop-wise to the freshly dried HT sample. The resultant wet solid was initially dried at ambient temperature for 12 h and subsequently dried at 100 °C for 10 h. Finally, the catalyst was calcined in air at 450 °C for 4 h followed by reduction in H₂ (30 mL/min) at 350 °C for 3 h.

4.3. Characterization techniques

The physico-chemical characterization of the catalyst and support were carried by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), temperature programmed reduction (TPR) etc. The X-ray diffraction patterns were obtained using PANalytical X'Pro dual goniometer equipped with an X'celator solid state detector. Nickel filtered Cu K α (λ = 1.5406 Å, 40 kV, 30 mA) radiation was used and the data collection was carried out using a flat holder in Bragg-Brentano geometry. The data was recorded in the 2 θ range of 5-90° with 0.02° step size. The surface areas of all the sample was investigated by N₂ sorption at -196 °C (Quanta chrome Autosorb IQ). Prior to sorption, the samples were evacuated at 200 °C for 3 h to a residual pressure of 2x10⁻³ torr. The isotherms were analyzed in the relative pressure (p/p₀) range of 0.05 to 0.30. Hydrogen chemisorption was also conducted using Quantachrome autosorb iQ instrument. Before chemisorption at 40 °C, catalyst was reduced insitu in H₂ flow at 350 °C. The amount of Ru 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 isopropyl alcohol, transferring a portion of it on to a silicon wafer and subsequently dried and gold coated before study. TEM images were collected using a FEI Technai TF-30 instrument operating at 300 kV. The samples for TEM measurement were prepared by placing a droplet of highly diluted suspension of the sample in isopropyl alcohol on a carbon coated copper grid and left for drying at room temperature. TPR studies of the catalysts was carried out using Micromeritics Autochem-2920 instrument in the temperature range 50-600 °C at a heating rate of 5 °C/min using 5% H₂ in He as the probe gas. The H₂ consumption in the TPR study was estimated quantitatively by the thermal conductivity detector that was calibrated before the TPR study. Prior to the TPR, the catalyst was pre-treated at 300 °C for 1h using 5% oxygen in helium gas mixture.

4.4. Evaluation of catalysts

Evaluation of catalysts was carried out using 100 mL capacity parr autoclave (SS316). In a typical experiment, 1 mmol (126 mg) of HMF, 25 mL of solvent and required amount of freshly reduced catalyst were introduced into the reactor vessel. After closing the reactor, the reactor was purged two to three times with hydrogen and filled with the same gas to the required hydrogen pressure. Subsequently, the reaction vessel was heated under stirring to the required temperature. During the reaction, the liquid samples were withdrawn periodically and analyzed by GC (Agilent 7890A) equipped with a flame ionization detector and CP Sil 8 CB capillary column (30 m length, 0.25 mm diameter). Product identification was done using authentic standards and by using GC-MS (Varian, Saturn 2200).

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References

- 1 G. W. Huber, S. Iborra and A. Corma, *Chem. Rev.*, 2006, **106**, 4044.
- 2 A. Corma, S. Iborra and A. Vely, *Chem. Rev.*, 2007, **107**, 2411.
- 3 J. N. Chheda, G.W. Huber and J. A. Dumesic, *Angew. Chem. Int. Ed.*, 2007, **46**, 7164.
- 4 K. Shimizu and A. Satsuma, *Energy Environ. Sci.*, 2011, **4**, 3140.
- 5 E. L. Kunkes, D. A. Simonetti, R. M. West, J. C. Serrano-Ruiz, C. A. Gärtner and J. A. Dumesic, *Science*, 2008, **322**, 417.
- 6 A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick Jr., J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer and T. Tschaplinski, *Science*, 2006, **311**, 484.
- 7 B. F. M. Kuster, *Starch*, 1990, **42**, 314.
- 8 Y. Román-Leshkov, C. J. Barrett, Z. Y. Liu and J. A. Dumesic, *Nature*, 2007, **447**, 982.
- 9 L. Deng, J. Li, D. M. Lai, Y. Fu and Q. X. Guo, *Angew. Chem. Int. Ed.*, 2009, **48**, 6529.
- 10 J. Q. Bond, D. M. Alonso, D. Wang, R. M. West and J. A. Dumesic, *Science*, 2010, **327**, 1110.
- 11 I. T. Horváth, J. Mehdi, V. Fábos, L. Boda and L. T. Mika, *Green Chem.*, 2008, **10**, 238.
- 12 J. P. Lange, W. D. van de Graaf and R. J. Haan, *ChemSusChem*, 2009, **2**, 437.
- 13 S. Song, R. Daniel, H. Xu, J. Zhang, D. Turner, M. L. Wyszynski and P. Richards, *Energy Fuels*, 2010, **24**, 2891.
- 14 T. Thananattananachon and T. B. Rauchfuss, *Angew. Chem. Int. Ed.*, 2010, **49**, 6616.
- 15 M. Chidambaram and A. T. Bell, *Green Chem.*, 2010, **12**, 1253.
- 16 T. S. Hansen, K. Barta, P. T. Anastas, P. C. Ford and A. Riisager, *Green Chem.*, 2012, **14**, 2457.
- 17 J. M. R. Gallo, D. M. Alonso, M. A. Mellmer and J. A. Dumesic, *Green Chem.*, 2013, **15**, 85.
- 18 W. Yang and A. Sen, *ChemSusChem*, 2010, **3**, 597.
- 19 A. Sen and W. Yang, US0307050A1, 2010.
- 20 W. Yang and A. Sen, *ChemSusChem*, 2011, **4**, 349.
- 21 S. Morikawa, *Noguchi Kenkyusho Jiho*, 1980, **23**, 39.
- 22 T. Thananattananachon and T. B. Rauchfuss, *Angew. Chem.*, 2010, **122**, 6766.
- 23 S. De, S. Dutta and B. Saha, *ChemSusChem*, 2012, **5**, 1826.
- 24 D. J. Braden, C. A. Henao, J. Heltzel, C. C. Maravelias and J. A. Dumesic, *Green chem.*, 2011, **13**, 1755.
- 25 L. Chen, Y. Zhu, H. Zheng, C. Zhang, B. Zhang and Y. Li, *J. Mol. Catal. A: Chem.*, 2011, **351**, 217.

- 26 T. Miyazawa, S. Koso, K. Kunimori and K. Tomishige, *Appl. Catal. A: Gen.*, 2007, **318**, 244.
- 27 F. Basile, L. Basini, G. Fornasari, M. Gazzano, F. Trifiro and A. Vaccari, *Chem Comm.*, 1996, 2435.
- 28 Q. Wang, H. H. Tay, Z. Guo, L. Chen, Y. Liu, J. Chang, Z. Zhong, J. Luo and A. Borgna, *Applied Clay Science*, 2012, **55**, 18. ¹⁵
- 29 a) R. Lanza, S. G. Jaras and P. Canu, *Appl. Catal. A: Gen.*, 2007, **325**, 57; b) M. G. Cattania, F. Parmigiani and V. Ragaini, *Surf. Sci.*, 1989, **211**, 1097; c) S. -H. Lee and D. J. Moon, *Catal. Today*, 2011, **174**, 10.
- 30 N. M. Bertero, A. F. Trasarti, C. R. Apesteguía and A. J. Marchi, *Appl. Catal. A: Gen.*, 2011, **394**, 228. ²⁰
- 31 R. A. W. Johnstone, A. H. Wilby and I. D. Entwistle, *Chem. Rev.*, 1985, **85**, 129.

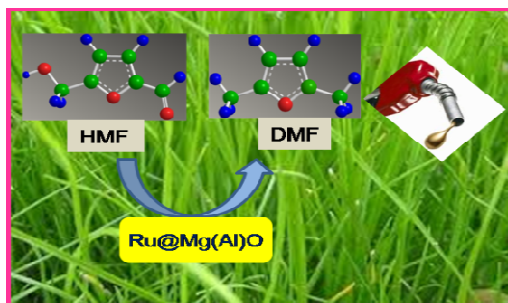
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Ruthenium nanoparticles containing hydrotalcite catalysts work efficiently for the conversion of biomass-derived HMF into liquid fuel 2,5-dimethylfuran.