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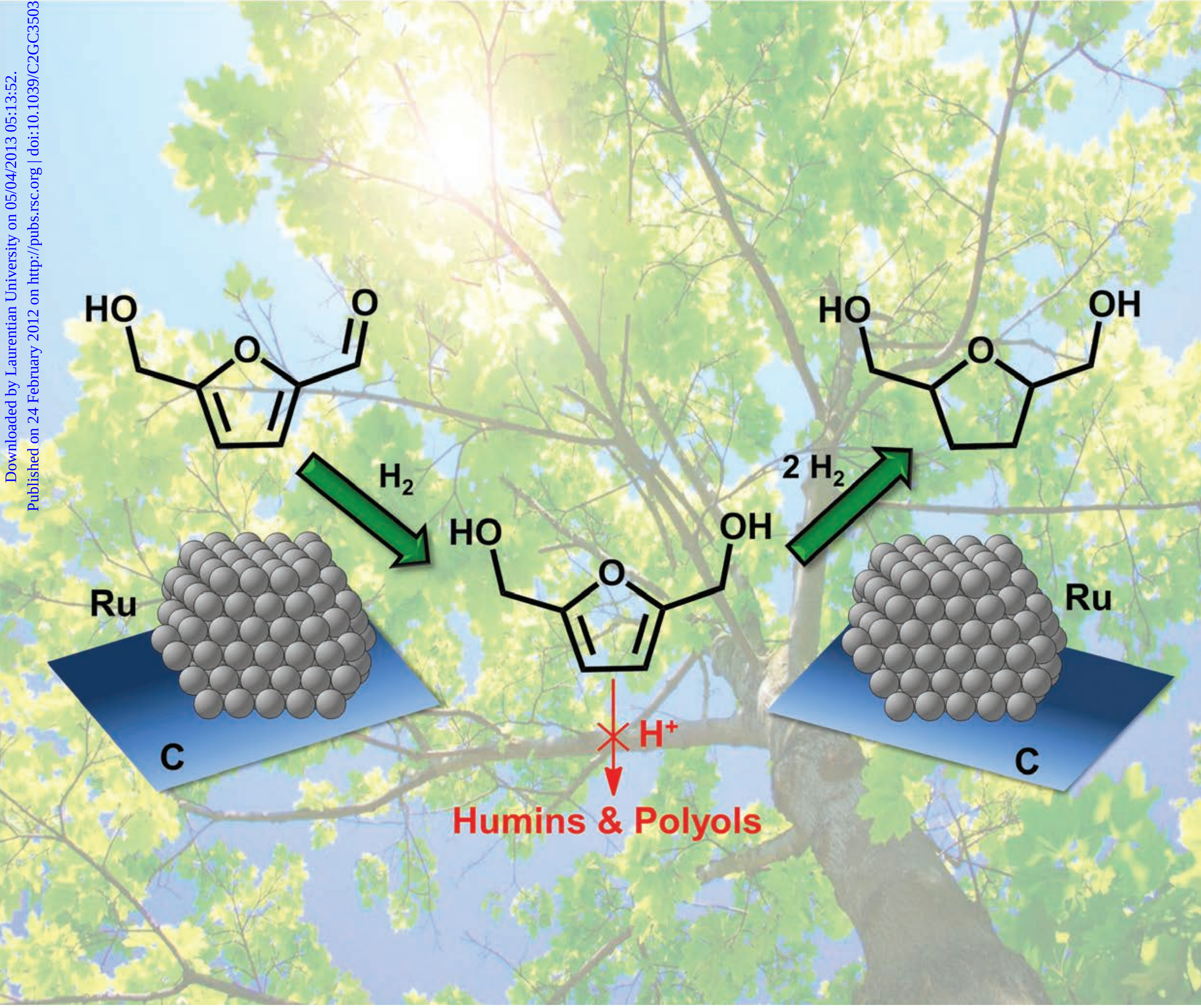

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PAPER

The selective hydrogenation of biomass-derived 5-hydroxymethylfurfural using heterogeneous catalysts†

Ricardo Alamillo, Mark Tucker, Mei Chia, Yomaira Pagán-Torres and James Dumesic*

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The products produced by hydrogenation of biomass-derived 5-hydroxymethylfurfural (HMF) are potential sustainable substitutes for petroleum-based building blocks used in the production of chemicals. We have studied the hydrogenation of HMF over supported Ru, Pd, and Pt catalysts in monophasic and biphasic reactor systems to determine the effects of the metal, support, solution phase acidity, and the solvent to elucidate the factors that determine the selectivity for hydrogenation of HMF to its fully hydrogenated form of 2,5-di-hydroxy-methyl-tetrahydrofuran (DHMTHF). We show that the selectivity to DHMTHF is affected by the acidity of the aqueous solution containing HMF. The major by-products observed are C_6-polyols formed from the acid-catalyzed degradation and subsequent hydrogenation of 2,5-dihydroxymethylfuran (DHMF), an intermediate hydrogenation product of HMF to DHMTHF. The highest yields (88–91%) to DHMTHF are achieved using Ru supported on materials with high isoelectric points, such as ceria, magnesia–zirconia, and γ-alumina. Supported catalysts containing Pt and Pd at the same weight percent as Ru are not as active for the selective hydrogenation to DHMTHF.

1. Introduction

The efficient production of biomass-derived fuels and chemicals is of technological importance for the transition to a more sustainable future. In this respect, 5-hydroxymethylfurfural (HMF) has been identified as a key precursor for the production of biofuels and high value chemicals.[1–3] Importantly, HMF can be hydrogenated to di-hydroxy-methyl-tetrahydrofuran (DHMTHF), a useful chemical with applications as a solvent,[4] a monomer,[5] or precursor to the production of other high-value chemicals.[6,7] For example, DHMTHF can be converted to 1,6-hexanediol, a valuable chemical for use in polymers and speciality chemicals, through the use of hydrogenolysis and dehydration reactions.[7–12] The conversion of HMF to 2,5-dihydroxymethylfuran (DHMF) or DHMTHF has been studied previously in the literature by several authors.[11,13] Schiavo *et al.* achieved high selectivities (80–100%) to either DHMF or DHMTHF using heterogeneous catalysts based on Ni, Cu, Pt, Pd, or Ru in neutral solution.[13] In an acidic solution using Ru or Pt as a catalyst, the major products were 1-hydroxyhexane-2,5-dione and 1,2,5-hexanetriol. Nakagawa and Tomishige studied the hydrogenation of HMF using Ni–Pd bimetallic catalysts and found that a Ni/Pd ratio of 7 led to high DHMTHF selectivities (96%).[11] Nakagawa and Tomishige reported that the hydrogenation of HMF can proceed to DHMTHF either by saturating the aldehyde first (forming DHMF), or by saturating the ring first (forming 5-hydroxymethyl-2,3,4,5-tetrahydro-2-furaldehyde (HMTF)).

The use of DHMTHF as a solvent has been shown to be effective for the dehydration of fructose to HMF, and a dual reactor design was proposed for the formation of DHMTHF from fructose. In the present paper, we have studied the hydrogenation of HMF to assess the feasibility of a dual-reactor system employing fructose dehydration combined with HMF hydrogenation for production of DHMTHF. We have also investigated the influence of catalyst support, solution acidity, solvent, and catalyst metal type on the selectivity to DHMTHF, and we have probed the primary mechanism to side products.

2. Experimental

2.1 Catalyst preparation

Catalysts were prepared by incipient wetness impregnation of supports with aqueous solutions of $Ru(NO)(NO_3)_3$ (Strem Chemical), $H_2PtCl_6 \cdot 6H_2O$ (Strem Chemical), or $Pd(NO_3)_2$ (Aldrich). The supports used were Vulcan XC-72 (Cabot Corp.), γ-Al_2O_3 (Strem), CeO_x (prepared as in ref. 14), magnesia–zirconia (as prepared in ref. 15) and fumed SiO_2 (Cab-O-Sil EH-5, Cabot Corp.). After impregnation, the catalysts were dried at 393 K overnight, reduced under flowing H_2 using a 3 hour ramp and a 5 hour hold at 573 K, and passivated with 2% O_2 in helium at 298 K. Ru-black (Ru-black) was purchased from Sigma Aldrich and used after reduction at 573 K for 5 hours followed by passivation using 2% O_2 in helium at 298 K.

University of Wisconsin-Madison, Department of Chemical and Biological Engineering, Madison, 53706 WI, USA. E-mail: dumesic@engr.wisc.edu; Fax: (+1) 608 262 5434

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2.2 Reaction studies

Studies of HMF hydrogenation were carried out using a 50 mL pressure vessel (Hastelloy C-276, Parr Instrument). In a typical experiment, 8 g of aqueous layer, 16 g of organic layer and a specified amount of catalyst were added into the pressure vessel (to simulate the composition of a bi-phasic reactor used for the dehydration of fructose to HMF[16]). The aqueous layer consisted of 5 wt% 5-hydroxymethylfurfural, HMF (99%, Aldrich) in water pre-saturated with 1-butanol (99.9%, Aldrich). The aqueous layer was filtered before reaction (to remove insoluble impurities from the commercial HMF), and in specific reactions, the feed was contacted with 1.5 g of a basic exchange resin, Amberlite IRA-400(OH) (Aldrich), before filtering. In some experiments, levulinic acid or sulfuric acid was added to the aqueous layer after the HMF solution was contacted with Amberlite IRA-400(OH) and filtered. The organic layer consisted of 1-butanol saturated with water. Alternatively, in several mono-phasic experiments, 24 g of the single phase solvent with 1.67 wt% HMF was added to the reaction vessel after filtering. The reactor was sealed, purged with He and then H_2, and subsequently pressurized with H_2 to 400 psi. The reactor was heated using a 30 minute ramp to 403 K and held for a specified amount of time before the reaction was quenched in an ice bath. The contents of the reactor were stirred with a magnetic stirrer bar and a magnetic stirrer plate.

2.3 Analytical methods

After reaction, the contents of the reactor were filtered, separated and analyzed using HPLC. Both the aqueous and organic layers were analyzed using a Waters e2695 HPLC system equipped with a 2998 photodiode array detector and 2414 refractive index detector. The products were separated using an Aminex HPX-87P column (Biorad) at 358 K, with Milli-Q water as the mobile phase at a flow rate of 0.6 mL min^{-1}. The conversion of HMF was monitored using a UV detector (320 nm), and the concentrations of products were monitored using a refractive index indicator. 1,2,5-Hexanetriol and 1,2,5,6-hexanetetrol were isolated from the reaction mixture by HPLC, dried using a rotary evaporator, and analyzed in D_2O using solution state NMR. For quantification purposes, the HPLC sensitivities for 1,2,5-hexanetriol and 1,2,5,6-hexanetetrol were assumed to be equal to that for 1,2,6-hexanetriol.

3. Results and discussion

3.1 Support effects with ruthenium catalysts

The hydrogenation of HMF was carried out using catalysts consisting of ruthenium supported on carbon and various oxides. In this study, a biphasic system composed of water and 1-butanol was chosen as the reaction solvent because it has previously been used in the production of HMF from fructose, and because this solvent is inert under hydrogenation conditions. A reaction temperature of 403 K was used because fructose dehydration to HMF readily occurs at this temperature, and this hydrogenation temperature would thus be suitable for coupling of fructose dehydration to HMF with the subsequent hydrogenation of HMF to DHMTHF.

A typical reaction profile for the hydrogenation of HMF over Ru/CeO_x is shown in Fig. 1. The selectivity to each product as a function of time is shown in Fig. 2. At a reaction time of 2 hours, complete conversion of HMF was achieved, and the primary products formed were DHMF and DHMTHF at selectivities of 81% and 4%, respectively. Upon increasing the reaction time to 6 hours, the DHMF was converted to DHMTHF, leading to overall selectivities of 32% and 48% to DHMF and DHMTHF, respectively. The other major products observed were the following polyols: 1,2,6-hexanetriol (1,2,6-HT), 1,2,5-hexanetriol (1,2,5-HT), and 1,2,5,6-hexanetetrol (1,2,5,6-HT) at 2%, 2%, and 11% selectivity, respectively. After increasing the reaction time to 12 hours, the HMF and DHMF were both fully converted, and the main products were DHMTHF (91% selectivity), 1,2,6-HT (3% selectivity), 1,2,5-HT (1% selectivity), and 1,2,5,6-HT (6% selectivity). After complete hydrogenation was achieved, a longer reaction time (*i.e.*, 20 hours) did not significantly change the product distribution, indicating that the triols and tetrol were formed by reactions in parallel to the formation of DHMTHF rather than in series (Fig. 3), as will be further discussed later (Section 3.3).

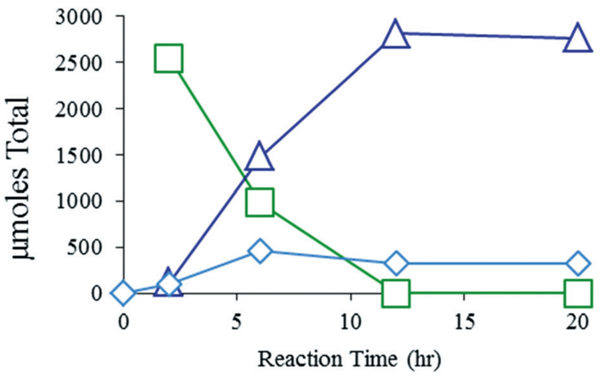

Fig. 1 Formation of DHMTHF (triangle), DHMF (square) and polyols (diamond) as a function of reaction time for the hydrogenation of HMF using 1 wt% Ru/CeO_x.

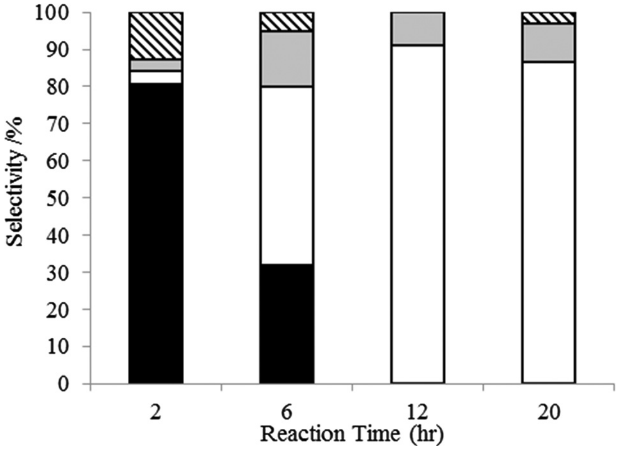

Fig. 2 Selectivity to DHMF (black), DHMTHF (white), polyols (grey) and unidentified products (striped) as a function of reaction time for the hydrogenation of HMF over Ru/CeO_x.

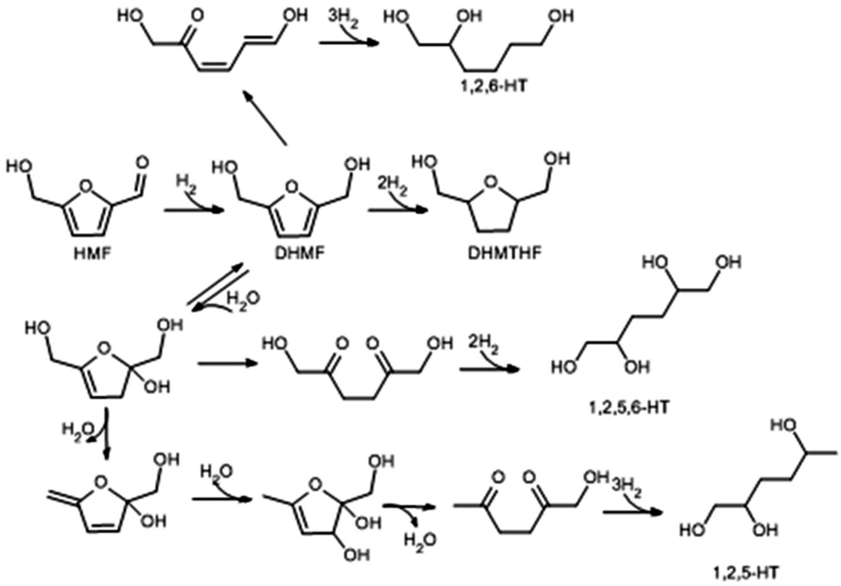

Fig. 3 Hydrogenation of HMF to DHMTHF with DHMF as an intermediate and the proposed mechanism for the formation of 1,2,6-hexanetriol, 1,2,5,6-hexanetetrol, and 1,2,5-hexanetriol. Mechanism based on Horvat *et al.*[17]

Table 1 Product distribution for HMF hydrogenation at full conversion for various supports and reaction times. All reaction were run with 200 mg of catalyst in 2 : 1 bi-phasic 1-butanol–water batch reactor at 403 K and 400 psi H_2

	Support	Reaction time (h)	HMF conversion (%)	Selectivity (%)					Total
				DHMF	DHMTHF	1,2,6-HT	1,2,5-HT	1,2,5,6-HT	
Oxide support, isoelectric point >7	CeO_x	2	100	81	4	0	1	2	87
		6	100	32	48	2	2	11	95
		12	100	0	91	3	1	5	100
		20	100	0	87	3	1	6	97
	Mg–Zr	2	99	94	2	0	0	2	99
		20	100	0	88	2	0	1	92
	γ-Alumina	2	92	81	5	0	0	2	88
		12	100	0	89	2	3	5	100
Non-oxide support	Vulcan carbon	1[a]	95	29	3	0	2	2	36
		10[a]	100	0	15	1	29	12	56
		1	100	0	51	2	9	28	90
		2	100	0	50	2	9	28	89
		10	100	0	56	2	9	27	94
	Ru-black	1[a]	100	0	53	13	13	15	94
		2[a]	100	0	46	13	13	11	84
		18[a]	100	0	48	9	13	13	83
Isoelectric point <7	Silica	1[a]	80	64	0	0	0	1	65
		2	100	0	53	3	13	20	89

[a] 50 mg of catalyst was used in this run.

Table 1 gives results for the hydrogenation of HMF using unsupported ruthenium (Ru-black) and ruthenium supported on Vulcan carbon and oxides including fumed silica (SiO_2), magnesia–zirconia (Mg–Zr), and γ-Al_2O_3. The reaction network shown in Fig. 3 adequately describes the results obtained for all of the catalysts, including (1) the presence of DHMF at low reaction times, (2) the appearance of the following polyols 1,2,5-HT, 1,2,6-HT, and 1,2,5,6-HT as byproducts, and (3) the stability of the completely hydrogenated products at long reaction times (for example when using Ru-black or Ru/Vulcan at long reaction times). The selectivity to DHMTHF varied considerably for the different catalysts. Of the oxide based supports, materials with high isoelectric points (Mg–Zr, CeO_x and Al_2O_3) produced DHMTHF at high selectivities of around 90%, while SiO_2 having a low isoelectric point produced DHMTHF with a lower selectivity. Unsupported Ru (Ru-black) and ruthenium supported on Vulcan carbon also exhibited low selectivities to DHMTHF (about 50%). Interestingly, the selectivity to DHMTHF changed substantially with the amount of Ru/Vulcan used, while keeping all other conditions constant (Table 1). For example, DHMTHF was the major product observed using 200 mg of catalyst (with a selectivity of about 50%), followed by 1,2,5,6-HT (30%), and 125 HT and 126 HT (9% and 2%). Decreasing the catalyst mass to 50 mg decreased the amount of DHMTHF produced to a selectivity of 15% (when all of the HMF and DHMF were converted). The selectivity to 1,2,5-HT increased to 29%, the amount of 1,2,5,6-HT decreased, and the amount of 1,2,6-HT remained low. Furthermore, the selectivity to observed products decreased from about 90% to 56%. These changes in selectivity with catalyst loading indicate the contributions of reactions occurring in the liquid solvent that are not catalyzed by metal. Due to the higher selectivities achieved using supports with higher isoelectric points, it is suggested that these undesirable reactions in solution are acid-catalyzed degradation reactions.

3.2 Effect of support and solution phase acidity

Based on the hypothesis that acid-catalyzed degradation reactions take place in solution during the hydrogenation of HMF, we have explored whether acidic impurities could be present in the HMF feed. If this is the case, the beneficial effect of using supports with high isoelectric points may be due to the adsorption of acidic species in solution. In this respect, HMF is commonly produced by the dehydration of monosaccharides in acidic solutions, with levulinic acid and formic acid being generated as byproducts.

Either the acid catalyst or these acidic byproducts could be present in the HMF feed. To study if acidic impurities are the cause of low selectivities for hydrogenation of HMF, the feed was treated with a basic ion-exchange resin before reaction, *i.e.*, using Amberlite IRA-400(OH). After treatment, the resin was removed by filtration, and the hydrogenation of HMF was carried out using either Ru/Vulcan or Ru-black as a catalyst. Treatment of the HMF feed with resin led to an increase of over 20% in the selectivity to DHMTHF using both Ru catalysts, as seen in Fig. 4. Furthermore, treatment of the feed with the resin resulted in an increase in pH from slightly acidic (pH 5) to neutral (pH 6–7). This increase in pH suggests that minor impurities of acid mixed with HMF decrease the selectivity to DHMTHF.

The selectivity to DHMTHF was also increased by adding solid materials with high isoelectric points to the Ru-black catalyst. When γ-Al_2O_3, with an isoelectric point of approximately 7–8, was added to the reaction mixture, the selectivity to DHMTHF increased from 46 to 85% at the expense of the polyols, as shown in Fig. 5. This effect was more pronounced when using magnesium oxide, which has an isoelectric point of 10–12, leading to a DHMTHF selectivity of 89%. The increase in DHMTHF selectivity in the presence of solid oxide materials with high isoelectric points demonstrates that the basicity of the catalyst support strongly affects the final product distribution in the hydrogenation of HMF.

As shown in Table 1, DHMTHF was formed with low selectivity (53%) when ruthenium supported on silica was used as a catalyst. In addition to the acidic impurities in solution, the low isoelectric point of silica could lead to a decrease in the selectivity to DHMTHF. Thus, the hydrogenation of HMF was studied using a feed that had been contacted with Amberlite IRA-400 (OH), and using Ru-black as a catalyst with the addition of 500 mg of silica. As seen in Fig. 6, the addition of silica decreased the selectivity to DHMTHF from 76% to 64% and increased the formation of polyols, indicating the important effect of the weak acidity of silica.

To elucidate the effects on the hydrogenation of HMF of specific types of acids, levulinic acid and H_2SO_4 were added to the reaction mixture that had been contacted with Amberlite IRA-400(OH), to isolate the effects of each acid. Levulinic acid is an example of an acidic degradation product of HMF, whereas H_2SO_4 was studied as an example of a homogeneous catalyst that can be used for the production of HMF. As shown in Fig. 6, addition of levulinic acid to the reaction mixture (1 : 4 wt : wt ratio of levulinic acid to HMF) resulted in a decrease in DHMTHF yield and an increase in the selectivity to the triols and tetrol, whereas the overall selectivity to known products remained constant. Addition of H_2SO_4 had a more significant

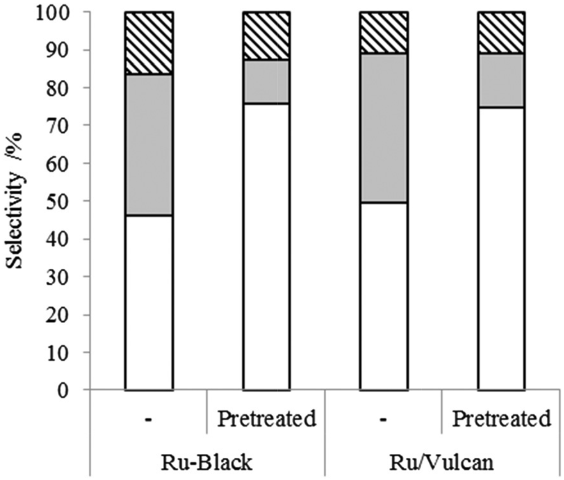

Fig. 4 Selectivity to DHMTHF (white), polyols (grey), and unidentified products (striped) in the hydrogenation of HMF over Ru-black and 1 wt% Ru/Vulcan without and with feed pretreatment with Amberlite IRA-400(OH).

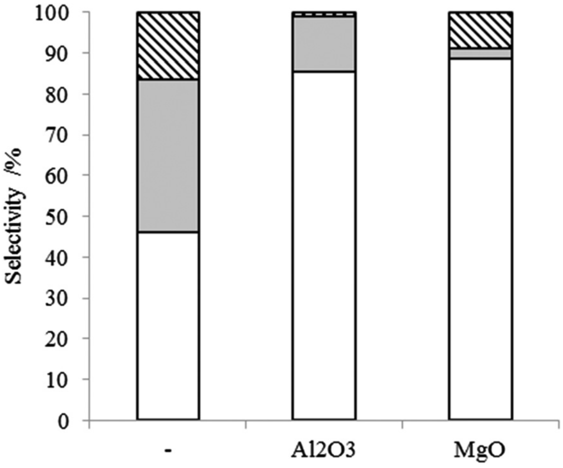

Fig. 5 HMF hydrogenation to DHMTHF (white), polyols (grey), and unidentified products (striped) using 50 mg of Ru-black as a catalyst and 500 mg of high-isoelectric point solids.

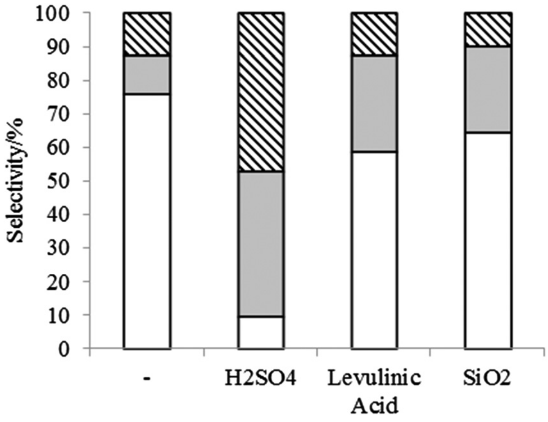

Fig. 6 Product selectivities for the hydrogenation of HMF to DHMTHF (white), polyols (grey) and unidentified (striped) over Ru-black (50 mg) in the presence of added acids. Feed was treated with 1.5 g Amberlite IRA-400(OH) prior to acid addition.

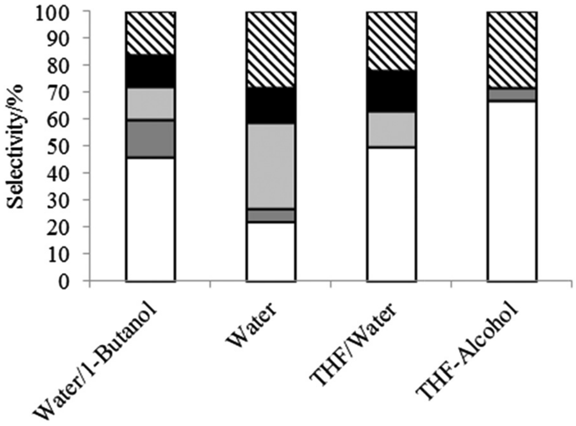

Fig. 7 HMF hydrogenation in different solvents using 50 mg Ru-black as a catalyst. Products include DHMTHF (white), 1,2,6-HT (dark grey), 1,2,5-HT (light grey), 1,2,5,6-HT (black), and unidentified products (striped).

effect on the selectivity to DHMTHF, which decreased from 76% to 9% with the addition of H_2SO_4 (0.084 M with respect to the aqueous layer, 3 times lower than the amount used in literature for the dehydration of fructose[2]). This decrease in DHMTHF selectivity was accompanied by an increase in the polyols selectivity, and the selectivity to observable products decreased. This decrease in selectivity to observable products may be due to formation of insoluble polymer of the reactive DHMF intermediate.

Because polyols are formed in parallel to the production of DHMTHF, it is possible that either the HMF or DHMF undergo acid-catalyzed degradation reactions. Accordingly, the hydrogenations of HMF and DHMF were each studied in a 1-butanol–water biphasic system with 0.011 M H_2SO_4 (with respect to the aqueous phase). Under these conditions, HMF did not undergo reaction after 10 minutes at 403 K. On the other hand, DHMF reacted rapidly, with 59% and 98% conversion after 4 and 10 minutes at 403 K. With these results, it appears that the production of 1,2,6-HT, 1,2,5-HT, and 1,2,5,6-HT originates from DHMF by acid catalyzed reactions, followed by hydrogenation of acid-catalyzed ring-opening and hydration–dehydration reactions.

Proposed mechanisms for the production of 1,2,6-HT, 1,2,5-HT, and 1,2,5,6-HT are shown in Fig. 3. The mechanisms for the formation of 1,2,5-HT, and 1,2,5,6-HT are based on the mechanism for conversion of HMF to levulinic acid proposed by Horvat *et al.*[17] The mechanism for the formation of 1,2,6-HT is based on ring opening of DHMF to form a conjugated ketone-diene, followed by hydrogenation. The mechanisms for the formation 1,2,5-HT and 1,2,5,6-HT require the presence of water. Therefore, the selectivity to DHMTHF should be affected by the solvent system, as studied below.

3.3 Solvent effects

Fig. 7 presents results for the hydrogenation of HMF using the water–1-butanol biphasic system, and single phase systems composed of water, a mixture of tetrahydrofuran (THF) with water, and tetrahydrofurfuryl alcohol (THF-alcohol). The overall weight percent of HMF in the reactor (1.7 wt%), the loading of the Ru-black catalyst (50 mg), and the reaction time (2 hours) were held constant. Both HMF and DHMF were completely converted in each of the reactions. It can be seen that the selectivity to DHMTHF decreased from 43% to 18% and the selectivity to 1,2,5-HT increased from 13% to 32%, when the solvent was changed from the water–1-butanol biphasic mixture to pure water.

These changes give support to the proposed reaction mechanism for the formation of 1,2,5-HT, which includes a hydration step. Surprisingly, the formation of 1,2,5,6-HT, which requires the net addition of water regardless of mechanism, remained nearly constant when changing from the water–1-butanol system to the pure water system. The overall selectivity to known products decreased when changing from water–1-butanol to water as the solvent, indicating the presence of additional degradation pathways in the presence of water.

The hydrogenation of HMF was studied in a solvent consisting of a THF–water mixture (4 : 1 THF–water), because this solvent system is selective for the production of HMF from fructose. The product distribution for THF–water was nearly the same as that of the water–1-butanol biphasic system. This result indicates that degradation reactions involving water are important in monophasic systems containing water, as well as in biphasic systems where one of the phases is water. This behavior is caused by the low partition coefficient of HMF in the 1-butanol–water system, (where the partition coefficient is equal to the concentration of HMF in the organic phase divided by the concentration in the aqueous phase).

Studies of HMF hydrogenation were also carried out using THF-alcohol as a solvent, because THF-alcohol is similar to the reaction product DHMTHF. Accordingly, the selectivity achieved using THF-alcohol as a solvent can give an indication of the selectivity that should be achieved when using DHMTHF as a solvent. As shown in Fig. 7, the use of THF-alcohol as a solvent gave rise to an increase in the selectivity of DHMTHF, likely as a result of the absence of water. In agreement with the mechanism of Fig. 3, 1,2,5-HT and 1,2,5,6-HT were not formed in the THF-alcohol solvent.

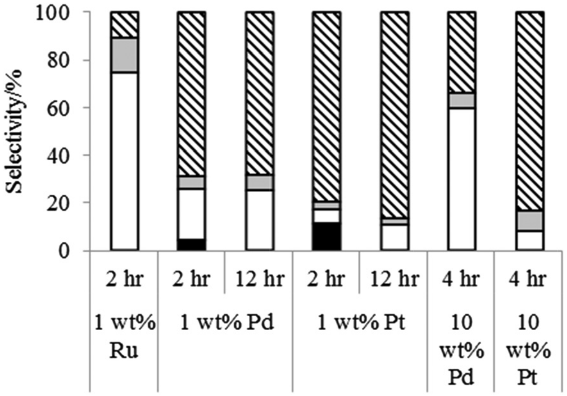

Fig. 8 HMF hydrogenation over Vulcan supported Ru, Pd, or Pt at various time points. Feed was purified with 1.5 g Amberlite IRA-400 (OH) before reaction. Products observed DHMF (black), DHMTHF (white), polyols (grey), and unidentified products (striped).

3.4 Effect of metal catalyst

Studies were conducted to probe how the selectivity for hydrogenation of HMF is affected by changing the nature of the metal component of the hydrogenation catalyst. All catalysts were studied using a biphasic system of water and 1-butanol, and the feed was contacted with Amberlite IRA-400(OH) before reaction to eliminate the effect of impurities in solution. The results are shown in Fig. 8. Using either palladium or platinum as the catalyst, the majority of the HMF was converted to unidentified products except when using higher loading of Pd. The HPLC spectra of the product mixture did not reveal any significant peaks, which may indicate that the undetected carbon is in the form of insoluble polymers. These polymers may be formed through the loss of formaldehyde from DHMF, followed by furfuryl alcohol polymerization, which is well known in the literature.[18,19] As evidence for this chemistry, we have detected the formation of formaldehyde dibutyl acetal (which was identified by GC/MS) when reacting DHMF in butanol under acidic conditions.

After a reaction time of 2 hours, DHMF was observed from the hydrogenation of HMF when using palladium and platinum as catalysts, whereas DHMF had been fully consumed when using ruthenium, indicating that at the same weight loading palladium and platinum catalysts were less active compared to the ruthenium catalyst (at least in terms of DHMF hydrogenation). As was seen in Table 1 when using a lower loading of Ru/Vulcan, a decrease in rate of hydrogenation is accompanied by a decrease in selectivity due to an increased relative rate of degradation reactions in solution. This behavior is consistent with an increased yield of unidentified products when using both a lower amount and/or weight loading of Ru/Vulcan or when using Pd/Vulcan or Pt/Vulcan.

The irreversible uptake of CO was measured for each catalyst (ESI,† Table 6) to calculate metal dispersion and particle size. Pt is known to catalyze both hydrogenation and C–C scission reactions during aqueous phase reforming, which can account for the lower selectivity to DHMTHF using Pt.[20,21] To probe the difference between Ru and Pd, HMF hydrogenation was studied using low catalyst amounts (50 mg) and low reaction times to calculate specific rates of HMF hydrogenation (ESI,† Table 6). Pd showed the highest rate of HMF hydrogenation relative to Pt and Ru. This behavior can be detrimental to the overall production of DHMTHF if the rate of DHMF hydrogenation is slow and permits time for this reactive intermediate to undergo degradation reactions. The relative rates of DHMF hydrogenation were estimated using furfuryl alcohol (FA) hydrogenation as a model reaction. Indeed, Ru showed a faster rate than Pd for FA hydrogenation. Accordingly, the overall selectivity to DHMTHF is dependent on both the rates of hydrogenation as well as solution acidity.

4. Conclusions

The selectivity for hydrogenation of HMF to DHMTHF is affected by the acidity of the aqueous solution containing HMF. In particular, the selectivity to DHMTHF decreases when acidic impurities (for example levulinic acid, an HMF degradation product) are present in the reaction mixture, or when metal oxides with low-isoelectric point are used as supports for Ru hydrogenation catalysts. The primary by-products observed are 1,2,5-HT, 1,2,5,6-HT, and 1,2,6-HT. These molecules appear to be formed by the hydrogenation of acid-catalyzed degradation products of dihydroxymethylfuran (DHMF). Importantly, high selectivities to DHMTHF can be achieved when the hydrogenation catalyst is comprised of ruthenium deposited on a support with a high isoelectric point oxide (*e.g.*, ceria).

Acknowledgements

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