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Decomposition of glucose with *in situ* deoxygenation in a low H_2 pressure environment – Pt. II: Bimetallic catalysts



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<i>Keywords:</i> Deoxygenation Water-gas-shift Glucose Decomposition Bimetallic catalysts	Bimetallic catalysts, CoFe, NiFe, PdFe, and PtCo were studied for their ability to perform <i>in situ</i> deoxygenation of glucose decomposition production at 350 °C. Catalysts were prepared via co-impregnation and sequential impregnation methods on SiO ₂ in combinations of 4 wt% and 0.5 wt% for the two metals. Easily identifiable furanic compounds in the products were used to establish an understanding of deoxygenation activity. Co-impregnated 0.5%Co4%Fe/SiO ₂ and sequentially impregnated (Fe first) 0.5%Ni4%Fe/SiO ₂ catalysts provided the most favourable results. Thanks to the alloying of Co and Fe which stabilized Fe, the 0.5%Co4%Fe/SiO ₂ catalyst required the Ni and Fe phases to remain uninterrupted to perform their synergistic roles which boosted DMF content and overall reduced solid residue.

1. Introduction

Traditional technologies for producing petroleum-compatible biofuels from lignocelluosic materials are heavily reliant on the use of hydrogen. Thermochemical processes like pyrolysis produce oxygenrich bio-oil which must be upgraded via hydroprocessing [1–7]. Although these processes claim to be renewable/sustainable they remain reliant on fossil fuels as > 95% of the world's H₂ is produced via fossil fuel resources [8].

The presence of CO₂, CO, H₂, H₂O, and light hydrocarbons in the outlets of lignocellulosic decomposition processes represents a missed opportunity [2]. CO and H₂O for example can potentially undergo water-gas-shift reaction (WGSR) and produce H₂ which can then be used for *in situ* deoxygenation. The concept of producing H₂ internally and using it to produce renewable fuels in not entirely new. For example, Dumesic's research group from the University of Wisconsin demonstrated the aqueous phase reforming of sugars such as glucose to produce hydrogen which was followed by upgrading with Pt catalyst [10–12]. Aside from requiring a potentially expensive catalyst; such a system would require initial processing of lignocellulosic material to first separate lignin and then produce water-soluble sugars from cellulose and hemicellulose. On the other hand, a thermochemical process involving *in situ* deoxygenation may utilize raw lignocellulosic material without the need of significant processing of the feedstock.

In Part 1 [9], we investigated the potential of performing a one-pot

reaction stage in which biomass is decomposed and the resulting products can immediately undergo deoxygenation in the presence of various monometallic catalysts. Using glucose as a model compound for cellulose, we reported the reduction of furfural into selectively deoxygenated products such as 2-methylfuran (2 M F) an 2,5-dimethylfuran (DMF) using a 4%Co/SiO₂. Although Ni catalysts were not as selective towards 2 M F and DMF, they were however beneficial for reducing the production of solid residue.

Bimetallic catalysts have received much attention for their activities in the selective deoxygenation of phenolic and furanic compounds derived from bio-oils [5]. Resasco and colleagues from the University of Oklahoma studied the use of supported Ni-Fe bimetallic catalysts for the selective deoxygenation of m-cresol and furfural and determined that Fe's oxophilic nature facilitated selective absorption via oxygen contain functional groups while Ni facilitated H₂ activation together permitting hydrogenolysis [13,14]. Pd-Fe bimetallic catalysts have also received much attention however Pd was reportedly responsible stabilizing Fe and preventing permanent oxidation [15–18]. Other bimetallic catalysts have included supported PtZn [19], supported NiCu [20,21], and PtCo nanocrystal [22] catalysts.

Herein, Pt. 2 of the decomposition of glucose with *in situ* deoxygenation in a low H_2 pressure environment focuses on the use of supported bimetallic catalysts: NiFe, CoFe, PdFe, and PtCo. As with Part 1, this study used glucose as a model for cellulose. Since Ni/SiO₂ and Co/SiO₂ were shown to yield the most ideal results in Part 1; within this

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study, NiFe and CoFe catalyst received much attention and were also studied for the impact that impregnation method (co-impregnation versus sequential/step-wise impregnation) has on the activity. Unlike NiFe bimetallic catalysts, CoFe catalysts have previously not received much or any attention within the literature for the use as a deoxygenation catalyst. They have however received some attention for their potential use for WGSR which may also be useful in the present system [23–25]. Although some of the aforementioned catalysts have been used in WGSR studies; the *in-situ* production of H₂ is not yet the primary focus for the catalysts. As such, a small source of H₂ is provided (37.6 kPaa) in order to maintain activity of deoxygenation catalysts. Future research may further investigate *in-situ* hydrogen production. Furanic compounds in the products, which have distinct structures and deoxygenation pathways, were used to establish an understanding of deoxygenation activity.

2. Experimental

2.1. Catalyst preparation

Various bimetallic catalysts were prepared using incipient wetness impregnation onto a SiO₂ supporting material (Aerosil 200). Both coimpregnation and step-wise impregnation methods were used. The catalysts that were prepared consisted of NiFe, CoFe, PtCo, and PdFe catalysts. Catalysts were prepared with one metal at 0.5 wt% and the other at 4 wt%. Catalysts were prepared using the following salts from Sigma Aldrich: nickel (II) nitrate hexahydrate, cobalt (II) nitrate hexahydrate, iron (III) nitrate nonahydrate, tetraamineplatinum (II) nitrate, and palladium (II) nitrate dihydrate. Before impregnation, the silica support was dried at 120 °C for 6 h and calcined at 550 °C for 4 h. After impregnation, catalysts were dried at 120 °C for 6 h and calcined in air at 550 °C for 6 h with heating rates of 5 °C/min.

Step-wise impregnation was performed by impregnating the first metal onto the support then performing calcination. Upon cooling of the material; the second impregnation was performed followed by another calcination process. Catalysts that were prepared via step wise impregnation were denoted as "SWM" where M represents the metal that was impregnated first (ie. 4%Ni0.5%Fe/SiO₂-SWFe – Fe was impregnated onto the support first followed by the 4%Ni).

For performance testing, catalysts were pelletized and crush to a size range of 40–60 mesh. Catalyst were reduced in flowing H₂ at 50 nm L/min at desired reduction temperatures with a heating rate of 10 °C/min. Temperatures used for reduction were 450 °C for NiFe/SiO₂, 550 °C for CoFe/SiO₂, 450 °C for PdFe/SiO₂, and 450 °C for PtCo/SiO₂ [13,14,18,26].

2.2. Activity tests

Activity tests were performed in accordance with Part 1 of the study [9]. Activity/performance tests were performed in a horizontal, stirred 55 mL stainless steel reactor for 1 h at 350 °C with 800 mg of glucose. Reduced catalyst catalysts were used in the reactor at a 1:5 catalyst to glucose ratio. 1-methylnaphthalene (1 MN) (Sigma-Aldrich) was used as a solvent (20:1 solvent to glucose ratio) to promote heat and mass transfer. 1 MN was once again selected as the solvent due to its high boiling point temperature and its stability at reaction conditions even within the presence of a catalyst showing no discernable changes in H₂ content and 1 MN related by-products within the liquid phase. 350 °C was selected as a reaction temperature as it represents a suitable temperature for both cellulose decomposition and WGSR [27–31]. Prior to reactions, the filled reactors were vacuum purged with He then filled with 37.6 kPaa of H₂ then topped off with He to a total pressure of 310 kPaa to prevent evaporation of the solvent.

Gases within the reactor were tested using a RGA200 mass spectrometer at room temperature after undergoing separation via a HP-PLOT/U column held at 30 $^{\circ}$ C. Upon separation from the liquid contents

from the reactor, the solid contents were washed with acetone and dried in an oven at 80 °C overnight. Liquid outputs were analyzed using GC–MS (Shimadzu GCMS QP5000) and GC-FID (Varian GC450). The hydrogen to carbon ratio of the solid residue was determined via CHNS analysis (Leco CHNS-932).

TGA analyses were performed using a TA Instruments TGA Q500 to determine the direct impact of selected catalysts on the decomposition/ weight loss of glucose. The catalysts and glucose were loaded into the TGA at a ratio of 1:5. The TGA was heated from room temperature to 950 °C at a rate of 5 °C/min under flowing He (50 nm L/min).

2.3. Catalyst characterization

Catalysts selected for characterization underwent TPR, XRD, and (S)TEM analyses with the objective of investigating the bimetallic catalyst structures and how the catalysts differ based on preparation method. Temperature programmed reduction (TPR) analyses were performed using an Autosorb 1-C with a RGA200 mass spectrometer as the detector. 150 mg of catalyst was loaded in a quartz u-cell and vacuum dried at 300 °C for 20 min under flowing helium (50 nm L/min). TPR analyses was then performed using 1% H₂ in He gas mixture at a flow rate of 50 nm L/min. The Quartz cell was heated from room temperature to 900 °C at a rate of 10 °C/min. X-ray diffraction (XRD) of reduced catalysts was performed at the UNB Geochemical and Spectrographic Facility using a Bruker AXS D8 XRD. XRD spectrums were gathered within the 2Theta range of 10-90° at a rate of 0.02°/ second.

(S)TEM analyses were performed at the UNB Microscopy and Microanalysis Facility with a JEOL JEM-2010 (S)TEM. Images were collected with a Gatan Ultrascan camera using Digital Micrograph. Metallic sites were identified on the supporting material (SiO₂) using both HRTEM (High Resolution TEM) and high angle annular darkfield STEM (HAADF-STEM) mode. With both techniques, a high contrast was observed between catalyst sites and the supporting SiO₂ material. Verification of the metallic sites was determined by collecting EDS spectra with an EDAX Genesis 4000 Energy Dispersive X-ray (EDS) analyser. In addition, mapping of the metallic sites was performed using the EDS detector whilst in STEM mode to further determine the existence and distribution of both metals across an area of material. An accelerating voltage of 200 kV was used for the imaging and analysis. Images were processed using an open source image processing platform, Fiji [32].

3. Results and discussion

3.1. Solid products

A high level of reduction of the solid content is desired to attain a liquid product and provide easy separation from the catalyst. Reduction of the solid content results from the conversion of glucose itself and the prevention of the formation of solid products such are char and heavy compounds and polymers attributed as tars. Catalysts may prevent this by supporting tar cracking/reforming reactions to eliminate heavy compounds in favour of liquid and gaseous products [33–39]. As demonstrated in Fig. 1, most bimetallic catalysts were shown to aid in the reduction of solid residue over tests with just glucose. This is also demonstrated in Fig. 2 where the H:C ratios of the solid residue were higher upon addition of the catalysts representing the possibility of less char formation.

As evidenced in Fig. 2, NiFe catalysts were the most capable at reducing output solid residue. Based on what was previously observed for monometallic catalysts in Part 1 [9], it is likely that the presence of Ni had a significant role. 0.5%Ni4%Fe-SWFe for example provided a similar reduction in solid residue to 0.5%Ni/SiO₂ as well as a very similar H:C ratio. Meanwhile, the co-impregnated and the SWNi variants of the 0.5%Ni4%Fe catalyst had comparatively lower levels of reduction in



Fig. 1. Percent removal of dry organic solids with bimetallic catalysts with data for 0.5%Ni/SiO₂ from Part 1 [9].



Fig. 2. H:C Molar Ratio in solid products.

solid residue. For these two catalysts, the Ni phase may not have been directly exposed like the SWFe catalyst and thus may have suffered from an interference with Fe. However, the second highest reduction in solid residue occurred on the 4%Ni0.5%Fe-SWNi catalyst which may not have had Ni-phase that was exposed as the 4%Ni0.5%Fe-SWFe variant which had slightly more solid residue. Meanwhile, the co-impregnated 4%Ni0.5%Fe catalyst suffered a loss in solid reduction compared to the 4%Ni/SiO₂ catalyst in Part 1. Co-impregnation may

produce a more uniform NiFe alloy phase rather than a strictly separate Ni-phase which is more active towards either the initial decomposition of glucose or tar cracking (see catalyst characterization in Section 3.4). When 0.5%Fe is layered on top of the 4%Ni, it may be possible that both Ni and Fe phases are exposed. The Fe phase may not completely cover the Ni phase possibly enabling a synergistic affect between the two metals in which each metal favours a different role in the reaction. This would explain why the SWNi performed slightly better than the SWFe layout which would have had a more completely exposed Ni phase.

CoFe catalysts appear to behave in the opposite way and favour coimpregnation over the step-wise impregnation methods. Co-impregnated 4%Co0.5%Fe reduced the organic solid content by "77% – slightly higher than the 4%Co/SiO₂ catalyst from the previous study with 74%. Even more subtle differences are witnessed for the two sequentially impregnated 4%Co0.5%Fe catalysts. It is noteworthy too that as monometallic catalysts, 0.5%Fe/SiO₂ and 4%Co/SiO₂ resulted in similar reductions in organic solid residue. Combing the two into a bimetallic catalyst apparently offered no significant improvement. Similar observations can be made for the 0.5%Co4%Fe catalysts.

For PdFe and PtCo, an odd observation was made where exposing the noble metals on top of the base metals provided slightly lower reduction in solid residue. However, in general, using bimetallic configurations of NiFe, CoFe, PdFe, and PtCo provides little advantage over their monometallic counterparts in terms of solid residue reduction. Especially in the cases of PdFe and PtCo catalysts, the additional costs of these catalysts outweigh the benefits.

To further understand the impact the catalysts, have on the decomposition of glucose, TGA was performed using 0.5%Ni4%Fe and 0.5%Co4%Fe catalysts. As demonstrated in Fig. 3, the catalysts, had a significant effect on the decomposition of glucose by reducing the temperatures at which substantial decomposition begins. Without a catalyst additive, the decomposition of glucose has two main periods of decomposition one at 215 °C and again at 293 °C where glucose undergoes a faster rate of decomposition. With the catalyst additives though, the first stage of decomposition had the higher rate of decomposition however it was not as significantly fast. As seen in Table 1, the results for the two chosen catalysts and their three variants did not have appreciable differences. Iron played an important role in influencing the decomposition of glucose as the results are mostly comparable to those of 4%Fe/SiO₂ from Part 1. In some cases, though, there are discernable differences such as for co-impregnated 0.5%Ni4%Fe and 0.5%Co4%Fe catalysts (as shown in Fig. 3) where the catalyst containing nickel achieved an overall lower residue content at the end of



Fig. 3. TGA results of glucose decomposition with and without 0.5%Ni4%Fe/SiO2 and 0.5%Co4%Fe/SiO2 catalyst. Catalysts added at 1:5 ratio with glucose.

Table 1

TGA results summary for glucose decomposition with catalyst additives. Temperature (T) program: $25 \degree C-900 \degree C$ at $5 \degree C/min$. Y = percent of solid remaining (does not include catalyst weight).

Catalyst	Initial	Initial Major Weight Loss				Valley			Second Major Weight Loss				
	T ^a (°C)	Y ^a (wt%)	T ^b (°C)	Y ^b (wt%)	(-dY/dT) ^b (%/K)	T ^c (°C)	Y ^c (wt%)	(-dY/dT)°(%/K)	T ^d (°C)	Y ^d (wt%)	(-dY/dT) ^d (%/K)	T ^e (°C)	Y ^e (wt%)
No Catalyst	178	99.6%	215	90.0%	0.49	242	79.4%	0.30	293	49.1%	0.92	417	16.4%
0.5%Ni4%Fe/SiO2	173	99.5%	211	81.6%	0.63	244	60.3%	0.46	253	54.6%	0.56	435	12.2%
0.5%Ni4%Fe/SiO ₂ SWFe	170	99.6%	194	89.5%	0.67	230	66.7%	0.40	242	60.8%	0.44	431	24.9%
0.5%Ni4%Fe/SiO ₂ SWNi	171	99.8%	200	87.2%	0.61	234	66.8%	0.42	246	60.5%	0.49	433	21.2%
0.5%Co4%Fe/SiO2	169	99.6%	195	87.9%	0.61	227	67.5%	0.43	245	57.9%	0.48	423	23.3%
0.5%Co4%Fe/SiO2 SWFe	172	99.6%	200	87.0%	0.64	236	64.4%	0.44	248	58.0%	0.51	434	18.8%
$0.5\%Co4\%Fe/SiO_2$ SWCo	171	99.7%	199	86.6%	0.68	234	64.2%	0.43	245	58.2%	0.47	435	20.7%

^a Point at which mass loss rate begins to exceed 0.05%/K.

^b First peak point on DTG curve.

^c Valley point on DTG curve between first and second peak.

^d Second peak point on DTG curve.

^e Point at which mass loss rate declines below 0.05%/K.

the analysis.

Given that 4%Fe likely played an important role in glucose decomposition, it is yet to be explained why the 0.5%Ni4%Fe-SWFe catalyst offered the highest reduction in solid residue during the activity tests. It is most likely that the catalyst reduced the formation of solids from heavy hydrocarbons or char. In Part 1, 0.5%Ni/SiO₂ was shown to reduce solid residue due to its tar cracking abilities and its overall catalyst site dispersion. Having been impregnated separately from the Fe phase; the 0.5%Ni phase on the 0.5%Ni4%Fe-SWFe may have been separated and uninfluenced by the 4%Fe phase allowing the 0.5%Ni phase to act on its own in tar cracking.

3.2. Gaseous products

One major purpose for the use of bimetallics in the proposed system is for the *in-situ* production of hydrogen. Bimetallic catalysts such as supported NiFe and PdFe catalysts have been studied for their activity in WGSR reactions [31,40–42]. Pt 1 demonstrated that monometallic catalysts can increase H₂ output during glucose decomposition. It was therefore anticipated that the synergy between two metals together would further improve the H₂ production over the monometallic catalysts.

Of all catalysts that were tested, 0.5%Co4%Fe catalysts had the highest output of H₂ exceeding double the initial H₂ and the H₂ production that was witnessed over monometallic catalysts in previous study (see Table 2). Overall, CoFe catalysts produced the most H₂ with co-impregnated 0.5%Co4%Fe offering the most H₂. Interestingly, in the

Table 2

Outputs of H2, CO2, and CO.

1	_, _,						
		0.5%(M1) 4%(M2)	0.5%(M1) 4%(M2) -SW (M2)	0.5%(M1) 4%(M2) -SW (M1)	4%(M1) 0.5%(M2)	4%(M1) 0.5%(M2) -SW (M2)	4%(M1) 0.5%(M2) -SW (M1)
H ₂ (kPaa)	Initial Input	38					
	No Catalyst	64					
	NiFe/SiO2	48	35	51	21	20	22
	CoFe/SiO ₂	78	70	64	66	58	61
	PdFe/SiO ₂		14	14			
	PtCo/SiO2		28	30			
CO ₂ (kPaa)	No Catalyst	99					
	NiFe/SiO2	163	138	118	100	122	136
	CoFe/SiO ₂	153	129	114	145	121	130
	PdFe/SiO ₂		103	122			
	PtCo/SiO2		109	108			
CO (kPaa)	No Catalyst	62					
	NiFe/SiO2	52	67	44	44	55	57
	CoFe/SiO ₂	53	47	44	56	52	44
	$PdFe/SiO_2$		37	42			
	PtCo/SiO2		44	39			

previous study, 0.5%Co and 4%Fe catalysts produced relatively low amounts of H₂. Combining the two however appears to have a greater impact due to either a synergistic effect or combined activity. Seeing as how no activity combination effect is witnessed for the 4%Co0.5%Fe catalyst, it is possible there is a synergistic role between the two metals which is most present when they are co-impregnated. A similar trend is also noted for CO₂ production highlighting the likelihood that WGSR occurred. The fact that the co-impregnation method provided the most H₂ suggests that there is a stronger relationship between the two metals when they are formed together perhaps as an alloy. It is suggested that this is due to the similar oxide structures of the two metals producing cobalt iron oxides Co_{3-x}Fe_xO₄.

Having the more noble metal in lower concentration than oxophillic Fe also appeared to benefit the NiFe catalysts in terms of H_2 output alone. The 0.5%Ni4%Fe configurations of NiFe had a higher output of H_2 than the 4%Ni0.5%Fe catalysts. Although 0.5%Ni produced more H_2 as a monometal than 4%Fe in Part 1, co-impregnation or impregnation of the Fe last is more beneficial for H_2 output signifying an importance in Fe exposure. Like CoFe, a similar trend is also noted for CO₂ production over the NiFe catalysts suggesting WGSR. According to Watanabe, et al. [42], NiFe catalysts behave synergistically for WGSR where water oxidizes the Fe and H_2 is produced meanwhile, Ni facilitates better CO absorption which leads to the oxygenation of CO to CO₂ via the oxidized Fe site. It may be possible that CoFe may also behave in a similar fashion where Co replaces the role of Ni.

For 4%Ni0.5%Fe it is noted that stepwise impregnation beginning with 4%Ni is most beneficial to produce CO_2 with no discernable

differences in H₂ production among all three impregnation methods used for 4%Ni0.5%Fe. One possibility to consider is that internal H₂ is being produced along with CO₂ via WGSR on the 4%Ni0.5%Fe catalysts however the H₂ may be rapidly consumed by other reactions. Seeing as how the H₂ output dips below the initial amount that was added – unlike what was seen on monometallic 4%Ni and 0.5%Fe catalysts in Part 1 – significant H₂ consumption is highly likely. Therefore, it is possible that the SWNi variant of the 4%Ni0.5%Fe catalyst produced more internal H₂ than the other two variants as signified by the higher CO₂ output.

When observing the results for the output of CO it is noted hat the output of CO does not correlate with that of CO_2 as expected. For a system purely based on WGSR, it is expected that the output of CO would decrease as the output of CO_2 increases. However, as seen in the results of some catalysts such as 4%Ni0.5%Fe, it is noted the trend of CO_2 increasing as per the impregnation method does not correspond with a decrease in CO. What is likely occurring is that the production and subsequent consumption of internal hydrogen leads to the production of more CO and H₂O. Therefore, it is not fair to say that a higher output of CO alone represents low WGSR activity here as WGSR could have already occurred producing H₂ which enabled the production of additional CO.

Similarly, for 0.5Pd4Fe, impregnating 4%Fe after 0.5%Pd appears to produce more CO_2 than the alternative step-wise impregnation method as well as monometallic 4Fe. Under the assumption that the 4% Fe covers the 0.5%Pd, this suggests that there is some synergistic relationship whereby Pd causes electron delocalization which stabilizes the Fe surface and preventing it from becoming permanently oxidized [15]. Alternatively, if Pd is directly exposed, it made become contaminated or easily coked. Similarly, to monometallic Pd, both configurations of 0.5%Pd4%Fe had an overall reduction of H₂ from initial input to output.

Combining Pt and Co together as a bimetallic catalyst negatively impacted the output of H_2 as both Pt and Co produced more as mono metals however, together, they appear to consume H_2 . Both stepwise configurations of 0.5%Pt4%Co catalysts produced the same amount of CO₂ however combining Co with Pt appears to offer no advantage over Fe. Therefore, the oxophilic nature of Fe serves an important role in the CoFe catalysts by as suggested earlier, serving the same role as Fe in NiFe catalysts – facilitating the oxygenation of CO to CO₂.

3.3. Liquids products

74%

NiFe/SiO2

As one may elude from the results reported for solid and gaseous products, the catalysts had an impact on the yield of liquid products. As seen in Fig. 4, the relative trend between the catalysts, for the most parts follows that of the organic solid conversion from Fig. 1 with a few

CoFe/SiO2

PdFe/SiO2



exceptions such as 4%Ni0.5%Fe/SiO₂ versus 4%Co0.5%Fe/SiO₂. With no surprise, 0.5%Ni4%Fe/SiO₂-SWFe had the highest yield of liquid products among all bimetallic catalysts, as this catalyst was active towards tar cracking. However, the liquid yield remained lower than that of 0.5%Ni/SiO₂ from Pt.1 due to its higher yields of CO and CO₂. Coimpregnated 0.5%Co4%Fe/SiO₂ yielded far less products in the liquid phase as it favoured the production of H₂ and CO₂. Along with the drop in CO production, it is suggested that the reduction in liquid phase products is due to a reduction in water content as water would have been consumed for water-gas-shift.

In the previous study for monometallic catalysts, it was determined that the Co catalysts were the most effective at performing in situ deoxygenation with the highest selectivities to 2 M F and DMF over furanic intermediates such as furfural. For $4\%\text{Co/SiO}_2$ in particular; 87.2% of the furanic compounds were 2 M F and DMF. As seen in Fig. 5, none of the bimetallic catalysts quite achieved the same selectivity, however various $4\%\text{Fe-containing catalysts yielded competitive results as high as <math>82\%$. For comparison, in the previous study, the fraction of 2 M F and DMF totalled 65.6%.

Combining 4%Fe and 0.5%Ni made a more competitive catalyst than either of the metals on their own. Overall, 0.5%Ni4%Fe catalysts out performed 4%Ni0.5%Fe which appeared to offer little improvement over monometallic 4%Ni in terms of 2 M F and DMF selectivity. This is likely related to higher production of internal H₂ with the 0.5%Ni4%Fe catalysts which had higher outputs of both H₂ and CO₂ suggesting higher degree of WGSR. Stepwise impregnation benefits this catalyst. When the 4%Fe phase was impregnated first, the result was a total elimination of the 5-methylfurfural intermediate and a higher selectivity towards DMF than the co-impregnated catalyst. Of the three variants, the 0.5%Ni4%Fe-SWFe catalyst had the lowest output of H₂ which as detailed here may have been due to an elevated rate of consumption via deoxygenation.

The selective deoxygenation function of NiFe catalysts have received much attention. Both metals have been suggested to serve important roles where Fe facilitates adsorption preferentially via the oxygen containing functional groups while Ni activates hydrogen for hydrogenolysis [13,14,26]. Therefore, it makes sense that both metals would have to be exposed. Impregnating 4%Fe after 0.5%Ni may have had a negative impact on Ni's ability to activate hydrogen and thus the selectivities of 2 M F and DMF are lower on the SWNi catalyst than the SWFe. The co-impregnated catalyst on the other hand may have suffered from a more intimate interaction between the two metals which may have formed a NiFe mixed or alloy phase.

Similar to the NiFe catalysts; the 0.5%Co4%Fe catalysts appeared to outperform the 4%Co0.5%Fe catalysts. The co-impregnated and SWFe variants of 0.5%Co4%Fe eliminated the output of the furfural. Unlike the NiFe catalysts, the co-impregnation method was very suitable for CoFe in general boosting competitively high 2 MF and DMF selectivities for both the 0.5%Co4%Fe and 4%Co0.5%Fe catalysts. This provides additional evidence that the CoFe catalysts benefit from a strong interaction between the two metals perhaps as an alloy. 4%Co0.5%Fe-SWFe produced interesting results in which the furnaic compounds consisted of a large portion (28.2%) of 2-acetylfuran - an unusual furanic compound that would signify either a major change in glucose decomposition or possibly a side reaction involving furfural. Trimethylfuran was noted as being present in the products likely due trans-alkylation reactions however in low amounts (< 5% of total furanics). Interestingly although the fraction of 2 M F achieved here was not as significant as 4%Co/SiO₂ in the previous study, 0.5%Co4%Fe/ SiO₂ had a lower furfural fraction at 0%.

As a monometallic catalyst; 0.5%Pd was not very effective at reducing the amount of furfural among all furanic compounds. However, 0.5%Pd and 4%Fe paired together significantly reduced the content of furfural, completely eliminating it when the 0.5%Pd phase was impregnated onto the support first. Like NiFe, PdFe catalysts have received a lot of attention in the selective deoxygenation of furanic and



■ 2MF ■ DMF ■ Furfural ■ 5-methylfurfural ■ Other Furanics

Fig. 5. Distribution of total furanic products.

phenolic compounds. The literature states that Pd alone was more active towards ring interaction however when modified with Fe, the catalyst favours selective deoxygenation of constituents attached to the aromatic ring [15–18]. Hensley et al. [15], described the roles of the two metals as Fe facilitating oxygenate absorption while Pd imposes an electron delocalization effect effectively stabilizing the Fe. As it outperformed the SWFe variant; it is suspected that the SWPd variant of 0.5%Pd4%Fe provided a stronger interaction between the two metals and/or was able to prevent Pd's interaction with the aromatic ring more effectively. Like the PtCo catalysts though which also had competitive results among all the catalysts, the PdFe catalysts appear to offer no significant advantages over the NiFe and CoFe catalysts which would justify the additional costs associated with using noble metal catalysts Pd and Pt.

3.4. Characterization

0.5%Ni4%Fe and 0.5%Co4%Fe were selected for further tests and characterizations due to the overall value that they provided. Despite having lower concentrations of expensive, active materials (Ni and Co), these catalysts provided very competitive results in terms of both gas and liquid products along with the potential to help reduce solid residue.

Due to the low concentrations of Ni and Co, TPR profiles (as shown in Fig. 6) were faint as iron itself generally has a faint profile. Interestingly though, the broad peaks which generally form at 450 °C and 600 °C for Fe were shifted and stretched when a second metal was used. For example – the 0.5%Ni4%Fe/SiO₂-SWFe catalyst had and an initial peak ~425 °C followed by a very broad peak ~700 °C. Clearly, there was an interaction between the two metals. The CoFe catalysts had very undiscernible peaks especially when prepared via stepwise impregnation.

XRD analyses of the 0.5%Co4%Fe and 0.5%Ni4%Fe catalysts (see



Fig. 6. TPR Profiles for 0.5%Ni4%Fe/SiO2 and 0.5%Co4%Fe/SiO2 catalysts.

Fig. 7) revealed that there was not an oxide phase present. Due to their low concentration; Ni and Co phases were not detectable on their own. XRD spectra for CoFe and NiFe alloys coincide with spectra for Fe therefore making it difficult to distinguish if the peaks at ~45° correspond only to Fe or if they indicate the presence of an alloy phase. For the two co-impregnated catalysts, the peak appears to be a double peak which could be described by the presence of both Fe and an alloy phase however the scale and resolution of these peaks are not strong enough to allow for verification.

HRTEM and STEM-HAADF analyses with were performed with EDS to determine the presence of Co/Ni and Fe in the catalysts and to establish if there were separated or together as alloy phases. HRTEM images – as shown in Fig. 8 – show no distinguishable deference



Fig. 7. XRD Spectra for 0.5%Ni4%Fe/SiO $_2$ and 0.5%Co4%Fe/SiO $_2$ catalysts.

between catalyst particles of different metals or the combination thereof. EDS proved to be the only method of indicating the presence of either metal or possibly both at one location. Dispersion of the metals appeared to be most significant on the SWFe catalysts as catalyst sites tended to be small and separated. The other two preparation methods (especially the SWNi/SWCo variants) yielded catalyst sites that were quite clustered perhaps. This effect was mostly independent on the selection of the most active metal (Ni vs. Co). For the co-impregnated samples, it was a regular occurrence to find sites that were composed of both metals. Meanwhile, for the step-wise impregnated samples, metallic sites consisted of both monometallic and bimetallic phases. Even the metals of lower concentrations (Co and Ni) were found separated.

STEM-HAADF images and EDS mappings were performed to further investigate the metallic site compositions. STEM-HAADF images

(Fig. 9a–c) clearly show the dispersion of the catalyst sites and their relative densities compared to the SiO_2 support. Corresponding EDS mappings (Fig. 9d–f) demonstrated distinct differences between co-impregnated and step-wise impregnated 0.5%Ni4%Fe. Fig. 9d shows that the Ni sites easily coincide with the Fe sites without separation, strongly suggesting that the two metals are together as an alloy. Fig. 9e and f on the other hand show a clear separation of the Ni and Fe sites for the 0.5%Ni4%Fe catalysts prepared via step-wise impregnated catalysts experienced alloying while the step-wise impregnated catalysts consisted of separate phases. EDS mapping of the CoFe catalysts was not possible as the spectra for Fe can interfere with that of Co.

Given the earlier observations, it can be concluded that 0.5%Co4% Fe/SiO₂ benefits most from alloying. This co-impregnated catalyst boosted competitive levels of deoxygenation and the highest output of H₂. Based on findings of other bimetallic catalysts, it is hypothesized that incorporating Co into Fe effectively helps stabilize Fe which facilitates absorption via oxygen containing functional group [15]. For $0.5\%Ni4\%Fe/SiO_2$ alloying Ni and Fe via co-impregnation, although competitive, was not as favourable as step-wise impregnation. Stepwise impregnation (SWFe) kept some of the 0.5%Ni phase separate from the Fe allowing for greater reduction in solid residue and achieved better deoxygenation. The SWFe catalyst however had lower output of H₂ perhaps due to higher consumption. Ni and Fe may need to be kept separate for them to perform separate roles for both solids decomposition and deoxygenation.

3.5. Magnetite tests

Of all the bimetallic catalysts that were tested, the two catalysts that proved to most interesting were the 0.5%Ni4%Fe/SiO₂-SWFe and 0.5%Co4%Fe/SiO₂ catalysts. The former provided the best reduction in organic solid residue at 83.7% reduction while the latter provided the highest output of H₂ at 78.2 kPaa. Both catalysts were competitive



Fig. 8. HRTEM Images of: (a) 0.5%Ni4%Fe/SiO₂ (b) 0.5%Ni4%Fe/SiO₂-SWFe (c) 0.5%Ni4%Fe/SiO₂-SWNi (d) 0.5%Co4%Fe/SiO₂ (d) 0.5%Co4%Fe/SiO₂-SWFe and (e) 0.5%Co4%Fe/SiO₂-SWCo.



Fig. 9. STEM-HAADF images and EDS mappings of 0.5%Ni4%Fe/SiO₂ catalysts. (a)-(c): STEM-HAADF images of NiFe, NiFe-SWFe, and NiFe-SWNi respectively. (d)-(f): EDS mappings of NiFe, NiFe-SWFe, and NiFe-SWNi respectively.

towards producing deoxygenated furanic compounds 2 M F and DMF. Like previous tests with $0.5\% \text{Ni/SiO}_2$ and $0.5\% \text{Re/SiO}_2$ in Part 1; these two catalysts were tested again without an initial charge of H₂ but instead with Fe₃O₄ fed at the same ratio as the catalysts. The intended purpose for the Fe₃O₄ was to produce internal H₂ (via WGSR), which the catalysts would be dependent upon.

The addition of the deoxygenation catalysts appeared to have only a small added affect on the outcome of the process as seen in Table 3. Adding the catalysts managed in slightly reduce the amount of organic solids from a 82.0% reduction to 85.2% upon addition of the NiFe catalyst and 86.3% for the CoFe catalyst. The NiFe catalyst seemingly increased the output of gases, especially CO_2 perhaps attributed to additional WGSR and reforming activity. However, where the CoFe catalyst mostly maintained the selectivity of furanic compounds. the NiFe catalyst seemed to reduce the selectivity of 2 M F and DMF in favour of other furanic compounds such as 2-acetylfuran.

Overall, the catalysts do not appear to add any significant bonus on top of the Fe_3O_4 . One issue that has been considered is that the hydrogen produced on the magnetite is not readily available to the added catalysts to provide activation. Ideally, WGS and deoxygenation reactions should occur on the same catalyst on nearby sites so that hydrogen can be produced on the surface and readily consumed for deoxygenation eliminating many mass transfer barriers.

Combining WGSR and deoxygenation on a single catalyst surface would mitigate the need for H₂ (from WGSR) or even water (from dehydration) to be desorbed from the catalyst surface - only CO₂. The mechanism would ideally proceed similarly to the WGSR mechanism suggested for NiFe/ CeO₂-ZrO₂ by Watanabe et al. [42], however, instead of the active material (NiFe) being oxidized by water, it is oxidized by the oxygenates undergoing hydrogenolysis. Catalysts would require an initial amount of hydrogen to provide activation to start hydrogenolysis. The oxygen on the surface may then transfer to an appropriate supporting material containing oxygen vacancies thereby temporarily stabilizing the active metal. CO is then required to reduce the catalyst producing CO₂. Surface CO may be derived either via the actual absorption of carbon monoxide or possibly via decarbonylation. In summary, water which is typically produced during hydrogenolysis is not immediately associated and desorbed from the surface, and essentially oxygen is instead removed as CO2. A summary of this theoretical process is demonstrated in Fig. 10 based on the mechanisms described by Watanabe et al. [42], for WGSR and Sitthisa et al. [14], for deoxygenation.

Table 3

Summary	of results	for tests	with mag	netite. N	iFe catalys	t = 0.5%	Ni4%Fe/SiO	D ₂ -SWFe.	CoFe cataly	vst =	0.5%Co4	%Fe/S	iO.

		-	-	
	Glucose	$Glucose + Fe_3O_4$	Glucose + Fe_3O_4 + NiFe Catalyst	$Glucose + Fe_3O_4 + CoFe Catalyst$
Gaseous Products:				
PH ₂ (kPaa)	3.8	9.1	10.0	10.5
PCO ₂ (kPaa)	96.5	181.7	200.3	170.6
PCO (kPaa)	52.0	47.5	53.4	51.3
Solid Residue:				
%OSC	75.8%	82.0%	85.2%	86.3%
H:C	0.76	0.96	0.97	0.90
Fraction of Total Furanic	Products:			
2 M F	28.4%	45.8%	41.9%	45.5%
DMF	25.9%	37.8%	32.5%	39.4%
Furfural	24.9%	0.9%	3.3%	2.0%
5-methylfurfural	14.2%	2.8%	4.0%	0.0%
Other Furanics	6.6%	12.7%	18.2%	13.2%



Fig. 10. Proposed combination of WGSR and Deoxygenation (furfuryl alcohol shown as example) on the surface of an active metal with an active support with oxygen vacancies. (A) Adsorption of furfuryl alcohol; adsorption and dissociation of H_2 . (B) Furfuryl alcohol is adsorbed via the oxygen of the hydroxymethyl group (likely on Fe of NiFe catalyst). (C) Hydrogenolysis of furfuryl alcohol. (D) 2 M F desorbed from the surface; oxygen is transferred to the active support's oxygen vacancy (such as CeO₂-ZrO₂). (E) CO is adsorbed onto catalyst surface (likely via Ni of NiFe); hydrogen atoms at any time may associate. (F) Oxygen back-transfer from support to active metal (Fe of NiFe); desorption of H_2 . (G) Oxidation of CO to produce CO₂. (H) Final desorption of CO₂.

4. Conclusions

Of all the catalysts that were studied herein, the superior catalysts were selected as $0.5\%Co4\%Fe/SiO_2$ and $0.5\%Ni4\%Fe/SiO_2$ -SWFe. Due to alloying of the two metals, $0.5\%Co4\%Fe/SiO_2$ offered competitive deoxygenation properties, eliminating furfural content all while boosting *in-situ* H₂ production. As an alloy, Co stabilizes Fe, preventing permanent oxide formation. On the other hand, sequential impregnation of $0.5\%Ni4\%Fe/SiO_2$ catalyst was favourable as it provided a distinct separation of the Ni and Fe phases allowing them to perform their individual roles. As a result, the $0.5\%Ni4\%Fe/SiO_2$ -SWFe catalyst provided competitive deoxygenation properties with elevated DMF fractions and was superior at reducing solid residue content. Aside from their ability to help reduce solid residue, catalysts with 4 wt% Co/Ni 0.5% provided underwhelming results. Pd4%Fe/SiO₂-SWPd also eliminated furfural content however H₂ consumption was a concern.

Future work should focus on improving catalyst site dispersion on supporting materials and the selection of appropriate materials that promote *in-situ* hydrogen production. A bifunctional catalyst that promotes both deoxygenation and WGSR instead of two separate catalysts would likely eliminate barriers associated with mass transfer of H_2 .

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