REGULAR ARTICLE



Base-free oxidation of 5-hydroxymethyl-2-furfural to 2,5-furan dicarboxylic acid over basic metal oxide-supported ruthenium catalysts under aqueous conditions

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MS received 10 May 2018; revised 13 August 2018; accepted 1 September 2018

Abstract. Polyethylene terephthalate (PET) is the third-largest globally produced polymer, and many efforts have been made to replace PET with a renewable polymer. One renewable alternative to PET is polyethylene furanoate (PEF), which is prepared using 2,5-furan dicarboxylic acid (FDCA) as a precursor instead of terephthalic acid (TPA). Biomass-derived hydroxymethyl-2-furfural (HMF) can be converted to 2,5-furan dicarboxylic acid (FDCA) through multiple oxidation reactions. Metal oxide-supported Ru catalyst prepared by simple methods for the oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furan dicarboxylic acid (FDCA) in the absence of a base under aqueous conditions is reported. This study clearly explains that the nature of basicity of the support has an important role on the selective oxidation of HMF to FDCA. Among the various materials studied magnesium oxide (MgO)-supported Ru catalyst afforded a 100% HMF conversion and more than 90% FDCA yield with 90 *psi* of O₂ at 160 °C in 4 h and it could be used 5 times without a significant drop of FDCA yields.

Keywords. Ruthenium; metal oxides; base-free oxidation; aqueous conditions; 5-hydroxymethylfurfural (HMF); 2,5-furan dicarboxylic acid (FDCA).

1. Introduction

The diminishing availability of petroleum resources is an increasing problem for the production of energy and chemicals that are essential for society. The worldwide reserves of petroleum resources are expected to be sufficient for another 40 years, which increased concerns about rising oil prices.¹ Biomass is the term used to describe all biological matter produced by photosynthesis using solar energy, and biomass is an alternative to petroleum resources. Abundant biomass resources are a promising alternative for the sustainable supply of valuable intermediates to chemical industries for the production of drugs and polymeric materials.² "Roadmap of Biomass Technologies," a report authored by 26 leading experts, predicted that by 2030, 20% of transportation fuels and 25% of chemicals will be produced from biomass.³ Plant biomass is a labourintensive and land-intensive resource with a variable economy due to rapidly growing utilization for the production of fuels and chemicals.⁴ Plant biomass-derived carbohydrates can be converted into fuels and chemicals *via* fermentation to bioethanol, enzyme-catalyzed conversion to hydrogen and anaerobic digestion to

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Electronic supplementary material: The online version of this article (https://doi.org/10.1007/s12039-018-1551-z) contains supplementary material, which is available to authorized users.



Figure 1. Synthesis of PET and PEF polymers.

methane.^{5–7} Every process has its own advantages and disadvantages during development, and research is ongoing to further expand the use of biomass. The conversion of carbohydrates to fuels and chemicals through 5-hydroxymethyl-2-furfural (HMF) is a catalytic method to utilize carbohydrate biomass in which oxidation leads to the replacement of polyethylene terephthalate (PET), the third-largest globally produced polymer.⁸ Several attempts have been made to replace PET using a renewable polymer, polyethylene furanoate (PEF), because PEF is a carbon neutral bio-based material, and its physical performance, such as glass transition temperature and gas permeability, is greater than PET (Figure 1).^{9,10}

HMF was identified as an intermediate chemical with the potential to be converted to the PEF polymer precursor, 2,5-furan dicarboxylic acid (FDCA). FDCA is obtained by full oxidation of both the formyl and hydroxymethyl groups of HMF to a carboxylic acid. HMF can be oxidized to FDCA with quantitative amounts of conventional oxidants such as KMnO4 or HNO₃.¹¹ Recently, enzyme-mediated preparation methods of FDCA were reported.¹²⁻¹⁴ However, most studies focus on heterogeneous catalysis using molecular oxygen as an oxidant under aqueous conditions; furthermore, several studies supported Au and Pt catalysts for this purpose.^{15–17} Moreover, excess inorganic bases such as NaOH or Na₂CO₃ were used in some processes.¹⁸⁻²¹ Hydrotalcite-supported Au nanoparticles gave 99% FDCA yield in the absence of a base, but its yield was significantly decreased during recycling.²² Several Pt and Au based catalysts found to be successful for the base free HMF oxidation but high cost of the precious metals is still an issue.²³⁻²⁶ Spinel oxides with active metal like cobalt and manganese were also successfully employed in this selective oxidation reaction; but in acetic acid solvent.²⁷ Ruthenium is a potential oxidizing metal; various ruthenium supported heterogeneous catalysts were used for HMF oxidation to 2,5-diformylfuran (DFF).^{28–31} However, ruthenium supported materials were not successful for HMF oxidation to FDCA

because complete oxidization to FDCA was impossible or ruthenium leaching caused the ruthenium to be unusable.^{32,33} Recently, Ru/C commercial catalyst showed the base free oxidation of HMF to FDCA with an 88% FDCA yield using high catalyst loading.³⁴ However, such a Ru/C catalyst needs activation before reuse. More recently, our group developed a new class of MnCo₂O₄ spinel supported Ru catalyst for selective oxidation of HMF into DFF or FDCA according to solvents.^{35,36}

Here we report exploration of basic metal oxidesupported Ru catalysts to use for this important reaction in the absence of a base.

2. Experimental

2.1 Materials

Magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O, 99%, ACS reagent), aluminium nitrate nonahydrtate (Al(NO₃)₃· 9H₂O, \geq 98%, ACS reagent), sodium hydroxide (NaOH, \geq 97%, ACS reagent), sodium bicarbonate (NaHCO₃, \geq 99.7%, ACS reagent), ruthenium(III) chloride (RuCl₃, Ru content 45–55%), 5-hydroxymethyl-2-furfural (HMF, 99%), MgAlhydrotalcite (Mg₆Al₂(CO₃)(OH)₁₆·4H₂O), MgO (97%, ACS reagent), ZrO₂ (powder, 99% trace metals basis), CeO₂ (powder, 99.995% trace metals basis) and La₂O₃ (99.99% trace metals basis) were purchased from Sigma-Aldrich (USA). All chemicals were directly used without further purification unless otherwise mentioned.

2.2 Methods

Powder X-ray diffraction (PXRD) was carried out on a Bruker M18XHF22 system using Cu K α radiation (λ =1.54056 Å). The operating voltage and current were 40 kV and 40 mA, respectively with a scanning speed of 2 deg/min, for data collection. The data were processed using the XPRESS (version 1.0.3) software. Transmission electron microscope (TEM) images were taken with a Maker FEI, model Technai G2 microscope with an acceleration voltage of 200 keV using carbon-coated 200 mesh copper grids. Total surface analysis of the materials obtained by NH₃ and CO₂ TPD was performed on an Autochem II 2920 (Micromeritics Corp.). Samples were pretreated using He at 100 °C for 1 h, continued with adsorption of NH3 or CO2 at 100 °C for 1 h, and followed by gas desorption from 100 °C to 800 °C (rate 10 °C/min). The specific surface area of the catalyst material was determined in a BET surface analyzer (Bruanuer-Emmett-Teller, ASAP2010, Micromeritics, USA) using N₂ as the adsorbent at liquid nitrogen temperature (77 K) in a relative pressure (P/P0) range of 0 to 0.25. The samples (in powder form) were degassed in the air for over 12h at 100 °C prior to analysis. XPS measurements were carried out on a Thermo Fischer Scientific K-alpha using monochromatized Al Ka radiation $(h\nu = 1486.6 \text{ eV})$ and processed using Thermo Avantage software. NMR analysis was performed on a Bruker Spectrospin 300 (Bruker Corporation, Germany) in a DMSO-d6 solvent. The conversion of HMF and the yield of the products, including FDCA were determined using high-performance liquid chromatography (HPLC, Agilent 1200 series) equipped with a refractive index (RI) detector and an Aminex HPX-87H column (Bio-Rad Laboratories, Inc.). The HPLC analysis conditions were as follows: eluent, 0.01 N H₂SO₄; flow rate, 0.6 mL/min; and column temperature, 45 °C. Prior to the HPLC analysis, all samples were subjected to dilution with water (HPLC grade) to prevent signal overload and damage to the system.

2.3 Synthesis of MgAlO

The material was prepared by co-precipitation under low supersaturation. In this method, two solutions, namely, solution (A) containing the desired amount of magnesium and aluminium nitrates and solution (B) having precipitating agents (i.e., NaOH and Na₂CO₃) were added slowly (1 mL/min) and simultaneously using Schott electronic titrator, at a constant pH 9.5 during addition under vigorous stirring at room temperature. The addition took approximately 90 min and the final pH was adjusted to 10 by adding few drops of precipitant solution. The samples were aged in the mother liquor at 65 °C for 18h in an oil bath, filtered, washed (until total absence of nitrates and sodium in the washing liquids) and dried in an air oven at 100–110 °C for 12h. This was calcined at 500 °C for 2h and named as MgAIO.

2.4 Ruthenium impregnation

Ruthenium was loaded on the support using wet impregnation method like the calculated amount of $RuCl_3$ (to achieve 2 wt% metal) was dissolved in 100 mL of water to which 2 g of support (MgAlO prepared above or other metal oxides purchased) was added and stirred at room temperature for 3 h. Filtered and washed with copious amount of water and dried in a vacuum oven at 30 °C.

2.5 Catalytic reactions

All the reactions were carried out in a 50 mL Parr reactor; HMF, solvent, and catalyst were added and the reactor was fleshed with O_2 for 3 times. Pressurized with O_2 again and heated up to the desired temperature to achieve the operating pressure; all the reactions were carried for 4 h with 650 rpm stirring. Immediately after the reaction reactor was cooled to room temperature and samples were analyzed with HPLC.

3. Results and Discussion

Ruthenium was simply loaded on the metal oxides using wet impregnation method as reported previously.²⁹ PXRD patterns of the synthesized Ru/metal oxides were the same as the metal oxides reported in the literature. No reflection was observed for ruthenium/ruthenium oxide in these materials, implying that the ruthenium is homogeneously loaded on the support. PXRD analysis of Ru/MgAlO and Ru/MgO showed mixed metal oxide and metal oxide phase and the right formation of mixed metal oxide MgAlO could be verified. Ru/La₂O₃ contains pure La₂O₃ phase along with some La(OH)₃ impurity phase. Ru/ZrO₂ and Ru/CeO₂ contain tetragonal zirconium phase and cubic CeO₂ phase, respectively (Figure 2). To understand the morphology and nature of ruthenium loading TEM was carried out and each material exhibited different morphology (Figure S1, Supplementary Information). Ru/MgAlO showed agglomerated small platelet materials forming a sponge-like structure and Ru/MgO showed larger platelet-like materials. Ru/La₂O₃ showed agglomerated coral-like structure rather than the platelet and both Ru/ZrO2 and Ru/CeO2 showed distorted sphere-like structure. Presence of ruthenium over these materials was confirmed by SEM-EDX analysis.

Oxidation of HMF was performed using synthesized materials as a catalyst in a water medium (Table 1).¹⁹ HMF bears two oxidizable moieties corresponding



Figure 2. Powder X-ray diffraction analysis of synthesized materials (with 2wt% Ru loading).

Table 1. Conversion of HMF and selectivity of products in the oxidation of HMFusing a Ru catalyst supported on various metal oxides.^a

Entry	Catalyst	HMF conversion (%) ^b	Yield (%) ^b				
			DFF	HMFCA	FFCA	FDCA	LA
1	Ru/MgAlO	100	0.5	0	0.2	99	0
2	Ru/MgO	88	2.8	0	21	58	5.4
3	Ru/La ₂ O ₃	4.6	0	0	1.4	0.8	2.4
4	Ru/CeO ₂	89	45	0	35	7.0	3.2
5	Ru/ZrO_2	100	86	0	14	0	0
6	RuCl ₃ ^c	100	7	0	26	18	30

^aReaction conditions: HMF (252 mg, 2 mM), catalyst (200 mg, 2 wt% Ru), H₂O (20 mL), O₂ (90 *psi*), 140 °C, 4 h.

^bDetermined by HPLC.

^cEquimolar to supported Ru.



Figure 3. Oxidation pathways from HMF to FDCA.

to formyl and hydroxymethyl groups. From HMF, oxidation of the hydroxymethyl group yields DFF, while oxidation of the formyl group yields 5-(hydroxymethyl)-2-furan carboxylic acid (HMFCA). Further oxidation of DFF and HMFCA can yield FDCA via 5-formyl-2-furan carboxylic acid (FFCA). Therefore, DFF, HMFCA, FFCA can be obtained as intermediates during the oxidation of HMF to FDCA (Figure 3).

Among the materials investigated, MgAlO support obtained from layered double hydroxide (LDH) was found to be highly active with a 100% HMF conversion and a 99% FDCA yield (Entry 1).²⁰ MgO supports showed high activity towards HMF conversion, but the yield of FDCA was moderate (58%) (Entry 2). Instead, DFF and FFCA intermediates produced by the partial oxidation of HMF still remained. La₂O₃ support has a very low HMF conversion of less than 5%, and a deformylated product, levulinic acid (LA), was obtained as a major product (Entry 3). ZrO₂ support has a low yield for FDCA, but DFF and FFCA were obtained in 45% and 35% yields, respectively (Entry 4). CeO₂ was not sufficient for the oxidation of HMF up to FDCA, but CeO₂ was converted mainly to DFF (86%) (Entry 5). Homogeneous ruthenium catalyzed a reaction in the presence of RuCl₃ prefers over oxidation of HMF to LA and FA rather than FDCA (Entry 6). In all supports, HMFCA was not found as an intermediate, which indicated that oxidation of HMF using metal oxides-supported Ru catalyst proceeds via DFF.

From these results, the order of Ru catalyst activity for HMF oxidation was determined according to supports: $MgAlO > MgO > ZrO_2$ $> CeO_2$ \gg La₂O₃. The surface area of these materials was measured to find the reason the activity (Table 2). The order of BET surface area of the materials were in the order of Ru/MgAlO > $Ru/MgO \gg Ru/La_2O_3 > Ru/ZrO_2 > Ru/CeO_2$ and it confirms that the high activity of MgAlO and MgO supports were due to its high surface area. But this analysis is not sufficient to explain the complete trend in the catalytic activity. Though these materials were different morphology as observed by TEM measurements reason for different catalytic activity might be due to different basic nature of the support.

To find the basicity of these materials temperature programmed desorption (TPD) were investigated (Table 3). TPD analysis of the catalysts indicates

Catalyst	BET surface area (m^2/g)	Pore volume (cm^3/g)	Aver. pore diameter (A)
Ru/MgO	73	0.372	203
Ru/MgAlO	200	0.394	79
Ru/La ₂ O ₃	13	0.051	156
Ru/CeO ₂	3.9	0.019	191
Ru/ZrO_2^2	4.5	0.018	157

Table 2. Surface properties of synthesized materials.

 Table 3.
 Temperature programmed desorption analysis of synthesized materials.

	NH ₃ TPD		CO ₂ TPD				
Name	Maximum desorption (°C)	Amount of HN ₃ (mmol/g)	Maximum desorption (°C)	Amount of CO ₂ (mmol/g)	Total acidity (mmol/g)	Total basicity (mmol/g)	
Ru/MgAlO	279	1.66	195	4.40		6.02	
C			217	0.22	1.66		
			346	1.40			
Ru/MgO	293	1.30	156	0.08		6.09	
•	354	1.80	221	0.11	3.10		
			340	5.90			
Ru/La ₂ O ₃	314	0.87	325	3.40		5.10	
	473	0.38	384	0.30	1.49		
	645	0.24	484	1.40			
Ru/ZrO ₂	313	0.19	_	_	0.21	0	
	510	0.02					
Ru/Ce ₂ O ₃	305	0.10	_	_	0.10	0	

that Ru/MgAlO, Ru/MgO, and Ru/La₂O₃ have total basicity of 6.02, 6.09, and 5.10 mmol/g, respectively while Ru/ZrO₂ and Ru/CeO₂ show no basic property. In addition, the MgAlO and MgO support contain only weak and moderate basic sites while La₂O₃ contains moderate and high basic sites. However, due to the presence of Lewis acidic character of lanthanum, La₂O₃ also contains moderate and high acidic sites, which can be the cause for low catalytic activity. In general, the catalyst supports with higher total basicity resulted in higher HMF conversion and FDCA yield.

Variation studies of temperature and O_2 pressure were performed to understand the influence of reaction parameters on the oxidation of HMF to FDCA over Ru/MgAlO (Figure S2, Supplementary Information). As the temperature increased, the HMF conversion increased with FDCA yield, and it was clearly explained that HMF oxidation passed through DFF and FFCA as previously mentioned. It was also clarified that 140 °C was the optimum temperature for the complete conversion of intermediates to FDCA. Pressure variation studies showed that 90 *psi* of O₂ pressure was enough for the complete conversion of HMF to FDCA; furthermore, it was confirmed that increase in O₂ pressure did not affect the product, i.e., the formed product was stable under high-pressure conditions in presence of a catalyst. However, the Ru/MgAlO catalyst filtered after the reaction washed with water and dried for reuse was not completely active for the consecutive cycles, which were also associated with a marginal amount of weight loss (Figure 4). ICP analysis was done for catalyst after first cycle which showed that 24.1% Ru reduction which clearly indicated the leaching of the active metal. This observation was different from materials reported in the literature, i.e., Au supported hydrotalcites (MgAl-OH), which was found to have reusable multiple cycles.²² To solve this problem, the Ru/MgAlO catalyst was calcined at different temperatures including 500 °C, 700 °C, and 900 °C, and the reusability was verified (Figure 4).

As the calcination temperature increases the structure of the oxide materials changes along with their acid/base properties. However, these catalysts were not found to be reusable, and some catalyst weight loss was observed after the first use. FDCA is a compound with high acidity ($pK_a = 2.28$), which can readily exchange the counter cation. Therefore, it was understood that Ru might be leached from the MgAlO support because Ru could be



Figure 4. Reusability of the Ru/MgAlO catalyst with different calcinations temperatures. Reaction conditions: HMF (252 mg, 2 mM), catalyst (200 mg, 2 wt% Ru), H₂O (20 mL), O₂ (90 *psi*), 140 °C, 4 h.

coordinated to the FDCA anion, as depicted in Figure 5. To confirm this phenomenon, commercial FDCA was stirred with a Ru/MgAlO catalyst at 100 °C in a water solvent, and it was observed that the catalyst was dissolved in the FDCA solution.

Since Ru/MgAlO failed to be reused for the oxidation of HMF to FDCA, Ru/MgO with acceptable activity was selected for further studies. Influence of catalyst loading was examined in order to increase HMF conversion. Expectedly, the catalyst loading enhanced the HMF conversion along with FDCA yield, and 400 mg of the catalyst was sufficient for the complete conversion of HMF with greater than 90% of FDCA yield using 90 *psi* of O_2 in 4h. Further, it needs to be mentioned here that the yield of the FDCA was also high (Figure 6).

Temperature variation studies of Ru/MgO were performed to understand the progress of the reaction (Figure 7). Its trend was similar to that of previous



Figure 6. Influence of catalyst amount on HMF oxidation using Ru/MgO catalyst. Reaction conditions: HMF (252 mg, 2 mM), Ru/MgO, H₂O (20 mL), O₂ (90 *psi*), 140 °C, 4 h.

materials, and FDCA yield was reached to a maximum at a reaction temperature of $160 \,^{\circ}$ C, whereas temperature over $160 \,^{\circ}$ C induced decomposition of HMF took place to give considerable amounts of levulinic acid and formic acid. Decomposition products formation was also observed in reactions with high reaction temperature and lower reaction time (2 h).

To further study the reusability of these materials immediately after the reaction, the catalyst was washed with water then dried and used for the next cycle. Figure 8 shows that these materials were reusable up to 5 cycles with a relatively identical activity. To understand the nature of ruthenium species responsible for the oxidation XPS analysis was done (Figure S3, Supplementary Information). It was noticeable that XPS analysis of Ru/MgO showed Ru $3d_{5/2}$ peak at 280.5 for the fresh catalyst while for the used one this reflection was at 279.5. This change in the peak position was due to



Figure 5. Proposed mechanism of leaching Ru and dissolving the metal oxide support.



Figure 7. Influence of temperature on HMF oxidation using the Ru/MgO catalyst. Reaction conditions: HMF (252 mg, 2 mM), Ru/MgO (200 mg), H₂O (20 mL), O₂ (90 psi), 4 h.



Figure 8. Reusability of the Ru/MgO catalyst on HMF oxidation. Reaction conditions: HMF (252 mg, 2 mM), Ru/MgO (400 mg), H₂O (20 mL), O₂ (90 *psi*), 160 °C, 4 h.

the electronic environment of the Ru metal was changed during the reaction but not associated with any change in the valance state of ruthenium.³⁷

HPLC profile of the reaction mixture during and after the reaction is given in Figure S4 (Supplementary Information). This clearly shows that the FDCA was the favorable product along with some intermediate oxidation products. In the industrial process, the formed product should be purified from the reaction mixture without using much energy. The product mixture was recrystallized and the purity of the FDCA was checked using ¹H and ¹³C NMR analysis (Figure S5, Supplementary Information). NMR results showed that recrystallized FDCA was pure and it can be further can

be used for polymerization reaction without any further purification.

4. Conclusion

In conclusion, the base free oxidation of HMF to FDCA using molecular oxygen was studied over different metal oxide supported ruthenium catalysts under aqueous conditions. Basicity of the support played an important role on the complete conversion of HMF to FDCA further, the presence of Lewis acid sites in the support leads to de-formylation reaction and weak basic sites leads to formation DFF. Among the 2 wt% Ru containing basic supports, MgAlO was found to be highly active; however, this support seriously dissolved during the reaction due to the highly acidic nature of the formed FDCA. On the other hand, a MgO-supported Ru catalyst, a bit less active than Ru/MgAlO, could be used 5 times with 90 psi of O₂ at 160 °C in 4 h without a significant drop of FDCA yields. FDCA formed during the reaction can be easily crystallized in water and which can be directly used for additional polymerization studies without any further purification.

Supplementary Information (SI)

Supplementary data is available for TEM, TEM-EDX, HPLC, XPS, and NMR studies. Supplementary Information is available at www.iac.ac.in/chemsci.

Acknowledgements

We acknowledge financial support for this research by the Internal Research Program (PEO18030) of Korea Institute of Industrial Technology (KITECH) and this work was supported by the National Research Council of Science & Technology (NST) grant by the Korea government (MSIP) (No. CMP-16-04-KITECH).

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