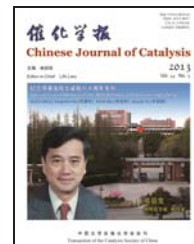


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Communication (Special Issue in Memory of the 80th Birthday of Professor Jingfa Deng)

Activated carbon-supported ruthenium as an efficient catalyst for selective aerobic oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran

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ABSTRACT

The aerobic oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-diformylfuran (DFF) was performed on an activated carbon-supported ruthenium (Ru/C) catalyst. The excellent DFF yield of 95.8% was achieved at 383 K and O₂ pressure 2.0 MPa in toluene. It exhibited superior activity and DFF selectivity than other C-supported noble metals (i.e. Pt, Rh, Pd, and Au) with comparable nanoparticle size. The Ru/C catalyst was stable and can be recycled by a simple hydrothermal treatment. Moreover, the product distribution in the HMF oxidation on Ru/C can be tuned by the use of water as solvent and the addition of hydrotalcite, giving either 5-formyl-2-furancarboxylic acid or 2,5-furandicarboxylic acid as the dominant product.

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Because of increasing attention to the use of biomass [1,2], 5-hydroxymethylfurfural (HMF) has been identified as one of the important biomass-based platform molecules for the sustainable production of chemicals and fuels [3,4]. HMF can be converted to a variety of useful chemicals, and one such example is 2,5-diformylfuran (DFF). Similar to HMF, DFF is a versatile intermediate and is used in the synthesis of fungicides, pharmaceuticals, and functional polymers with numerous applications [5–8].

Selective aerobic oxidation of HMF forms DFF, but the presence of the more reactive aldehyde group in HMF makes it difficult to get high yields of DFF from this reaction. To improve this selectivity, a number of homogeneous and heterogeneous catalysts have been explored to date [9–17]. Moreau et al. [9] reported that HMF was converted to DFF with 93% selectivity

and 91% conversion on V₂O₅/TiO₂ with a high weight ratio of catalyst to HMF (i.e. 2:1 by weight), reflecting the low catalytic activity. By using homogeneous VOSO₄/Cu(NO₃)₂ catalysts in acetonitrile, Ma et al. [10] obtained a nearly quantitative yield of DFF at 353 K but suffered from a difficult catalyst recovery. Takagaki et al. [14] achieved a 92% yield of DFF with a hydrotalcite (HT)-supported Ru(OH)_x catalyst (Ru(OH)_x/HT) in DMF. Antonyraj et al. [17] reported a ~97% DFF yield on RuCl₃/Al₂O₃. However, the Ru(OH)_x/HT and RuCl₃/Al₂O₃ catalysts were deactivated significantly when recycled [14,17]. A similarly high DFF yield has also been reported recently by Yang et al. [15] with MnO₂-based catalysts in dimethyl sulfoxide (DMSO). However, DMSO tends to undergo disproportionation to noxious and toxic Me₂SO and Me₂S under oxidizing conditions [18,19]. Herein, we report that activated car-

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bon-supported Ru (Ru/C) acts as an efficient and recyclable heterogeneous catalyst for selective aerobic oxidation of HMF to DFF in toluene with yields as high as ~96% under mild conditions.

Ru/C was prepared by incipient wetness impregnation of activated carbon with an aqueous solution of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, followed by evaporation and drying at 383 K in air overnight, and subsequent reduction in a flow of 20% H_2 in N_2 at 623 K for 4 h [20]. Similarly, Pt/C, Pd/C, and Rh/C were prepared for comparison [20]. The metal loadings of these catalysts were 3 wt%. In accordance with our previous report, 1 wt% Au/C was prepared by a single-step borohydride reduction [21]. HMF oxidation reactions were carried out in a Teflon-lined stainless steel autoclave (50 ml). Typically, 1 mmol HMF (98%) and 40 mg catalyst were added to 10 ml toluene in the autoclave. The reactants and products were analyzed by HPLC using a UV detector and an Alltech OA-1000 organic acid column [13]. HMF reaction activities were reported as molar HMF conversion rates per mole of dispersed metal per hour and selectivities on a carbon basis. The Ru contents in the catalysts and in the filtrate after the HMF oxidation reaction were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Profile Spec, Leeman Labs). X-ray photoelectron spectra (XPS) of Ru 3p were collected on an AXIS Ultra spectrometer (Kratos, Manchester, UK) using an Al anode (Al K_{α} , $h\nu = 1486.6$ eV) operating at 150 W.

Figure 1 shows how the oxidation activities and selectivities to DFF and 5-formyl-2-furancarboxylic acid (FFCA) vary with the HMF conversions over Ru/C at 383 K and 2.0 MPa O_2 . The DFF selectivity was essentially constant at 95.8% even when the HMF conversion increased from 21.3% to 100%. The selectivity toward FFCA was always small and increased slightly from 0.7% to 1.5%. These results show that DFF selectivity is stable on Ru/C in toluene, and thus DFF was obtained in yields as high as 95.8%. Moreover, this excellent DFF yield was obtained at high activity (15.8 h^{-1}), which is much greater than $\sim 3.8 \text{ h}^{-1}$ observed for $\text{Ru}(\text{OH})_x/\text{HT}$ catalyst (at 393 K under flowing oxygen) [14], showing the superiority of Ru/C for catalyzing the HMF oxidation to DFF.

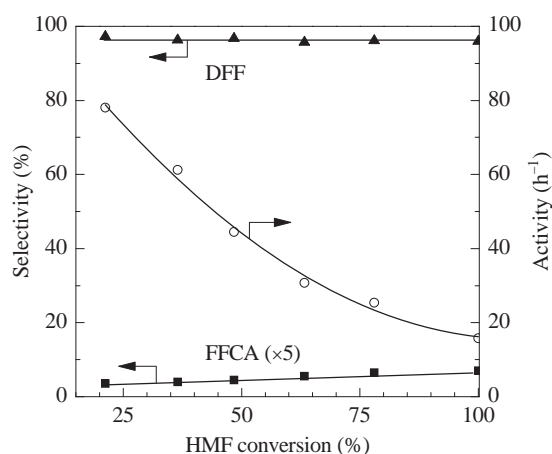


Fig. 1. Changes in the activity and selectivity for DFF and FFCA with HMF conversion over Ru/C (383 K, 2.0 MPa O_2 , 1.0 mmol HMF, 40 mg Ru/C, 10 ml toluene, 0.3–7.0 h).

Table 1

Activity and product selectivity in the aerobic oxidation of HMF in toluene on carbon-supported Ru, Pt, Pd, Rh, and Au nanoparticles of comparable size.

Entry	Catalyst	Particle size (nm)	Activity (h^{-1})	Selectivity (%)	
				DFF	FFCA
1	Ru/C	1.7 (1.8) ^a	61.2	96.2	0.9
2	Pt/C	2.3	44.0	72.6	0.4
3	Pd/C	1.7	4.9	53.1	0.6
4	Rh/C	1.8	5.0	40.8	0.7
5	Au/C	3.5	28.2	32.5	1.0
6	C ^b	—	1.1% ^c	22.1	0.4

Reaction conditions: 383 K, $p(\text{O}_2) = 2.0$ MPa, 1.0 mmol HMF, 40 mg catalyst (120 mg for Au/C), 10 ml toluene, ~30% HMF conversion.

^aThe number in parenthesis is the Ru particle size for Ru/C after five reaction cycles.

^b0.043 g of C was used.

^cThe conversion after HMF oxidation for 30 min.

For comparison, several other noble metals, Pt, Pd, Rh, and Au, supported on C were also examined in the HMF oxidation. As shown in Table 1, characterization of these catalysts by TEM shows that the metal particles were 1.8–2.3 nm in diameter, except for Au/C (3.5 nm Au), and were similar to the size of Ru/C (1.7 nm). Pt/C was active for the HMF oxidation, but with a lower activity (44.0 h^{-1}) and DFF selectivity (72.6%) than Ru/C (61.2 h^{-1} and 96.2%) at similar HMF conversions (~30%) in the kinetic regime. Au/C was also active (28.2 h^{-1}), but it gave a DFF selectivity as low as 32.5%. Pd/C and Rh/C exhibited very low activities (4.9 and 5.0 h^{-1}) and DFF selectivities (53.1% and 40.8%) under the same reaction conditions.

The stability and recyclability of Ru/C were examined at 383 K and 2.0 MPa O_2 in the kinetic controlled regime (i.e. at ~30% HMF conversion). To recycle, the catalyst was simply washed with water. As shown in Fig. 2, the HMF oxidation activity decreased from 61.2 to 53.7 h^{-1} in the second run, and continuously to 26.0 h^{-1} in the fifth run, while the DFF selectivity remained almost unchanged. To understand this decline in activity, the filtrate after each run was measured by ICP-AES and showed no detectable leaching of Ru. The oxidation of HMF

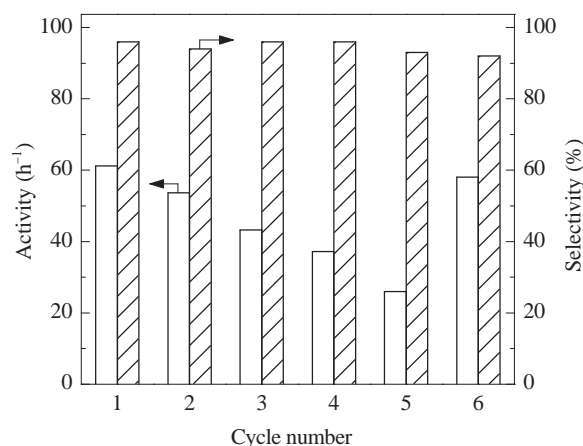


Fig. 2. Activity and DFF selectivity for the recycle examination of HMF oxidation on Ru/C at ~30% HMF conversion (383 K, 2.0 MPa O_2 , 1.0 mmol HMF, 40 mg Ru/C, 10 ml toluene). Ru/C was filtered and simply washed with water for cycles 2–5, and for the 6th cycle it was treated under hydrothermal conditions at 383 K for 4 h.

stopped once Ru/C was removed from the reaction solution, confirming the heterogeneous nature of the Ru/C catalysis. Moreover, TEM images of the used Ru/C catalyst demonstrated that the mean diameters of the Ru nanoparticles remained essentially unaltered (1.7 nm vs 1.8 nm, Table 1, entry 1). XPS analysis revealed no significant change in the oxidation state of the Ru particles after being recycled. Taken together, these results mean the structure of the Ru/C catalyst is stable, and thus the observed activity loss during recycling cannot be due to the change in the structure and oxidation state of the Ru particles or due to being leached out of the catalyst.

Because Ru/C is stable, we theorized that the loss in activity may be due to the strong adsorption of the acid byproducts such as FFCA and maleic acid (MA) at the Ru active sites. To verify this, the fresh Ru/C catalyst was stirred in the filtered reaction solution at 298 K before it was examined for a second run, which resulted in similar activity loss (~20%, 46.1 h⁻¹). More directly, in a separate reaction, the addition of a small amount of FFCA and MA (2 equivalents of the amount produced at 100% HMF conversion) led to a significant decline in the activity (~50%, 30.6 h⁻¹). This confirms that the activity loss of Ru/C is due to the blockage of the Ru active sites by the acidic byproducts formed during the HMF oxidation. Accordingly, the catalyst which had been used for five successive cycles was treated under hydrothermal conditions at 383 K for 4 h to remove the adsorbed acids, and the activity was almost completely recovered (Fig. 2, cycle 6). This demonstrates the high recyclability of the Ru/C catalyst, which is superior to the reported Ru(OH)_x/HT catalyst that loses ~80% of its activity in the second cycle at ~50% DFF yield [14]. Similar activity loss was observed on RuCl₃/Al₂O₃, but the activity was harder to recover even after treatment with NaOH solution [17].

Moreover, HMF can be further oxidized to FFCA and 2,5-furandicarboxylic acid (FDCA) on Ru/C by performing the reaction in water instead of toluene in otherwise identical reaction conditions. As shown in Table 2, FFCA and FDCA were obtained with 51.9% and 8.1% selectivities, respectively, at 100% HMF conversion in water. Such changes in the product distribution are due to the facile hydration of aldehyde group to a geminal diol in water, which tends to be further oxidized to acids [22,23]. Addition of hydrotalcite (Mg:Al = 3:1) further improved the yields of FFCA to 82.8% and FDCA to 75.3% after the HMF oxidation at 383 K for 6 h and at 403 K for 8 h, respec-

Table 2

Aerobic oxidation of HMF in water on Ru/C.

Entry	Additive ^a	Time (h)	Conversion (%)	Selectivity (%)		
				DFE	FFCA	FDCA
1	—	7	100	28.8	51.9	8.1
2	hydrotalcite	6	100	1.4	82.8	5.4
3 ^b	hydrotalcite	8	100	—	2.9	75.3

Reaction conditions: 383 K, 2.0 MPa O₂, 1.0 mmol HMF, HMF/metal = 80 (mol/mol), 10 ml H₂O.

^a 0.2 g hydrotalcite (Mg/Al = 3).

^b The reaction temperature was 403 K.

tively.

In conclusion, Ru/C is an effective and recyclable catalyst for the aerobic oxidation of HMF to DFF, affording DFF in ~96% yield in toluene. High yields of FFCA and FDCA can also be obtained from Ru/C in water in the presence of hydrotalcites. Detailed studies of the structural requirements and reaction mechanism of the HMF oxidation on Ru/C are reported elsewhere [24].

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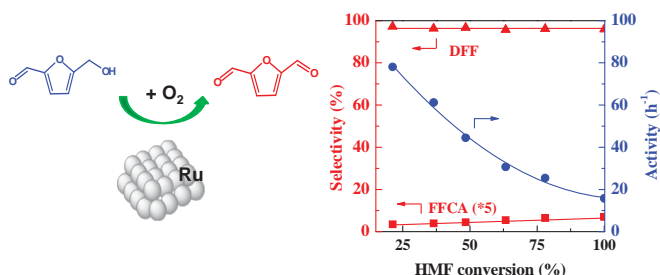
Graphical Abstract

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Activated carbon-supported ruthenium as an efficient catalyst for selective aerobic oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran

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Peking University

Ru/C is an effective and recyclable catalyst in the aerobic oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-diformylfuran (DFF), affording a high DFF yield of 95.8% in toluene.



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Ru/C催化5-羟甲基糠醛选择氧化高效合成2,5-呋喃二甲醛

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摘要: 在活性炭负载金属钌(Ru/C)催化剂上实现了5-羟甲基糠醛的高效选择氧化。以甲苯为反应溶剂, 在383 K和2.0 MPa O₂的反应条件下, 2,5-呋喃二甲醛(DFP)收率高达95.8%。与活性炭负载的具有相似粒径的Pt, Rh, Pd, Au等其它贵金属催化剂相比, Ru/C具有更加优良的活性和DFP选择性。同时Ru/C催化剂结构稳定, 具有良好的重复使用性能。在相似的反应条件下, 采用水代替甲苯作为溶剂, 同时添加少量水滑石固体碱, 可便捷地将主要产物从DFP调变为5-甲酰基-2-呋喃甲酸或2,5-呋喃二甲酸, 显示出Ru/C催化剂在控制5-羟甲基糠醛选择氧化反应产物方面的优异性能。

关键词: 生物质; 5-羟甲基糠醛; 2,5-呋喃二甲醛; 选择氧化; 钌催化剂

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利用生物质代替日益消耗的化石资源有助于实现油品和化学品的可持续生产^[1,2]。作为一类重要的生物质基平台分子^[3,4], 5-羟甲基糠醛(HMF)可以转化生成2,5-呋喃二甲醛(DFP)等多种重要的化学品。DFP具有多种用途, 可以用于合成杀菌剂、药品和功能性高分子等^[5-8]。

DFP可以通过选择氧化HMF的羟基而制得, 但是HMF分子中存在活性更高的醛基, 因而通过氧化反应从HMF高收率地合成DFP具有一定的困难。因此, 很多均相和非均相催化剂都被用于这个反应, 试图解决这一问题^[9-17]。Moreau等^[9]将V₂O₅/TiO₂作为催化剂, HMF转化率和DFP选择性分别可达91%和93%, 但需要较高的催化剂用量(催化剂/HMF质量比 = 2/1), 催化剂活性较低。Xu课题组^[10]在乙腈溶剂中采用均相的VO₂SO₄/Cu(NO₃)₂催化剂, 在353 K下DFP收率接近100%, 但分离不便。Ebitani课题组^[14]使用水滑石(HT)负载的Ru(OH)_x(Ru(OH)_x/HT)作为催化剂, 在*N,N*-二甲基甲酰胺(DMF)溶剂中获得了92%的DFP收率。Cho课题组^[17]在RuCl₃/Al₂O₃上取得了~97%的DFP收率。然而, 这些催化剂在循环使用时活性均明显下降。最近, 在二甲亚砜(DMSO)溶剂中, 以八面体分子筛构型的MnO₂作为催化

剂也得到相似的高收率^[15]。但DMSO在氧气气氛下加热容易歧化, 生成有害的Me₂SO₂和Me₂S^[18,19]。本文以活性炭负载Ru金属纳米粒子(Ru/C)作为HMF选择氧化的催化剂, 在甲苯中反应, DFP收率可达95.8%, 且催化剂具有良好的活性和循环使用性能。

采用浸渍法制备Ru/C催化剂。将活性炭加入到适量的RuCl₃水溶液中, 振荡并待水分蒸发后置入383 K烘箱过夜。所得固体用20% H₂-80% N₂混合气在623 K下还原4 h^[20]。作为对比, 用类似方法制备了Pt/C, Pd/C和Rh/C催化剂^[20]。这些催化剂的金属负载量均为3%(质量分数)。1% Au/C催化剂采用NaBH₄一步还原法制备^[21]。HMF氧化反应在内置聚四氟乙烯衬管的反应釜(50 ml)中进行。投料量为1 mmol HMF(98%), 40 mg催化剂和10 ml甲苯。反应产物使用HPLC和UV检测器进行分析, 色谱柱为Alltech OA-1000有机酸柱^[13]。催化剂和HMF氧化反应溶液中的Ru含量使用电感耦合等离子体原子发射光谱(ICP-AES)进行检测(Profile Spec, Leeman Labs)。催化剂的X射线光电子能谱(XPS)表征在AXIS Ultra型电子能谱仪(Kratos, Manchester, UK)上进行, 操作条件为Al靶(Al K_α, *hν* = 1486.6 eV), 150 W。

图1为在383 K和2.0 MPa O₂下Ru/C催化剂的催化活

性以及DFF和5-甲酰基-2-呋喃甲酸(FFCA)选择性与HMF转化率之间的关系。由图可见,当HMF转化率从21.3%增至100%时,DFF选择性基本稳定在95.8%,而FFCA选择性仅从0.7%增至1.5%。这一结果表明,在甲苯溶剂中,DFF选择性可以在Ru/C催化剂存在下保持稳定,最终在HMF完全转化时,其收率可达95.8%。而且,Ru/C催化剂的活性可达 15.8 h^{-1} ,远高于Ru(OH)_x/HT催化剂的 $\sim 3.8\text{ h}^{-1}$ (反应条件:393 K, O₂压0.1 MPa)^[14]。

作为对比,本文将Pt, Pd, Rh和Au担载在活性炭上,也用于HMF的选择氧化反应中。TEM结果显示(见表1),除了Au/C中Au粒径(3.5 nm)略大外,其它催化剂的金属粒子粒径均在1.8~2.3 nm,与Ru/C粒径(1.7 nm)接近。各催化剂性能的比较在相似的较低HMF转化率($\sim 30\%$)下进行,以排除浓度差异和扩散的影响。由表可见,Pt/C也具有较高的活性(44.0 h^{-1})和DFF选择性(72.6%),但分别低于Ru/C的 61.2 h^{-1} 和96.2%。另外,Au/C的活性为 28.2 h^{-1} ,但DFF选择性仅为32.5%。Pd/C和Rh/C的活性(4.9 和 5.0 h^{-1})和DFF选择性(53.1%和40.8%)均较低。

在383 K和O₂压2.0 MPa下,调节HMF转化率为 $\sim 30\%$ 的动力学控制区间测试了Ru/C催化剂的结构稳定性和循环使用性能。循环使用前,回收的Ru/C采用去离子水洗涤并真空干燥。如图2所示,反应活性在第2次使用时从 61.2 h^{-1} 降至 53.7 h^{-1} ;至第5次时进一步降至 26.0 h^{-1} ,DFF选择性则基本保持稳定。为了考察活性下降的原因,我们首先对每次反应后的滤液进行ICP-AES测定,没有观察到Ru的流失。将Ru/C从反应体系中分离出来,反应即停止进行,说明Ru/C在催化反应过程中的多相特性。TEM结果显示,反应后的Ru/C催化剂中Ru粒径几乎保持不变(见表1)。XPS结果也表明,反应前后Ru的价态没有发生明显的改变。可见,Ru/C催化剂的结构稳定,循环使用时其活性的降低不是源自Ru纳米粒子的结构

和价态的改变或者Ru的流失。

我们推测,催化剂活性的降低可能来自反应的副产物如FFCA和马来酸(MA)对Ru活性位的强吸附作用。为了验证这一想法,我们将新鲜的Ru/C催化剂先在室温下于反应滤液中搅拌,然后用于HMF反应,发现了类似的活性降低(转化率 $\sim 20\%$ 时活性为 46.1 h^{-1})。直接加入少量FFCA和MA(约相当于HMF 100%转化时各自生成量的2倍)则导致活性的显著降低($\sim 50\%$ 时 30.6 h^{-1})。因此,循环使用时Ru/C活性的降低可以归结为反应副产物对Ru活性位的占据。与此对应,将循环使用5次后的Ru/C在383 K下水热处理4 h,即可除去吸附的副产物并使活性几乎完全恢复(见图2)。这表明Ru/C具有良好的循环使用性能。而文献中报道的Ru(OH)_x/HT催化剂在50%的DFF收率下,第二次循环使用即发生 $\sim 80\%$ 的活性损失^[14]; RuCl₃/Al₂O₃也存在类似的现象^[17],且催化剂在使用后即使经过NaOH溶液处理仍无法恢复其活性。

在相同反应条件下将溶剂由甲苯换成水,HMF可被进一步氧化成FFCA和2,5-呋喃二甲酸(FDCA)。如表2所示,在水中当HMF完全转化时,FFCA和FDCA的收率分别为51.9%和8.1%。这一产物分布的变化是由于在水中醛基容易水合生成偕二醇,并倾向于进一步被氧化成酸^[22,23]。添加固体碱如水滑石(Mg/Al = 3)可以进一步提高FFCA和FDCA的收率:383 K下反应6 h,FFCA收率可达82.8%;403 K下反应8 h,FDCA收率可达75.3%。由此可见,改变反应条件即可很好地调节Ru/C催化剂上HMF反应产物的分布,从而制得所需目标产物。

综上所述,Ru/C是HMF选择氧化合成DFF有效且可良好循环使用的催化剂,在甲苯中DFF收率可达95.8%;当将溶剂换成水并加入水滑石时,可高收率地得到FFCA和FDCA。关于Ru/C催化剂结构和HMF氧化反应机理等方面的研究结果可参看文献[24]。