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Tuning of Selectivity and Activity in Aerobic Oxidation and Oxidative Esterification of 5-Hydroxymethylfurfural by Gold Nanoparticles Supported on Nanoporous Polymer Host Matrix

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Abstract: The aerobic oxidation and oxidative esterification of 5hydroxymethylfurfural (HMF) catalyzed by gold nanoparticles (AuNPs) supported on a semicrystalline nanoporous multiblock copolymer matrix consisting of syndiotactic poly(styrene)-cis-1,4poly(butadiene) (sPSB) have been investigated. Depending on the reaction parameters (support nanoporosity, presence of water, solvent, temperature, co-catalyst, oxygen pressure) the HMF conversion can be finely addressed to the formation of the desired oxidation product, such as 2,5-diformylfuran (DFF), 5-formylfuran-2carboxylic acid (FFCA), methyl 5-(hydroxymethyl)furan-2carboxylate (MHMFC), dimethyl furan-2,5-dicarboxylate (DMFC) and furan-2,5-dicarboxylic acid (FDCA); under optimized reaction conditions, AuNPs-sPSB resulted highly effective and selective since the polymer support acts as a conveyor and concentrator of the reactants toward the catalytic sites.

Introduction

The U.S. Department of Energy (DOE) includes 5-(hydroxymethyl)-2-furancarboxaldehyde (HMF), furfural (FF), and 2,5-furandicarboxylic acid (FDCA) in the "Top 10+4" list (as addition to the original top 10 list) of biobased chemicals.^[1] Most of the work in HMF synthesis is focused on the conversion of monosaccharides into HMF; this compound is currently produced from fructose with a cost of 460 USD/ton.^[2] When obtained at high efficiency, the follow-up products will become attractive options to replace petrochemical analogues for the synthesis of bioderived polymers, fine chemicals and biofuels.^[3] 5-hydroxymethyl-2-furoic acid (HMFA), 2,5-diformylfuran (DFF) and 2,5-di(hydroxymethyl)furan (DHMF) are the most versatile intermediate chemicals of high industrial potential since they are six-carbon monomers that could replace, *e.g.* adipic acid,

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alkyldiols or terephthalic acid in polymer synthesis.[3h]

DFF is an attractive building block that has been polymerized to polypinacols and polyvinyls and used for the synthesis of antifungal agents, pharmaceuticals and ligands.^[3b, 4] Selective oxidation of HMF to DFF is challenging because of ready oxidation of the aldehyde to carboxylic acid functionality when reaction is carried out in water with strong oxidants.[3b, 5] Green methods, which avoid the use of stoichiometric toxic reagents as chromium salts, have been proposed but satisfactory results are far to be reached. The salen-Mn(III) catalyst (5 mol%) allows 63-89% yields using sodium hypochlorite as oxidant at pH 11.3 and room temperature.^[6] Aerobic oxidation of HMF was performed with CuCl₂ in N.N-dimethylformamide (DMF) using catalytic amount of TEMPO; the yields are rather scarce (55%) but significantly increase when stronger oxidants as HNO₃/O₂ have been employed.^[7] More interesting results have been obtained with heterogeneous catalysts based on vanadium compounds, such as V₂O₅/TiO₂^[8] under harsh conditions (170 °C; 1.5 MPa of oxygen) or VOPO₄ in dimethyl sulfoxide (DMSO a 150°C.^[9] DFF synthesis from fructose or glucose was also attempted using Amberlyst15 and ruthenium/hydrotalcite^[4] or gold-ruthenium nanoparticles supported on reduced graphene oxide^[10].

Only recently FFCA has been obtained with high selectivity (90%) from aerobic oxidation of HMF over CuO/CeO $_2$ in water.^[3b]

Looking at the cascade of products resulting from HMF oxidation, 5-hydroxymethyl 2-furancarboxylic acid (HMFCA) can be considered intermediate to FDCA and is typically obtained under mild oxidation conditions. Highly selective oxidation to HMFCA was reported using *Acetobacter rancens* or *Serratia liquefaciens*; 2.6 mmol of HMF were oxidized with 97% conversion in 26 h using 182 mg of whole cells.^[11]

FDCA is likely the most interesting target, identified by DOE^[1a] as a key bioderived platform molecule for the production of chemicals and monomers, such as succinic acid, 2,5-furandicarbonyl dichloride and dimethyl furan-2,5-dicarboxylate (DMFC).^[3b, 3c, 3e, 3g, 12] Noble metal nanoparticles supported on metal oxides were found very efficient in aerobic oxidation of HMF to FDCA.^[3] Supported platinum catalysts were first used in the presence of an external base producing nearly quantitative FDCA yields.^[13] Recently, supported gold catalysts have shown interesting catalytic performances for the aerobic oxidation of alcohols^[14] and HMF^[5b, 15]. The Au/TiO₂ catalyst oxidizes HMF to FDCA in 71% yield at room temperature.^[16] Au/CeO₂ was more active and selective: however similarly to the platinum catalysts the addition of an external base (1-20 equiv. of NaOH) and high oxygen pressure (1.0-2.0 MPa) are required.^[15k] Recently, Gupta

et al. reported the base free oxidation over gold catalysts supported on hydrotalcites.^[15m]

Esterification of HMF leads to interesting products for industry. Alkyl esters of FDCA were patented as polymer plasticisers.^[17] BASF and Avantium launched in joint venture poly(ethylene furanoate) (PEF), a polyester from FDCA and ethylene glycol as alternative to poly(ethylene terephthalate) (PET) for soft drink bottles.^[18] PEF can be also produced from transesterification of DMFC with ethylene glycol. DuPont and ADM combined their efforts for the production of DMFC and its copolymerization with 1,3-propandiol to poly(trimethylene furandicarboxylates) (PTF).^[19] Direct esterification of HMF to DMFC was performed with Au/TiO2 in a sodium methoxide methanol solution at 130 °C.^[15] The base-free oxidative esterification of HMF was also successfully obtained using Au/CeO₂ in methanol at 130°C and 1.0 MPa of oxygen pressure.[15k]

Recently, we reported on catalysis by gold nanoparticles supported on multiblock copolymer consisting of syndiotactic polv(styrene)-*cis*-1.4-polv(butadiene) (AuNPs-sPSB).^[20] The polymer matrix presents excellent mechanical properties, chemical and thermal stability, physical crosslinks and a complex polymorphism.^[21] Five crystalline forms were discovered, namely α , β , γ , δ and ϵ , where the latter two present nanopores ($\emptyset < 2$ nm) and nanochannels in the crystalline lattice, which allow obtaining co-crystalline structures by clathration of small organic molecules as THF, aromatics and halocarbons [21a, $^{22]}$ whereas $\alpha,\,\beta$ and $\gamma\,$ are not permeable. The permeability of the δ and ϵ crystalline phases determined high activity and selectivity in the reduction of nitroarenes to anilines^[20a] and oxidation of alcohols^[20b, 20c]. In the light of these results, we aimed to investigate HMF oxidation catalysed by this peculiar catalyst.

Results

Synthesis of the catalysts. The polymeric support sPSB^[23] and the AuNPs-sPSB catalyst^[20] were prepared according to the previously reported procedures. The wide angle x-ray diffraction (WAXD) analysis of the "as synthesized" catalyst allowed to assess the average size of the AuNPs of 5.7 nm, estimated with the Scherrer equation, and the nanoporous δ crystalline form of the polymer support containing THF molecules in the voids of the crystalline phase (Figure S1a). A thermal treatment at 170 °C affords a moderate increment of the nanoparticle size to 8.0 nm and the formation of multigeminate defective particles, which are more active in oxidation reactions compared to the prestine spherical particles.^[20c, 24] Moreover, the annealing of the catalyst converts the crystalline phase of the polymer support from δ to β form (Figure S1b) which was finally converted into the porous crystalline form ϵ (Figure S1c) after stirring in chloroform/water solvent mixture.^[20] At the end of the synthetic procedure the AuNPs resulted homogeneously dispersed in the polymer matrix with average size of 10.3±3.1 nm, assessed by TEM and WAXD analysis (Figures 1, S1c and S2).



Figure 1. TEM micrograph of AuNPs-sPSB (ϵ form) after thermal annealing at 170°C for 5h and treatment in chloroform/water solvent mixture.



Figure 2. Effect of the crystalline phase of the polymeric support on selectivity and activity in: a) HMF oxidation (entries S1-3 of Table S1); b) HMF oxidative esterification with methanol (entry 4 of Table 2 and S1-2 of Table S5).

Table 1. Oxidation of HMF under dry conditions.											
$HO \qquad O_{2} \qquad O_{2} \qquad O_{2} \qquad O_{2} \qquad O_{2} \qquad O_{1} \qquad O_{2} \qquad O_{2} \qquad O_{1} \qquad O_{2} \qquad O_{1} \qquad O_{2} \qquad O_{1} \qquad O_{2} \qquad O_{2} \qquad O_{1} \qquad O_{2} \qquad O_{2} \qquad O_{1} \qquad O_{2} \qquad$											
Entry ^[a]	Catalyst	Base	т	Conversion ^[b]	Selec	ctivity ^[b]	TON ^[c]	TOF ^[d]			
					DFF	FFCA					
			[°C]	[%]	[%]	[%]		[h ⁻¹]			
1	AuNPs-sPSB	Cs ₂ CO ₃	40	17	80	20	4.2	0.3			
2	AuNPs-sPSB	Cs ₂ CO ₃	50	32	73	27	8.0	0.5			
3	AuNPs-sPSB	Cs ₂ CO ₃	60	47	74	26	11.7	0.7			
4	AuNPs-sPSB	Cs ₂ CO ₃	70	72	67	33	18.0	1.1			
5	AuNPs-sPSB	Cs ₂ CO ₃	80	78	80	20	19.5	1.2			
6	AuNPs-sPSB	Cs ₂ CO ₃	90	75	60	40	18.7	1.2			
7	AuNPs-sPSB	Cs ₂ CO ₃	100	84	26	74	25.0	1.6			
8	AuNPs-sPSB	Cs ₂ CO ₃	110	78	5	95	19.5	1.2			
9	AuNPs-sPSB	Cs ₂ CO ₃ (2 equiv.)	80	>99	40	60	25.0	1.6			
10	AuNPs-sPSB	Cs ₂ CO ₃ (4 equiv.)	80	>99	18	82	25.0	1.6			
11	AuNPs-CB ^[g]	Cs ₂ CO ₃	80	58	9	91	14.5	0.9			
12 ^[e]	AuNPs-CB	Cs ₂ CO ₃	110	65	23	71	16.2	1.0			
13	AuNPs-TiO ₂	Cs ₂ CO ₃	80	59	23	77	14.7	0.9			
14 ^[f]	AuNPs-TiO2	Cs ₂ CO ₃	110	75	<1	69	18.7	1.2			
15	AuNPs-sPSB	-	80	32	77	23	8.0	0.5			
16	AuNPs-sPSB	-	110	52	49	51	13.0	0.8			
17	AuNPs-CB	-	80	0	-	-	-	-			
18 ^[g]	AuNPs-CB ^[g]	-	110	43	29	54	10.7	0.7			
19 ^[g]	AuNPs-TiO ₂	-	80	20	6	9	5.0	0.3			
20 ^[g]	AuNPs-TiO ₂	-	110	72	15	23	18.0	1.1			

[a] Reaction conditions: anhydrous HMF (0.127·mmol); AuNPs-sPSB ([Au] = 2wt%; HMF/Au molar ratio = 25); Cs₂CO₃ (0.127·mmol); DMF (2 mL); molecular sieves (\approx 50 mg); reaction time = 16 h. [b] Determined by ¹H NMR analysis. [c] Turnover number (moles of reacted HMF/moles of Au). [d] Overall turnover frequency (TON/reaction time). [e] FDCA (yield =7.9 mol%; selectivity = 22.1 mol%). [f] FDCA (yield = 4.0 mol%; selectivity = 6.2 mol%). [g] Not identified by products.

Oxidation of HMF to DFF and FFCA. The screening of the AuNPs-sPSB performances in HMF oxidation was carried out in N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMA), using oxygen pressure of 1.5 MPa and Cs₂CO₃ as cocatalyst. The role of the polymer crystalline phase was preliminary investigated. The AuNPs-sPSB catalyst prepared in the nanoporous phases δ and ϵ exceeds the performance of the β form (Table S1) and produces FFCA as the main reaction product. Considering that water leads to oxidation of aldehyde to carboxylic acid functionality via hemiacetal intermediate species, HMF and the solvent were anhydrified and the molecular sieves added for trapping the stoichiometric amount of water resulting from alcohol oxidation or adventitious water (Table 1). In the range of temperature 25-100 °C the HMF conversion smoothly increases and becomes quantitative at 100°C (entries 1-8 of Table 1; Figure 3a). The selectivity in DFF is good (73-80%) and roughly constant in the temperature range of 40-90 °C, and then to decrease at higher temperature in favour of FFCA.

Conventional external bases, typically employed in the HMF oxidation, such as KOH, NaOH Na₂CO₃, K₂CO₃, led to worse activity and selectivity than Cs₂CO₃ (Figure 4a and Table S2). When the number of equiv. of Cs₂CO₃ is increased, the conversion increases but the selectivity changes in favour of FFCA (Figure 4b; compare entries 5, 9-10 and 15 of Table 1). Under the optimized conditions of entry 5 in Table 1, the TOF value increases as the oxygen pressure was increased from 0.1 MPa to 3.5 MPa, reaching the maximum value at 2,5 MPa, then to plateaux at higher pressure where oxidation of HMF to FFCA becomes progressively more and more consistent (Figure 5; Table S3).



Figure 3. Effect of temperature on yield and selectivity in HMF oxidation carried out in: a) DMF (entries 1-8, Table 1); b) DMA (entries 1-8, Table S4).

When compared to the commercial gold catalysts, consisting of AuNPs supported on carbon black (AuNPs-CB) or titania (AuNPs-TiO₂) with average size of the nanoparticles of 9 nm and 5 nm, respectively, the activity and selectivity of AuNPs-sPSB are higher producing prevailingly DFF at 80°C (compare entry 5 with 11 and 13 of Table 1) and FFCA at 110°C (compare entry 8 with 12 and 14 of Table 1) (see Figure 6). The performances of AuNPs-sPSB do not generally depend on solvent employed, e.g. DMA vs DMF (Figure 3b); remarkably a quantitative conversion of HMF into FFCA was obtained at 110°C (entry 9, Table S4). Noteworthy, AuNPs-sPSB is still active in the absence of external bases in both the solvents leading to DFF at 80 °C and FFCA at 110°C with good HMF conversion (Figure 6; entries 15-16 of Table 1); under the same conditions AuNPs-CB and AuNPs-TiO₂ are less selective and show good activity only at high temperature (Figure 6).

The presence of water in the reaction media, coming from wet HMF (entry 10, Table S4) or purposely added (entry 11, Table S4), results in the formation of FFCA with high selectivity. The same compound was obtained in high yield at 80°C when using a strong excess (6 equiv.) of Cs_2CO_3 (entry S12 Table S4).



Figure 4. Oxidation of HMF in DMF: a) yields and selectivity from different external bases (entries 3 of Table 1 and S1-4 of Table S2); b) yields and selectivity and yield at variance of the Cs_2CO_3 concentration (entries 15, 5, 9-10 of Table 1).



Figure 5. Effect of oxygen pressure on HMF conversion into DFF or FFCA (entries S1-6 of Table S3 and 5 of Table 1).

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Figure 6. Selectivity and yields in HMF oxidation in DMF catalyzed by different gold catalyst in presence of Cs_2CO_3 (a; entries 5, 8, 11-12, 13-14 of Table 1) and in absence (b; entries 15-20, Table 1) of cocatalyst base.

Oxidative esterification of HMF to MHMFC and DMFC. Oxidative esterification of HMF to the dimethyl ester derivative DMFC is another interesting synthetic target. AuNPs-sPSB was preliminary screened in methanol at variance of temperature (entries 1-3, Table 2). At 25°C MHMFC is obtained with excellent yield and selectivity (entry 1, Table 2); under this condition the alcoholic functionality is thus not oxidized. The increase of temperature to 70°C increased the oxidation rate of this functional group producing the expected DMFC (entry 2, Table 2). Oddly, a further increase of temperature to 110°C produced a worsening of the activity (entry 3, Table 2). The addition of DMF improved the polymer matrix swelling and MHMFC was obtained in higher yield and selectivity at 25°C (entry 4, Table 2); under the same conditions, AuNPs-CB is completely inactive (entry 5; Table 2) and AuNPs-TiO₂ is less active and selective (entry 6, Table 2). When the reaction temperature is increased, the HMF conversion was moderate (\approx 50%, entries 9-14 of Table 2; Figure 7) and selectivity poor, with the reaction mixture containing equimolar amounts of DMFC and MHMFC. Similar findings were obtained in DMA/methanol in the temperature range of 25-90 °C (entries 15-23 of Table 2; Figure 7). Interestingly the selective formation of DMFC was obtained at 100-110 °C (entries 22-23, Table 2) in this mixture of solvents; at the oxygen pressure of 3.5 MPa (entry 30, Table 2) the quantitative esterification of HMF was observed in 5 h, with the remarkable TOF value of 5 h⁻¹. Noteworthy the recovered catalyst is even more active with a TOF of 7.2 h⁻¹ (entry 31, Table 2). When using sodium methoxide as co-catalyst the conversion and selectivity in DMFC (entry 29, Table 2) was similarly high.

In methanol and Cs₂CO₃ as base, AuNPs-sPSB showed better activity and selectivity than AuNPs-CB and AuNPs-TiO₂ (compare entry 23 with 24-25 in Table 2; Figure 8); in the absence of an external base AuNPs-sPSB preserved a discrete activity but selectivity is lower (compare entry 26 with 27-28 in Table 2 and see Figure 8).





Figure 7. Oxidative esterification of HMF at variance of temperature in: a) DMF/methanol (entries 4,7-14, Table 2); b) DMA/methanol (entries 15-23, Table 2).

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Table 2. Oxidative esterification of HMF with methanol under dry conditions.

	НО	0 $\frac{0}{1}$ $0_2 + 1$	сн₃он но						
		HMF Au	NPs	ÓCH₃ H MHMFC	l₃co´ ∖_ /́ D	OCH₃ MFC			
Solvent	Entry ^[a]	Catalyst	т	Conversion ^[b]	Selecti	vity ^[b]	TON ^[c]	TOF ^[d]	
					MHMFC	DMFC	_		
[v/v]			[%]	[%]	[%]	[%]		[h ⁻¹]	
	1	AuNPs-sPSB	25	>99	78	22	25.0	1.6	_
MeOH	2	AuNPs-sPSB	70	>99	56	44	25.0	1.6	,
	3	AuNPs-sPSB	110	33	51	49	8.2	0.5	
	4	AuNPs-sPSB	25	86	96	4	21.5	1.3	_
	5	AuNPs-CB	25	0		-	0	0	
	6	AuNPs-TiO ₂	25	33	67	33	8.2	0.5	
	7	AuNPs-sPSB	40	66	96	4	16.5	1.0	
	8	AuNPs-sPSB	50	61	92	8	15.2	1.0	
DMF/MeOH	9	AuNPs-sPSB	60	55	90	10	13.7	0.9	
(4/1 ///)	10	AuNPs-sPSB	70	44	76	24	11.0	0.7	
	11	AuNPs-sPSB	80	43	49	51	10.7	0.7	
	12	AuNPs-sPSB	90	52	52	48	13.0	0.8	
	13	AuNPs-sPSB	100	50	51	49	12.5	0.8	
	14	AuNPs-sPSB	110	48	49	51	12.0	0.7	
	15	AuNPs-sPSB	25	35	64	36	87	0.5	
	16	AuNPs-sPSB	40	53	51	49	13.2	0.8	
	17	AuNPs-sPSB	50	65	55	45	16.2	1.0	
	18	AuNPs-sPSB	60	64	52	48	16.0	1.0	
	19	AuNPs-sPSB	70	68	40	60	17.0	1.0	_
	20	AuNPs-sPSB	80	83	48	52	20.7	13	
	21	AuNPs-sPSB	90	37	57	43	9.2	0.6	
	22	AuNPs-sPSB	100	76	31	69	19.0	12	
DMA/MeOH	23	AuNPs-sPSB	110	89	10	90	22.2	1.4	
(-1,1,0,0)	24	AuNPs-CB	110	40	19 ^[f]	52 ^[f]	10.0	0.6	
	25	AuNPs-TiO ₂	110	55	21 ^[f]	45 ^[f]	13.7	0.9	
	26 ^[e]	AuNPs-sPSB	110	56	11 ^[f]	47 ^[f]	14 0	0.9	
	27 ^[e]	AuNPs-CB	110	1	>99	-	0.2	≈0	
	28 ^[e]	AuNPs-TiO ₂	110	16	47 ^[f]	20 ^[f]	4.0	0.2	
	29 ^[g]	AuNPs-sPSB	110	94	-	>99	23.5	1.5	
	30 ^[h]	AuNPs-sPSB	110	>99	-	>99	25.0	5.0	
	310	AuNPs-sPSB	100	36	31	69	35.8	7.2	

[a] Reaction conditions: anhydrous HMF (0.127·mmol); AuNPs-sPSB ([Au] = 2wt%; HMF/Au molar ratio = 25); Cs₂CO₃ (0.127·mmol); anhydrous solvent (2.5 mL); P_{O2} (1.5 MPa); molecular sieves (\approx 50 mg); reaction time = 16 h. [b] Determined by ¹H NMR analysis. [c] Turnover number (moles of reacted HMF/moles of Au). [d] Overall turnover frequency (TON/reaction time). [e] Without co-catalyst base. [f] Not identified products. [g] sodium methoxide as base. [h] P_{O2} = 3.5 MPa, reaction time = 5 h. [i] P_{O2} = 3.5 MPa, reaction time = 3 h.



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Table 3. Oxidation of HMF in presence of water.



Entry ^[a]	Solvent	т	PO ₂	t	Conversion ^[D]	Selectivity ^[0]					TONICI	TOF ^[d]		
						DFF	HMFCA	FFCA	FDCA	MFCA	DMFC			
	[v/v]	[°C]	[MPa]	[h]	[%]	[%]	[%]	[%]	[%]	[%]	[%]		[h-1)	
1	H ₂ O	100	3.5	15	74	7	40	46	7	-	-	18.5	1.2	-
2	H ₂ O/DMA (4:1)	100	3.5	15	83	5	42	34	19	-	-	20.7	1.3	
3 ^{e]}	H ₂ O/DMA/CH ₃ OH (1:4:1)	90	1.5	24	78	-	-	32	20	38	10	19.5	1.2	
4 ^[e]	H ₂ O/DMA/CH ₃ OH (1:4:1)	110	1.5	16	>99	-	· .	10	77	6	7	25.0	1.6	
5 ^[e]	H ₂ O/DMA/CH ₃ OH (1:4:1)	110	1.5	24	>99				>99	-	-	25.0	1.6	
6 ^[f]	H ₂ O/DMA/CH ₃ OH ^[f] (1:4:1)	110	1.5	16	>99	-	-	-	>99	-	-	25.0	1.6	

[a] Reaction conditions: HMF (0.127 mmol); AuNPs-sPSB ([Au] = 2 wt%; HMF/Au molar ratio = 25); Cs₂CO₃ (0.127 mmol); solvent (2.5 mL); PO₂ = 1.5 MPa. [b] Determined by ¹H NMR. [c] Turnover number (moles of reacted HMF/moles of Au). [d] Overall turnover frequency (TON/reaction time). [e] 3 mL of solvent mixture. [f] KOH as base (1.25 equiv. w.r.t. HMF).





Figure 8. Oxidative esterification of HMF with methanol catalyzed by different catalytic systems with (histogram bars marked with w; entries 23-25, Table 2) and without (histogram bars marked with w/o; entries 26-28, Table 2) cocatalyst base.

Figure 9. Product distribution in oxidation of HMF in water (entry 1, Table 3), water/DMA (entry 2, Table 3) and water/DMA/methanol (entries 3-5, Table 3).



The AuNPs-sPSB catalyst is scarcely effective and selective in HMF oxidation in water because of the poor swelling of the polymer support in this solvent (entry 1 of Table 3; Figure 9). The addition of DMA enhances the permeability of the polymer support and DFF, HMFCA, FFCA and finally DFCA were successfully obtained, although in low yields and selectivity, through the route a-f of Table 3. The oxidative esterification of HMF produced FDCA with selectivity of 20 % in 24 h at 90°C in water/DMA/methanol solution (entry 4, Table 3) where the oxidation intermediates MFCA (38%), DMFC (10%) and FFCA (32%) were also detected. Increasing temperature to 110°C the conversion of HMF was complete in 16 h (entry 4, Table 3) and the exclusive formation of FDCA was observed in 24 h (entry 5, Table 3). When using KOH as external base, the selective formation of FDCA (entry 6, Table 3; Figure 9) was obtained with a TOF of 1.56 h^{-1} via the route *g*-*i* of Table 3. To explain these findings, we propose that oxidation of HMF to DFF is fast; both water and methanol can compete for the nucleophilic attack to the carbonvls of DFF to produce the *aem*-diol and hemiacetal intermediates, respectively. The hydrophobic nature of the polymer host matrix^[25] favours the latter and oxidation to DMFC is obtained as a consequence. Finally, the base catalyzed hydrolysis of DMFC produces FDCA in high yield and selectivity. Finally, the recycle of AuNPs-sPSB has been tested under the reaction conditions of entry 5 in Table 1. The catalyst preserved the activity for at least four runs, although the selectivity switches toward the formation of FFCA (see Table S6).

Discussion

The oxidation and oxidative esterification of HMF follow a complex reaction pathway (Scheme 1) comprising several reaction steps and intermediates. Oxidation of the aldehyde function proceeds always faster than the alcoholic one leading to HMFCA (in water) and MHMFC (in methanol) via the formation of the gem-diol and hemiacetal intermediates, respectively (routes a and c of Scheme 1). Oxidation of the alcoholic function occurs under more drastic conditions of temperature or external base concentration. [15c]. The complex and peculiar scenario observed with the AuNPs-sPSB catalyst tightly depends on the crystalline morphology and the properties of the polymeric support (see Figure 10) which allow addressing the course of reaction differently from the AuNPs-TiO₂ and AuNPs-CB catalysts. Anhydrification of the reagents and solvents, the addition of molecular sieves and the hydrophobic nature of the hydrocarbon polymer support^[25] allow the selective oxidation of HMF to the challenging oxidation product DFF. The higher selectivity of AuNPs-sPSB compared to AuNPs-CB and AuNPs-TiO₂, is likely due to the hydrophobic host matrix that hampers diffusion of the water solvent to the metal catalyst and the formation of the gem-diol species, as a consequence; on the contrary, FFCA is rapidly formed at high temperatures because of the enhanced reactivity the stoichiometric amount of water resulting from the first oxidation step. Intriguingly, the oxidative process does not further proceed to FDCA. The increase of the base concentration (Figure 4) and oxygen pressure (Figure 5) promotes FFCA formation without affecting FDCA yield; under the same reaction conditions AuNPs-CB and AuNPs-TiO2 produced a mixture of DFF, FDCA and FDCA with lower efficiency (Figure 6a).

Figure 10. WAXD pattern of the AuNPs-sPSB catalyst (a) with the corresponding diffractograms after catalytic test in DMF at 50 °C (b), 70 °C (c), 90 °C (d) and 110 °C (e), compared to the corresponding diffractograms after catalytic test in DMA at: 50 °C (b'), 70 °C (c'), 90 °C (d') and 110 °C (e').



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The polymeric support also produces some differences in the oxidation reactions performed in DMF and DMA. The oxidative esterification of HMF under dry conditions (Table 2) shows that the activity and selectivity of the catalyst are different at temperature higher than 100°C; while in DMF the conversion does not exceed 50% as well as the selectivity in DMFC, the performances in DMA are higher, leading to a HMF conversion of 89% with a selectivity in DMFC of 90%. Remarkably the first oxidation step leading to MHMFC is fast at 25 °C in methanol and DMF/methanol, where the catalytic performances are remarkably higher than those of the commercial catalysts AuNPs-CB and AuNPs-TiO2. To understand these results the crystalline phase of the polymeric support was analysed at the beginning and the end of the catalytic runs; the WAXD spectra are shown in Figure 10. The "as synthesized catalyst" is observed in the porous ε crystalline form that is stable at room temperature during the catalytic runs performed in methanol; this could explain the high oxidation rate observed at room temperature with AuNPs-sPSB. The swelling of the catalyst in DMF or DMA caused the formation of the not permeable crystalline γ and β forms, where the latter persists in DMF up to 110 °C, while amorphization of the polymer host occurs in DMA (compare the WAXD patterns e and e' in Figure 10). Thus the different catalytic performances observed at high temperature can be related to the morphology of the polymer support produced by the two solvents. The conversion of the ε form into the β form occurs nearby 170 °C in solid state, a temperature much higher than the glass transition (T_g) of polystyrene (\approx 105°C) which is the main phase of the polymeric support; this is a further evidence of the effective swelling of the support in these solvents that strongly affects the accessibility of the catalytic sites to the reagents.

Interestingly the oxidation runs carried out in DMA/water/methanol led to an unexpected reaction pathway. The conventional distribution of oxidation products is observed in entry 2 (DMA/water solvent) where the classical course of reaction via the routes a and b of Table 3 can be proposed. When methanol is added to the reaction solvent (entry 3), the distribution of the reaction products changed and both DMFC and MFCA, resulting from the route c, appeared in the reaction mixture. The increase of the reaction temperature yielded FDCA

as the main reaction product that becomes the only product at longer reaction time. We propose that FDCA, in the presence of methanol, results from route c and that under this condition the hemiacetal oxidation proceeds faster than the gem-diol intermediate species. Experimental evidences for the different reactivity of the latter two intermediates were not previously reported. Surprisingly, the investigated catalytic systems, AuNPs-sPSB, AuNPs-CB and AuNPs-TiO₂ are all active in the absence of base. Under not optimized condition the AuNPssPSB catalyst yields HMF conversion of 52% at 110°C producing equimolar amounts of DFF and FFCA. The external base is typically considered fundamental in alcohol oxidation since the deprotonation of the alcohol stabilizes its adsorption onto the gold surface and promotes hydride migration from the carbinol carbon atom to the gold surface. External base free gold catalyst were obtained using hydrotalcite support; in this case a HMF conversion of 80% into prevailingly HMFCA was reported.[15m].

The recycle of the AuNPs-sPSB catalyst was tested under the reaction conditions of entry 5 in Table 1, in which the selective formation of DFF was obtained under moderate temperature (80°C); considering that the crystalline polymeric support is stabilized by simple physical crosslinks, in principle one could expect nanoparticle deactivation/leaching in DMF at 80°C. After the fourth catalytic runs (see Table S6) the HMF conversion is completely preserved; however a shift in selectivity toward FFCA was progressively monitored as the number of recycling tests increased. To clarify this issue the recovered catalysts was investigated by WAXD, after washing with methanol and drying in vacuo. Reflections for crystalline Cs₂CO₃ entrapped in the polymer matrix (Figure S2) were actually detected, highlighting the increase of the Cs_2CO_3/Au molar ratio along with recycling tests. This finding is in good agreement with the results of Figure 4b where the selectivity in FFCA increases as the number of equiv. of external base is increased. Thus additional catalytic tests were carried out after the first run without adding the external base; as expected the selectivity in DFF resulted unaffected after two catalytic tests.

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Conclusions

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In this work, a survey of the challenging reactivity of HMF over gold nanoparticles supported on semicrystalline polymorphic polymer matrix is shown. The AuNPs-sPSB catalyst is highly effective and selective in addressing the conversion of HMF into the desired oxidation product. The peculiar nanoporous and semicrystalline polymer matrix allowed a fine control on the reactivity of HMF by judicious choice of the reaction conditions. Compared to the commercially available gold-based catalysts, AuNPs-sPSB offers the possibility of a fine control of the reaction product by a simple tuning of the reaction parameters.

HMF oxidation to DFF was efficiently obtained under anhydrous conditions, moderate reaction temperature (40-80°C), low base content (1 equiv.) and oxygen pressure of 1.5 MPa. The switch of selectivity toward FFCA occurs under more severe conditions (110°C, 2.5-3.5 MPa and/or base excess) and is favoured by water resulting from the first oxidation step to DFF leading to the *gem*-diol intermediate.

In the oxidative esterification of HMF with methanol, the polymorphic behavior of the polymer support plays and important role in addressing the course of the reaction. AuNPssPSB is highly efficient in the synthesis of MHMFC at room temperature where the nanoporous δ and ϵ crystalline phases exceeded the performances of the not permeable $\boldsymbol{\beta}$ phase and of the commercial catalysts, AuNPs-CB and AuNPs-TiO2, suggesting that the porous polymer matrix acts as conveyor and concentrator of reactants towards the catalytic sites (see Figure 2b). The choice of the solvent is fundamental at high reaction temperature in determining the polymer support phase and the corresponding activity/selectivity. DMA yielded amorphization of the polymer phase allowing the synthesis of DMFC in high yield at high temperature (entry 23, Table 2, Figure 7). On the contrary DMF converted the nanoporous crystalline phase ε into the β and γ crystalline forms which are not permeable, determining a loss of catalytic activity and selectivity. Direct oxidation of HMF to FDCA in water is unsatisfactory because of the poor swelling of the polymer matrix in this solvent. The addition of DMA and KOH allowed the efficient oxidative esterification of HMF to DMFC followed by base catalyzed hydrolysis of the latter leading to readily synthesis of DFCA with good yields. Moreover, preliminary encouraging results were obtained in the oxidation runs carried out in DMF and DMA in absence of an external base.

Experimental Section

General procedures and materials. The manipulation of air- and moisture-sensitive compounds has been performed under nitrogen atmosphere using standard Schlenk techniques and an MBraun glovebox. Toluene (99.5%, Sigma-Aldrich) was dried over calcium chloride, refluxed for 48 h over sodium and finally distilled before use in the synthesis of sPSB copolymers. Tetrahydrofuran (99.5%, Sigma-Aldrich) was dried over potassium hydroxide, refluxed for 48 h over sodium/benzophenone and distilled before use in the synthesis of the AuNPs-sPSB catalysts. Silica (Sigma-Aldrich) and molecular sieves (3 Å, Sigma-Aldrich) were activated respectively by treatment at 400 °C in air and at 200 °C in vacuo. 5-(hydroxymethyl)furfural (≥ 99 %; Sigma-Aldrich) was dried by exposure in vacuo to phosphorous pentoxide. Methanol (HPLC grade; Sigma-Aldrich) and ethanol (99.8 %; Sigma-Aldrich) were anhydrified by refluxing for 1 h over magnesium turning, activated with iodine, and distillation under nitrogen atmosphere. N,Ndimethylformamide (99.8%, Sigma-Aldrich) and N,N-dimethylacetamide (99%, Sigma-Aldrich) have been purified by stirring for 12 h over calcium

hydride before distillation under reduced pressure and stored over molecular sieves. Tetrachloroauric acid trihydrate (≥49.0% Au basis, Sigma-Aldrich), sodium triethylborohydride (1.0 M in THF; Sigma-Aldrich), chloroform (HPLC grade; Romil), water (HPLC grade; Romil), acetonitrile (HPLC grade; Sigma-Aldrich), cesium carbonate (97.9%, Sigma-Aldrich), potassium hydroxide (90%, Sigma-Aldrich), sodium hydroxide (98%, Sigma-Aldrich), sodium carbonate anhydrous (99.5, Sigma-Aldrich), potassium carbonate anhydrous (99.9, Sigma-Aldrich), Oxygen (5.0 grade; Linde) were used as received. The gold catalysts AuNPs-CB (Strem Chemicals; 1 wt%Au, onto amorphous carbon black support) and AuNPs-TiO2 (Strem Chemicals; 1 wt%Au, onto titania support) were characterized by WAXD analysis and found comprising AuNPs with the average size of 9,0 nm and 5.nm, respectively. Deuterated solvents were purchased from Euriso-Top or Sigma-Aldrich and used as received. sPSB copolymer^[23a-c, 26] and AuNPs-sPSB catalyst^[20] (gold content of 2 wt% determined by atomic absorption spectroscopy according to the literature procedure^[20c]) have been synthesized and characterized according to the reported procedures. Catalytic tests were carried out, unless otherwise stated, with AuNPs-sPSB in the ϵ crystalline form.

Instrumentation and methods. NMR spectra have been collected on AVANCE Bruker spectrometers (600, 400, 300 and 250 MHz for ¹H). The chemical shifts have been referenced to tetramethylsilane as external reference, using the residual protio signal of the deuterated solvents. NMR diagnostic signals for reagents and products (δ in ppm, DMSO-d₆, 25 °C): i) 5-hydroxymethylfurfural (HMF) ¹H NMR: 4.57 (2H, d, J = 6.0 Hz s), 6.57 (1H, d, J = 3.5 Hz), 7.41 (1H, d, J = 3.5 Hz), 9.56 (1H, s); ¹³C NMR: 56.4 (1C), 109.5 (1C), 121.5 (1C), 152.2 (1C), 154.1 (1C), 177.7 (1C). ii) 2,5-diformylfuran (DFF) ¹H NMR: 7.57 (2H, s), 9.83 (2H, s); ¹³C NMR: 121.5 (2C), 163.7 (2C), 180.2 (2C).^[27] iii) 5-formylfuran-2carboxylic acid (FFCA) ¹H NMR: 6.56 (1H, d, J = 3.3 Hz), 7.39 (1H, d, J = 3.3 Hz), 9.55 (1H, s).^[13] iv) methyl 5-(hydroxymethyl)furan-2-carboxylate (MHMFC) ¹H NMR : 3.78 (3H, s), 4.47 (2H, s), 6.47 (1H, d, J = 3.2 Hz), 7.19 (1H, d, J = 3.2 Hz); ¹³C NMR: 52.2 (1C), 56.2 (1C), 109.1 (1C), 119.2 (1C), 143.3 (1C), 157.7 (1C), 158.1 (1C).[28] v) dimethyl furan-2,5dicarboxylate (DMFC) ¹H NMR: 3.88 (6H, s), 7.32 (2H, s); ¹³C NMR: 52.1 (2C), 118.7 (2C), 146.6 (2C), 158.2 (2C).^[29] vi) 5-hydroxymethyl 2furancarboxylic acid (HMFCA) ¹H NMR (δ in ppm, D₂O+CD₃CN, 25 °C): 4.47 (2H, s), 6.35 (1H, d, J = 3.4 Hz), 6.82 (1H, d, J = 3.4 Hz); ¹³C NMR (δ in ppm, D₂O, 25 °C): 55.9 (1C), 109.2 (1C), 114.6 (1C). vii) 5-(methoxycarbonyl)furan-2-carboxylic acid (MFCA) ^{1}H NMR (δ in ppm, CDCl₃, 25 °C): 3.56 (3H, s), 6.62 (1H, d, *J* = 3.6 Hz), 6.82 (1H, d, *J* = 3.6 Hz); ¹³C NMR: 51.2 (1C), 113.4 (1C), 118.1 (1C). viii) furan-2,5dicarboxylic acid (FDCA) ¹H NMR (δ in ppm, CDCI₃, 25 °C): 6.56 (2H, s); ¹³C NMR: 113.5 (2C). Wide angle x-ray diffraction (WAXD) patterns have been obtained in reflection mode with an automatic Bruker D8 powder diffractometer using the nickel-filtered Cu K_{α} radiation. Transmission electron microscopy (TEM) has been carried out with a Tecnai 20 microscope from FEI operating at 200 kV. The specimens for TEM analysis have been sonicated in 2-propanol and then transferred (10 µL) onto a copper grid covered with a lacey carbon film supplied from Assing. The size distribution analysis of the AuNPs has been performed with the software Photoshop CS5 Extended. Atomic absorption spectroscopy (AAS) analysis has been performed on a PerkinElmer AAnalyst 100 spectrophotometer using an Au hollow cathode lamp (Perkin-Elmer).

General procedure for oxidation of HMF to DFF or catalyzed by AuNPs-sPSB (entry 5 of Table 1). A 60 mL stainless steel pressure reactor, equipped with a magnetic stirring bar, has been charged with Cs_2CO_3 (42 mg), AuNPs-sPSB (50 mg) and molecular sieves (50 mg). The reactor has been sealed, pressurized with oxygen at 0.5 MPa and depressurized at ambient pressure for five times to condition the inner atmosphere, charged under oxygen flux with an anhydrous solution of HMF (16 mg) in DMF (2.0 mL) and finally pressurized with oxygen to 1.5 MPa. The reaction was run under stirring at 80°C for 16 h. The reactor has been cooled with ice, oxygen pressure slowly released and the mixture analysed by ¹H-NMR spectroscopy using DMSO- d_8 as solvent and anisole as external standard. Yields: DFF 61.9 % and FFCA 15.8 %.

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General procedure for direct esterification of HMF with methanol catalyzed by AuNPs-sPSB (entry 23, Table 2). A 60 mL stainless steel pressure reactor, equipped with a magnetic stirring bar, has been charged with Cs₂CO₃ (42 mg), AuNPs-sPSB (50 mg) and molecular sieves (50 mg). The reactor has been sealed, pressurized with oxygen at 0.5 MPa and depressurized at ambient pressure for five times to condition the inner atmosphere, charged under oxygen flux with an anhydrous solution of HMF (16 mg) in methanol (0.5 ml) and DMA (2.0 mL) and finally pressurized with oxygen to 1.5 MPa. The reaction was run under stirring at 110°C for 16 h. The reactor has been cooled with ice, the oxygen pressure slowly released and the mixture analysed by ¹H-NMR spectroscopy using DMSO-d₆ as solvent and anisole as external standard. Yields: DMFC 80.2 % and MHMFC 8.6 %.

General procedure for HMF oxidation to FDCA catalyzed by AuNPssPSB (entry 5, Table 3). A 60 mL stainless steel pressure reactor, equipped with a magnetic stirring bar, has been charged with Cs₂CO₃ (42 mg) and AuNPs-sPSB (50 mg). The reactor has been sealed, pressurized with oxygen at 0.5 MPa and depressurized at ambient pressure for five times to condition the inner atmosphere, charged under oxygen flux with a solution of HMF (16 mg), water (0.5 mL), methanol (0.5 mL), DMA (2.0 mL), finally pressurized with oxygen at 1.5 MPa and stirred at 110 °C for 24 h. The reactor has been cooled with ice, oxygen pressure slowly released and the mixture analysed by ¹H-NMR spectroscopy using DMSO-d₆ as solvent and diglyme as external standard. Yield: FDCA >99.9%.

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Keywords: gold nanoparticles • oxidation • esterification • HMF • nanoporous.

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Entry for the Table of Contents

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The aerobic oxidation and oxidative esterification of HMF catalyzed by gold nanoparticles supported on a semicrystalline nanoporous polymer matrix have been investigated. The selectively permeable support allows a fine regulation of the environment surrounding the catalytic sites allowing a fine control on the oxidation process.



Antonio Buonerba, Salvatore Impemba, Antonella Dentoni Litta, Carmine Capacchione, Stefano Milione and Alfonso Grassi*

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Tuning of Selectivity and Activity in Aerobic Oxidation and Oxidative Esterification of 5-Hydroxymethylfurfural by Gold Nanoparticles Supported on Nanoporous Polymer Host Matrix