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Fabien Grasset, Benjamin Katryniok, Sébastien Paul, Veronique Nardello-Rataj, Marc Pera-Titus, et al.. Selective oxidation of 5-hydroxymethylfurfural to 2,5- diformylfuran over intercalated vanadium phosphate oxides. RSC Advances, Royal Society of Chemistry, 2013, 3, pp.9942-9948. <10.1039/c3ra41890a>. <hal-00859535>

HAL Id: hal-00859535

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Submitted on 9 Sep 2013

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PAPER

Selective oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran over intercalated vanadium phosphate oxides†

Cite this: *RSC Advances*, 2013, **3**, 9942

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The selective oxidation of 5-hydroxymethylfurfural (5-HMF) to 2,5-diformylfuran (DFF) was studied over vanadium phosphate oxide (VPO)-based heterogeneous catalysts in the liquid phase. The selectivity to DFF was highly increased when using intercalated vanadium phosphate oxides under mild conditions (1 atm of oxygen, 110 °C) in an aromatic solvent. We found that the length of the intercalated ammonium alkyl chain had no clear influence on the catalytic performances, and a maximum yield of 83% could be achieved over C₁₄VOPO₄ and C₁₄VOHPO₄ after 6 h of reaction. Recycling of the catalyst was successfully performed, and we further obtained some insights in the reaction pathway: while the desired oxidation reaction indeed proceeded over the catalyst, the formation of by-products was linked to the presence of free radicals in solution.

Received 18th February 2013,
Accepted 25th April 2013

DOI: 10.1039/c3ra41890a

www.rsc.org/advances

Introduction

The economy of the industrialised and emerging countries hangs almost entirely on the use of fossil raw materials, with more than 90% of organic chemicals issued from crude oil transformations.¹ Some of these molecules are used to synthesize polymers, which have grown in importance since World War 2. For example, polyethylene terephthalate (PET), discovered in the early 1940's, is a common component of a multitude of nowadays' consumer goods, such as plastic bottles.² However, the national dependency on crude oil importation, the depletion of resources and climate change have triggered the research of alternative strategies for manufacturing chemicals.³ Carbohydrates, which represent

75% of the 180 Gt of renewable biomass produced each year, is the most important class of organic compounds in terms of volume.⁴ Among them, simple sugars like glucose and fructose can be obtained by hydrolysis of waste wood cellulose or inulin, avoiding competition with the food chain. Fructose dehydration has been extensively studied for the production of 5-hydroxymethylfurfural (5-HMF), which is one of the key bio-based platform chemicals identified by the U.S. DoE.^{1,5,6} Indeed, its structure contains a hydroxyl and a formyl moieties together with a furan ring, opening an avenue for chemical reactions. However, this rich chemistry also makes 5-HMF suffer from poor stability.^{3,4,7} In contrast, 2,5-diformylfuran (DFF) produced by oxidation of the hydroxymethyl group of 5-HMF proved to be indefinitely stable under its crystalline form.⁷ Interestingly, DFF can be used either as a monomer,⁷ or as a starting material for the synthesis of ligands,⁸ drugs,⁹ and antifungal agents¹⁰ (Scheme 1). The oxidation of 5-HMF to DFF with Ba(MnO₄)₂ or NaOCl as oxidizing agents in the presence of a Mn catalyst has been reported in the literature.^{4,11} However, this reaction requires stoichiometric amounts of oxidant, which generates considerable amounts of wastes.^{4,11} Alternative homogeneous catalytic systems have been developed using molecular oxygen (or air) as oxidant, including Co/Mn/Zr/Br,¹² vanadium,^{13,14} or Mn(III)-salen catalysts.¹¹ A better separation of the products from the catalytic system can be achieved using heterogeneous catalysts, which are often based on vanadium. For example, immobilization of VO(acac) on poly(4-vinylpyridine) provides high selectivity to DFF (>99%) after 24 h of reaction under air at 130 °C in

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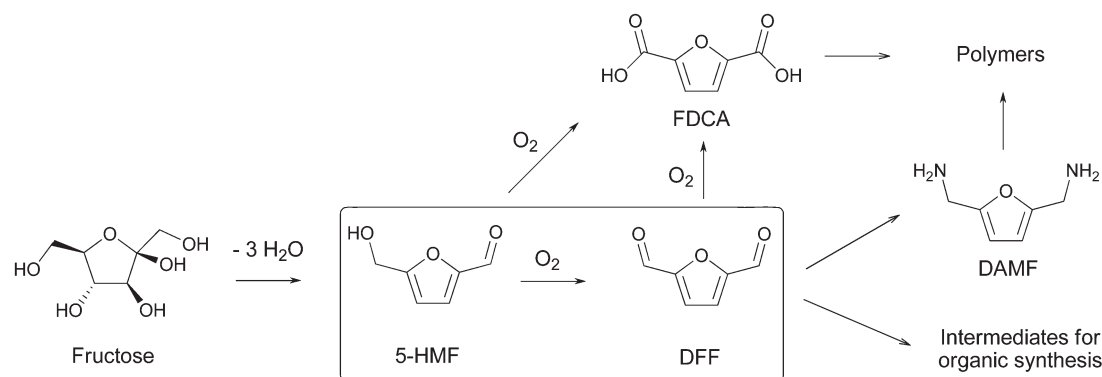
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† Electronic supplementary information (ESI) available: Powder XRD patterns, elemental analysis, characterization of products and proposed reaction mechanism. See DOI: 10.1039/c3ra41890a



Scheme 1 Transformation of fructose to value added chemicals via oxidation of 5-HMF to DFF.

DMSO.¹⁵ However, the addition of pyridine to the reaction medium was mandatory to prevent vanadium leaching and to attain high 5-HMF conversions. V_2O_5 has also been used in toluene at 170 °C under air ($P = 1$ bar), giving 91% of 5-HMF conversion and 69% of selectivity to DFF. The use of V_2O_5 supported on TiO_2 increases the yield to DFF up to 97% at 110 °C in toluene after 1.5 h of reaction under air ($P = 1.6$ bar).¹⁶ This result was however obtained under non-ideal conditions, with an important weight ratio of 2 between the catalyst and 5-HMF. A systematic study on VO_x supported on various oxides (TiO_2 , MgO , Al_2O_3 ...) revealed that a high VO_x surface density leads to the formation of V_2O_5 crystallites on the support and increases the selectivity to DFF.¹⁷ The authors postulated a Mars-Van Krevelen mechanism, the rate-determining step being the re-oxidation of the vanadium species. Recently, V_2O_5 supported on an H-beta zeolite was used to successfully perform the oxidation of 5-HMF to DFF, showing more than 99% of selectivity at 84% of 5-HMF conversion.¹⁸ Nevertheless, both heterogeneous and lixiviated species were found responsible for this performance. Oxidation of 5-HMF obtained by dehydration of fructose without any purification (except the removal of the dehydration catalyst) has been performed using various vanadium catalysts such as $VOHPO_4 \cdot 0.5H_2O$ in DMSO at 150 °C under air.^{19,20} Yields as high as 61% based on 5-HMF were obtained after 13 h. Nonetheless, the produced DFF was found to be contaminated with Me_2SO_2 and Me_2S , and further purification by vacuum sublimation and Soxhlet extraction was required to obtain pure crystalline DFF.

Carlini *et al.* found that $VOPO_4 \cdot 2H_2O$ could oxidize 5-HMF in methylisobutylketone (MIBK), displaying 50% of selectivity at 98% of 5-HMF conversion under oxygen ($P = 1$ bar) at 80 °C after 6 h of reaction.²¹ The use of MIBK revealed to be especially advantageous, since 5-HMF can be produced by the catalytic dehydration of fructose in water/MIBK mixtures.^{22–25} The selectivity was further improved by performing the reaction in *N,N*-dimethylformamide (DMF) at 100 °C, leading to DFF with 93% selectivity, but with a comparatively low 5-HMF conversion of 56% after 6 h.²¹ In contrast, the same authors reported almost no conversion of 5-HMF over $VOPO_4 \cdot 2H_2O$ when the reaction was performed in water. In

the present work, we report encouraging results on long alkyl chain trimethylammonium intercalated vanadium phosphorus oxides (I-VPO) for the efficient selective oxidation of 5-HMF to DFF under relatively mild conditions using conventional and green solvents. Herein, we raise the hypothesis that intercalation could drive the catalytic systems to mesostructured phases, which could then impact their oxidation properties. Mechanistic aspects of the reaction were also explored.

Experimental

Materials

V_2O_5 , H_3PO_4 (85%), 2-butanol, toluene, *m*-xylene, *p*-xylene, cyclopentylmethylether (CpOMe), 2-methyltetrahydrofuran (MeTHF), and 2,5-diformylfuran (DFF) were obtained from Aldrich. Decyl-, dodecyl-, tetradecyl-, hexadecyl-trimethylammonium bromides (abbreviated as $C_{10}TAB$, $C_{12}TAB$, $C_{14}TAB$, $C_{16}TAB$, respectively), *tert*-butyl acetate (*t*BuOAc), and acetonitrile were purchased from Alfa Aesar. Methylisobutylketone (MIBK) was purchased from Laboratoires Verbièse. 5-HMF was provided by Shanghai Chempartner Co, LTD. All the chemicals were used without further purification.

$VOPO_4 \cdot 2H_2O$ was prepared following the method described by Kamiya *et al.*²⁶ V_2O_5 (11.8 g) and H_3PO_4 (85%, 104.6 g) were refluxed in H_2O (275 mL) for 16 h. The resulting solid was isolated by vacuum filtration, washed with acetone (3 x 200 mL), and dried under static air at room temperature for 2 days to finally yield $VOPO_4 \cdot 2H_2O$, as confirmed by powder XRD (Fig. S1).†

$VOHPO_4 \cdot 0.5H_2O$ was prepared according to the procedure described by Kim *et al.*²⁷ V_2O_5 (11.8 g) and H_3PO_4 (85%, 16.5 g) were refluxed in 2-butanol (250 mL) for 16 h. The resulting solid was isolated by vacuum filtration, washed with acetone (3 x 200 mL), and dried under static air at room temperature for 2 days, yielding $VOHPO_4 \cdot 0.5H_2O$ as confirmed by powder XRD (Fig. S2).†

The intercalated compounds (I-VPOs) were synthesized using a method already described by Doi and Miyake.²⁸ $VOPO_4 \cdot 2H_2O$ or $VOHPO_4 \cdot 0.5H_2O$ (1 eq.) were added to an

aqueous solution (30 mL) of C_n TAB, (1 eq.) at room temperature. The pH was adjusted to 7.5 using concentrated NH_4OH before the mixture was heated to 75 °C for 48 h. The resulting solids were recovered by filtration, washed with water (5 x 100 mL), and dried in an oven under static air (50 °C, 2 days). The samples were labelled $C_nVO(H)PO_4$, where n indicates the length of the alkyl chain (10, 12, 14, or 16, respectively). They were analysed by powder XRD (Fig. S3 and S4) and elemental analysis (Table S1).†

Characterisations

Powder XRD patterns were recorded on a Bruker D8 Advance diffractometer using $Cu-K\alpha$ radiation ($\lambda = 0.154$ nm) as X-ray source in the 2θ range of 0.5–80° (0.02°/s, 0.5 s/step).

The textural properties of the samples were determined by nitrogen physisorption at 77.4 K on a Micromeritics ASAP 2010 porosimeter. The specific surface areas were calculated using the BET (Brunauer-Emmett-Teller) method in the pressure range $0.06 < P/P_0 < 0.20$. The total pore volumes were determined from the data recorded at $P/P_0 = 0.99$. Prior to the analyses, the samples were outgassed at 130 °C for 3 h.

V, P, N and Br elemental analyses were performed at the Service Central d'Analyses du CNRS (Villeurbanne, France).

Evaluation of catalytic performance

Atmospheric pressure oxidation of 5-HMF was performed in 30 mL glass tubes equipped with a reflux condenser using the following general procedure. Typically, the catalyst (30 mg) was introduced in the reaction tube and 3 consecutive vacuum/oxygen cycles were performed. A solution of 5-HMF (0.1 M, 3 mL) was added and the mixture was heated to the desired temperature under oxygen atmosphere while stirring (800 rpm). At the end of the experiment, the tube was cooled down to room temperature and a clear solution was recovered by syringe filtration.

Experiments of high-pressure 5-HMF oxidation were also performed in a Hastelloy C 35 mL reactor equipped with a mechanical stirring. Typically, the catalyst (45 mg) and a solution of 5-HMF (0.1 M, 9 mL) were introduced to the reactor and 3 consecutive pressurization cycles with oxygen/evacuation were performed. Then, the mixture was heated to the desired temperature under stirring (800 rpm) and the oxygen pressure was adjusted to 10 bar. At the end of the experiment, the reactor was cooled to room temperature, depressurized, and the clear solution was recovered by syringe filtration.

The analysis of the recovered solutions were performed on a Varian CP 3800-Saturn 2000 GC-MS equipped with a CP Wax 58 (FFAP)CB capillary column (column length: 25 m, internal diameter: 0.25 mm, film thickness: 0.20 μ m). External calibration curves based on commercial samples were used for 5-HMF and DFF quantifications.

Results and discussion

Preparation and characterisation of the catalysts

The introduction of alkyltrimethylammonium into $VOPO_4 \cdot 2H_2O$ or $VOHPO_4 \cdot 0.5H_2O$ results in the formation of

Table 1 Textural properties of vanadium phosphate oxides compounds as inferred by N_2 physisorption at 77.4 K

Compound	BET specific surface ($m^2 g^{-1}$)	Pore Volume ($cm^3 g^{-1}$) ^a
$VOPO_4 \cdot 2H_2O$ ²¹	<1	—
$VOHPO_4 \cdot 0.5H_2O$	9	0.007
$C_{14}VOPO_4$	18	0.021
$C_{14}VOHPO_4$	27	0.094

^a determined at $P/P_0 = 0.99$.

mesostructured I-VPOs, whereby the basal spacing is known to increase with the alkyl chain (3.2 nm for C_{12} TAB to 4.1 nm for C_{18} TAB in $VOPO_4 \cdot 2H_2O$).^{26,28} The powder XRD patterns of the I-VPOs showed indeed no reflections above $2\theta = 10^\circ$, and strong reflections at $2\theta \approx 8^\circ$ in addition to peaks attributed to mesostructured phases at $2\theta < 5^\circ$ (Fig. S3 and S4), which is in agreement with the previous work of Datta *et al.* on the intercalation of C_{16} TAB into $VOPO_4 \cdot 2H_2O$.²⁹ As a matter of example, the textural properties of intercalated $VOPO_4 \cdot 2H_2O$ and $VOHPO_4 \cdot 0.5H_2O$ using C_{14} TAB compared to the parent solids were analysed by nitrogen physisorption, as this surfactant is commonly used in ammonium intercalation studies. The results presented in Table 1 show that the specific surface area after intercalation is significantly promoted with respect to the initial VPO solids.

Catalytic activity

$VOPO_4 \cdot 2H_2O$ and $VOHPO_4 \cdot 0.5H_2O$ were used as reference catalysts, since both phosphates have already been described for the oxidation of 5-HMF to DFF.^{19–21} A standard 5-HMF oxidation procedure was then established based on MIBK as solvent to investigate the catalytic performance of I-VPO and enable direct comparison with the results reported by Carlini *et al.*²¹ taken as benchmark. Moreover, the influence of the temperature and nature of the solvent were examined. In addition to conventional solvents such as acetonitrile or xylenes, we also screened 2 more eco-friendly solvents, namely cyclopentylmethylether (CpOME) and 2-methyltetrahydrofuran (MeTHF).

Oxidation of 5-HMF (0.1 M in MIBK) over $VOPO_4 \cdot 2H_2O$ and $VOHPO_4 \cdot 0.5H_2O$ gave a high conversion of 5-HMF but yielded numerous by-products (more than 20) resulting in a poor selectivity to DFF, *i.e.* below 10% (Table 2, entries 2, 3 and 4). Among the different by-products formed, formic acid, acetic acid and 5-(2-furaldehyde)methyl formate (FMF) were mainly detected. The sole by-products observed by Carlini *et al.*,²¹ namely 5-acetoxymethyl-2-furaldehyde (AMF), 5,5'-[oxybis(methylene)]bis-2-furaldehyde (OBMF) and levulinic acid, were not detected in our experiments. Although acetic acid was not observed by Carlini *et al.*, these authors suggested its role as intermediate in AMF formation. In the present study, AMF was not observed, but the formed by-product was clearly identified as FMF (Fig. S6–10†). Hence, formic acid is more likely to act as intermediate in the formation of FMF, this hypothesis being supported by the study of Du *et al.*³⁰ The use of intercalated VPOs, *i.e.* $C_{14}VOPO_4$ and $C_{14}VOHPO_4$, in MIBK led to low

Table 2 Catalytic oxidation of 5-HMF by vanadium phosphorus oxides^a

Entry	Catalyst	Solvent	T/°C	5-HMF conversion (%)	DFF selectivity (%)
1	—	MIBK	80	—	—
2	VOPO ₄ ·2H ₂ O	MIBK	80	92	7
3 ^b	VOPO ₄ ·2H ₂ O	MIBK	80	99	<5
4	VOHPO ₄ ·0.5H ₂ O	MIBK	80	80	11
5	C ₁₄ VOPO ₄	MIBK	80	23	24
6	C ₁₄ VOHPO ₄	MIBK	80	6	99
7	C ₁₄ VOPO ₄	MIBK	110	96	20
8	C ₁₄ VOHPO ₄	MIBK	110	61	43
9	C ₁₄ VOPO ₄	Acetonitrile	80 ^c	69	20
10	C ₁₄ VOPO ₄	^t BuOAc	80 ^c	51	7
11	C ₁₄ VOPO ₄	MeTHF	80 ^c	50	27
12	C ₁₄ VOPO ₄	CpOMe	106 ^c	96	8
13	C ₁₄ VOPO ₄	<i>m</i> -Xylene	110	99	67
14	C ₁₄ VOPO ₄	<i>p</i> -Xylene	110	99	63
15	C ₁₄ VOPO ₄ ^d	Chlorobenzene	110	96	73
16	C ₁₄ VOPO ₄	Toluene	110	99	82
17	C ₁₄ VOHPO ₄	Toluene	110	99	83
18 ^e	C ₁₄ VOPO ₄	Toluene/water	100	<5	99
19	VOPO ₄ ·2H ₂ O	Toluene	110	82	7
20	VOHPO ₄ ·0.5H ₂ O	Toluene	110	91	5
21	—	Toluene	110	—	—
22	C ₁₄ VOPO ₄ ^d	Toluene	110	91	87
23 ^f	C ₁₄ VOHPO ₄	Toluene	110	56	80
24 ^g	C ₁₄ VOPO ₄	Toluene	110	91	85
25 ^{21,h}	VOPO ₄ ·2H ₂ O	MIBK	80	98	50
26 ^{21,i}	VOPO ₄ ·2H ₂ O	DMF	100	56	93

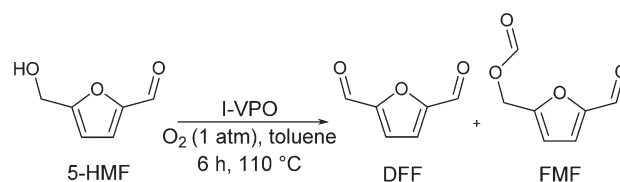
^a [HMF] = 0.1 M, solvent (3 mL), catalyst (30 mg), 6 h, oxygen (1 atm). ^b [HMF] = 0.4 M, solvent (3 mL), catalyst (60 mg). ^c Reduced reaction temperature due to lower boiling point. ^d Catalyst (15 mg). ^e toluene (2 mL), water (2 mL), catalyst (20 mg), 6 h, oxygen (1 atm). ^f catalyst (15 mg), helium (1 atm). ^g solvent (9 mL), catalyst (45 mg), 6 h, oxygen (10 bar). ^h [HMF] = 0.4 M, solvent (30 mL), catalyst (600 mg), 6 h, oxygen (1 atm). ⁱ [HMF] = 0.2 M, solvent (50 mL), catalyst (300 mg), 6 h, oxygen (1 atm).

5-HMF conversions (23 and 6%, respectively), but with a significantly better selectivity (Table 2, entries 5 and 6). This slight improvement in the selectivity was ascribed to the reduced oxidative properties of the samples. Indeed, the intercalation process relies on the substitution of water molecules in the VPO structure by tertiary alkyl-ammonium chains.^{31,32} This intercalation process implies a decrease in the *P/V* ratio, and the generation of new mesostructured phases, which can moderate the oxidation properties of the catalyst and decrease in turn the formation of side products as well as the conversion.^{28,29} In order to increase the catalytic activity of I-VPOs in MIBK, the reaction temperature was increased to 110 °C, whereby the yield significantly increased to 19% and 26% (Table 2; entries 7 and 8) for C₁₄VOPO₄ and C₁₄VOHPO₄, respectively.

In a second step, several solvents were screened—namely acetonitrile, *tert*-butyl acetate, CpOMe, 2-MeTHF, *meta*- and *para*-xylene, chlorobenzene, and toluene in the oxidation of 5-HMF over C₁₄VOPO₄ taken as example and under the optimized conditions (110 °C). Among the tested solvents (Table 2, entries 9–16), only the aromatic ones offered good DFF selectivity (>63%) at full conversion (Table 2, entries 13–16). In contrast, the use of oxygenated solvents (Table 2, entries 10–12) resulted in the formation of large amounts of degradation products originating either from 5-HMF and/or from the solvent itself. This enlightens that these polar solvents are not inert under the chosen experimental oxidative conditions, and may react with the catalyst or chemical species

produced by action of the catalyst on 5-HMF (Scheme 2). This latter hypothesis is more likely, since the use of VOPO₄·2H₂O in toluene or MIBK without 5-HMF barely produced any product. Blank experiments revealed also that without a catalyst, no 5-HMF was converted. The introduction of water (Table 2, entry 18) prevented the oxidation of 5-HMF (conversion less than 5%), in agreement with the results of Carlini *et al.*²¹

As the best performance was obtained in toluene, this solvent was employed for further experiments with the other VPO catalysts (C₁₄VOHPO₄, VOPO₄·2H₂O and VOHPO₄·0.5H₂O). In the case of the two non-intercalated VPOs (Table 2; entries 19 and 20), noticeable amounts of benzaldehyde and benzyl alcohol were formed by oxidation of toluene, whereas only low amounts of DFF were formed (selectivity of 7% and 5% over VOPO₄·2H₂O and VOHPO₄·0.5H₂O, respectively). The main products were FMF and benzyl formate, appearing most likely from the esterifica-

**Scheme 2** 5-HMF oxidation products over intercalated VPOs.

tion of formic acid with 5-HMF and benzyl alcohol formed by oxidation of toluene, respectively.

In contrast, the use of I-VPOs in toluene resulted in an increase of 5-HMF conversion as well as in the selectivity to DFF, while both I-VPOs showed a comparable yield to DFF of 82–83% (Table 2, entries 16 and 17). The only observed by-product in these cases was FMF (Scheme 2). The results were found independent of the initial vanadium oxidation state (V^{5+} for $VOPO_4 \cdot 2H_2O$ and $C_{14}VOPO_4$; V^{4+} for $VOHPO_4 \cdot 0.5H_2O$ and $C_{14}VOHPO_4$), which strongly evidences that both oxidation states are involved during the catalysis supposedly *via* a Mars-Van Krevelen mechanism as claimed by Nie *et al.*^{17,33} Halliday *et al.* also reported that both V^{4+} ($VOHPO_4 \cdot 0.5H_2O$) and V^{5+} (V_2O_5 , γ - $VOPO_4$) enabled the oxidation of 5-HMF to DFF in DMSO at 150 °C under air (1 atm) with almost the same DFF yield ($\approx 60\%$).^{19,20}

The influence of the reaction atmosphere was studied using helium or high pressure of oxygen (Table 2, entries 22–24). No differences were observed between the tests under atmospheric pressure or 10 bar of oxygen. In contrast, the use of helium (atmospheric pressure) yielded a significant decrease in the conversion (56%), while the selectivity remained high (80%). This highlights the fact that oxygen is indeed mandatory to complete a catalytic cycle.

Influence of the catalyst loading and recycling

The conversion of 5-HMF was studied with different catalyst-to-substrate weight ratios ($C_{14}VOPO_4/5\text{-HMF}$) in the range of 0.13–0.80 at 110 °C in toluene and under 1 atm. of O_2 . As expected, the reduction of the catalyst/5-HMF ratio slowed down the substrate conversion (Fig. 1), but the selectivity remained constant above 80% during the runs, as exemplary shown in Fig. 2 for $C_{14}VOPO_4$ (weight ratio $C_{14}VOPO_4/5\text{-HMF} = 0.40$). This result is in agreement with the work of Nie *et al.* on VO_x/TiO_2 ,¹⁷ who reported that the selectivity to DFF is independent on the 5-HMF conversion. $C_{14}VOPO_4$ (weight ratio of $C_{14}VOPO_4/5\text{-HMF} = 0.26$) and $C_{14}VOHPO_4$ (weight ratio of $C_{14}VOHPO_4/5\text{-HMF} = 0.26$) gave the same results, which may indicate that the equilibrium between the different oxidation states of the vanadium species is quickly reached. Visually, $C_{14}VOPO_4$ is light brown, whereas $C_{14}VOHPO_4$ is dark

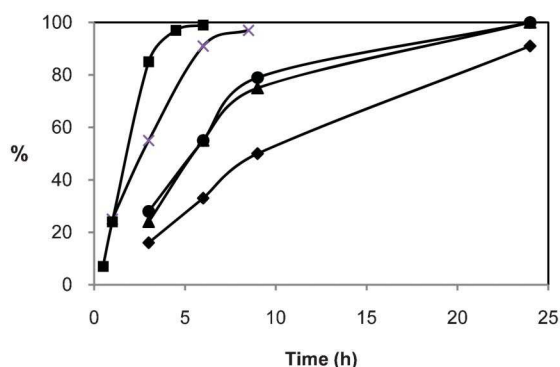


Fig. 1 5-HMF conversion under O_2 (1 atm.) at 110 °C in toluene with $C_{14}VOPO_4$ (weight ratio I-VPO/5-HMF = 0.80 (■), 0.40 (×), 0.26 (●), 0.13 (◆)) and $C_{14}VOHPO_4$ (weight ratio I-VPO/5-HMF of 0.26) (▲).

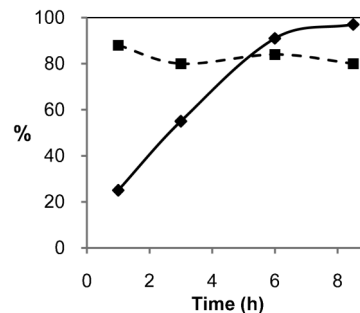


Fig. 2 5-HMF conversion (◆) and DFF selectivity (■) with $C_{14}VOPO_4$ (weight ratio I-VPO/5-HMF = 0.40) under O_2 (1 atm.) at 110 °C in toluene.

green.²⁸ At the end of the test, both catalysts were dark green, which indicates that they contain both V^{5+} and V^{4+} species. This observation is consistent with the XPS results reported by Datta *et al.* for the reduction of intercalated VPOs by 2-propanol revealing a gradual decrease of the vanadium average oxidation state from 4.95 to 4.64.²⁹

In order to demonstrate the recyclability of the catalysts, the $C_{14}VOPO_4$ intercalated sample was recovered after a first run by centrifugation. Before reuse, the solid was washed with toluene three times and dried overnight at 70 °C. It was then used under the same reaction conditions (110 °C; toluene; 1 atm. of O_2 , catalyst/substrate weight ratio of 0.40). The performance of the recycled catalysts decreased with respect to the initial values (Fig. 3). The catalyst in the first recycle run exhibited 81% conversion against 91% in the initial run, but with a similar selectivity (*ca.* 88%). On the other hand, the re-use of $C_{14}VOPO_4$ recovered for the second time gave not only a lower 5-HMF conversion (62%), but also a reduced selectivity to DFF of 74%. Thus, a modification of the catalyst can be anticipated, notably *via* the leaching of the intercalated chains by the reincorporation of water molecules generated during the oxidation process into the catalyst, yielding to changes in the XRD patterns for $2\theta < 8^\circ$ (Fig. S3–S5).^{29,33} The leaching of $C_{14}TAB$ was evidenced by elemental analysis of the liquid phase, which revealed traces of bromine and nitrogen ($<0.3\%$). However, the V/P weight ratio remained unchanged before and after reaction (Table S1, ESI†). The change in structure might then reduce the number of accessible reactive

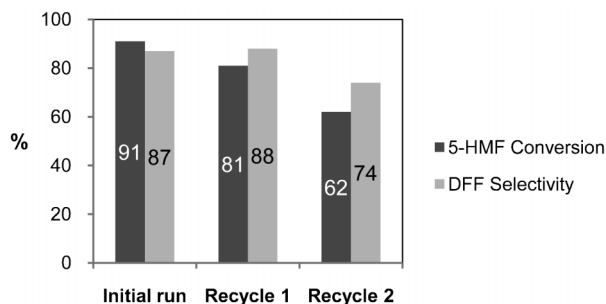


Fig. 3 Recycling test with $C_{14}VOPO_4$ (weight ratio I-VPO/5-HMF = 0.40); reaction conditions: 110 °C; toluene; O_2 (1 atm.); 6 h.

Table 3 Performance of intercalated VPOs in catalytic oxidation of 5-HMF^a

Entry	Catalyst	5-HMF conversion (%)	DFF selectivity (%)
1	C ₁₀ VOPO ₄	85	76
2	C ₁₂ VOPO ₄	90	82
3	C ₁₄ VOPO ₄	91	87
4	C ₁₄ OHVOPO ₄	90	82
5	C ₁₆ VOPO ₄	90	84

^a [HMF] = 0.1 M, toluene (3 mL), catalyst (15 mg), 6 h, oxygen (1 atm).

vanadium centres, explaining the observed decrease in the 5-HMF conversion and selectivity to DFF.

Influence of the nature of ammonium intercalates

As stated above, the basal spacing in intercalated mesostructured VPO phases increases with the alkyl chain length. In order to study the influence of the basal spacing on the catalytic properties, intercalated VOPO₄·2H₂O using different alkyl chain lengths (C₁₀TAB, C₁₂TAB, C₁₄TAB and C₁₆TAB) were prepared. Furthermore, C₁₄OHVOPO₄ was prepared using C₁₄TAOH to replace the counter-anion Br⁻ by HO⁻. The as-prepared catalysts were evaluated in the catalytic oxidation of 5-HMF in toluene at 110 °C with a catalyst/5-HMF weight ratio of 0.40. All the samples exhibited both high 5-HMF conversions (>85%) and selectivity to DFF (>76%) (Table 3). In fact, the catalysts displayed a very similar catalytic activity indicating a weak impact of the alkyl chain length. The use of hydroxide counter-ion instead of bromide did not significantly impact the catalytic performance either (Table 3, entries 3 and 4). C₁₄VOPO₄ was then selected for the tests, with the purpose of elucidating the reaction mechanism.

Reaction mechanism

Homogeneous oxidation of 5-HMF by vanadium compounds involves an active role of the redox couple V⁵⁺/V⁴⁺.¹⁴ The reduction of V⁵⁺ to V⁴⁺ by 5-HMF coupled to further re-oxidation of V⁴⁺ to V⁵⁺ by O₂ through a Mars-Van Krevelen mechanism has been highlighted using the heterogeneous

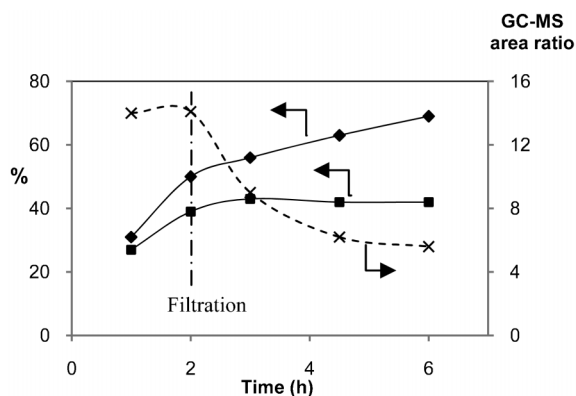


Fig. 4 Filtration of C₁₄VOPO₄ after 2 h of reaction and evolution of the filtrate under O₂ (1 atm) at 110 °C; Conversion (○); DFF yield (■); GC-MS peak areas ratio DFF/AMF (×).

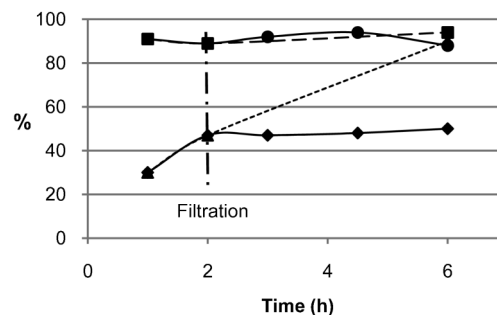


Fig. 5 Filtration of C₁₄VOPO₄ after 2 h of reaction and evolution of the filtrate under O₂ (1 atm) at 110 °C in the presence of BHT. 5-HMF conversion with (◆) and without filtration (▲ dotted line). DFF selectivity with (●) and without filtration (■ dotted line).

catalyst VO_x/TiO₂.¹⁷ On the guidance of these studies, we first checked about the heterogeneous nature of our reaction. A 0.1 M 5-HMF toluene solution was reacted with C₁₄VOPO₄ for 2 h at 110 °C under O₂ (*P* = 1 atm.). Then, the catalyst was separated by filtration, and the filtrate was re-introduced into the reaction vessel for 4 h. As an interesting result, we observed that the conversion of 5-HMF still progressed in the filtrate, yielding exclusively FMF, while no evolution of the DFF yield was observed (Fig. 4). In addition, benzyl formate was also detected after filtration. This result suggests that the oxidation of 5-HMF to DFF proceeds on the vanadium heterogeneous catalyst, whereas the formation of by-products proceeds *via* a homogeneous reaction of 5-HMF.

In order to check whether free radicals are involved in the formation of these by-products, the same experiment was performed in the presence of 2,6-di-*tert*-butyl-4-methylphenol (BHT) used as a radical scavenger. C₁₄VOPO₄ exhibited a slightly better performance as observed before in the absence of scavenger, with more than 90% of selectivity to DFF at 90% of 5-HMF conversion after 6 h (Fig. 5). However, if the reaction medium was filtrated after 2 h and the filtrate transferred back into the reaction vessel, no evolution was observed, *i.e.*, around 50% of conversion and 90% of selectivity (Fig. 5), meaning that neither FMF nor benzyl formate were formed. This result suggests that the species responsible for the formation of by-products probably results from a radical pathway. Furthermore, according to the study of Du *et al.*, the genesis of FMF catalysed by soluble vanadium species can be ruled out. As a matter of fact, these authors reported that the catalytic oxidation of 5-HMF with soluble VO(acac)₂ species was not affected by the presence of BHT, namely, the same conversion and product selectivity were obtained.³⁰ Finally, no vanadium was detected in solution by elemental analysis (no leaching).

Since no by-product formation corresponding to the oxidation of toluene (benzyl alcohol and benzaldehyde) was observed in the absence of 5-HMF, the free radical species responsible for by-product formation must originate from the interaction of 5-HMF and C₁₄VOPO₄. No carboxylic acid derived from 5-HMF was observed and DFF was stable in the reaction medium. Thus, one can assume that the corresponding radical is formed on the hydroxymethyl group of 5-HMF

(Scheme S2, ESI†), this hypothesis being in good agreement with the observation of Du *et al.* on the reactive position of the 5-HMF in homogeneous oxidation with VO(acac)₂.³⁰ This radical can further react with a vicinal V⁵⁺ to give DFF and a reduced vanadium centre (*i.e.* V⁴⁺) (Scheme S3, ESI†).

An oxidative degradation pathway leading to formic acid from 5-HMF may be proposed, as previously supposed in the literature, to explain the formation of FMF by esterification of 5-HMF.³⁰ In addition, the formation of benzyl formate in the filtration experiment without radical scavenger (*vide supra*) could also be explained by condensation of benzyl alcohol on formic acid. Additional work would be required to confirm and explain the reaction pathways to the by-products. The fact that oxidation of 5-HMF performed in an oxygenated solvent such as MIBK or CpOMe gave poor selectivity to DFF (Table 2, entries 7 and 12) can be then attributed to the weak stability of these solvents toward both oxidative conditions and presence of free radicals.

Conclusion

Intercalation of alkyltrimethylammonium ions in VOPO₄·2H₂O generated heterogeneous catalysts that performed the oxidation of 5-HMF to DFF with higher yields (83%) when using molecular oxygen at 110 °C in toluene compared to their non-intercalated VPO mother precursors (<6%). Oxygenated or polar solvents favoured 5-HMF degradation pathways. The formation of FMF was ascribed to a radical mechanism involving 5-HMF decomposition in solution, whereas the formation of DFF proceeded at the surface of the catalyst. Degraded recyclability of the catalyst may be attributed to the leaching of intercalated ammonium ions and change in the catalyst structure.

Acknowledgements

We thank Pr. Elisabeth BORDES-RICHARD, Dr Matthieu CORBET and Dr Damien CARTIGNY for fruitful discussions. This work was supported by CNRS and E2P2L (Solvay China). The "Fonds Européen de Développement Régional (FEDER)", "CNRS", "Région Nord-Pas-de-Calais" and "Ministère de l'Éducation Nationale de l'Enseignement Supérieur et de la Recherche" are gratefully acknowledged for contributing to the funding of X-ray diffractometers.

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