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Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Published on 09 August 2017. Downloaded by University of Windsor on 10/08/2017 14:33:46



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Over the past decade, great efforts have been devoted in the field of biomass valorisation to the development of reductive processes for the sustainable production of bio-fuel additives and chemicals. Catalytic transfer hydrogenation, which uses alcohols as the hydrogen source, offers an interesting approach that avoids the use of both high H₂ pressure and precious metal catalysts. In this work, the vapour-phase production of 2-methylfuran from biomass-derived furfural (FU), using methanol as the H-transfer agent and FeVO4 catalyst, was studied. At a temperature of 320°C it was possible to achieve 80% yield to 2-methylfuran, with small amounts of 2,5-dimethylfuran and 2-vinylfuran as by-products. Catalyst characterization highlighted that FeVO4 reduction took place under the studied conditions, leading to the in-situ development of the true active phase. The study of the reaction network permitted us to infer on the relative contribution of H-transfer and hydrogenation, the latter from the in-situ generated formaldehyde and H₂, to 2-methylfuran formation. The reported results indicate the potential application of H-transfer with FeVO4 catalysts as an efficient process for the selective de-oxygenation of biomass-derived molecules.

1. Introduction

In recent decades the continuing growing global demand for petrochemical products and fossil fuels, with the associated increase in CO₂ emission, has forced researchers to seek some renewable alternative feedstock for the production of chemicals and fuels ^{1,2}. In this field, the conversion of non-food lignocellulosic second-generation biomasses such as wood chips and agricultural and municipal wastes into chemicals and fuels has gained increasingly more importance. Indeed, lignocellulose can be converted into different chemicals and liquid fuels via biological and chemical pathways ³. Furan derivatives play an important role in the transformation of this renewable feedstock 4-7. For instance, furfural (FU), which is available on an industrial scale via the hydrolysis-dehydration of the hemicellulose part of lignocellulosic biomass ^{8,9}, is a key precursor for the synthesis of derivatives with applications in the fuel and polymer industries ¹⁰. The FU upgrade processes involve the selective hydrogenation of the carbonyl group into the corresponding unsaturated furfuryl alcohol (FAL), which finds application in industry for the production of resins and fine chemicals ^{11,12}, and into 2-methylfuran (MF) (Scheme 1), used as a renewable fuel. Indeed, this furan compound has

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superior properties as compared to bio-ethanol because of its

higher energy density and octane values ¹³. The octane



J. Name., 2013, 00, 1-3 | 1

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Electronic Supplementary Information (ESI) available: See DOI: 10.1039/x0xx00000x

Scheme 1. Production of 2-methylfuran (MF) from xylose and furfural (FU).

An alternative approach for the reduction of the FU carbonyl group to produce FAL and MF, bypassing the need for high hydrogen pressure and noble metal-based catalysts, is the Meerwein–Ponndorf–Verley (MPV) reaction, in which an alcohol is used as the hydrogen source. Indeed, under appropriate conditions, the reaction can be highly chemoselective towards carbonyl groups.²⁰⁻²²

Catalysts studied for this reaction may be divided into three main groups: Lewis basic, Lewis acid, and metal-supported catalysts²³⁻²⁵.

Di Cosimo and co-workers reported on the use of MgO as selective catalyst for the conversion of a wide range of unsaturated ketones to the corresponding alcohols using isopropanol as the hydrogen source ²⁶.

Hermans et al. have reported that Cu, Ni and Pd supported on Fe_2O_3 are active in the catalytic transfer hydrogenation of FU to produce a mixture of FAL, MF and 2-methyltetahydrofuran (MTHF) both in batch and continuous flow reactor, using 2-propanol as the hydrogen donor. They demonstrated that the high activity of Pd/Fe₂O₃ is due to strong metal-support interaction ²⁷.

Additionally, Vlachos and co-workers reported on the vapourphase hydrodeoxygenation of FU to MF with 50-60% selectivity using MoC as the catalyst ²⁸. They also described a liquid-phase catalytic transfer hydrogenation of FU over Ru/C and Ru/RuO catalysts, using various alcohols as hydrogen sources. ²⁹

Nevertheless, there are only a few studies in literature concerning the vapour-phase production of MF from FU with heterogeneous catalysts, and most of them require noble metal-supported catalysts, together with high hydrogen pressure and reaction temperature. Therefore, the development of a continuous catalytic process based on non-noble metal catalysts for the hydrodeoxygenation of FU to MF is a very attractive topic. Moreover, the use of H-transfer instead of classical hydrogen sources, thus increasing the sustainability of the entire process.

In this specific field, we recently reported on the use of methanol as a clean and efficient H-transfer reactant for carbonyl reduction in the liquid phase ³⁰. Compared to other molecules used in H-transfer, methanol showed the advantage of producing gaseous components as the only co-products. Using high-surface area MgO as a simple, easily recoverable and reusable catalyst for FU reduction, a 100% FAL yield was obtained.

As an alternative, mixed iron-vanadium mixed oxides could be used for the catalytic transfer hydrogenation on FU. Indeed, these materials were reported to be able to activate methanol in several reactions, for potential industrial applications. For example, Asahi Company reported that $FeVO_4$ is a very active and stable catalyst for the gas-phase methylation of phenol to *o*-cresol using methanol as the alkylating agent ³¹. It was demonstrated that the strong de-hydrogenating properties of the catalyst make possible the in-situ formation of a high quantity of formaldehyde, which is vietheicle real (hydroxyl)alkylating agent. Furthermore, Andérsson and real workers reported that FeVO₄ is very active and selective in methanol oxidation to formaldehyde ³².

Herein, we report on the vapour-phase reduction of FU to MF. The reaction was carried out in a continuous reactor by means of H-transfer from methanol to FU and $FeVO_4$ as the catalyst. Only 2,5-dimethylfuran and 2-vynilfuran were formed as by-products, and catalyst pre-treatment under reducing conditions was found to be fundamental for increasing MF selectivity, while limiting heavy compounds production. Moreover, the study of the reaction network was conducted by feeding reaction intermediates and various H-transfer molecules and molecular hydrogen, as well.

2. Experimental

2.1. Catalyst preparation

A FeVO₄ catalyst was prepared by co-precipitation from an aqueous solution containing the corresponding metal precursors, to obtain an atomic ratio Fe³⁺/V⁵⁺ equal to 1. For the synthesis of 20 g FeVO₄, a solution containing 47.32 g of Fe(NO₃)₃*9H₂O (Sigma Aldrich, 99% purity) in 105 ml of distilled water was prepared. A second solution containing 13.70 g NH₄VO₃ (Sigma Aldrich, 99% purity) in 105 ml of distilled water was prepared and added dropwise under vigorous stirring to the Fe solution. The pH of the resulting solution (14%) to precipitate the FeVO₄ precursor. After 1 h of aging under stirring, the resulting precipitate was filtered and washed with an excess of water and dried overnight at 110°C. The dried solid was ground and calcined at 650°C in static air for 3 h.

2.2. Catalyst characterization

BET specific surface area. The BET surface area of catalysts was determined by means of N_2 absorption–desorption at liquid N_2 temperature, using a Sorpty 1750 Fison instrument. 0.3 g of the sample was used for the measurement, and the sample was outgassed at 150°C before N_2 absorption.

X-ray diffraction analyses (XRD). XRD powder patterns of the catalysts were recorded with Ni-filtered Cu K α radiation (λ = 1.54178 Å) on a Philips X'Pert vertical diffractometer equipped with a pulse height analyser and a secondary curved graphite-crystal monochromator.

Thermogravimetric/differential thermal analyses (TGA/ DTA). TGA/DTA analyses of fresh and spent catalysts were carried out using a SDT Q 600 instrument, to identify the amount of heavy compounds absorbed on the catalyst surface. 5-10 mg of sample were typically used, from room temperature up to 700°C, with a heating rate of 10°C min⁻¹ in air.

Raman spectroscopy. Laser Raman spectra were recorded at room temperature using a Renishaw 1000 spectrometer equipped with a Leica DLML microscope (5x, 20x, 50x lenses were used) and a CCD detector. Samples were excited with a Published on 09 August 2017. Downloaded by University of Windsor on 10/08/2017 14:33:46

diode laser beam (782 nm or 514 nm). Raman spectra were recorded in the spectral window 500-2000 $\rm cm^{-1}.$

Atomic absorption. The elemental analysis was carried out with a VARIAN SpectrAA 100 (equipped with a graphite tube atomizer); the solutions resulting from the mineralization process performed with hot aqua regia on both fresh and spent catalysts were analysed to determine the real Fe/V ratio.

In-situ DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) experiment with mass spectrometer. The IR apparatus used was a Bruker Vertex 70 with a Pike DiffusIR cell attachment. Spectra were recorded using a MCT detector after 128 scans and 2 cm⁻¹ resolution. The mass spectrometer used was an EcoSys-P from European Spectrometry Systems. In most cases the catalyst was loaded into the sample holder and the cell was closed and inserted into the DRIFT apparatus. A pretreatment up to 320-450°C in helium flow was then performed to remove any molecules adsorbed on the material, mainly carbon dioxide and water. The sample was then cooled down to 85°C and the spectra of the pure catalyst was recorded and used as a background for the following measurement. A first set of experiments was performed at 85°C by feeding methanol in a helium flow and vaporising it using heating strips. Then methanol was stopped and only helium was flowed inside the IR cell. This way, the low-temperature adsorption and desorption process was monitored. The second set of experiments was performed with a low-temperature adsorption and a programmed temperature desorption during which the following temperatures were monitored: 125°C, 175°C, 225°C, 275°C, and 320°C.

2.3. Vapor-Phase catalytic tests

Catalytic tests were conducted in a continuous-flow fixed-bed micro-reactor (Pyrex, length 38 cm, internal diameter 1/3 inch). The catalyst (30-60 mesh particles) was placed into the reactor in a quantity appropriate for changing the contact time from 0.1 to 1.0 s, and then heated to the desired reaction temperature (250-400°C) under N_2 flow (54 ml min⁻¹). The catalytic reaction was started by the vaporisation of methanol (WWR Chemicals) and FU (Sigma-Aldrich) in a 10/1 molar ratio using nitrogen as the carrier gas (54 ml min⁻¹). FU was purified via distillation prior to being fed into the flowing gas stream. The total volumetric inlet flow rate was held constant at 60 ml min⁻¹ and the molar concentrations of FU, methanol, and nitrogen were respectively 1, 10, and 89%. In all cases, results were taken after 1 h reaction time. Analyses of reactants and products were carried out as follows: the outlet stream was scrubbed for 1 h in cold acetonitrile, which was maintained at -26°C by a F32 Julabo thermostat. The condensed products were analysed by means of HPLC, using an Agilent Technologies 1260 Infinity instrument equipped with a DAD UV-Vis detector and an Agilent POROshell 120 C-18 column. Non-condensable gases (CO, CO₂, CH₄ and H₂) were analysed on-line with a PerkinElmer Clarus 500 gas chromatograph equipped with a TCD detector and a Carbosphere® 80/100

$$Furfural Conversion = \frac{\dot{n}_{furfural}^{ln} - \dot{n}_{furfural}^{out}}{\dot{n}_{furfural}^{ln}}$$

$$Products Selectivity = \frac{\dot{n}_{out}^{out}}{\dot{n}_{furfural}^{in} - \dot{n}_{furfural}^{out}}$$

$$C - Loss = 100 - \sum_{l} Product Selectivity$$

Preliminary tests were conducted, making it possible to exclude any problems originating from interparticle and intraparticle diffusion limitations. More specifically, some catalytic tests were conducted by changing the catalyst particle size for the same catalyst weight/inlet flow ratio; no effect on catalyst performance was observed. The catalytic tests performed while keeping the contact time constant but doubling or halving the total volumetric flow and catalyst volume, compared to the conditions typically used, showed no performance changes.

3. Results and Discussion

3.1. Bulk catalyst features

The catalyst was characterised via different techniques such as BET surface area, atomic absorption, X-ray diffraction, and Raman spectroscopy. After calcination at 650°C, the catalyst showed a specific surface area of 12 m²g⁻¹, a value in agreement with that reported by other authors ^{33,34}.

XRD patterns of the dried precursor and the calcined material are compared in Figure S1. The dried sample showed an amorphous structure: no reflection was registered, while the calcined catalyst presented a well-defined FeVO₄ triclinic structure with traces of segregated iron oxide phase (hematite).

The Raman analysis confirmed these results. The spectrum reported in Figure 1 can be divided into four spectral regions which agree well with those reported in literature for crystalline FeVO₄ ³³: (i) at Raman shift 1050-880 cm⁻¹, there are bands attributable to terminal V=O bond stretching; (ii) at 880-700 cm⁻¹, to V—O--Fe bond stretching; (iii) at 700-550 cm⁻¹ to V—O--Fe and V--O--Fe stretching; and (iv) at < 550 cm⁻¹, to the deformation of V—O--V bonds and Fe—O stretching. In addition to these bands, at 1300 cm⁻¹ a weak broad band can be attributed to α -Fe₂O₃ ³⁵, indicating the possible segregation of a small quantity of hematite.

The elemental analysis indicated the presence of a Fe/V molar ratio equal to 1.09 ± 0.02 in fresh catalyst. This value is slightly higher than the theoretical one, thus highlighting the possible loss of some vanadium during catalyst synthesis. Indeed, the analysis of the solution obtained after filtration and washing of the catalyst showed the presence of very low amount of vanadium thus justifying the slight excess of iron in the solid.

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Figure 1. Raman spectrum of calcined FeVO₄.



Figure 2. DRIFT spectra recorded after methanol adsorption and desorption at the temperature of 320°C. During adsorption methanol was continuously fed over the catalyst while, during desorption, only He was fluxed. Legend: (a) DRIFT spectra registered during methanol adsorption, (b) DRIFT spectra registered during methanol desorption.

3.2. Hydrodeoxygenation of FU with FeVO₄ catalyst: effect of reaction temperature

The gas phase hydrodeoxygenation of FU was carried out using methanol as the hydrogen source.

The strong interaction between methanol and FeVO₄ was demonstrated by means of in-situ DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) experiments. Indeed, by feeding continuously the alcohol during the adsorption at low temperature (Figure S2), we demonstrated that methanol was mainly physi-adsorbed as methoxy species (IR bands at 2930 and 2828 cm⁻¹) ^{36,37}. The same behaviour was also confirmed at high temperature, but for very short time only (Figure 2); during adsorption, the main IR bands relating

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to the presence of both methoxy and molecular ic physic adsorbed methanol were identified. For prolonged adsorption desorption times, the appearance of broad bands at 1670-1500 cm⁻¹, 1350-1300 cm⁻¹ and 1713-1772 cm⁻¹ ³⁸ could be attributed to C-O vibration of molecular formaldehyde, providing evidence for the formation of chemi-adsorbed formate and formaldehyde species, thus confirming the ability of the catalyst to activate and dehydrogenate methanol at this temperature. Furthermore, the intensity of the IR bands remained unchanged during desorption, indicating that the interaction between activated methanol and catalyst was strong.

We first studied the influence of the reaction temperature. In these catalytic tests, MF was the main product detected, with small amounts of 2,5-dimethylfuran (DMF) and 2-vinylfuran (VINFU).

Since the product selectivity changed significantly during the first hour of reaction (Figures S3_A and S3_B), catalyst performances were compared at the second hour. Figure 3 shows FU conversion and product selectivity based on temperature (range 250-400°C).

At a low temperature (250°C), the hydrogenation of FU to MF occurred with very low efficiency. Indeed, the conversion of FU was lower than 50% and the overall selectivity to the identified products was around 25% (\approx 20% selectivity to MF). The low selectivity to MF and the high C loss indicate the poor ability of the catalyst to activate methanol for temperatures lower than 300°C. Indeed, the C loss could be ascribed to the formation of heavy carbonaceous compounds deriving from the degradation of FU.

When the temperature was increased up to 300-350°C, the efficiency of the H-transfer increased significantly. In this temperature range, we registered a notable increase in FU conversion and a remarkable enhancement of the overall selectivity to reduction products to up to approximately 75% (\approx 65% selectivity to MF). The formation of heavy compounds, due to FU degradation, was less than 20-30%.



Figure 3. Effect of reaction temperatures on FU conversion and product selectivity in the second hour of reaction, catalyst $FeVO_4$. Feed composition: FU 1%, CH_3OH 10%, N_2 89%; Pressure 1 atm, overall gas residence time 1.0 s. Symbols: \blacklozenge FU conversion, \blacksquare MF selectivity, \blacksquare DMF selectivity, \blacksquare VINFU selectivity, \blacksquare C loss.

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The presence of the oligomeric compounds adsorbed on the used catalyst surface was confirmed by Raman spectroscopy (Figure S4), with the characteristic D3 band at 1600cm⁻¹, which is ascribable to the presence of amorphous carbon species ³⁹. No products of ring hydrogenation or decarbonylation were formed.

The ability of FeVO₄ to activate methanol for temperatures higher than 300°C was confirmed by the results in Figure S5, which shows the number of moles of light compounds formed, based on time, at 250°C and 320°C. The negligible amount of CO, CO₂, CH₄, and H₂ produced at 250°C agrees with the results in Figure 3. As a matter of fact, in addition to the main reaction involving the H-transfer to MF, the process was accompanied by the decomposition of formaldehyde, which is produced by methanol dehydrogenation, into light gaseous compounds, CO, CO₂, CH₄, and H₂. In a previous work, we demonstrated that in similar reaction conditions formaldehyde was decomposed following the formal set of reactions reported in Scheme 2 40,41.

$CH_2O \rightarrow CO + H_2$	(1
$CO + H_2O \rightarrow CO_2 + H_2$	(2
2 CH ₂ O → CH ₃ O-C(O)H	(3
$CH_3OC(O)H \rightarrow CO_2 + CH_4$	(4
$HCOOH \rightarrow CO_2 + H_2$	(5
$HCOOH \rightarrow CO + H_2O$	(6
$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$	(7

Scheme 2. Summary of main reactions involving methanol in the catalytic H-transfer of FU ^{40,41}.

The formaldehyde generated as the co-product of H-transfer decomposes, leading to the formation of CO and H₂ (Reaction 1). Alternatively, two adsorbed CH₂O molecules may disproportionate to formate and a methoxy species, yielding methylformate (reaction 3) (the latter can also be formed by Tishchenko dimerization), which decomposes at high temperatures to CH₄ and CO₂ (reaction 4). Formic acid may also form through the oxidation of formaldehyde by Fe³⁺, and decompose to CO₂ and H₂ (reaction 5) or CO and H₂O (reaction 6). Moreover, water gas shift (WGS) (reaction 2) or methanol reforming (reaction 7) cannot be disregarded.

The high amount of CH_4 produced, higher than that of CO_2 , suggests the occurrence of a disproportionation involving two methanol molecules to yield an equimolar amount of methane, formaldehyde, and water. Ueda et al. have recently reported similar results over vanadium and molybdenum oxides, using various alcohols, including methanol and ethanol, to produce the corresponding alkanes and aldehydes in equimolar ratio ^{42,43}.

Lastly, when FU was reduced with methanol at 400°C, the total conversion of the substrate was registered. The main product detected was MF with a selectivity of 62%. However, a lower carbon balance was registered due to the degradation of FU to carbonaceous compounds.

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With the aim of studying the effect of reaction conditions on the amount of carbonaceous deposits, TGAs¹Were carried⁷Out on the spent catalysts (Figure 4).



Figure 4. Thermogravimetric analysis (TGA) in nitrogen: (--) fresh $FeVO_4$ calcined at 650°C; $FeVO_4$ used in catalytic test (--) at 250°C, (--) at 320°C and (--) at 400°C.

Thermograms were obtained by heating up the samples in a nitrogen flow, instead of air, in order to avoid the re-oxidation of the catalyst that would invalidate the results. Thus, it is necessary to take into account that some carbonaceous compounds could remain on the catalyst after TGA due to the anaerobic condition utilized (see the section concerning the effect of reaction time on catalyst structure).

As expected, the fresh catalyst calcined at 650°C (black line) did not show any weight loss. Conversely, all the used catalysts showed a weight loss that could be related to the amorphous desorption/decomposition of the carbon deposited during reactivity tests; however, the weight loss was a function of the temperature used for FU reduction. In fact, after heating up to 150-170°C, samples showed a common and marginal initial weight loss (2-3 wt %) which is related to the desorption of some physisorbed water. However, upon increasing the temperature, an evident weight loss (≈ 10 wt %), in the range 200-450°C, was observed for the sample used at 250°C; a further and limited weight loss (≈ 3-4 wt %) was then registered while heating up the sample to 700°C. This latter weight loss could be related to the removal of the heavier oligomeric carbonaceous species, whereas that registered at lower temperatures could be connected to the desorption of lower molecular mass deposits. It may be hypothesized that the catalyst oxidises carbonaceous residua, while being itself reduced because of anaerobic conditions.

It is also shown that, in the case of the sample used at 250°C, the formation of the lighter carbonaceous deposits was largely improved. The sample used at 320°C showed a lower weight loss (\approx 5-6 wt %) in the range 200-450°C, and a similar weight loss in the high temperature region. These results can be correlated to the trend of C loss observed in function of reaction temperature (Figure 3). Indeed, the formation of heavy carbonaceous deposits (oligomeric species deriving from the condensation of several furanic species) could represent the main contribution to C loss.

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Lastly, it should be pointed out that increasing the reaction temperature from 250°C to 400°C significantly increased the temperature at which carbonaceous deposits were eliminated. This could be connected to the formation of compounds with more ordered structures.

These results confirm that the catalyst has the best performance in the temperature range between 300 and 350°C. In particular, at 320°C a conversion higher than 95% was registered, with a selectivity to MF of around 70%; moreover, a fairly good C balance was obtained (C loss 25%).

3.3. Hydro-deoxygenation of FU with FeVO₄ catalyst: effect of reaction time

The effect of reaction time on catalyst performance was examined by conducting tests for 6 h at the optimised reaction temperature (320°C) (Figure 5). FU conversion slightly decreased during the first 3 hours of reaction; then, starting from the 4th hour, a rapid FU conversion decline was observed and a final value of 55% was reached. This drop in conversion may be correlated to the previously discussed accumulation of C residues (Figure 4 and S4).

With regard to the products formed, a notable difference in selectivity was observed between the first and following hours of reaction, thus highlighting a different catalyst behavior over time. Indeed, in the first hour of reaction, a C loss of 63% and a selectivity to MF of 32% only were registered; starting from the second hour, the C loss dropped to 25%, with a significant increase in MF (66%), DMF and VINFU yields.

A further evidence of the change in catalytic behaviour occurring during the first hour can be inferred from Figure S5, showing the light gaseous compound amounts. CO and CO₂ exhibited an initial rapid increase up to a maximum value at 15 and 30 minutes, respectively. After this maximum, their concentration rapidly decreased. The high amounts of CO and CO₂ initially produced are probably due to the oxidation of methanol by the catalyst.



Figure 5. Effect of reaction time on FU conversion and product selectivity for FeVO₄ catalyst. Feed composition: FU 1%, CH₃OH 10%, N₂ 89%; Pressure 1 atm, 320°C, overall gas residence time 1.0 s. Legend: \blacklozenge FU conversion, \blacksquare MF selectivity, \blacksquare DMF selectivity, \blacksquare VINFU selectivity, \blacksquare C loss.

In order to gain better insight into this hypothesis, we performed a catalytic test in which only Methanol/Was field at 320°C for 1h. Figure S6 shows the number of moles of light compounds formed, based on the time; methanol and furfural were then fed under usual conditions.

The trend of light compounds, obtained by feeding methanol alone, was very similar to that registered in the test performed by co-feeding methanol and FU (Figure S5). Therefore, during the first hour of reaction, methanol preferentially reacts with the catalyst, thus decreasing the amount of methanol available as the H source for the reduction of FU. In these conditions, FU was mainly degraded, leading to the high C loss registered (Figure 5).

In order to further validate this hypothesis and evidence modifications to FeVO₄ occurring during the first hours of reaction, we characterised samples subjected to different treatments by means of XRD and elemental analysis. The analysis of the catalysts used, either during FU reduction or with methanol alone, showed a very similar Fe/V atomic ratio (1.08), a value very close to that of the fresh sample (1.09), thus ruling out any loss of vanadium or iron during the first hour of reaction.

Furthermore, a test carried out by feeding methanol only over a fresh FeVO₄ catalyst was performed in order to evaluate the reduction degree of the sample; the latter was calculated by taking into account reaction stoichiometries and yields to all products. In fact, the O content in the outlet stream was higher than that contained in the inlet methanol stream, an evidence that confirmed the release of O^{2-} from the catalyst because of metal ions reduction. The experimental reduction degree estimated with this method was 30% (Figure S7 A and B). The patterns of the two used samples, after reaction with either methanol alone or with the FU/methanol mixture (Figure 6), were very similar and, at the same time, different from that one of the fresh catalyst (Figure S1).

The analysis of the diffraction pattern confirms the formation of a pure spinel structure. However, the only two known spinels containing iron and vanadium are Fe_2VO_4 and FeV_2O_4 (so called coulsonites), and neither of them completely match with the pattern of our spent catalyst; in coulsonites, iron can be present either as Fe^{3+} or Fe^{2+} , and vanadium as V^{3+} or V^{2+} .

Overall, the analysis of the used catalyst confirmed the same Fe/V ratio as for the fresh one, and showed the formation of a single spinel structure with a reduction extent of 30%. All this led us to conclude that the composition of the spinel in the used catalyst was $Fe^{II}Fe_{0,5}^{III}V_{1,5}^{III}O_4$. Nevertheless, further insitu studies are currently being carried out in order to confirm this hypothesis.



Figure 6. XRD patterns of reduced $FeVO_4$ samples. Reference patterns: (•) Fe_2VO_4 , (*) FeV_2O_4 .

3.4. Effect of catalyst pre-reduction

Since catalyst characterisation demonstrated that FeVO₄ was reduced by methanol during the first hour of reaction, the effect of catalyst pre-reduction was studied in order to check whether it can affect catalytic properties. In particular, catalyst pre-reduction was obtained by feeding methanol alone for 1 h at 320°C; then FU and methanol were fed again and activity was monitored as usual for 6 h. Results (Figure 7) demonstrated that catalyst pre-reduction improved the performance. In fact, it was not just a higher MF selectivity compared to the untreated catalyst that was registered during the first hour of reaction, but also a greater stability with lower deactivation extent during the 6 h reaction time.

Accordingly, a notably lower C loss was observed and a final value of 80% conversion was registered after 6 h. With the fresh catalyst, final conversion was just 55%. The improved catalyst stability was due to the lower amount of heavy carbonaceous compounds formed with the pre-reduced sample during the initial period, the latter being due, in turn, to the catalyst's higher efficiency in methanol activation for H-transfer.



Figure 7. Effect of reaction time on FU conversion and product selectivity for pre-reduced $FeVO_4$ catalyst, feeding only methanol at 320°C for 1 h (bold line), and non-pre-reduced catalyst (dotted line). Feed composition: FU 1%, CH₃OH 10%, N₂ 89%; Pressure 1 atm, overall gas residence time 1.0 s. Legend: \blacklozenge FU conversion, \blacktriangle MF selectivity, \blacksquare sum of DMF and VINFU selectivity, \blacksquare C loss.

3.5. Study of the reaction network

We conducted experiments aimed at elucidating the reaction network. More specifically, we wanted to investigate the reasons why we never detected FAL, which is supposed to be the intermediate for MF formation.

First, we studied the effect of contact time (Figure 8). Results were taken at the optimised temperature (320°C), having prereduced the catalyst with methanol and changing the contact time from 0.01 to 1.0 s. FU conversion increased from 16% at 0.01 s contact time up to 100%. At 0.01 s, MF was the main product with 32% selectivity; however VINFU and FAL, the latter with 2% selectivity, were also formed. Upon increasing FU conversion, MF selectivity increased up to 75% when contact time was set at 1 s. At the same time a lower Class was observed, from 63% down to 18%. DMF and VINFO were produced in low amounts (\approx 5%) while FAL was no longer formed at contact times higher than 0.01 s, due to its consecutive transformation.



Figure 8. Effect of contact time on FU conversion and product selectivity for FeVO₄ catalyst. Feed composition: FU 1%, CH₃OH 10%, N₂ 89%; Pressure 1 atm, Temperature 320°C, overall gas residence time 1.0 s. Legend: \blacklozenge FU conversion, \blacksquare FAL selectivity \blacktriangle MF selectivity, \blacklozenge DMF selectivity, \blacklozenge VINFU selectivity, \blacklozenge C loss.

Some catalytic tests were conducted using different substrates (FU, FAL, MF, and DMF) as starting reagents, at 320° C, with both pre-reduced and fresh FeVO₄ (Table 2).

Entry 1 is the result obtained in the standard catalytic test after 1 h reaction time, using the pre-reduced catalyst. This can be compared with the result obtained by feeding FAL with methanol (entry 2). Also with FAL, the total conversion of the substrate was registered; MF and DMF were produced with 60% and 4% selectivity, respectively: values very similar to those obtained by feeding FU. This further supports the hypothesis that in FU reduction to MF, FAL is the reaction intermediate.

FU and FAL were then made to react, in the absence of methanol, on the pre-reduced catalyst (Table 2 - entries 3 and 5). These experiments demonstrate that, in the absence of the H-transfer reactant, these substrates undergo degradation; indeed, the C loss registered was 70% or higher in both cases. However, also in this case we observed the formation of MF from FU and FAL, despite the absence of methanol. The analysis of the gas stream (Figure S8) showed the presence of CO₂, CH₄, and H₂. Therefore, it can be hypothesized that during the first half hour of reaction some adsorbed methanol, deriving from the previous catalyst reduction treatment, was available as the H source for the reduction of FU or FAL to MF. The same catalytic tests were performed by feeding FU and FAL, in the absence of methanol, with the fresh FeVO₄ (Table 2 - entries 4 and 6). In these conditions, only small amounts of FU and MF formed from FAL (both with 6% selectivity) and C loss was very high. The equimolar formation of FU and MF could be due to FAL disproportionation; this reaction might contribute to MF and FU formation also with the pre-reduced catalyst (entry 5). TG/DT analysis of the spent catalyst (Figure

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		Conversion (%)	Products Selectivity (%) DOI: 10.1039/C						
Entry	Substrate		FU	FAL	MF	DMF	VINFU		
				O	H			C loss	
1	FU + CH₃OH ª	99	-	0	75	5	2	18	
2	FAL + CH ₃ OH ^a	100	2	-	60	4	0	34	
3	FU ^a	31	-	0	21	0	0	79	
4	FU ^b	35	-	0	0	0	0	100	
5	FAL ^a	85	5	-	25	0	0	70	
6	FAL ^b	56	6	-	6	0	0	88	
7	MF + CH ₃ OH ^a	21	0	0	-	42	0	58	
8	MF ^a	0	0	0	-	0	0	0	
9	DMF + CH ₃ OH ^a	13	0	0	0	0	0	100	
10	DMF ^a	0	0	0	0	-	0	0	

Table 2. Reactivity experiments carried out by feeding different reactants: FU or FAL or MF or DMF 1%, CH_3OH 10% , N_2 89% or 99%; pressure 1 atm, temperature 320°C, overall gas residence time 1,0 s, reaction time 1 h.

a. Catalyst pre-reduced by feeding methanol at 320°C for 1 h.

b. Catalyst calcined in static air at 650°C

S9) in air showed a weight loss of \approx 3% in the temperature range 290-360°C which, coupled with an exothermic DTA peak, demonstrated the combustion of carbonaceous deposits. The absence of MF

in FU reduction with the fresh catalyst confirms the hypothesis that the formation of MF with the pre-reduced catalyst (entries 3 and 5) was due to the presence of pre-adsorbed methanol.

The catalytic tests performed by feeding MF and methanol (Table 2 – entry 7) showed that the reduced catalyst is able to convert MF into DMF through a hydroxyalkylation process that involves MF and formaldehyde, the latter having been formed by methanol dehydrogenation. Furthermore, some experiments carried out by feeding MF and DMF without methanol (Table 2 – entry 8 and 10) demonstrated that both compounds are stable and did not undergo consecutive degradation reactions.

Indeed, no substrate conversion was registered in the catalytic tests performed by feeding either MF or DMF. However, in the presence of methanol, DMF was converted by the 13% (Table 2 – entry 9) and completely transformed into heavy carbonaceous compounds adsorbed over the catalyst surface; this behaviour was probably ascribable to the in-situ formation of formaldehyde that favours consecutive reactions on DMF.

Based on this study, it is possible to conclude that: i) FAL is the intermediate for the transformation of FU into MF; however, FAL is very reactive, and is very rapidly reduced to MF without

desorbing in the gas phase; indeed, it was observed only in traces at a very low contact time (0.01s); ii) MF can be transformed into DMF by reacting with the in-situ-generated formaldehyde; the intermediate 2-methyl-5-hydroxymethylfuran, deriving from the electrophilic attack of formaldehyde, is also rapidly reduced to DMF; iii) VINFU formed only from FU in the presence of methanol (Table 2 – entry 1).

We then tested the reactivity of FU and FAL on the prereduced catalyst with different H sources: formaldehyde, isopropanol, acetone, and hydrogen. Table 3 shows the results of these experiments, collected during the first hour of reaction and compared with the results obtained with methanol as the H source.

It is interesting to note that the use of methanol (Table 3 – entry 1) led to the formation of MF with a yield (74%) which was even higher than that registered with isopropanol (Table 3 – entry 2), despite the latter being considered a much more active H-transfer reactant than methanol. It may be hypothesized that formaldehyde could also be directly involved in the mechanism of MF formation from FU. Conversely, with the much more reactive FAL, similar yields to FU were obtained with methanol and isopropanol (Table 3 – entries 6 and 7).

The direct involvement of formaldehyde in MF formation with the co-production of CO_2 through a disproportionation involving the two aldehydes, in a way similar to that previously

				Cor		View Article Online DOI: 10.1039/C7GC01749A			
			FU	FAL	MF	DMF	VINFU		
Entry	Substrate	H-source	0					с	MF Yield (%)
				Он				loss	
1		CH₃OH	99	0	75	5	2	18	74
2		2- propanol	93	0	60	0	0	40	56
3	FU	acetone	58	0	8	0	0	92	5
4	_	CH₂O (a)	79	0	70	4	0	26	55
5		H ₂	55	0	17	0	0	83	9
6		CH₃OH	2	100	60	4	0	34	60
7	FAL	2- propanol	2	97	58	0	0	40	56
8	_	CH₂O (a)	1	97	60	8	0	31	58
9		H ₂	1	100	33	0	0	66	33

(a) CH₂O from formalin solution in water: 37% w/w CH₂O, 7-8% w/w CH₃OH.

Table 3. FU/FAL conversion and product distribution as a function of the hydrogen source used. Reaction conditions: 1% FU or FAL, 10% H source, 89% N₂, 1 atm, temperature 320°C, overall gas residence time 1.0s, reaction time 1h. Pre-reduced catalyst.

reported for salicylic aldehyde reduction⁴¹ was demonstrated by reacting FU and FAL with formaldehyde (entries 4 and 8); the same reaction occurred only at a minor extent with acetone, the co-product of FU reduction with isopropanol (entry 3).

The results of the experiments carried out with H_2 (Table 3 – entries 5 and 9) confirmed the higher reactivity of FAL, and showed that substrate reduction may also occur with H_2 ; the yield to MF, however, was much lower than that obtained with methanol. Nevertheless, these results demonstrate that a

contribution to MF formation deriving from the in-situ generated H_2 should be also taken into account.

It is also worth noting that DMF formed in experiments conducted with methanol and formaldehyde, whereas VINFU formed exclusively with methanol. This confirms that the formation of the former compound involves the aldehyde, via an hydroxyalkylation step, whereas the latter forms by reaction between FU and methanol.

A possible mechanism for VINFU formation might occur by the formation of the intermediate furfural methyl hemiacetal, as shown in Scheme 3 ³⁰. Hemiacetal could then be dehydrated into the corresponding enol, which would rapidly rearrange to furylmethyl ketone; the latter is reduced by methanol to the corresponding alcohol, which is finally dehydrated to VINFU.

In order to support the mechanism proposed, we conducted an experiment entailing a direct feed of furylmethyl ketone and methanol onto the FeVO₄ catalyst at 320°C. The GC-MS analysis of the products revealed the formation of VINFU and ethylfuran; the latter may form by hydrogenolysis of the alcohol. When the same experiment was conducted without methanol, no VINFU formed.

The formation of the hypothesized ketone was demonstrated by reacting a hemiacetal, trifluoroacetaldehyde methyl hemiacetal (unfortunately, the hemiacetal formed by reaction between furfural and methanol is not commercially available), without methanol. Hemiacetal was readily dehydrated to the ketone (in this case, trifluoroacetone).



Scheme 3. Possible reaction pathways for the formation of VINFU from FU in the presence of methanol on $FeVO_4$ catalyst.

These tests support the hypothesized mechanism for the formation of VINFU.

The overall network for the vapour-phase reduction of FU with methanol and the $FeVO_4$ catalyst is summarised in Scheme 4. MF can form via three different routes:

 The classic H-transfer two-step mechanism with the reduction of FU to FAL and of FAL to MF. Indeed, under normal conditions FAL is not isolated as an intermediate, to the classic H-transfer mechanism, the in-site generated formaldehyde and H₂ played a direct role in the state of MF.

Furthermore, it has to be highlighted that the mixture of MF, DMF and VINFU could be directly used as fuel-additive thanks to the high energy content, high RON (higher than that of ethanol and 97-RON commercial gasoline), excellent auto-ignition behavior ¹³.



Scheme 4. Overall reaction pathways for the transformation of FU on FeVO₄ catalyst in the presence of CH₃OH as H source.

because of its very high reactivity, also because of the possible involvement of formaldehyde (co-product of the MPV reaction) in the immediate reduction of FAL to FU (see the following point);

- ii) The disproportionation reaction involving the in-situgenerated formaldehyde, with reduction of FU to MF and co-production of CO₂;
- iii) The hydrogenation of FU and FAL to MF involving the insitu-generated H_2 .

DMF forms by the hydroxyalkylation of MF with formaldehyde, and the reduction of the alcohol. VINFU forms by reaction between FU and methanol to the corresponding hemiacetal, which is then dehydrated to furylmethyl ketone and finally reduced again via H-transfer.

4. Conclusions

FeVO₄ is a very active catalyst in the gas-phase production of 2-methylfuran from biomass-derived furfural using methanol as the H-transfer reactant. 320°C was the optimum reaction temperature at which the selectivity to MF was the highest and, at the same time, the formation of heavy carbonaceous residues was minimised. The deposition of the latter was the main cause of catalyst deactivation.

A simple procedure of $FeVO_4$ pre-reduction with methanol increased both catalyst stability and MF selectivity. Indeed, it was demonstrated that the catalyst was reduced by methanol to form a reduced oxide with spinel structure.

Due to its high activity, FeVO₄ offers an alternative to MF production from FU with a high yield without the need for H_2 at high pressure and precious metal catalysts. The formation of MF occurred via three different reaction pathways. In addition

Acknowledgements

INSTM is acknowledged for co-financing the project.

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