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A one-pot approach for conversion of fructose to 2,5-diformylfuran by combination of Fe_3O_4 -SBA-SO₃H and K-OMS-2[†]

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We have demonstrated an efficient, selective and environmentally benign heterogeneous catalyst (K-OMS-2) for aerobic oxidation of 5-HMF to 2,5-DFF. In addition, a combination of Fe₃O₄-SBA-SO₃H and K-OMS-2 successfully catalyzed direct synthesis of 2,5-DFF from fructose *via* acidcatalyzed dehydration and successive aerobic oxidation in one-pot reaction.

With increasing depletion of fossil resources and growing concern about environmental issues, biomass has attracted the attention of chemists as an important feedstock for the renewable production of fuels and bulk chemicals.¹ 5-Hydroxymethyl-furfural (5-HMF), which is an important bridge molecule linking biomass to fuels and chemicals, can be obtained from biomass-based carbohydrates² and transformed to many other compounds. For example, aerobic oxidation of 5-HMF to 2,5-diformylfuran (2,5-DFF) has attracted much attention due to the various applications of 2,5-DFF. It can not only be used to synthesize pharmaceutical intermediates,³ fungicides,⁴ and heterocyclic ligands,⁵ but also can be used as a monomer for making multifunctional materials.⁶ Therefore, synthesis of 2,5-DFF from biomass-based carbohydrates is important.

The reported routes for 2,5-DFF synthesis have mostly been based on aerobic oxidation of pure 5-HMF. Many classic oxidants, such as pyridinium chlorochromate (PCC),⁷ NaOCl,⁸ and 2,2,6,6-tetramethylpiperidine-1-oxide (TEMPO)⁹ show good performance for 2,5-DFF synthesis. However, from the viewpoint of cost and sustainability, air or molecular O₂ is more interesting as an oxidant. A number of catalyst systems using air or O₂ as oxidant have been developed for the oxidation of 5-HMF to 2,5-DFF, including vanadium-based catalysts, such as V₂O₅,¹⁰ VOPO₄·2H₂O,¹¹ V-containing polymeric catalyst¹² and Cu-(NO₃)₂/VOSO₄.¹³ Other catalyst systems, such as metal/bromide (Co/Mn/Br) catalyst,¹⁴ polymer-supported IBX amide¹⁵ and Ru/HT¹⁶ have also been reported for the same application. These studies have contributed to the development of catalyst systems for oxidation of 5-HMF to 2,5-DFF. However, the high energy cost for isolation and purification of 5-HMF still limits scale-up production of 2,5-DFF.

Biomass-derived carbohydrates are a sustainable chemical feedstock and can be used to synthesize 5-HMF *via* acid-catalyzed dehydration. Thus, a one-pot process for synthesis of 2,5-DFF from cheap carbohydrates may be more efficient. Several efficient catalyst systems have been reported for this transformation, such as H-form cation exchange resin/V-based catalysts,¹⁰ CrCl₃·6H₂O/NaBr/NaVO₃·2H₂O¹⁷ and Amberlyst-15/polymer-supported IBX amide.¹⁵ Very recently, Takagaki *et al.* combined hydrotalcite, Amberlyst-15, and Ru/HT for direct synthesis of 2,5-DFF from carbohydrates. The yields of 2,5-DFF were up to 49% from fructose and 25% from glucose, respectively.¹⁶

Recently, Son *et al.* reported that K-OMS-2 (a porous manganese oxide with a composition of $KMn_8O_{16}\cdot nH_2O$) or H-K-OMS-2 ($H_{0.2}K_{0.8}Mn_8O_{16}\cdot nH_2O$) could be used as a cheap and nontoxic heterogeneous catalyst for selective oxidization of benzylic alcohols to aldehydes or ketones (Fig. 1).²⁰ Inspired by Son's work, we found that a combined catalyst of Fe₃O₄-SBA-SO₃H (a magnetic solid acid) and K-OMS-2 can efficiently convert fructose to 2,5-DFF in a one-pot fashion (Scheme 1). Fe₃O₄-SBA-SO₃H catalyzes fructose dehydration into 5-HMF by removal of water, and K-OMS-2 catalyzes an efficient and selective oxidation of 5-HMF to 2,5-DFF.

Table 1 lists the results for 2,5-DFF formation via aerobic oxidation of 5-HMF under different reaction conditions with the







Scheme 1 The one-pot approach for synthesis of 2,5-DFF from fructose by a combination of Fe_3O_4 -SBA-SO₃H and K-OMS-2.

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Entry	Catalyst	Catalyst (g)	Solvent	Yield (%)
1	H-K-OMS-2	0.05	DMSO	46
2	K-OMS-2	0.05	DMSO	43
3	H-K-OMS-2	0.1	DMSO	99 $(92)^{e}$
4	K-OMS-2	0.1	DMSO	99 (92) ^e
5^c	H-K-OMS-2	0.1	DMSO	57
6 ^{<i>c</i>}	K-OMS-2	0.1	DMSO	39
7^d	K-OMS-2	0.1	DMF	99
8	K-OMS-2	0.1	MIBK	38
9	K-OMS-2	0.1	Toluene	19
10	MnO_2	0.1	DMSO	4

^{*a*} 1 mmol 5-HMF, 0.05–0.1 g (~0.38–0.75) equiv K-OMS-2/H-K-OMS-2, 3 mL solvent, 10 mL min⁻¹ O_2 . React at 110 °C for 6 h. ^{*b*} Selectivity of all oxidation reactions were 100%. ^{*c*} Air as primary oxidant. ^{*d*} Reaction time was 8 h. ^{*e*} Isolated yield in the parenthesis.

K-OMS-2 or H-K-OMS-2 catalyst. Reaction parameters, such as solvent, temperature, reaction time, and catalyst loading, have been examined. As reported in previous literature, K-OMS-2 has the ability to absorb aldehydes, so the yields of 2,5-DFF were detected after the catalyst was washed with DMSO several times. It was found that the catalyst loading was an important factor. In the presence of molecular oxygen (10 mL min⁻¹), 5-HMF (1 mmol) and catalysts K-OMS-2/H-K-OMS-2 (0.05 g), the yield of 2,5-DFF was about 45% with 100% selectivity at 110 °C for 6 h (entries 1, 2). Subsequently, when we increased the catalyst loading to 0.1 g, 5-HMF was transformed completely to 2,5-DFF with 100% selectivity (entries 3, 4). However, by using air as the oxidant instead of molecular oxygen. 5-HMF was not converted completely, even after 12 h (entries 5, 6). This observation showed that molecular oxygen has a higher activity than air in this system. In addition, when we used air as the oxidant, H-K-OMS-2 was more efficient than K-OMS-2 because the Brønsted acid sites in H-K-OMS-2 promote the oxidation process, maybe by affecting the Mn-O bond strength.^{18,19} However, there was no significant difference between the two catalysts if molecular oxygen was used, it may be that the higher oxidizing ability of molecular oxygen minimised the effect of catalyst nature. Thus, in the following experiments we used K-OMS-2 as the catalyst, and molecular oxygen as the oxidant.

Solvents also have a significant effect on 2,5-DFF formation. According to Table 1, solvents with strong polarity and high boiling point (such as DMSO and DMF) were favorable. When 5-HMF (1 mmol) and catalyst K-OMS-2 (0.1 g) were heated at 110 °C for 6 h in DMSO under 10 mL min⁻¹ O₂, the yield of 2,5-DFF was up to 99%. For DMF, we needed to prolong the reaction time to 8 h for complete conversion of 5-HMF (entry 7). However, if other solvents such as MIBK (methyl isobutyl ketone) and toluene were used, the yields of 2,5-DFF were reduced to 38% and 19% (entries 8, 9). The effect of reaction time and temperature has also been studied (Fig. S1, ESI†).

According to Son's work, the interesting oxidation properties of K-OMS-2 is due to the coexistence of Mn^{4+} , Mn^{3+} and Mn^{2+} ions in the material.²⁰ Mechanistic studies by Son *et al.* point to a Mars–van Krevelen mechanism of oxidation for the catalytic oxidation of alcohols by heterogeneous catalyst K-OMS-2 and

the reaction process undergoes a simultaneous transfer of two electrons. The active sites may be derived from the Mn^{3+} ions in the tunnel sites of K-OMS-2. A redox mechanism was proposed for K-OMS-2-catalyzed conversion of 5-HMF to 2,5-DFF. 5-HMF is oxidized by $Mn^{4+}O_2^{-}$, simultaneously $Mn^{4+}O_2^{-}$ is reduced to a Mn^{3+} ion which is reoxidized by O_2 . In the whole process, the removal of a secondary H atom is the rate-control-ling step.¹⁹ Eqn (1)–(4) summarize this process:

$$\begin{array}{c} O & H \\ & O \\ &$$

 $HO_2^- + H^+ \xrightarrow{fast} H_2O_2 \longrightarrow H_2O + 1/_2O_2$ (3)

 $Mn^{3+} + O_2 \xrightarrow{slow} Mn^{4+}O_2^{-1}$

Catalyst Regenerate

Total Reaction:

In the rate-controlling step, the positive charge has been dispersed. According to related knowledge of solvent effects, the electronic pairs of O, N, S in strong polarity solvents can attract and disperse the positive charge of the cations. Thus, strong polarity solvents (such as DMSO and DMF) promote the ratecontrolling step of 5-HMF oxidation and affect the conversion of 5-HMF.

MnO₂ has been used as a catalyst for comparison with K-OMS-2 (entry 10). As shown in Table 1, MnO₂ was not efficient for aerobic oxidation of 5-HMF to 2,5-DFF in this reaction system. This is probably due to the different structure of the two materials and the different forms of Mn in these two materials. Fig. S2 and S3[†] show the N₂ adsorption–desorption isotherms of K-OMS-2 and MnO₂. The K-OMS-2 sample exhibits a type I isotherm, which is a characteristic of a mesoporous material but MnO₂ has a much smaller pore size (Fig. S2, S3, ESI[†]). In addition, K-OMS-2 has a much larger BET surface area (77.2106 m² g⁻¹) than MnO₂ (BET surface area: 0.1324 m² g⁻¹). (Table S1, ESI[†]). The XPS patterns also provide evidence for the existence of Mn³⁺ in K-OMS-2 (Fig. S4, ESI[†]).

The K-OMS-2 catalyst was recovered by centrifugation, washed with DMSO and then recycled for further reaction. The yields of 2,5-DFF were plotted against reuse times, indicating that the activity of the catalyst is not decreased after being reused five times (Fig. S5, ESI[†]). The possibility for loss of the K-OMS-2 catalyst during the oxidation reaction was also tested. The reaction was stopped after 1 h, and K-OMS-2 was filtered. The filtrate was reacted again for another 6 h under the same reaction conditions. The results show that the 5-HMF conversion and 2,5-DFF yield do not change after K-OMS-2 was removed (Fig. S6, ESI[†]). Simultaneously, the IR spectra and XRD spectra

Table 2 One-pot synthesis of 2,5-DFF from fructose using SBA-SO₃H and K-OMS-2^a

Entry	Substrate	Acid catalyst	Oxidation catalyst	Conversion (%)	5-HMF yield (%)	2,5-DFF yield (%)
1	Fructose	Fe ₃ O ₄ -SBA-SO ₃ H		>99	81	0
2^b	Fructose		K-OMS-2	>99	0	0
3^c	Fructose	Fe ₃ O ₄ -SBA-SO ₃ H	K-OMS-2	>99	<5	<5
4^d	Fructose	Fe ₃ O ₄ -SBA-SO ₃ H	K-OMS-2	>99	0	80
5^d	Glucose	Fe ₃ O ₄ -SBA-SO ₃ H	K-OMS-2	>99	0	<5
$6^{d,e}$	Inulin	Fe ₃ O ₄ -SBA-SO ₃ H	K-OMS-2	>99	18	29

^{*a*} 1 mmol substrate, 0.1 g (~0.1 equiv) Fe₃O₄-SBA-SO₃H, 0.1 g (~0.75 equiv) K-OMS-2, 3 mL DMSO, 10 mL min⁻¹ O₂. Reaction at 110 °C. ^{*b*} O₂ flow for 6 h. ^{*c*} One step reaction in O₂ flow for 8 h. ^{*d*} Two-step reaction without catalyst separation. After 2 h reaction in air, K-OMS-2 was added in O₂ flow for 6 h. ^{*e*} 0.108 g water was added before beginning the reaction.

of fresh and regenerated catalyst also indicated that there was no loss of catalyst activity after being reused five times (Fig. S7, S8, ESI†). In addition, scale-up conditions showed a good result for the heterogeneous catalyst system. After 2 g 5-HMF and 2 g K-OMS-2 were heated at 110 °C for 6 h in the presence of molecular oxygen or air, the 2,5-DFF yield was 70% and 20% with 100% selectivity, respectively (Table S2, ESI†).

Furthermore, we have examined the one-pot synthesis of 2,5-DFF from fructose by using Fe₃O₄-SBA-SO₃H and K-OMS-2. Fe₃O₄-SBA-SO₃H is a magnetic solid acid catalyst, and has been previously reported for cellulose hydrolysis by our group.²¹ The advantage of this catalyst is that it is easy to separate from other solid catalysts due to its magnetic properties. As shown in Table 2, using Fe₃O₄-SBA-SO₃H can produce 5-HMF from fructose with 81% yield at 110 °C in DMSO (entry 1). A combination of Fe₃O₄-SBA-SO₃H and K-OMS-2 afforded 2.5-DFF directly from fructose. However, the coexistence of Fe₃O₄-SBA-SO₃H and K-OMS-2 in the initial stage of reaction resulted in trace formation of 2,5-DFF (entry 3). The low yield of 2,5-DFF from fructose in the one-step reaction may be due to the formation of humins or the undesired oxidation of fructose by K-OMS-2 in the presence of molecular oxygen. Further tests showed that K-OMS-2 did indeed lead to oxidation of fructose to unknown compounds (entry 2). To overcome this problem, we carried out a two-step but still one-pot reaction. Gratifyingly, the yield of 2,5-DFF was up to 80% by stepwise addition of catalysts, i.e. Fe₃O₄-SBA-SO₃H and K-OMS-2 without any intermediate separation (entry 4). As shown in Fig. 2, the addition of Fe₃O₄-SBA-SO₃H resulted in the disappearance of fructose and simultaneous formation of 5-HMF. Further addition of K-OMS-2 without catalyst separation under molecular oxygen flow afforded 2,5-DFF from aerobic oxidation of 5-HMF. The two heterogeneous catalysts could be recovered by centrifugation, washed with ethanol and water, dried in oven, and then separated by using a magnet for further reuse (Fig. 3). After being reused five times, the activities of the two catalysts show no significant decrease (Fig. S9, ESI[†]).

Glucose and inulin were also used as substrates for 2,5-DFF synthesis, the yields of 2,5-DFF from glucose and inulin were \sim 5% and 29%, respectively (entries 5, 6). The reaction conditions for glucose was the same as fructose, but for inulin, we added a little water before beginning the reaction for conversion of inulin to fructose. The yield of 2,5-DFF from glucose was so low due to Fe₃O₄-SBA-SO₃H having no ability to transform glucose to fructose. The yield of 2,5-DFF from inulin was not



Fig. 2 A plot of 5-HMF yield, 2,5-DFF yield for the transformation of fructose as a function of reaction time. K-OMS-2 was added after 2 h under O_2 flow (10 mL min⁻¹). Reaction conditions, 1 mmol fructose, 0.1 g Fe₃O₄-SBA-SO₃H, 0.1 g K-OMS-2, 3 mL DMSO, 110 °C.



Fig. 3 The separation of Fe_3O_4 -SBA-SO₃H and K-OMS-2 simply by a magnet.

high because the existence of water poisoned the oxidation catalyst K-OMS-2 and leaded to incomplete oxidation of 5-HMF in the second step.

In conclusion, we demonstrated an inexpensive, efficient, selective, easily regenerable and environmentally benign heterogeneous catalyst (K-OMS-2) for aerobic oxidation of 5-HMF to 2,5-DFF with 99% yield and 100% selectivity. In addition, a combination of Fe_3O_4 -SBA-SO₃H and K-OMS-2 catalysts successfully catalyzed direct synthesis of 2,5-DFF from fructose *via* acid-catalyzed dehydration and successive aerobic oxidation in a one-pot reaction. Stepwise addition of catalysts gave 2,5-DFF in 80% yield. These two heterogeneous catalysts could be easily separated by using a magnet and re-used for further reaction (Fig. 3).

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Notes and references

- A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411;
 J. N. Chheda, G. W. Huber and J. A. Dumesic, *Angew. Chem.*, 2007, **119**, 7298, (*Angew. Chem., Int. Ed.*, 2007, **46**, 7164);
 B. Kamm, *Angew. Chem.*, **2007**, **119**, 5146, (*Angew. Chem., Int. Ed.*, 2007, **46**, 5146);
 T. Stahlberg, W. Fu, J. M. Woodley and A. Riisager, *ChemSusChem*, 2011, **4**, 451;
 Y. T. Cheng, J. Jae, J. Shi, W. Fan and G. W. Huber, *Angew. Chem., Int. Ed.*, 2012, **51**, 1387.
- 2 Y. Roman-Leshkow, J. N. Chheda and J. A. Dumesic, *Science*, 2006, 312, 1933; H. B. Zhao, J. E. Holladay, H. Brown and Z. C. Zhang, *Science*, 2007, 316, 1597; J. B. Binder and R. T. Raines, *J. Am. Chem. Soc.*, 2009, 131, 1979; G. Yong, Y. Zhang and J. Y. Ying, *Angew Chem., Int. Ed.*, 2008, 47, 9345; X. L. Tong and Y. D. Li, *ChemSusChem*, 2010, 3, 350; S. Q. Hu, Z. F. Zhang, Y. X. Zhou and B. X. Han, *Green Chem.*, 2009, 11, 1746.

- 3 K. T. Hopkins, W. D. Wilson, B. C. Bendan, D. R. McCurdy, J. E. Hall, R. R. Tidwell, A. Kumar, M. Bajic and D. W. Boykin, *J. Med. Chem.*, 1998, 41, 3872.
- 4 M. Del Poeta, W. A. Schell, C. C. Dykstra, S. Jones, R. R. Tidwell, A. Czarny, M. Bajic, A. Kumar, D. Boykin and J. R. Perfect, *Antimicrob. Agents Chemother.*, 1998, **42**, 2495.
- 5 D. T. Richter and T. D. Lash, Tetrahedron Lett., 1999, 40, 6735.
- 6 O. W. Howarth, G. G. Morgan, V. McKee and J. Nelson, J. Chem. Soc., Dalton Trans, 1999, 12, 2097.
- 7 L. Cottier, G. Descotes, J. Lewkowski and R. Skowronski, Pol. J. Chem., 1994, 68, 693.
- 8 A. S. Amarasekara, D. Green and E. McMillan, *Catal. Commun.*, 2008, 9, 286–288.
- 9 L. Cottier, G. Descotes, J. Lewkowski, R. Skowronski and E. Viollet, J. Heterocycl Chem., 1995, 32, 927.
- 10 G. A. Halliday, R. J. Young and V. V. Grushin, Org. Lett., 2003, 5, 2003.
- 11 C. Carlini, P. Patrono, A. M. R. Galletti, G. Sbrana and V. Zima, *Appl. Catal. B*, 2005, **289**, 197.
- 12 O. Casanova, A. Corma and S. Iborra, Top. Catal., 2009, 52, 304.
- 13 J. P. Ma, Z. T. Du, J. Xu, Q. H. Chu and Y. Pang, *ChemSusChem*, 2011, 4, 51.
- 14 W. Partenheimer and V. V. Grushin, Adv. Synth. Catal., 2001, 343, 102.
- 15 H. J. Yoon, J. W. Choi, H. S. Jang, J. K. Cho, J. W. Byun, W. J. Chung, S. M. Lee and Y. S. Lee, *Synlett*, 2011, 165.
- 16 A. Takagaki, M. Takahashi, S. Nishimura and K. Ebitani, ACS Catal., 2011, 1, 1562.
- 17 X. Xiang, L. H. Yu, Y. Yang, B. Guo, D. M. Tong and C. W. Hu, *Catal. Lett.*, 2011, **141**, 735.
- 18 V. D. Makwana, Y. C. Son, A. R. Howell and S. L. Suib, J. Catal., 2002, 210, 46.
- 19 G. Qiu, H. Huang, S. Dharmarathna, E. Benbow, L. Stafford and S. L. Suib, *Chem. Mater.*, 2011, 23, 3892.
- 20 Y. C. Son, V. D. Makwana, A. R. Howell and S. L. Suib, *Angew. Chem.*, *Int. Ed.*, 2001, **40**, 4280.
- 21 D. M. Lai, L. Deng, J. J B. Liao, Q. X. Guo and Y. Fu, *ChemSusChem*, 2011, 4, 55; D. M. Lai, L. Deng, Q. X. Guo and Y. Fu, *Energy Environ. Sci.*, 2011, 4, 3552.