

Cr-MIL-101 encapsulated Keggin phosphomolybdic acid as catalysts for one-pot synthesis of 2,5-diformylfuran from fructose

Jun Zhao, Jayakumar Anjali, Yibo Yan, Jong-Min Lee*

School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore, 637459, Singapore *KEYWORDS : 5-hydroxymethylfurfural, 2,5-diformylfuran, metal-organic framework, biomass, phosphomolybdic acid*

ABSTRACT: The direct conversion of fructose to 2,5-diformylfuran(DFF) is a tandem reaction which consists of fructose dehydration to 5-hydroxymethylfurfural(HMF) catalyzed by acid catalysts and subsequent oxidation of HMF to DFF by redox catalysts. Phosphomolybdic acid encapsulated in MIL-101(PMA-MIL-101), with high Bronsted acidity and moderate redox potential, is evaluated as a promising catalyst for the one-pot strategy for synthesizing DFF directly from fructose. The results demonstrate that PMA-MIL-101 is an efficient and recyclable bifunctional for DFF production from fructose in DMSO, showing high activity and selectivity towards direct transformation from fructose to DFF, and it can be reused. A satisfactory DFF yield of 75.1% is obtained over 2PMA-MIL-101 in a one-pot and one-step reaction under optimal reaction conditions.

Bio-refining is an important approach for the current needs of energy and chemicals for various applications. A growing interest has been recently dedicated to obtaining these valuable fuels and chemicals from biomass resources.^[1] Carbohydrates, which can be generated from renewable biomass, are deemed as promising feedstocks for the production of chemical building blocks.^[2] 5-Hydroxymethylfurfural (HMF), which is obtained from the acid catalyzied dehydartion of carbohydrates, has been identified as a key platform chemical for the deep exploitation and utilization of biomass resources due to its rich chemical properties.^[3] The selective oxidation of hydroxyl group of HMF leads to the formation of 2,5-Diformylfuran (DFF), which is expected to be used as a monomer for polymeric materials and considered as a potential intermediate for fungicides, heterocyclic ligands, furan-based resins and pharmaceuticals.^[4]

The common synthetic methods of DFF were mainly based on the selective oxidation of HMF. Various oxidants, such as NaOCl, BaMnO₄, pyridinium chlorochromate, and 2,2,6,6tetramethylpiperidine-1-oxide were reported to be used in the oxidation of HMF to DFF.^[5] Typical catalysts, such as Co/Mn/Zr/Br,^[6] SiO₂-supported vanadylphosphate,^[7] Mn-salen, V₂O₅,^[8] Ru/HT,^[9] K-OMS-2,^[10] Ru/C,^[11] Ag-OMS-2,^[12] PVP-Pd NP,^[13] VO₈/TiO₂,^[14] Cu(NO₃)₂/VOSO₄,^[15] Fe₃O₄/Mn₃O₄^[16] and RuCo(OH)₂CeO₂^[17] exhibited good activity. However, to produce DFF from HMF is an uneconomical and energy intensive process because of the high price of HMF and the difficulties in purification of HMF. Therefore, the industrial mass production of DFF from HMF has not been realized.

The direct synthesis of DFF from carbohydrates provides an alternative approach to overcome the above disadvantages. The process involves a two-step reaction: dehydration of carbohydrates to HMF and oxidation of HMF to DFF, in which the first step is an acid catalyzed reaction and the second one is an oxidation reaction. Thus the combination of acidic catalysts and oxidative catalysts were applied for the one-pot synthesis of DFF from carbohydrates. For instance, H-form cation-exchange resin and vanadium based catalysts,^[18] Amber-

lyst-15 and Ru/HT,^[19] CrCl₃ 6H₂O/NaBr and NaVO₃ 2H₂O,^[20] Fe₃O₄-SBA-SO₃H and K-OMS-2,^[10] Amberlyst-15 and polymer supported IBX amide^[21] have been investigated as bifunctional catalysts for the one-pot production of DFF from fructose. However, since the oxidative catalysts can promote the oxidative degradation of fructose and formation of humins, in order to obtain the highest possible DFF yield, the oxidation catalysts have to be added into the reaction after the fructose has been converted to HMF in the presence of acidic catalysts, resulting in a one-pot but two-step method conversion of fructose to DFF.^[10, 18]

Recently, it was noticed that heteropoly acids showed excellent performance in acid and oxidation catalysis for the hydrocarbons. Keggin-type polyoxometalates, such as H₃PW₁₂O₄₀, and FePW₁₂O₄₀, have been applied in the dehydration of fructose to HMF.^[22] Moreover, Mo-containing Keggin heteropolyacids can also promote the aerobic oxidation of HMF to DFF.^[23] However, heteropoly aicds can dissolve in most liquids and form a homogeneous reaction system which causes difficulties for the separation and reuse of the catalysts. In the last decade, metal-organic-frameworks(MOFs) have attracted numerous researchers' attention in the world and were widely used in gas storage, drug delivery and dye adsorption.^[24] The chromium terephthalate metal-organic framework, MIL-101, is one of the most porous materials reported to date. In addition, polyoxometalate(POM) can be introduced into the pores of MIL-101 and generate a POM embedded MOF, which is catalytically active towards oxidation of alkanes and alkenes.^[25] Very recently, phosphotungstic acid (PTA) encapsulated into MOF exhibits good catalytic performance for acidcatalyzed reactions, such as esterifications and dehydrations.^[26]



Scheme 1. Conversion of fructose into HMF and DFF.

ChemCatChem

Herein, phosphomolybdic acid was encapsulated into MIL-101(PMA-MIL-101) by a one-pot synthesis method and used as bifunctional catalysts for the conversion of DFF from fructose in a one-pot and one-step approach (see supporting information). The Fourier Transform Infrared Spectroscopy (FTIR) (Figure S1), X-ray diffraction (XRD) measurement (Figure S2) and Raman spectra (Figure S3) confirmed the formation of PMA-MIL-101 and MIL-101 retained its structure when the synthesis was carried out in the presence of PMA. The fructose undergoes acid-catalyzed dehydration to produce HMF and aerobic oxidation of HMF to form DFF through the PMA-MIL-101 in ambient oxygen (Scheme 1).



Figure 1. Catalytic dehydration of fructose to HMF over PMA-MIL-101. Reaction conditions: 30mg catalyst, 200mg fructose, 5mL DMSO, 110°C, 1h.

Intimal experiments were conducted to study the catalytic performance of PMA-MIL-101 catalysts toward fructose dehydration. In a typical process, 200mg of fructose was dissolved in 5mL DMSO and heated to 110°C with 30mg of PMA-MIL-101 as a catalyst. The catalytic reaction results were shown in Figure 1. According to the related research results, the interaction between DMSO and fructose can facilitate the selective dehydration of fructose to HMF. Besides, DMSO can also help to protect HMF from further rehydration to formic acid and levulinic acid.^[27] Thus, it can be seen in Figure 1 that fructose can be converted to HMF without any acid catalysts. Since MIL-101 contains coordinatively unsaturated meatal centers as Lewis acids and also catalytically active sites suspended on the organic linkers, the addition of MIL-101 increased the reaction speed.^[28] Bronsted acids are also active for the dehydration of carbohydrates especially for the conversion of fructose to HMF.^[29] Therefore, the reaction process is further accelerated when PMA-MIL-101 was applied as catalysts and the fructose conversion and DFF yield increased as the loading amount of PMA raised. Obviously, 0.5PMA-MIL-101, with a PMA loading of 9.5%, was more active than pure MIL-101. After one-hour reaction, the HMF yield was 44%. HMF yield of 60.1% was obtained when the PMA loading increased to 10.4%. To further confirm the activity of PMA, the reaction was carried out in the presence of PMA (PMA dosage is the same as the PMA loading on 2PMA-MIL-101). A fructose conversion of 81% and DFF yield of 64% were obtained, indicating the good activity of PMA on the dehydration of fructose to HMF. However, the

further increasing of PMA loading on MIL-101 did not bring higher HMF yield due to the remarkable drop of the surface area of the catalysts (Table S2). Higher PMA loading can promote the dehydration of fructose to HMF but also lead to the decrease of surface area and the pore size which are unfavorable for the contact between the reactant and active sites, and may lead to some diffusion limitations.



Figure 2 HMF oxidation to DFF over PMA-MIL-101. Reaction conditions: 30mg catalyst, 63mg HMF, 5mL DMSO, $O_2=20mL/min$, 140°C, 20h.

After the above study on fructose dehydration to HMF, the aerobic oxidation of HMF to DFF was further investigated. In a typical process, 0.5mmol HMF was dissolved in DMSO and heated to 140°C with 30mg PMA-MIL-101 as catalysts for 20 h under an oxygen flow rate of 20mL/min. The catalytic performance of PMA-MIL-101 in the aerobic oxidation of HMF to DFF is shown in Figure 2. MIL-101 was widely used in the oxidation of hydrocarbons, such as cyclohexene, indane, dibenzothiophene, et al.^[30] According to the related reports, the carboxylic acid groups in MIL-101 can activate molecular oxygen.^[31] In addition, it is reported that the acids formed by the thermolysis of DMSO may act as catalysts in HMF oxidation.^[27a] HMF conversion of 65.1% and DFF yield of 47.2% was obtained when pure MIL-101 was used as the catalyst in Figure 2. Keggin-type heteropoly acids were reported to be effective in the aerobic oxidation of HMF to DFF.^[32] A HMF conversion of 90.8% and DFF yield of 88.2% were obtained when PMA was used as the catalysts (PMA dosage is the same as the PMA loading on 2PMA-MIL-101), indicating the high activity of PMA on the oxidation of HMF to DFF. The relationship between the activity of PMA-MIL-101 and the PMA loading was investigated. Importantly, when the MIL-101 supported PMA catalysts were applied in the reaction, the vield of DFF and HMF conversion enhanced greatly compared with MIL-101. 87.5% HMF conversion and 82.6% DFF yield were obtained when 0.5PMA-MIL-101, with a PMA loading of 9.5%, was used as the catalyst. The selectivity of DFF increased from 72.6% (MIL-101) to 94.4% (0.5PMA-MIL-101). With increasing the loading of PMA, the yield of DFF increased, reaching a maximum of 91% (2PMA-MIL-101), and then decreased to 81.7% (3PMA-MIL-101) due to the decline of surface area and pore size in this process (Table S2).



Figure 3. One-pot and one-step synthesis of DFF from fructose. Reaction conditions: 40mg catalyst, 200mg fructose, 5mL DMSO, $O_2=20mL/min$, 150°C, 7h.

PMA-MIL-101 was used as the bifunctional catalyst in the one-pot and one-step synthesis of DFF from fructose. In a typical experiment, 200mg fructose was dissolved in 5 mL DMSO with 40mg PMA-MIL-101 and then heated to 150°C, with oxygen bubbling at a rate of 20 mL/min. The experiment results are showed in Figure 3. In the presence of MIL-101, HMF was the main product after the reaction for 7h at 150°C due to the limited catalytic oxidation ability of MIL-101, giving a HMF yield of 54.1% and DFF yield of 13.6%. As expected, the DFF yield increased significantly after the loading of PMA on the MIL-101. When 0.5PMA-MIL-101 was added as the catalyst, the DFF yield reached 52.22% and HMF yield declined noticeably from 54.1% (MIL-101) to 3.2%. Further increasing the PMA loading afforded full HMF conversion and higher DFF yield. DFF yield of 75.1% was achieved when 2PMA-MIL-101 was used as a catalyst under the same reaction conditions. Similar to the reaction results of fructose dehydration to HMF and HMF oxidation to DFF, the yield of the target product increased with the increasing of PMA loading, reaching a maximum value and then decreased slightly. In addition, the color of the reaction solution turned from green or light green before the reaction to dark brown after the reaction, indicating the formation of humins due to the degradation of HMF and the oxidation of fructose in the initial stage of the reaction, which is supposed to lead to a low carbon balance.

2



Figure 4. Fructose conversion into HMF and DFF as a function of reaction time. Reaction conditions: fructose 200mg, catalytic 40mg, DMSO 5mL, O_2 =20mL/min, 150°C.

The time course for the one-pot and one-step conversion of fructose to DFF was investigated by determining the change of the content of fructose in Figure 4, HMF and DFF in specified time intervals during the reaction process. It is well known that the reaction consists of two steps: the dehydration of fructose to HMF and the aerobic oxidation of HMF to DFF. Under the combined action of DMSO and Bronsted and Lewis acid of PMA-MIL-101, HMF formed quickly, reaching a maximum yield in 0.5h. Then the reaction entered the second step, in which HMF was continuously consumed and the yield of DFF increased accordingly. $[PMo_{12}O_{40}]^{3-}$ was reported to be the active species which promoted the cleavage of the O-H bond in the hydroxyl group and cleavage of the C-H bond in the methylene group of HMF in this step.^[32] The successful synthesis of DFF from fructose was attributed to the excellent tolerance of PMA to organic by-products in the reaction system and moderate redox ability of PMA which might otherwise lead to the strong decomposition of fructose and HMF resulting in a large number of by-products.

Entry	Catalyst (mg)	T(°C)	t(h)	Fructose conv. (%)	HMF yield(%)	DFF yield(%)
1	40	140	7	100	26.5	53.4
2	20	150	7	100	14.1	69
3	40	150	7	100	0.8	75.1
4	60	150	5	100	3.1	72.4
5	80	150	5	100	4.9	70.2
6	40	160	2	100	27.3	53.9

Table 1 Fructose conversion to DFF under different reaction conditions.



Reaction conditions: fructose 200mg, O₂=20mL/min.

In the presence of 2PMA-MIL-101, the reaction conditions affecting the catalytic performance were investigated and the results were summarized in Table 1. It can be seen that the yield of the products was greatly affected by the reaction time, reaction temperature and catalyst amount. A HMF yield of 26.5% and DFF yield of 53.4% were obtained in 7h at 140°C (Entry 1), while a comparable result was achieved in only 2h when it was reacted at 160°C (Entry 6), and all the HMF can be converted to DFF in 5 h (Entry 7), resulting in a final DFF yield of 73.7%. Our previous study on the dehydration of fructose to HMF by using PMA-MIL-101 has proven that the dehydration step runs fast under the investigated temperature range, so the reaction temperature affects the final yield of DFF by affecting the reaction rate of HMF oxidation to DFF. A 14.07% HMF yield and 69% DFF yield were obtained in 7h when a 20mg catalyst was applied in the reaction under 150°C (Entry 2), while an above 70% yield of DFF with little HMF remains can be achieved in even shorter time by increasing the catalyst amount to 40, 60 and 80mg (Entry 3,4,5). Overall, the results showed that the catalytic performance was steady.

Figure 5. Reusability of 2PMA-MIL-101 with the reaction conditions described in Figure 3.

The reusability and stability of PMA-MIL-101 was investigated in the one-pot and one-step conversion of fructose to DFF. The used catalyst was separated from the reaction mixture by centrifugation, and washed by ethanol and deionized water, respectively. The wet catalyst was dried in an oven at 65°C overnight. Generally, the catalyst affords stable performance and the fructose conversion maintained at almost 100% during the recycling test in Figure 5. However, there was a drop of DFF yield to about 10% in the second run. The ICP analysis of the filtrate after the catalytic reaction showed a 9% loss of the Mo in the catalyst. This loss could be caused by the leaching of Mo from the catalyst and the loss of the very fine particles of PMA-MIL-101 due to the stirring during the recycling reaction. The loss of the catalyst during the recycling operation was another reason behind the decrease of the DFF yield. Since the dehydration of fructose to HMF runs fast and the reaction time was long enough for the fully conversion of fructose, the reduction of the catalyst amount with the increase of the reuse cycles mainly influences the oxidation of HMF to DFF. Therefore, more and more HMF remained in the reaction products, resulting in the decrease of DFF yield. After the second run, the DFF yield decreasing was slowed down gradually and the catalytic performance tended to become stable.

In conclusion, considerable efforts have been made to the synthesis of DFF from fructose by a one-pot and one-step approach in recent years. However, it is still challenging to achieve a satisfactory DFF yield due to the difficulties in generating acid sites and oxidative active sites on one support to form bifunctional catalysts, and reduce the side-reactions meanwhile. In this study, phosphomolybdic acid was encapsulated in a metal-organic framework MIL-101 and used as a bifunctional catalyst for the direct transformation of fructose to DFF. The as-synthesized catalysts processed both Bronsted acidity and oxidability, which synergistically facilitated the dehydration of fructose and the aerobic oxidation of HMF. PMA loading is a key factor which influences the catalytic performances. Under optimal reaction conditions, a DFF yield of 75.1% was achieved over 2PMA-MIL-101 after 7h in DMSO. The catalyst could be recycled and reused without significant loss of the catalytic activity. This one-pot and onestep synthesis of DFF from fructose highlights a good prospect for lower costs and energy consumption in biomass carbohydrate conversion without separation of reaction intermediates.

ASSOCIATED CONTENT

Supporting Information. Experimental details, Table S1-S2 and Figures S1-S3.

AUTHOR INFORMATION

Corresponding Author

* Telephone: +65-6513-8129. Fax: +65 6794-7553. E-mail: jmlee@ntu.edu.sg.

ACKNOWLEDGMENT

This work is supported by the National Research Foundation (NRF), Prime Minister's Office, Singapore under its Campus for Research Excellence and Technological Enterprise (CREATE) program, as well as the AcRF Tier 1 grant (RGT27/13), Ministry of Education, Singapore.

REFERENCES

a) E. Hodgson, D. Nowakowski, I. Shield, A. Riche, A. Bridgwater, J. Clifton-Brown, I. S. Donnison, *Bioresource technology* 2011, *102*, 3411-3418; b) A. M. R. Galletti, C. Antonetti, V. De Luise, M. Martinelli, *Green Chemistry* 2012, *14*, 688-694; c) J. Hancsók, M. Krár, S. Magyar, L. Boda, A. Holló, D. Kalló, *Microporous and Mesoporous Materials* 2007, *101*, 148-152.

[2] H.-T. N. Hao, O. P. Karthikeyan, K. Heimann,

Energies **2015**, *8*, 6350-6364.

- [3] a) R.-J. van Putten, J. C. van der Waal, E. De Jong, C. B. Rasrendra, H. J. Heeres, J. G. de Vries, *Chemical reviews* 2013, *113*, 1499-1597;
 b) Y. Román-Leshkov, J. N. Chheda, J. A. Dumesic, *Science* 2006, *312*, 1933-1937.
- [4] a) K. T. Hopkins, W. D. Wilson, B. C. Bender, D. R. McCurdy, J. E. Hall, R. R. Tidwell, A. Kumar, M. Bajic, D. W. Boykin, *Journal of Medicinal Chemistry* 1998, *41*, 3872-3878; b) M. Del Poeta, W. A. Schell, C. C. Dykstra, S. K. Jones, R. R. Tidwell, A. Kumar, D. W. Boykin, J. R. Perfect, *Antimicrobial agents and chemotherapy* 1998, *42*, 2503-2510; c) M. Baumgarten, N. Tyutyulkov, *Chemistry A European Journal* 1998, *4*, 987-989; dA. Gandini, N. M. Belgacem, *Polymer International* 1998, *47*, 267-276.
- [5] a) A. S. Amarasekara, D. Green, E. McMillan, *Catalysis Communications* 2008, *9*, 286-288; b)
 L. Cottier, G. Descotes, E. Viollet, J. Lewkowski, R. Skowroñski, *Journal of heterocyclic chemistry* 1995, *32*, 927-930; c) Y. Zhu, M. Lu, *RSC Advances* 2015, *5*, 85579-85585; d) L. Cottier, G. Descotes, J. Lewkowski, R. Skowroñski, *Organic preparations and procedures international* 1995, *27*, 564-566.
- [6] W. Partenheimer, V. V. Grushin, *Advanced Synthesis & Catalysis* **2001**, *343*, 102-111.
- [7] C. Carlini, P. Patrono, A. M. R. Galletti, G. Sbrana, V. Zima, *Applied Catalysis A: General* 2005, *289*, 197-204.
- [8] C. A. Antonyraj, B. Kim, Y. Kim, S. Shin, K.-Y. Lee,
 I. Kim, J. K. Cho, *Catalysis Communications* 2014, *57*, 64-68.
- [9] J. Artz, S. Mallmann, R. Palkovits, *ChemSus-Chem* **2015**, *8*, 672-679.
- [10] Z.-Z. Yang, J. Deng, T. Pan, Q.-X. Guo, Y. Fu, *Green Chemistry* **2012**, *14*, 2986-2989.
- [11] Y. Román-Leshkov, C. J. Barrett, Z. Y. Liu, J. A. Dumesic, *Nature* 2007, 447, 982-985.
- [12] G. D. Yadav, R. V. Sharma, *Applied Catalysis B: Environmental* **2014**, *147*, 293-301.
- B. Siyo, M. Schneider, M.-M. Pohl, P. Langer, N. Steinfeldt, *Catalysis letters* 2014, *144*, 498-506.
- [14] S. Zhang, W. Li, X. Zeng, L. Lin, *Journal of Bio-process Engineering and Biorefinery* 2014, *3*, 23-34.
- [15] J. Ma, Z. Du, J. Xu, Q. Chu, Y. Pang, *ChemSus-Chem* **2011**, *4*, 51-54.
- [16] B. Liu, Z. Zhang, K. Lv, K. Deng, H. Duan, *Applied Catalysis A: General* **2014**, *472*, 64-71.

- [17] Y. Wang, B. Liu, K. Huang, Z. Zhang, *Industrial & Engineering Chemistry Research* 2014, *53*, 1313-1319.
- [18] G. A. Halliday, R. J. Young, V. V. Grushin, Organic letters 2003, 5, 2003-2005.
- [19] S. Dabral, S. Nishimura, K. Ebitani, *ChemSus-Chem* **2014**, *7*, 260-267.
- [20] X. Xiang, L. He, Y. Yang, B. Guo, D. Tong, C. Hu, *Catalysis Letters* **2011**, *141*, 735-741.
- [21] H.-J. Yoon, J.-W. Choi, H.-S. Jang, J. K. Cho, J.-W. Byun, W.-J. Chung, S.-M. Lee, Y.-S. Lee, *Synlett* 2011, 2011, 165-168.
- [22] Q. Zhao, L. Wang, S. Zhao, X. Wang, S. Wang, *Fuel* **2011**, *90*, 2289-2293.
- [23] a) Y. Liu, L. Zhu, J. Tang, M. Liu, R. Cheng, C. Hu, *ChemSusChem* 2014, *7*, 3541-3547; b) R. Liu, J. Chen, L. Chen, Y. Guo, J. Zhong, *ChemPlusChem* 2014, *79*, 1448-1454.
- [24] a) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* 2002, *295*, 469-472; b) P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J. F. Eubank, D. Heurtaux, P. Clayette, C. Kreuz, *Nature materials* 2010, *9*, 172-178; c) X.-X. Huang, L.-G. Qiu, W. Zhang, Y.-P. Yuan, X. Jiang, A.-J. Xie, Y.-H. Shen, J.-F. Zhu, *CrystEngComm* 2012, *14*, 1613-1617.
- [25] a) N. Maksimchuk, M. Timofeeva, M. Melgunov, A. Shmakov, Y. A. Chesalov, D. Dybtsev, V. Fedin, O. Kholdeeva, *Journal of Catalysis* 2008, *257*, 315-323; b) N. V. Maksimchuk, K. A. Kovalenko, S. S. Arzumanov, Y. A. Chesalov, M. S. Melgunov, A. G. Stepanov, V. P. Fedin, O. A. Kholdeeva, *Inorganic chemistry* 2010, *49*, 2920-2930; c) N. V. Maksimchuk, O. A. Kholdeeva, K. A. Kovalenko, V. P. Fedin, *Israel Journal of Chemistry* 2011, *51*, 281-289.
- [26] a) Y. Zhang, V. Degirmenci, C. Li, E. J. Hensen, *ChemSusChem* 2011, *4*, 59-64; b) Q. Deng, G. Nie, L. Pan, J.-J. Zou, X. Zhang, L. Wang, *Green Chemistry* 2015, *17*, 4473-4481.
- [27] a) C. Laugel, B. Estrine, J. Le Bras, N. Hoffmann,
 S. Marinkovic, J. Muzart, *ChemCatChem* 2014, *6*, 1195-1198; b) S. H. Mushrif, S. Caratzoulas,
 D. G. Vlachos, *Physical Chemistry Chemical Physics* 2012, *14*, 2637-2644.
- [28] S.-H. Huo, X.-P. Yan, Analyst 2012, 137, 3445-3451.
- [29] Y. J. Pagan-Torres, T. Wang, J. M. R. Gallo, B. H. Shanks, J. A. Dumesic, *Acs Catalysis* **2012**, *2*, 930-934.

ChemCatChem

- a) N. V. Maksimchuk, K. A. Kovalenko, V. P. Fedin, O. A. Kholdeeva, *Chemical Communications* 2012, *48*, 6812-6814; b) A. Santiago-Portillo, S. Navalón, F. G. Cirujano, F. X. L. i. Xamena, M. Alvaro, H. Garcia, *ACS Catalysis* 2015, *5*, 3216-3224; c) A. Gomez-Paricio, A. Santiago-Portillo, S. Navalon, P. Concepcion, M. Alvaro, H. Garcia, *Green Chemistry* 2016, *18*, 508-515.
- [31] G. Lv, H. Wang, Y. Yang, T. Deng, C. Chen, Y. Zhu, X. Hou, *ACS Catalysis* 2015, *5*, 5636-5646.
- [32] L.-K. Ren, H.-Q. Yang, C.-W. Hu, *Catalysis Science & Technology* **2016**.

This article is protected by copyright. All rights reserved.