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COMMUNICATION

Selective Oxidation of Glycerol to Formic Acid in Highly Concentrated Aqueous Solutions with Molecular Oxygen using V-substituted Phosphomolybdic Acids

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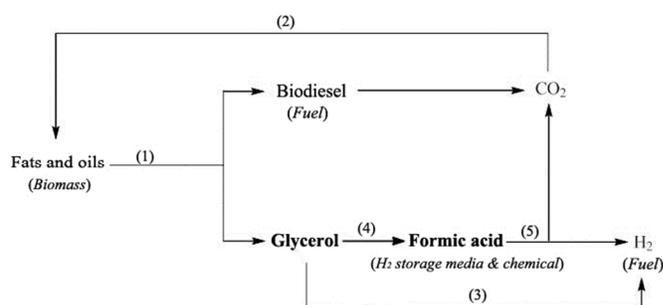
Jizhe Zhang,^a Miao Sun,^b and Yu Han^{* a}

Formic acid is an important commodity chemical as well as a promising medium for hydrogen storage and hydrogen production. In this paper, we report that formic acid can be produced through selective oxidation of glycerol, a low-cost by-product of biodiesel, by using vanadium-substituted phosphomolybdic acids as catalysts and molecular oxygen as the oxidant. Significantly, this catalytic system allows for high-concentration conversions and thus leads to exceptional efficiency. Specifically, 3.64 g of formic acid was produced from a 10 g of glycerol/water (50/50 in weight) solution.

In the context of the future hydrogen economy, effective production of hydrogen (H₂) from readily available and sustainable resources is of crucial importance.^{1, 2} Currently, H₂ is mainly produced from nonrenewable natural gases, petroleum and coal through reforming process, while technologies for producing H₂ from water by solar energy are not yet mature.³ The possibility of generating H₂ from biomass that is both abundant and ecologically sustainable has attracted substantial research efforts in the last decade, and various technologies have been developed including fermentation,⁴ enzymatic conversion,^{5, 6} gasification,⁷ and steam/aqueous reforming.^{8, 9} However, high-yield, low-cost production of H₂ from biomass remains a challenge. As a traditional commodity chemical in high demand in the chemical, pharmaceutical and agricultural industries, formic acid (FA) has recently received particular attention because it was demonstrated to be an efficient storage medium for H₂.¹⁰⁻¹² With the development of new processes that allow selective decomposition of FA into H₂ and CO₂,¹³⁻²¹ it is also possible to consider FA as a precursor to hydrogen production, although this is economically and ecologically meaningful only when FA can be produced from renewable feedstock using low-cost processes.

The significantly increased global demand for biodiesel results in the large surplus of glycerol, the main byproduct in manufacturing biodiesel fuels by the triglyceride transesterification process. As a consequence, the price of crude glycerol has dropped markedly in the last 10 years from ~USD 0.25 per pound to ~USD 0.05 per pound.²²⁻²³ This makes glycerol a promising feedstock to be converted to various high-valued products.²⁴ The current price of FA is comparable to that of the refined glycerol (approximately USD

0.30 per pound). Given that the price of glycerol will certainly fall further along with the increase of biodiesel production, it is desirable to develop a route to selective conversion of glycerol to FA as a useful commodity chemical as well as an intermediate compound for hydrogen production. It is worth noting that the use of glycerol to produce H₂ would fully integrate biodiesel into the renewable fuel concept, considering that in addition to itself, the H₂ obtained from its by-product is also a clean fuel (Scheme 1).^{8, 25-28} Hydrogen generation from glycerol has been investigated by means of aqueous/gas phase reforming.²⁵⁻³¹ These processes suffer from low yields of H₂ or high reaction temperatures,^{25, 28} and they can only be applied to very diluted (~1%) aqueous solutions.^{8, 26} Processes that enable selective reforming of concentrated glycerol solutions at low temperatures remain to be developed.



Scheme 1. Schematic illustration of the renewable fuel concept based on biomass conversion: (1) triglyceride transesterification; (2) photosynthesis; (3) aqueous/gas phase reforming; (4) catalytic oxidation; and (5) dehydrogenation of FA.

Here, we report that glycerol can be selectively oxidized to FA in an aqueous solution with molecular oxygen by using vanadium-substituted phosphomolybdic acids as catalysts. Given that many efficient catalytic systems have been developed for dehydrogenating FA to generate H₂, the selective conversion of glycerol to FA offers an alternative route to the direct extraction of H₂ from glycerol (Scheme 1). In comparison with conventional reforming processes, this catalytic system requires a lower temperature (423 K) and leads to higher selectivity; more importantly, it can work with highly

concentrated aqueous solutions of glycerol (up to 75 wt%) to give rise to much higher conversion efficiencies, i.e., higher potential H₂ yields per unit volume of the reactor. The liquid product FA also holds advantages over H₂ for its ease of storage and transportation and its readiness to release H₂ when needed.

In our recent studies, we have demonstrated that many Keggin-type heteropoly acids (HPAs) can effectively convert biomass substrates under oxidative conditions due to their strong Brønsted acidity, while the reaction pathway is largely determined by the type of addenda atom in the HPA catalyst.³²⁻³⁴ For example, we reported the direct conversion of cellulose to glycolic acid with high yields (~50%) using molecular oxygen in a water medium in which a phosphomolybdic acid (H₃PMo₁₂O₄₀) acts as a bi-functional catalyst to catalyze both the hydrolysis of cellulose and the subsequent oxidation reactions. Further study indicated that the product selectivity of this system changed from glycolic acid to FA if some molybdenum (Mo) atoms in the H₃PMo₁₂O₄₀ catalyst were substituted by vanadium (V).³⁴ Similar results were also reported by other research groups³⁵⁻³⁷ and were attributed to the selective oxidative cleavage of C-C bonds by the V atoms in HPA. Inspired by these previous works, we attempted to use vanadium-substituted phosphomolybdic acids (H_{3+n}PV_nMo_{12-n}O₄₀) as catalysts to convert glycerol through oxidation. The reactions were carried out at 423 K for 3 hours under 2 MPa – 4 MPa O₂ in a Teflon-lined stainless autoclave reactor (75 mL) that contained 10 g of an aqueous solution of glycerol with a designated concentration and 0.1 mmol of catalyst.

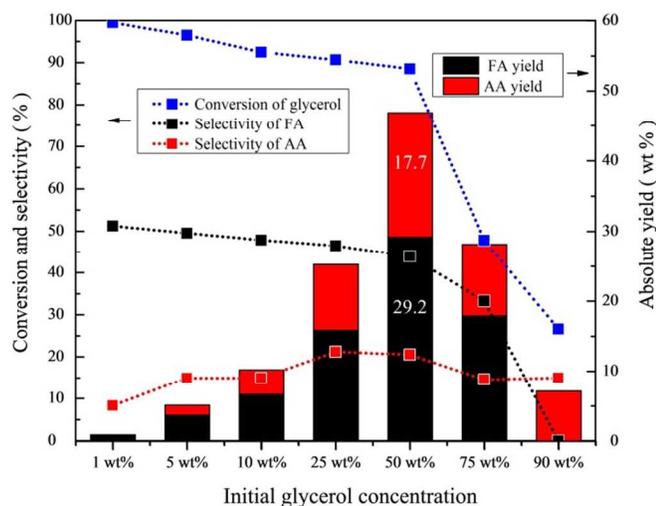


Figure 1. Selective oxidation of glycerol in an aqueous solution over the H₄PV₁Mo₁₁O₄₀ catalyst. Reaction conditions: 10 g of glycerol solution with a designated concentration; 0.1 mmol of catalyst; at 423 K and a constant O₂ pressure of 2 MPa for 3 h.

We first used mono-V-substituted phosphomolybdic acid (H₄PV₁Mo₁₁O₄₀) to convert glycerol in aqueous solutions of different concentrations ranging from 1 wt% to 90 wt%. Full conversion of glycerol was achieved in the 1 wt% solution with three major products detected in the liquid phase, including FA (selectivity: 51.2%), acetic acid (selectivity: 8.3%), and formaldehyde (selectivity: 7.2%), while the only product detected in the gas phase was CO₂. When a 5 wt% glycerol solution was used for conversion, 98% of the glycerol was converted with nearly unchanged product selectivities. However, it is worth noting that the absolute yields of the products, which are defined as their weight percentages relative to the initial reaction mixture, were markedly increased in this case due to the five times higher substrate

concentration (Figure 1). Further increasing the concentration of the glycerol substrate resulted in gradually decreased conversion, disappearance of formaldehyde in the products, and continuously increased absolute yields of FA and acetic acid (AA). As shown in Figure 1, the maximum absolute yields (29.2 wt% for FA and 17.7 wt% for AA) were obtained in the system that initially contained 50 wt% of glycerol. These values are exceptionally high, considering that conventional oxidative biomass conversion reactions are usually performed in diluted solutions (< 5 wt%).³⁸⁻⁴⁰ With the initial glycerol concentration exceeding 50 wt%, the conversion as well as the selectivity of FA dramatically decreased, giving rise to lower absolute yields of FA (Figure 1). When a 90 wt% glycerol solution was used in the reaction, for example, the conversion of glycerol was 25% and AA was the only detectable product in the liquid phase (Figure 1). These results suggest that higher water content in the reaction system favors the formation of FA. We note that glycerol has been converted through selective oxidation to various high-value chemicals, such as glyceric acid,⁴¹ tarttronic acid,^{42,43} ketomalonic acid,⁴⁴ and dihydroxyacetone^{45,46}, and that the use of HPAs to catalyze the dehydration of glycerol to acrolein⁴⁷⁻⁴⁹ or glycerol acetylation⁵⁰ has also been reported. However, to the best of our knowledge, conversion of glycerol to FA with such a high selectivity and efficiency has never been achieved prior to this study. Actually, the conversion of glycerol to FA was not attractive before because of the comparable values of the two compounds.⁵¹ With the slump of the glycerol's price, this conversion route has drawn more attention and several systems have been investigated very recently. For example, Shen *et al.* reported the formation of formic acid from glycerol using a hydrothermal reaction at 250 °C with H₂O₂ as an oxidant;⁵² Liu *et al.* reported the selective oxidation of glycerol to formic acid catalyzed by Ru(OH)₄/r-GO in the presence of FeCl₃;⁵³ the conversion of glycerol to FA using a phosphomolybdic acid catalyst was mentioned but not specifically discussed in reference 37. In these previous studies, however, the reactions were all carried out in highly diluted solution, resulting in much lower conversion efficiency in comparison with our system. Moreover, the yield of AA, another useful chemical with important applications, is also remarkable in our system.

Table 1. Oxidative conversions of various substrates catalyzed by V-substituted phosphomolybdic acids^a

Catalysts	Substrate	Conc. (wt%)	Conversion (%)	Selectivity (%)	
				FA	AA
HPMoV ₁ ^[a]	Glycerol	50	90.6	41.2	19.2
HPMoV ₂ ^[a]	glycerol	50	93.0	48.5	13.0
HPMoV ₃ ^[a]	glycerol	50	94.8	51.3	11.2
HPMoV ₁ ^[b]	glycerol	1	99.5	51.2	8.3
HPMoV ₂ ^[b]	glycerol	1	100	55.2	2.9
HPMoV ₃ ^[b]	glycerol	1	100	60.0	2.8
HPMo ^[b]	glycerol	1	-	-	-
HPMoV ₁ ^[b]	Lactic acid	1	100	7.4	38.2
HPMoV ₁ ^[c]	methanol	1	5.8	5.2	-
HPMoV ₁ ^[c]	formaldehyde	1	43.9	83.8	-
HPMoV ₁ ^[b]	formic acid	50	4.7	-	-

^a Reaction conditions: 10 g aqueous solution of the substrate with a designated concentration; 0.1 mmol of catalyst; for 3 h. Besides FA and AA, trace amount of formaldehyde, glycolic acid and other unidentified products are detected in the liquid phase. ^[a] 423 K and 4 MPa O₂. ^[b] 423 K and 2 MPa O₂. ^[c] 453 K and 2 MPa O₂.

We found that the conversion efficiency of glycerol to FA can be further enhanced by increasing the vanadium content in the phosphovanadomolybdic catalyst. Under identical reaction conditions, multi-V-substituted phosphomolybdic acid catalysts ($H_5PV_2W_{12}O_{40}$ and $H_6PV_3Mo_9O_{40}$) gave rise to more FA and less AA than their mono-substituted counterpart. The FA selectivity increases in the following order: $H_6PV_3Mo_9O_{40} > H_5PV_2W_{12}O_{40} > H_4PV_1Mo_{11}O_{40}$, and this trend applies to both concentrated (50 wt%) and diluted (1 wt%) glycerol solutions (Table 1). The highest absolute yield of FA (36.4 wt%), which corresponds to a selectivity of 51.3% from the 50 wt% glycerol solution, was achieved by $H_6PV_3Mo_9O_{40}$ (Table 1). The fact that the V-free phosphomolybdic acid is catalytically inactive under the same reaction conditions (Table 1) further demonstrates the crucial role of vanadium in this reaction.

The oxidative C-C bond cleavage of primary alcohol and vicinal diols catalyzed by $H_5PV_2W_{12}O_{40}$ was believed to follow an electron transfer and oxygen transfer (ET-OT) reaction mechanism.⁵⁴ Meanwhile, previous studies suggested that in the conversion of glucose to FA catalyzed by $H_5PV_2W_{12}O_{40}$, the intermediates are aldehyde-group-containing compounds and there is more than one mechanism involved in the reaction.^{35,37} A recent study of the use of an AuPd/TiO₂ catalyst for selective oxidation of glycerol proposed that FA and AA were generated through the oxidative decomposition of lactic acid, which was the major product of that system.⁵⁵ In our system, we found that lactic acid can indeed be converted to FA and AA with high selectivities (7.4 % and 38.2 %, respectively) (Table 1). On the other hand, when methanol and formaldehyde were used as the substrates, slower conversions with lower FA yields were observed, as compared with the cases of glycerol (Table 1). This result excludes methanol or formaldehyde from being the intermediates for the production of FA in this system. However, the exact reaction pathway of selective oxidation of glycerol to FA and AA over vanadium-substituted phosphomolybdic acids remains unclear, due to the complexity of this reaction. We also investigated the stability of FA in this catalytic system by using FA (50 wt% in water) as the substrate, and found that only ~ 5% of FA was decomposed under the reaction conditions. This result reveals that FA is rather stable in this system. Therefore, the CO₂ produced in this reaction is not from the dehydrogenation of FA, as supported by the observation that varying the glycerol/catalyst ratio did not much change the selectivity of FA (Figure 1). In addition, we can conclude from this result that the absence of FA in the products of high concentration (e.g., 90 wt%) glycerol conversion is not due to its decomposition but more likely associated with the low water content in the reaction system.

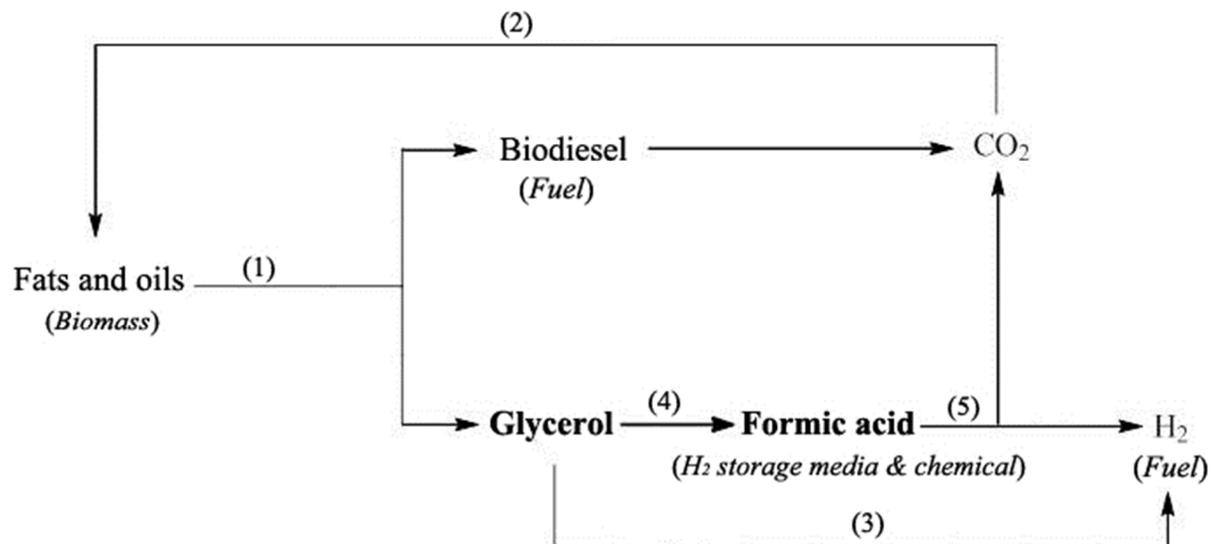
Conclusions

We demonstrated that V-substituted phosphomolybdic acid catalysts enable the selective oxidation of glycerol to formic acid in highly concentrated aqueous solutions using molecular oxygen. The preliminary results show that the absolute yield of formic acid could reach 36.4 wt% of the initial reaction mixture, representing exceptionally high conversion efficiency. This reaction provides an alternative route to the production of H₂ from glycerol, given that formic acid can be readily and selectively converted to H₂. In comparison with conventional reforming processes, this process requires lower energy input while offering higher selectivity and yield. Taking advantage of the large surplus of glycerol, it fully integrates biodiesel in the renewable fuel concept. A noteworthy advantage of the HPA catalysts used in this study is that they can be recovered in solid form after reactions by distilling the products and solvent out, and their good reusability has been demonstrated in our previous studies.³⁴

Notes and references

- ^a Advanced Membranes and Porous Materials Center, Physical Science and Engineering Division, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia
E-mail: yu.han@kaust.edu.sa
- ^b Cooperate Research and Development Center in King Abdullah University of Science and Technology, Saudi Aramco, Thuwal 23955-6900 Saudi Arabia
1. A. A. Evers, the Hydrogen Society, *Hydrogeit Verlag*, 2012.
2. J. Rifkin, the Hydrogen Economy, *Penguin Putnam Inc.*, 2002.
3. A. J. Esswein and D. G. Nocera, *Chem Rev*, 2007, **107**, 4022-4047.
4. T. A. Ngo, T. H. Nguyen and T. V. B. Ha, *Renew Energ*, 2012, **37**, 174-179.
5. J. S. Martin del Campo, J. Rollin, S. Myung, Y. Chun, S. Chandrayan, R. Patino, M. W. W. Adams and Y. H. P. Zhang, *Angew Chem Int Edit*, 2013, **52**, 4587-4590.
6. J. Woodward, M. Orr, K. Cordray and E. Greenbaum, *Nature*, 2000, **405**, 1014-1015.
7. D. Castello and L. Fiori, *Bioresource Technol*, 2011, **102**, 7574-7582.
8. P. R. de la Piscina and N. Homs, *Chem Soc Rev*, 2008, **37**, 2459-2467.
9. R. D. Cortright, R. R. Davda and J. A. Dumesic, *Nature*, 2002, **418**, 964-967.
10. F. Joo, *Chemsuschem*, 2008, **1**, 805-808.
11. B. Zaidman, H. Wiener and Y. Sasson, *Int J Hydrogen Energ*, 1986, **11**, 341-347.
12. R. Williams, R. S. Crandall and A. Bloom, *Appl Phys Lett*, 1978, **33**, 381-383.
13. S. Zhang, O. Metin, D. Su and S. H. Sun, *Angew Chem Int Edit*, 2013, **52**, 3681-3684.
14. Z.-L. Wang, J.-M. Yan, Y. Ping, H.-L. Wang, W.-T. Zheng and Q. Jiang, *Angewandte Chemie International Edition*, 2013, **52**, 4406-4409.
15. Y. Y. Cai, X. H. Li, Y. N. Zhang, X. Wei, K. X. Wang and J. S. Chen, *Angew Chem Int Edit*, 2013, **52**, 11822-11825.
16. Q. Y. Bi, X. L. Du, Y. M. Liu, Y. Cao, H. Y. He and K. N. Fan, *J Am Chem Soc*, 2012, **134**, 8926-8933.
17. K. Tedsree, T. Li, S. Jones, C. W. A. Chan, K. M. K. Yu, P. A. J. Bagot, E. A. Marquis, G. D. W. Smith and S. C. E. Tsang, *Nat Nanotechnol*, 2011, **6**, 302-307.
18. M. Ojeda and E. Iglesia, *Angew Chem Int Edit*, 2009, **48**, 4800-4803.
19. X. C. Zhou, Y. J. Huang, W. Xing, C. P. Liu, J. H. Liao and T. H. Lu, *Chem Commun*, 2008, 3540-3542.
20. B. Loges, A. Boddien, H. Junge and M. Beller, *Angew Chem Int Edit*, 2008, **47**, 3962-3965.
21. C. Fellay, P. J. Dyson and G. Laurenczy, *Angew Chem Int Edit*, 2008, **47**, 3966-3968.
22. B. J. Kerr, W. A. Dozier, K. Bregendahl, Proceedings of the 23rd Annual Carolina Swine Nutrition Conference. Raleigh, NC, 2007. Nutritional value of crude glycerin for nonruminants; pp. 6-18.
23. F. Yang, M. A. Hanna, R. Sun, *Biotechnol Biofuels*, 2012, **5**, 13.
24. (a) E. Arceo, P. Marsden, R. G. Bergman and J. A. Ellman, *Chem Commun*, 2009, 3357-3359; (b) C. H. C. Zhou, J. N. Beltramini, Y. X. Fan and G. Q. M. Lu, *Chem Soc Rev*, 2008, **37**, 527-549; (c) M.

- Pagliari, R. Ciriminna, H. Kimura, M. Rossi and C. Della Pina, *Angew Chem Int Edit*, 2007, **46**, 4434-4440.
25. S. Adhikari, S. Fernando and A. Haryanto, *Catal Today*, 2007, **129**, 355-364.
26. G. W. Huber and J. A. Dumesic, *Catal Today*, 2006, **111**, 119-132.
27. G. W. Huber, J. W. Shabaker and J. A. Dumesic, *Science*, 2003, **300**, 2075-2077.
28. S. Czernik, R. French, C. Feik and E. Chornet, *Ind Eng Chem Res*, 2002, **41**, 4209-4215.
29. P. V. Tuza, R. L. Manfro, N. F. P. Ribeiro and M. M. V. M. Souza, *Renew Energ*, 2013, **50**, 408-414.
30. P. J. Dietrich, T. P. Wu, A. Sumer, J. A. Dumesic, J. Jellinek, W. N. Delgass, F. H. Ribeiro and J. T. Miller, *Top Catal*, 2013, **56**, 1814-1828.
31. D. L. King, L. A. Zhang, G. Xia, A. M. Karim, D. J. Heldebrant, X. Q. Wang, T. Peterson and Y. Wang, *Appl Catal B-Environ*, 2010, **99**, 206-213.
32. J. Z. Zhang, X. Liu, M. Sun, X. H. Ma and Y. Han, *Acs Catal*, 2012, **2**, 1698-1702.
33. J. Z. Zhang, X. Liu, M. N. Hedhili, Y. H. Zhu and Y. Han, *Chemcatchem*, 2011, **3**, 1294-1298.
34. J. Zhang, M. Sun, X. Liu and Y. Han, *Catal Today*, 2014, **233**, 77-82.
35. J. Li, D. J. Ding, L. Deng, Q. X. Guo and Y. Fu, *Chemsuschem*, 2012, **5**, 1313-1318.
36. J. Albert, R. Wolfel, A. Bosmann and P. Wasserscheid, *Energ Environ Sci*, 2012, **5**, 7956-7962.
37. R. Wolfel, N. Taccardi, A. Bosmann and P. Wasserscheid, *Green Chem*, 2011, **13**, 2759-2763.
38. G. L. Brett, Q. He, C. Hammond, P. J. Miedziak, N. Dimitratos, M. Sankar, A. A. Herzing, M. Conte, J. A. Lopez-Sanchez, C. J. Kiely, D. W. Knight, S. H. Taylor and G. J. Hutchings, *Angew Chem Int Edit*, 2011, **50**, 10136-10139.
39. A. Villa, G. M. Veith and L. Prati, *Angew Chem Int Edit*, 2010, **49**, 4499-4502.
40. R. M. Painter, D. M. Pearson and R. M. Waymouth, *Angew Chem Int Edit*, 2010, **49**, 9456-9459.
41. S. Carrettin, P. McMorn, P. Johnston, K. Griffin and G. J. Hutchings, *Chem Commun*, 2002, 696-697.
42. B. Katryniok, H. Kimura, E. Skrzynska, J. S. Girardon, P. Fongarland, M. Capron, R. Ducoulombier, N. Mimura, S. Paul and F. Dumeignil, *Green Chem*, 2011, **13**, 1960-1979.
43. C. L. Bianchi, P. Canton, N. Dimitratos, F. Porta and L. Prati, *Catal Today*, 2005, **102**, 203-212.
44. R. Ciriminna and M. Pagliaro, *Adv Synth Catal*, 2003, **345**, 383-388.
45. S. Hirasawa, H. Watanabe, T. Kizuka, Y. Nakagawa and K. Tomishige, *J Catal*, 2013, **300**, 205-216.
46. Y. Kwon, Y. Birdja, I. Spanos, P. Rodriguez and M. T. M. Koper, *Acs Catal*, 2012, **2**, 759-764.
47. B. Katryniok, S. Paul, M. Capron, V. Belliere-Baca, P. Rey and F. Dumeignil, *Chemsuschem*, 2012, **5**, 1298-1306.
48. M. H. Haider, N. F. Dummer, D. Z. Zhang, P. Miedziak, T. E. Davies, S. H. Taylor, D. J. Willock, D. W. Knight, D. Chadwick and G. J. Hutchings, *J Catal*, 2012, **286**, 206-213.
49. B. Katryniok, S. Paul, M. Capron and F. Dumeignil, *Chemsuschem*, 2009, **2**, 719-730.
50. P. Ferreira, I. M. Fonseca, A. M. Ramos, J. Vital and J. E. Castanheiro, *Appl Catal B-Environ*, 2009, **91**, 416-422.
51. P. McMorn, G. Roberts, G. Hutchings, *Catal Lett*, 1999, **63**, 193-197.
52. Y. L. Zhang, M. Zhang, Z. Shen, J. F. Zhou, X. F. Zhou, *J Chem Technol Biot*, 2013, **88**, 829-833.
53. J. L. Xu, Y. F. Zhao, H. J. Xu, H. Y. Zhang, B. Yu, L. D. Hao, Z. M. Liu, *Appl Catal B-Environ* 2014, **154**, 267-273.
54. A. M. Khenkin and R. Neumann, *J Am Chem Soc*, 2008, **130**, 14474-14476.
55. J. L. Xu, H. Y. Zhang, Y. F. Zhao, B. Yu, S. Chen, Y. B. Li, L. D. Hao and Z. M. Liu, *Green Chem*, 2013, **15**, 1520-1525.



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