多金属氧酸盐纳米纤维催化O₂氧化5-HMF

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2019-05-28 收稿, 2019-09-19 修回, 2019-10-17 接受, 2019-11-05 网络版发表

国家自然科学基金(201115180)资助

摘要 2,5-二甲基呋喃(DFF)是一种用途广泛的化合物, 可作为前体用于合成各种高附加值产品, 可通过氧化5-羟甲基糠醛(HMF)得到. 然而, 5-羟甲基糠醛的有氧氧化有不同的途径, 从而会产生DFF, 2,5-呋喃甲酸(FDCA)或马来酸酐(MA)等产物. 迄今为止, 均相和非均相金属催化剂均被作为氧化剂用于对HMF氧化为DFF的研究. 特别是含钒的多金属氧酸盐(POMs)被发现可以氧化HMF生产DFF, MA等一系列产品. 本文通过采用静电纺丝和表面活性剂成孔技术合成了介孔纳米纤维H₅PMo₁₀V₂O₄₀/meso-ZrO₂(f)并通过IR, ³¹P MAS NMR, XRD, SEM, TEM, N₂吸附-脱附测试对其进行了表征. H₅PMo₁₀V₂O₄₀/meso-ZrO₂(f)纳米纤维, 其在氧气作为氧化剂氧化5-羟甲基糠醛(5-HMF)到2,5-二甲酰基呋喃(DFF)反应中表现出高的催化活性和产物的选择性, 源于复合催化剂良好的氧化还原性、Lewis酸中心、Brønsted酸中心及纳米纤维高的比表面积.

关键词 多金属氧酸盐, 纳米纤维, 氧气氧化, 5-羟甲基糠醛(5-HMF)

5-羟甲基糠醛(5-HMF)是C₆糖类脱水产物, 被美国科学院评为TOP10的生物基可再生平台化合物. 5-HMF分子在呋喃环2,5位置上分别有1个醛基和1个羟甲基^[1], 可以进行如加氢、氧化、C-O键的氢解、重排、分解和聚合等不同类型的反应; 其氧化反应可以产生各种衍生物, 如2,5-呋喃二甲酸(FDCA)、2,5-双(羟甲基)-四氢呋喃(DHMTF)、二甲基呋喃(DMF)、2,5-呋喃二甲醛(DFF)和乙酰丙酸等^[2-5]. DFF是现代工业中有价值的前体, 广泛应用于Schiff碱、医药中间体、抗真菌剂、有机导体和聚乙烯醇交联剂的制备. 但由于FDCA是DFF继续氧化的产物, 选择性地制备DFF困难. 因此, 控制5-HMF的催化氧化定向转化制备DFF是目前需要突破的前沿课题.

多金属氧酸盐(polyoxometalates, POMs)因其有较强的酸性和氧化还原性, 被广泛用于催化反应中^[6]. H₅PMo₁₀V₂O₄₀(HPMoV)是一种典型的Keggin型多金属

氧酸盐, 具有强的氧化还原性能, 被广泛用于生物质能源的氧化转化中. 单纯的HPMoV很难催化氧气定向制备DFF. ZrO₂是唯一同时具有酸性、碱性及氧化性和还原性的金属氧化物, 而且它易于产生氧空穴, 将它作为催化剂的载体, 可和活性组分之间产生相互作用, 提高催化剂的性能.

本研究制备HPMoV/meso-ZrO₂(f)纳米纤维, 并研究其在氧化5-HMF中的性能, 建立多中心的复合催化剂对其转化的影响关系, 为多金属氧酸盐基催化材料的设计合成提供借鉴.

1 实验

(i) 催化剂的制备. 0.6 g聚环氧乙烷-聚环氧丙烷-聚环氧乙烷三嵌段共聚物(P123)溶解到3.4 mL乙醇中作为A溶液待用. 1.6 g ZrClO₂·8H₂O溶解于2 mL蒸馏水中, 加入4 mL乙醇搅拌20 min作为B溶液待用. H₅PMo₁₀

引用格式: 李月, 李一鸣, 张雪艳, 等. 多金属氧酸盐纳米纤维催化O₂氧化5-HMF. 科学通报, 2020, 65: 940-947

Li Y, Li Y M, Zhang X Y, et al. POMs nanofibers for the oxidation of 5-HMF with O₂ (in Chinese). Chin Sci Bull, 2020, 65: 940-947, doi: 10.1360/TB-2019-0109

V_2O_4 参照文献[7,8]合成. 称取一定质量的HPMoV溶解到2.5 mL水中作为C溶液待用. 将B溶液缓慢加入A溶液中搅拌2 h后, 滴加C溶液, 室温下剧烈搅拌12 h. 向溶液中缓慢加入10 g 10%的PVA溶液, 60°C水浴加热条件下搅拌4 h得到溶胶液.

HPMoV/ ZrO_2 /PVA溶胶溶液作为前驱体用于静电纺丝制备复合纳米纤维^[9,10]. 将收集的HPMoV/ ZrO_2 /PVA在350°C煅烧6 h除去模板和聚合物, 得到不同HPMoV负载量的HPMoV/meso- ZrO_2 (*n*-f)(*n*=5%, 14%, 23%, 28%和35%, f表示纳米纤维)纳米纤维.

(ii) 催化氧气氧化5-HMF. 5-HMF(126 mg, 1 mmol), 催化剂(80 mg)与5 mL的二甲基亚砜(DMSO)放入到高压反应釜中, 温度达到120°C后通入1.0 MPa的 O_2 , 磁力搅拌下反应7 h. 反应结束后反应体系冷却至室温, 通过离心将催化剂与产物进行分离. 将分离出的催化剂分别用DMSO和乙醇洗涤多次后置于烘箱中干燥, 用于重复使用. 利用高效液相色谱(HPLC)检测5-HMF产率及产物产率. 5-HMF产率及产物利用HPLC分析仪(紫外检测器)进行检测与分离. 流动相为乙腈与0.1%的乙酸溶液(*v*:*v*=10:90), 流速为0.9 mL min⁻¹, 在280 nm波长处进行检测.

(iii) 仪器与方法. 红外光谱(Agilent Technologies Cary 630 FT/IR红外光谱仪)、固体紫外漫反射光谱(UV-2600 UV-vis spectrophotometer (Shimadzu), 200~800 nm)、X射线粉末衍射光谱(Rigaku D/max-2000 VPC X-ray衍射仪, Cu K α , λ =0.154178 nm, 扫描范围5°~90°)、固体磷核磁(NMR Bruker AVANCE III 400 MB, 202.5 MHz)、热重分析仪(Perkin-Elmer

TGA7)、电感耦合等离子体原子发射光谱仪(LEEMAN Prodigy)、比表面积分析仪(ASAP 2020M型, 90°C脱气处理8 h后在77 K条件下进行 N_2 吸附测定)及扫描电子显微镜(SEM, HITACHI SU8010)、透射电子显微镜(TEM, JOEL JEM-2020).

2 结果与讨论

2.1 结构表征

红外谱图(图1(a))在1100~700 cm⁻¹范围内出现Keggin结构特征峰, 与母体HPMoV(1056, 954, 866和730 cm⁻¹)相比, 1065, 944和835 cm⁻¹处特征峰峰位有所偏移, 证明 $PMo_{10}V_2O_{40}^{5-}$ 阴离子与 ZrO_2 载体间存在一定的相互作用^[11], HPMoV/meso- ZrO_2 (f)纳米纤维结构稳定, 不是简单的附着形成, 可以保证HPMoV在催化反应中不溶脱. ZrO_2 737 cm⁻¹处的 Zr-O伸缩振动峰偏移到800 cm⁻¹处^[12], 证明POMs阴离子和骨架间存在一定的相互作用. 图1(b)给出 ZrO_2 , HPMoV/meso- ZrO_2 (5-f), HPMoV/meso- ZrO_2 (14-f), HPMoV/meso- ZrO_2 (23-f), HPMoV/meso- ZrO_2 (28-f), HPMoV/meso- ZrO_2 (35-f)和HPMoV的吡啶吸附红外谱图. 由图可以看出, 在1545和1450 cm⁻¹的振动吸收归因于复合材料的Brønsted酸和Lewis酸的振动吸收. ZrO_2 在1450 cm⁻¹处出现振动吸收, 说明其具有Lewis酸性. 随着HPMoV负载量递增, 催化剂的总酸量呈现递增的趋势. 其中, Lewis酸/Brønsted酸摩尔比随着HPMoV负载量增多逐渐减小. 根据电位滴定法测得催化剂的酸性分别为: HPMoV/meso- ZrO_2 (5-f)(0.17 mmol g⁻¹)<HPMoV/meso- ZrO_2 (14-f)

图1 (网络版彩色)HPMoV/meso- ZrO_2 (f)红外光谱(a)和的吡啶吸附红外光谱(b). ① ZrO_2 -f; ② HPMoV/meso- ZrO_2 (5-f); ③ HPMoV/meso- ZrO_2 (14-f); ④ HPMoV/meso- ZrO_2 (23-f); ⑤ HPMoV/meso- ZrO_2 (28-f); ⑥ HPMoV/meso- ZrO_2 (35-f); ⑦ HPMoV
Figure 1 (Color online) FT-IR spectra of HPMoV/meso- ZrO_2 (a) and pyridine adsorption FT-IR spectra of HPMoV/meso- ZrO_2 (b). ① ZrO_2 -f; ② HPMoV/meso- ZrO_2 (5-f); ③ HPMoV/meso- ZrO_2 (14-f); ④ HPMoV/meso- ZrO_2 (23-f); ⑤ HPMoV/meso- ZrO_2 (28-f); ⑥ HPMoV/meso- ZrO_2 (35-f); ⑦ HPMoV

(0.22 mmol g^{-1}) < meso-ZrO₂(f) (0.36 mmol g^{-1}) < HPMoV/meso-ZrO₂(23-f) (0.41 mmol g^{-1}) < HPMoV/meso-ZrO₂(28-f) (0.47 mmol g^{-1}) < HPMoV/meso-ZrO₂(35-f) (0.51 mmol g^{-1}) < HPMoV (2.66 mmol g^{-1}). Lewis/Brønsted的比分别为1.1:1, 0.71:1, 0.24:1, 0.11:1, 0.02:1.

HPMoV/meso-ZrO₂(*n*-f)固体紫外-可见漫反射光谱(图2(a))在215和270 nm出现Keggin特征峰, 归属于Mo-O的荷移跃迁^[13,14], 证明多阴离子被成功固载到ZrO₂纳米纤维上. 图2(b)分别给出HPMoV和HPMoV/meso-ZrO₂(23-f)的固体磷核磁谱. 与母体HPMoV($\delta -4.55$)相比, HPMoV/meso-ZrO₂(23-f)在-4.95处出现一个尖峰和-2.41处一个肩峰, 表明制备过程中多阴离子的Keggin结构保持不变, 且与ZrO₂骨架间存在一定的相互作用^[12]. 复合物HPMoV/meso-ZrO₂(*n*-f)X射线粉末衍射光

谱(图3(a))表明在HPMoV负载量低于23%时, 15°~39°出现无定型ZrO₂宽的衍射峰, 证明POMs阴离子以分散态存在于ZrO₂载体上^[12]. 当HPMoV负载量达到35%时, 在8.75°, 17.26°, 27.63°, 28.44°出现HPMoV的特征衍射峰, 表明HPMoV以聚集态被固载在ZrO₂上. 图3(b)给出了HPMoV的热重曲线, HPMoV在710°C发生分解, 保证了多金属氧酸盐在高温煅烧去除模板剂时, 结构不会被破坏.

复合材料的形貌通过SEM和TEM进行表征(图4和5), 可以看出复合材料均是直径在200~400 nm范围内的纳米纤维. HPMoV/meso-ZrO₂(23-f)的TEM(23%)中可以看出纳米纤维具有均匀的孔结构, X射线能谱分析(EDAX, 图5(b))中得出Zr, P, Mo, V的含量分别为31.02%, 0.62%, 8.70%和1.04%, 对应P:Mo:V摩尔比为

图2 (网络版彩色)HPMoV和HPMoV/meso-ZrO₂(*n*-f)的X射线粉末衍射光谱(a)与HPMoV的热重曲线(b). ① HPMoV; ② HPMoV/meso-ZrO₂(35-f); ③ HPMoV/meso-ZrO₂(28-f); ④ HPMoV/meso-ZrO₂(23-f); ⑤ HPMoV/meso-ZrO₂(14-f); ⑥ HPMoV/meso-ZrO₂(5-f); ⑦ meso-ZrO₂-f
Figure 2 (Color online) The XRD spectra of HPMoV/meso-ZrO₂(*n*-f) (a) and the TGA curve of HPMoV (b). ① HPMoV; ② HPMoV/meso-ZrO₂(35-f); ③ HPMoV/meso-ZrO₂(28-f); ④ HPMoV/meso-ZrO₂(23-f); ⑤ HPMoV/meso-ZrO₂(14-f); ⑥ HPMoV/meso-ZrO₂(5-f); ⑦ meso-ZrO₂-f

图3 (网络版彩色)HPMoV和HPMoV/meso-ZrO₂(*n*-f)固体紫外-可见漫反射光谱(a)与HPMoV/meso-ZrO₂(23)的固体磷核磁(b). ① HPMoV; ② HPMoV/meso-ZrO₂(35-f); ③ HPMoV/meso-ZrO₂(28-f); ④ HPMoV/meso-ZrO₂(23-f); ⑤ HPMoV/meso-ZrO₂(14-f); ⑥ HPMoV/meso-ZrO₂(5-f)
Figure 3 (Color online) The DR-UV-vis spectra of HPMoV/meso-ZrO₂(*n*-f) (a) and the ³¹P MAS NMR of HPMoV/meso-ZrO₂(23) (b). ① HPMoV; ② HPMoV/meso-ZrO₂(35-f); ③ HPMoV/meso-ZrO₂(28-f); ④ HPMoV/meso-ZrO₂(23-f); ⑤ HPMoV/meso-ZrO₂(14-f); ⑥ HPMoV/meso-ZrO₂(5-f)

图4 HPMoV/meso-ZrO₂(*n*-f)的SEM。(a) HPMoV/meso-ZrO₂(5-f); (b) HPMoV/meso-ZrO₂(14-f); (c) HPMoV/meso-ZrO₂(23-f); (d) HPMoV/meso-ZrO₂(28-f); (e) HPMoV/meso-ZrO₂(35-f)

Figure 4 The SEM images of HPMoV/meso-ZrO₂(5-f) (a), HPMoV/meso-ZrO₂(14-f) (b), HPMoV/meso-ZrO₂(23-f) (c), HPMoV/meso-ZrO₂(28-f) (d) and HPMoV/meso-ZrO₂(35-f) (e)

图5 (网络版彩色)HPMoV/meso-ZrO₂(23-f)的TEM图(a)和EDAX能谱(b)

Figure 5 (Color online) The TEM image of HPMoV/meso-ZrO₂(23-f) (a) and the EDAX of HPMoV/meso-ZrO₂(23-f) (b)

1:10:2, 表明复合材料保持Keggin结构, HPMoV的负载量为23%。

复合材料HPMoV/meso-ZrO₂(f)的氮气吸附-脱附等温线(图6(a))表明, 复合物表现第四类型吸附-脱附等温线: 在 $P/P_0 = 0.45 \sim 0.90$ 处存在H1滞留环, 说明该类催化剂具有常规介孔结构^[15]。HPMoV/meso-ZrO₂(*n*-f)的孔径分布曲线(图6(b))可以看出, 复合材料表现出均匀的孔尺寸且孔径大小与HPMoV的负载量有直接关系, 随着HPMoV负载量的增多(5%~35%)孔径逐渐减小(3.86~3.16 nm)。

2.2 氧气氧化5-HMF的催化活性

考察了不同催化剂对5-HMF的氧化反应的活性及产物选择性的影响(图7)。发现没有催化剂时, 9 h 5-

HMF的转化率只有3.7%, 同时仅有0.4%的DFF产生, 说明氧气的氧化能力低。使用ZrO₂介孔纳米纤维作为催化剂, 9 h 5-HMF转化率和DFF产率分别达到43.1%和28.3%, 表明ZrO₂-f氧化催化能力有限, 但其一定的Lewis酸性(0.36 mmol g⁻¹, 催化剂的总酸量和Lewis酸性分布利用电位滴定和吡啶吸附红外方法测定^[16])有利于DFF的生成^[17]。HPMoV作为均相催化剂(总酸量2.66 mmol g⁻¹), 9 h催化5-HMF转化率为99.9%, DFF产率达到49.4%。利用HPMoV/meso-ZrO₂(*n*-f)作为催化剂, 5-HMF的转化率和DFF的产率均表现随HPMoV负载量变化而变化的性质, 即和复合催化剂总酸量、Lewis/Brønsted(L/B)酸之比呈现一定的关系。随着HPMoV负载量从5%增加到23%, 复合催化剂的酸量从0.17 mmol/g提高到0.41 mmol/g, 反应7 h 5-HMF转化

图6 (网络版彩色)HPMoV/meso-ZrO₂(*n*-f)的氮气吸附-脱附等温线(a)和孔径分布曲线(b). ① HPMoV/meso-ZrO₂(35-f); ② HPMoV/meso-ZrO₂(28-f); ③ HPMoV/meso-ZrO₂(23-f); ④ HPMoV/meso-ZrO₂(14-f); ⑤ HPMoV/meso-ZrO₂(5-f); ⑥ meso-ZrO₂-f
Figure 6 (Color online) N₂-sorption analysis revealed the porosity (a) and textural properties (b) of HPMoV/meso-ZrO₂(*n*-f). ① HPMoV/meso-ZrO₂(35-f); ② HPMoV/meso-ZrO₂(28-f); ③ HPMoV/meso-ZrO₂(23-f); ④ HPMoV/meso-ZrO₂(14-f); ⑤ HPMoV/meso-ZrO₂(5-f); ⑥ meso-ZrO₂-f

图7 (网络版彩色)不同催化剂的催化活性随时间变化曲线及产物分布曲线. (a) HMF转化率曲线; (b) DFF产率曲线; (c) HMFCA产率曲线; (d) FDCA产率曲线

Figure 7 (Color online) The oxidation of 5-HMF and product distribution curve in the different catalysts. The conversion of 5-HMF (a), yields of DFF (b), HMFCA (c) and FDCA (d)

率和DFF选择性从60.1%和96.3%变化为96.4%和93.3%。继续提高HPMoV负载量到35%，5-HMF的转化率提高到97.7%，而DFF选择性下降到75.8%。HPMoV/meso-ZrO₂(35-f)总酸量随HPMoV负载量的提高而增加到0.51 mmol/g，但也仅对5-HMF的产率促进不到2%，

而DFF的选择性降低近20%。说明对于复合催化剂HPMoV/meso-ZrO₂(*n*-f)，Brønsted酸性对于提高5-HMF转化有利，而酸性的比例影响产物的选择性：5%负载量对应L/B比为1.1:1，23% 对应L/B比为0.24:1，和35% 对应L/B比为0.04:1。即提高复合催化剂的L酸性，可以

提高DFF的选择性。同时催化剂的Lewis酸性也影响到5-羟甲基-2-呋喃甲酸(HMFCA)的产率,但没有和HPMoV的担载量呈现一定的关系。从FDCA的产率看,强的Brønsted酸性催化剂有利于FDCA的产生。但对于HPMoV/meso-ZrO₂(*n*-f), HMFCA和FDCA的产率均没有超过10%和5%,说明该类催化剂表现出高的5-HMF选择性氧化为DFF。当L/B比为0.24:1时,复合纳米纤维HPMoV/meso-ZrO₂(23-f)表现出最高的DFF产率89.9%。因此,控制复合催化剂的L/B比可以提高DFF的选择性。不具有一维纳米纤维结构的复合催化剂HPMoV/meso-ZrO₂(23)在5-HMF氧化反应中也表现出一定的催化活性,7 h 5-HMF的转化率和DFF的产率分别为76.2%和59.6%,与纳米纤维复合催化剂活性的差异源于纳米纤维高的比表面积(59.2 m² g⁻¹)。HPMoV/meso-ZrO₂(23-f)随反应时间延长,5-HMF转化率和DFF产率呈现递增的趋势,当反应时间为7 h时,5-HMF转化率为96.4%,DFF产率为89.9%。继续延长反应时间到8或9 h,5-HMF的转化率接近100%,DFF的产率分别减少了2.4%和8.6%,表明过度延长反应时间DFF会发生过度氧化。最优反应条件为:126 mg 5-HMF, 80 mg催化剂,反应温度120℃,5 mL DMSO,反应时间7 h,得到5-HMF转化率为96.4%,DFF产率为89.9%。

复合纳米纤维催化剂在5-HMF催化氧化反应中表现出良好的循环使用性和高稳定性。重复使用10次后,催化活性没有明显的降低(图8),10次反应中HPMoV的总溶脱量仅为2.4%。反应后³¹P固体核磁(图9(a))、SEM(图9(b))及TEM(图9(c))结果表明,催化剂保持其原始结构和形貌,说明催化剂具有良好的结构和形貌的稳定性。利用ICP测定反应后溶液,未检测到Mo和V元素,

图8 (网络版彩色)催化剂HPMoV/meso-ZrO₂(23)的重复使用性能
Figure 8 (Color online) Cycling runs in the oxidation of 5-HMF in the presence of HPMoV/meso-ZrO₂(23)

说明催化剂在反应过程中没有脱落,进一步证明了催化剂的稳定性。

2.3 氧气氧化5-HMF的可能反应机理

通过猝灭实验研究了本反应机理^[18]。图10(a)可以看出,NaN₃存在条件下,5-HMF的转化率仅为5.4%,而另外两种猝灭剂几乎对5-HMF的氧化无影响,说明该反应是催化剂促进氧气产生单线态氧自由基。为了进一步确定单线态氧自由基的产生,用1,3-二苯基苯并呋喃(DPBF)为猝灭剂^[18]对催化剂/O₂体系通过随时间变化的紫外吸收光谱进行测试(图10(b))。黑暗条件下,不加入HPMoV/meso-ZrO₂(23)时,归属于DPBF的417 nm处吸收峰仅有非常微弱的降低;而加入HPMoV/meso-ZrO₂(23)和氧气的溶液,因产生的单线态氧与DPBF发生反应,导致DPBF浓度下降,417 nm处的吸收带明显

图9 (网络版彩色)催化剂HPMoV/meso-ZrO₂(23)反应前后³¹P MAS NMR(a)、SEM图(b)和TEM图(c)。① 反应后;② 反应前
Figure 9 (Color online) The ³¹P MAS NMR of HPMoV/meso-ZrO₂(23) (a), SEM of HPMoV/meso-ZrO₂(23) after the reaction (b), and TEM of HPMoV/meso-ZrO₂(23) after the reaction (c). ① After the reaction; ② before the reaction

图10 (网络版彩色)催化反应猝灭实验(a)和DPBF随时间变化的紫外吸收曲线(b)
Figure 10 (Color online) Quenching experiments (a) and UV absorption curve of DPBF with time (b)

降低,最后在3 h后DPBF在417 nm处吸收峰完全消失表明,该反应活性物种是由于HPMoV/meso-ZrO₂(23)促进氧气产生单线态氧自由基。

3 结论

利用静电纺丝技术合成了HPMoV/meso-ZrO₂(f)纳

米纤维,并发现在氧气氧化5-HMF的反应中表现高反应活性。其活性主要来源于:HPMoV适当的氧化还原能力;介孔纳米纤维材料高的比表面积;ZrO₂载体的Lewis酸性;适当的L/B比,HPMoV/meso-ZrO₂(23)对于催化氧气氧化5-HMF表现出高的活性和产物DFF的选择性。

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Summary for “多金属氧酸盐纳米纤维催化O₂氧化5-HMF”

POMs nanofibers for the oxidation of 5-HMF with O₂

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2,5-Diformylfuran (DFF) is a versatile compound that can be used as a precursor in the synthesis of various value-added products, which can be obtained from aerobic oxidation of 5-hydroxymethylfurfural (HMF). However, aerobic oxidation of 5-HMF gives rise to several pathways and products containing DFF, 2,5-furandicarboxylic acid (FDCA), or maleic anhydride (MA). To date, both homogeneous and heterogeneous metal catalysts have been explored for the oxidation of HMF to DFF with various oxidants. It was found that materials containing vanadium showed higher efficiency with conversions ranging from 84% to 100% and DFF yields of 82%–99.9% at 120–140°C for 3–11 h in dimethyl sulfoxide (DMSO). Selective oxidation of 5-HMF depended on the nature of the catalysts and supports. Polyoxometalates (POMs) are widely applied in catalysis especially in catalytic transformation of biomass. Especially, POMs containing vanadium had been found to be potential for oxidation of HMF to produce a series of products including DFF and MA. The diversity in structure and components allows POMs to be most active in acidic and redox catalysis. Compared to their homogeneous catalysis, heterogeneous systems showed more favorable in easy separation and reuse, introduction of special active sites belonging to supports, enhancement in surface area. Under such circumstances, heterogeneous POM catalysts are developed using microporous, mesoporous and macroporous SiO₂, TiO₂ and ZrO₂ as supports. Compared to powdered mesoporous materials, electrospun nanofibers are good candidates because of their high surface-to-volume ratios. Herein, trifunctional H₅PMo₁₀V₂O₄₀/meso-ZrO₂(f) had been synthesized using combined electrospinning and surfactant pore-forming technology, which were characterized by IR, ³¹P MAS NMR, XRD, SEM, TEM, and N₂ adsorption-desorption measurement. Combination of IR, ³¹P MAS NMR, XRD, BET surface areas, SEM and TEM could confirm that POM molecules were loaded on ZrO₂ nanofibers (200–400 nm) with mesoporous structure. It was found that decorating ZrO₂ nanofibers by H₅PMo₁₀V₂O₄₀ generated enhanced catalytic activity by emerging their unique individual properties of redox ability, Brønsted acidity, Lewis acidity, and nanofiber structure with higher surface area. H₅PMo₁₀V₂O₄₀/meso-ZrO₂(f) materials were evaluated in aerobic oxidation of 5-HMF to DFF. The conversion of HMF followed the order: HPMoV/meso-ZrO₂(5-f) (0.17 mmol g⁻¹, 60.1%) < HPMoV/meso-ZrO₂(14-f) (0.22 mmol g⁻¹, 79.8%) < meso-ZrO₂(f) (0.36 mmol g⁻¹, 92.3%) < HPMoV/meso-ZrO₂(23-f) (0.41 mmol g⁻¹, 94.2%) < HPMoV/meso-ZrO₂(28-f) (0.47 mmol g⁻¹, 95.6%) < HPMoV/meso-ZrO₂(35-f) (0.51 mmol g⁻¹, 96.4%) < HPMoV (2.66 mmol g⁻¹, 99.9%), which followed the increase of HPMoV loading hence the Brønsted acidity. The DFF yields depended on their Lewis acidity as HPMoV/meso-ZrO₂(35-f) (B/L=0.04:1, yield=74.6%) < HPMoV/meso-ZrO₂(28-f) (B/L=16.8:100, yield=80.2%) < HPMoV/meso-ZrO₂(23-f) (B/L=0.11:1, yield=89.9%) < HPMoV/meso-ZrO₂(14-f) (B/L=0.71:1, yield=74.5%) < HPMoV/meso-ZrO₂(5-f) (Lewis acidity/Brønsted basicity = 1.1:1, yield=56.8%). Therefore, balancing the L/B ratio could control the DFF generation. As results, H₅PMo₁₀V₂O₄₀/meso-ZrO₂(23) nanofiber (23, represented the POM amount) was found to be most active in aerobic oxidation of 5-HMF to give 89.9% yield of DFF at 96.4% conversion in DMSO at 120°C for 7 h. The mechanism study showed that the generated O₂ was the active site in this aerobic oxidation being catalyzed by H₅PMo₁₀V₂O₄₀. Moreover, H₅PMo₁₀V₂O₄₀/meso-ZrO₂(f) showed good stability and duration for being reused at least ten times without leaching of POMs from ZrO₂ nanofibers.

polyoxometalates, nanofibers, oxygen oxidation, 5-HMF

doi: [10.1360/TB-2019-0109](https://doi.org/10.1360/TB-2019-0109)