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无机-有机杂化铜钒酸盐 $Cu_2(eIM)_6[V_4O_{12}]$的合成及其硫醚氧化催化性能

李季坤[1*], 魏传平[1], 胡长文[2*]

1. 泰山学院化学化工学院, 泰安 271021;
2. 北京理工大学化学与化工学院, 原子分子簇科学教育部重点实验室, 北京 100081
* 联系人, E-mail: lijk0212@163.com; cwhu@bit.edu.cn

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摘要 在三乙胺存在下, 以中性的六核钒氧簇$V^{IV}_2V^{V}_4O_{14}(eIM)_8$(eIM=1-乙基咪唑)为钒源, 与$Cu(OAc)_2·H_2O$反应调控合成了无机-有机杂化的铜钒酸盐$Cu_2(eIM)_6[V_4O_{12}]$(**1**), 并利用X射线单晶衍射、傅里叶转换红外光谱、元素分析及X射线粉末衍射等对其结构进行了表征, 进一步考察了其在硫醚氧化反应中的催化性能. 结果表明, 在以环境友好的H_2O_2为氧化剂的条件下, 化合物**1**对硫醚选择性氧化表现出很好的催化活性. 值得指出的是, 通过控制反应条件, 利用相同的氧化剂, 硫醚能以较高转化率和选择性分别氧化制备亚砜或砜, 而**1**作为非均相催化剂在保持结构稳定的同时至少能循环使用3次而没有明显的活性降低.

关键词 无机-有机杂化, 铜钒酸盐, 非均相催化, 硫醚氧化

多酸, 即多金属氧酸盐(polyoxometalates, POMs)是一类多核配合物, 因其具有可逆接受电子和质子的能力、簇骨架结构、尺寸的可调变性以及高的化学稳定性等优异的物理化学特性[1,2], 在催化[3,4]、材料[5,6]、生物[7]及能源[8]等领域有着广泛的应用前景. 作为POMs的重要分支, 钒酸盐多样的结构、多重的价态以及多变的配位构型使其成为设计和组装基于POMs的无机-有机杂化材料的优选构筑模块[9]. 过渡金属杂化钒酸盐由于金属-有机单元和钒氧簇之间的协同作用使其在功能材料制备领域有潜在的应用价值, 但由于其结构多样, 很难在晶体结构和合成条件之间找出必然的联系, 使其调控合成面临很多挑战. Arriortua课题组[10]通过合理控制反应条件, 在杂化钒酸盐的调控合成领域做了有益的探索, 揭示了杂化钒酸盐Ni(II)/Bpe/V_xO_y和Ni(II)/4,4′-Bpy/V_xO_y(Bpe=1,2-二(4-吡啶基)乙烯, Bpy=4,4′-联吡啶)中V的配位环境以及超分子结构与反应体系的pH、反应物浓度以及温度等合成条件之间的联系, 他们出色的工作促使我们进一步研究该类材料的调控合成并拓展其应用领域.

另一方面, 通过硫醚选择性氧化制备的亚砜和砜是重要的化学反应中间体, 可用于合成生物分子[11]、手性助剂[12]以及过氧转移剂[13,14]等. 同时, 硫醚的氧化也是石油化工行业油品脱硫[15]以及化学战剂芥子毒气(二氯二乙硫醚)氧化降解[16]所关注的问题. 以环境友好的H_2O_2为氧化剂选择性氧化硫醚, 不仅能避免传统氧化剂的等剂量或过量使用以及产生对环境有害的副产物[17~19], 还能进一步提高产物

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Li J K, Wei C P, Hu C W. Synthesis and catalytic property of inorganic-organic hybrid copper vanadate $Cu_2(eIM)_6[V_4O_{12}]$ in selective oxidation of sulfides (in Chinese). Chin Sci Bull, 2018, 63: 3342–3349, doi: 10.1360/N972018-00613

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亚砜或砜的选择性. 因此, 从环保和经济性角度出发, 我们需要大力发展以H_2O_2为氧化剂的高效的硫醚选择性氧化体系.

含钒的化合物或POMs在很多氧化催化反应中表现出良好的催化性能, 而对无机-有机杂化钒酸盐催化性能研究的例子并不多见[20,21]. 2015年, 本课题组[22]在无机-有机杂化钒酸盐的调控合成及催化性能方面也做了探索性研究, 利用相同起始原料, 通过精细调控反应条件, 合成了3个不同结构的1-甲基咪唑(mIM)配位铜钒酸盐化合物α-Cu(mIM)$_4$[V_2O_6], β-Cu(mIM)$_4$[V_2O_6]和Cu(mIM)$_2$[V_2O_6], 进一步研究了其硫醚氧化催化性能. 结果表明, α-Cu(mIM)$_4$[V_2O_6]在非均相条件下能高效、高选择性的催化硫醚氧化生成相应的亚砜产物, 且经过多次循环使用而催化活性没有明显的降低.

为了丰富无机-有机杂化钒酸盐的调控合成策略, 进一步探索催化剂结构与催化活性与选择性之间的关系, 本文利用有机溶剂中溶解度较好的中性六核钒氧簇$V^{IV}_2V^{V}_4O_{14}$(eIM)$_8$为钒源, 通过调控反应条件, 制备得到具有四核钒氧簇的无机-有机杂化的铜钒酸盐Cu$_2$(eIM)$_6$[V_4O_{12}](**1**), 研究了其硫醚氧化催化性能. 值得指出的是, 通过调控氧化剂H_2O_2的用量以及反应温度等条件, 可以高选择性的分别制备相应的亚砜或砜(图1), 该研究为无机-有机杂化钒酸盐催化剂的实际应用提供了实验数据参考.

1 实验

(ⅰ) 试剂与仪器. 所用化学药品和试剂均直接购买, 使用之前未进一步纯化. $V^{IV}_2V^{V}_4O_{14}$(eIM)$_8$采用本课题组[23]已报道的方法制备. 催化剂的C, H和N采用Perkin-Elmer 2400元素分析仪, Cu, V元素分析采用JYULTIMA2分析仪测试; 傅里叶转换红外光谱(FT-IR)通过溴化钾压片法在Nicolet 6700型红外光谱仪上测定; X射线粉末衍射光谱(PXRD)由Bruker D8 Advance衍射仪, 采用Cu Kα射线光源(λ=1.54056 nm)测试; X射线单晶衍射(SXRD)数据使用Bruker-AXS CCD单晶衍射仪常温下测试, 采用Mo Kα射线光源(λ=0.71073 nm), 通过半球策略进行衍射点收集, 对所收集的数据进行经验吸收校正, 结构解析与精修使用SHELXS-2014和SHELXL-2014软件程序.

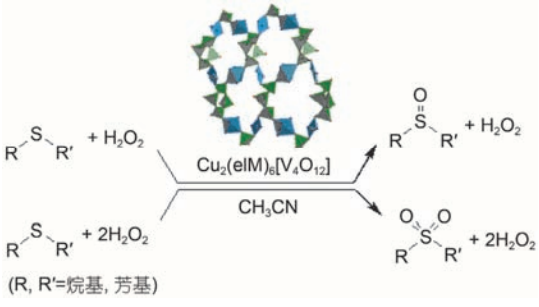


图 1 (网络版彩色)以Cu$_2$(eIM)$_6$[V_4O_{12}]为催化剂的硫醚选择性氧化示意图

Figure 1 (Color online) The diagram of sulfides selective oxidation catalyzed by Cu$_2$(eIM)$_6$[V_4O_{12}]

(ⅱ) 化合物Cu$_2$(eIM)$_6$[V_4O_{12}](**1**)的合成. 将130 mg(0.1 mmol)$V^{IV}_2V^{V}_4O_{14}$(eIM)$_8$溶于12 mL无水甲醇中, 加入0.5 mL三乙胺, 50℃下在圆底烧瓶中搅拌10 min作为溶液A; 另取一烧杯, 将40 mg(0.2 mmol) Cu(OAc)$_2$·H_2O溶于5 mL无水甲醇中搅拌作为溶液B. 将B溶液缓慢滴加到A溶液中, 在回流状态下加热6 h, 混合液冷却并过滤, 滤液在室温下静置挥发, 1周后得到深蓝色块状晶体. 产率: 65%(以V为基准). $C_{30}H_{48}Cu_2N_{12}O_{12}V_4$的元素分析结果计算值: C, 32.77%; H, 4.40%; N, 15.29%, Cu, 11.56%; V, 18.53%; 实验值: C, 32.25%; H, 4.62%; N, 15.12%; Cu, 11.24%; V, 18.16%.

(ⅲ) 化合物**1**的晶体数据. $C_{30}H_{48}Cu_2N_{12}O_{12}V_4$, M_r=1099.63. 单斜晶系, 空间群*C2/c*; *a*=22.7921(13) Å, *b*=10.3487(6) Å, *c*=19.6782(11) Å; β=109.8540(10); *V*=4365.6(4) Å^3; *Z*=8; ρ=1.673 g cm^{-3}; *T*=298(5) K; R_1=0.0424; wR_2=0.1175; GOF(F^2)=1.017. 详细晶体学数据请参阅剑桥晶体结构数据库CCDC1845074.

(ⅳ) 硫醚选择性催化氧化. 亚砜: 硫醚(0.25 mmol, 1 equiv.)溶解到1 mL乙腈中, 化合物**1**(8.0 μmol, 3.2 mol%), H_2O_2(1.2 equiv.), 45℃下反应4 h; 砜: 硫醚(0.25 mmol, 1 equiv.)溶解到1 mL乙腈中, 化合物**1**(8.0 μmol, 3.2 mol%), H_2O_2(2.5 equiv.), 60℃下反应6 h. 硫醚转化率和产物选择性以1,3-二氯苯为内标物, 通过气相色谱(GC-2014C, 日本岛津)进行分析, 测试条件: 以N_2为载气, 色谱柱为Rtx-1701型毛细管柱, 样品进样量为0.4 μL, 氢离子火焰检测器(FID).

2 结果与讨论

2.1 催化剂结构表征

SXRD分析表明, 化合物Cu$_2$(eIM)$_6$[V_4O_{12}](**1**)的

不对称分子结构单元$Cu_{0.5}(eIM)_2Cu_{0.5}(eIM)V_2O_6$含有2个$Cu^{II}$离子(晶体数据中Cu原子占有率均为0.5), 1个$[V_2O_6]^{2-}$阴离子簇和3个eIM配体(图2). **1**中的Cu原子有四和六配位2种配位方式, 这在无机-有机杂化的钒酸盐结构中是比较少见的, 其中Cu1具有四配位的平面正方形几何构型, 由来自2个eIM配体的2个N原子和来自2个$[VO_4]$四面体的2个O原子形成, 而Cu2具有六配位的八面体几何构型, 由来自4个eIM配体的4个N原子和来自2个$[VO_4]$四面体的2个O原子形成(图2). 在$[V_2O_6]^{2-}$簇中, V1和V2都具有扭曲的$[VO_4]$四面体的几何构型, 其中V1的配位原子有2个来自于相邻$[VO_4]$四面体的桥O, 另外2个端O则分别与Cu1和Cu2配位, 而V2的配位原子则有2个分别来自于2个相邻$[VO_4]$四面体的桥O和2个未参与配位的端O.

化合物**1**是一个具有二维平面网状超分子结构的无机-有机杂化铜钒酸盐, 其超分子结构的形成可以通过以下两步来描述: 首先, 4个相邻的$[VO_4]$四面体通过共角的O原子相连形成$[V_4O_{12}]^{4-}$簇, 在$[V_4O_{12}]^{4-}$拟平面的同一侧, 处在$[V_4O_{12}]^{4-}$簇对位上的2个$[VO_4]$四面体利用端氧O1与$Cu[(eIM)_2]^{2+}$连接沿*c*轴形成1个一维(1D)的"之"字形链状结构, 在$[V_4O_{12}]^{4-}$拟平面的另一侧, 2个相同的$[VO_4]$四面体利用另1个端氧O3与$Cu[(eIM)_4]^{2+}$连接沿*c*轴形成第2个1D的"之"字形链状结构; 然后, 2种不同类型的1D"之"字形链以$[V_4O_{12}]^{4-}$簇为节点连接在一起沿*bc*面形成一个二维(2D)平面网状超分子结构(图S1). 价键理论计算结果表明, 化合物**1**中V原子的价态都是+V价, 而Cu的价态都是+II价, 这与化合物整体电荷平衡及结构分析结果一致.

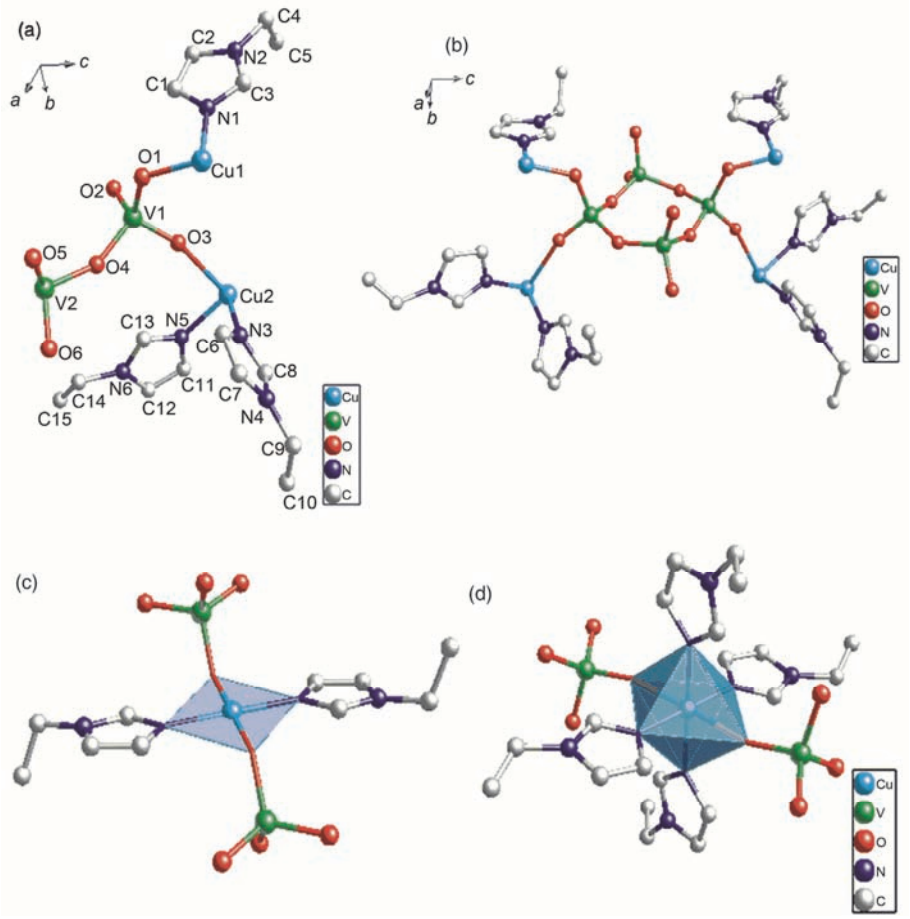


图 2 (网络版彩色)化合物**1**的晶体结构. (a) $Cu_2(eIM)_6[V_4O_{12}]$的不对称结构单元; (b) $Cu_2(eIM)_6[V_4O_{12}]$的分子结构; (c) Cu1的平面正方形配位几何构型; (d) Cu2的八面体配位几何构型

Figure 2 (Color online) The crytstal strctures of **1**. (a) Asymmetrical structural unit of $Cu_2(eIM)_6[V_4O_{12}]$; (b) the Molecular structure of $Cu_2(eIM)_6[V_4O_{12}]$; (c) square plane coordination geometry of Cu1; (d) octahedral coordination geometry of Cu2

化合物**1**的红外光谱特征振动吸收峰主要来自eIM配体和钒酸盐基团. 如图3所示, 1500~1600 cm^{-1}处的特征峰归属为eIM配体中C=C键和C=N键的伸缩振动, 而3124 cm^{-1}处出现的振动吸收峰则与C=C–H键相关; 波数在1000 cm^{-1}以下的吸收峰大部分归属于无机基团的振动吸收和两种类型的O原子的振动吸收: O_t(端氧)和O_b(桥氧), V=O_t伸缩振动及V–O–V和V–O–Cu的振动吸收峰则出现在935, 820, 775, 655 cm^{-1}等位置[24,25]. 化合物**1**的PXRD数据表明(图4), 目标产物与通过单晶结构模拟的数据能较好地吻合, 说明大量合成的化合物纯度较高, 适合用作催化剂. 热重量分析(TG)表明, 化合物**1**在140 ℃以下保持稳定, 在150~340 ℃表现一步缓慢失重过程, 对应于结构中1-乙基咪唑的失去, 本阶段实际失重52.69%与理论值52.46%也基本一致(图S2).

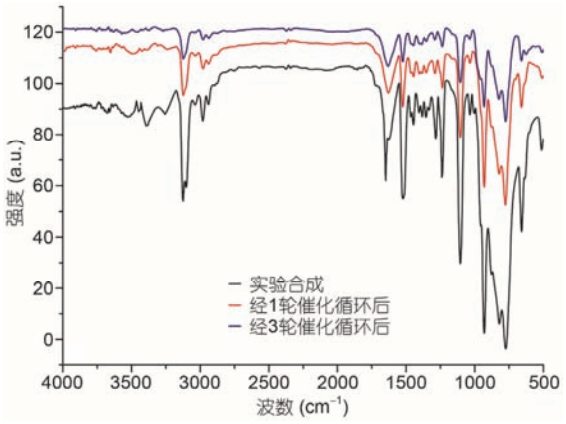


图 3 (网络版彩色)实验合成与经 1 轮和 3 轮催化循环后化合物 **1** 的FT-IR数据对比图

Figure 3 (Color online) The comparison of experimental synthesized FT-IR pattern with the FT-IR patterns collected after 1 and 3 catalytic cycles of **1**

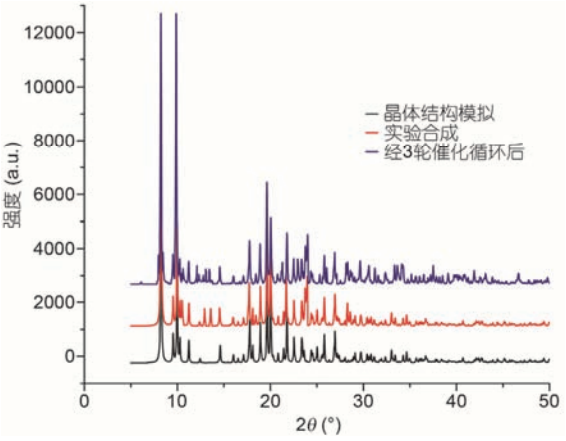


图 4 (网络版彩色)通过晶体结构模拟的XPRD数据与实验合成及 3 轮催化循环后化合物 **1** 的XPRD数据对比图

Figure 4 (Color online) The comparison of simulated XPRD pattern with the XPRD patterns of experimental synthesized and collected after 3 catalytic cycles of **1**

2.2 氧化催化性能

有机化合物的选择性氧化是由原材料转化成高附加值产品的非常重要的途径. 本文选取硫醚的氧化来考察铜钒酸盐$Cu_2(eIM)_6[V_4O_{12}]$(**1**)的催化性能, 催化剂在使用前先用H_2O_2(30%), 在45 ℃下乙腈溶液中搅拌活化30 min(催化剂/H_2O_2=1∶2, 物质量之比), 然后分离干燥备用. 以甲基苯基硫醚氧化为甲基苯基亚砜为模型反应, 在非均相反应条件下, 通过对催化剂用量、氧化剂用量、反应温度及时间等因素的优化, 甲基苯基硫醚的转化率达到98.5%, 相应亚砜的选择性高达97.5%(表1).

为了验证化合物**1**中各组分在硫醚氧化催化反应中的作用, 利用$V^{IV}_2V^{V}_4O_{14}(eIM)_8$(与化合物**1**具有相似的$[V_4O_{12}]^{4-}$阴离子簇)作催化剂, 得益于均相催化的反应条件, 甲基苯基硫醚的转化率达到99%以上, 但相应亚砜的选择性却降到91.5%(此反应条件下, 亚砜容易进一步氧化为砜). 而当选用与化合物**1**中$[Cu_2(eIM)_6]^{4+}$有当量组分的$Cu(OAc)_2·H_2O$和eIM(物质量之比为1∶3)为催化剂时, 甲基苯基硫醚的转化率和相应亚砜的选择性分别达到31.5%和100%(表1). 实验结果表明, 化合物**1**中的钒酸盐多阴离子簇对催化剂的反应活性有主要贡献, 而铜配合物的阳

表 1 不同催化剂或无催化剂作用下甲基苯基硫醚转化为甲基苯基亚砜[a)]

Table 1 Conversion of methyl phenyl sulfide to sulfoxide with different catalysts or without catalysts

催化剂	转化率(%)	选择性(%)[b)]	反应体系
化合物**1**	98.5	97.5	非均相
$V^{IV}_2V^{V}_4O_{14}(eIM)_8$	>99	91.5	均相
$Cu(OAc)_2·H_2O$+eIM (二者物质量之比=1∶3)[c)]	31.5	100	均相
无催化剂	12.5	100	–

a) 反应条件: 甲基苯基硫醚(0.25 mmol, 1 equiv.), 催化剂(8.0 μmol, 3.2 mol%), H_2O_2(1.2 equiv.), 乙腈(1 mL), 45 ℃, 4 h; b) 亚砜的选择性. 副产物砜通过GC-MS测定; c) Cu的含量等价于化合物**1**

离子部分则有助于提高催化剂的选择性, 两组分之间的协同作用, 使化合物**1**成为高活性和高选择性的非均相氧化催化剂.

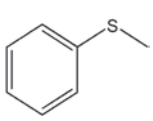
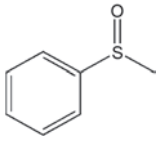
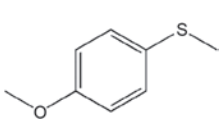
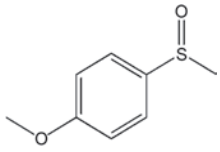
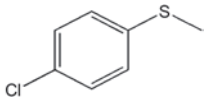
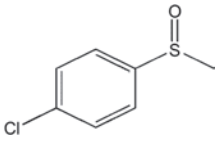
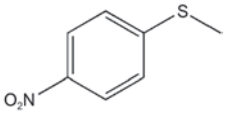
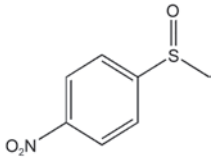
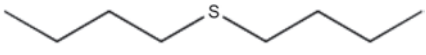
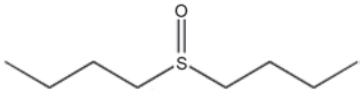
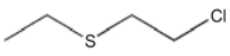
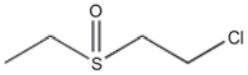
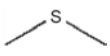
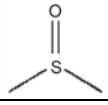
循环利用是非均相催化剂的最大优势, 鉴于化合物**1**在甲基苯基硫醚氧化反应中表现出的优异催化性能, 进一步考察了其稳定性. 在反应结束后, 化合物**1**可以利用先离心后过滤的方法简便地从反应体系中分离出来, 分离后的催化剂经过乙腈洗涤干燥后可直接用于催化循环反应. 催化剂在经过3次循环使用以后, 甲基苯基硫醚的转化率依然能达到96.5%, 相应亚砜的选择性保持在97.0%, 实验结果表明催化剂的活性和选择性没有明显地降低. 催化循环后催化剂的FT-IR(图3)和XPRD数据(图4)表明催化剂的结构没有太大的改变, 说明催化剂在该催化氧化体系中是比较稳定的.

化合物**1**在甲基苯基硫醚氧化反应中表现出的较高催化活性促使我们进一步扩大硫醚底物范围, 验证其催化反应的普适性. 化合物**1**对多种不同硫醚的氧化均具有较高的催化活性, 当在甲基苯基硫醚的苯环对位上引入空间位阻较小的供电或吸电基团后, 催化活性没有出现明显的降低且相应产物亚砜也保持了很高的选择性(表2, 第2~4条目). 在应用于脂肪族硫醚催化氧化时, 选择有代表性的二正丁基硫醚、2-氯乙基乙基硫醚(CEES, 化学战剂硫芥子气模拟物)以及二甲基硫醚作为反应底物, 发现硫醚的转化率较高, 但相应亚砜的选择性有所降低(表2, 第5~7条目).

通过调控反应条件, 利用相同的氧化剂氧化硫醚分别合成相应亚砜和砜的研究并不多见. 鉴于化合物**1**在硫醚氧化制备亚砜反应中表现出的优异催化活性和选择性, 进一步探索了其硫醚氧化制备砜的

表 2 化合物 1 催化的多种硫醚氧化为亚砜的反应[a)]

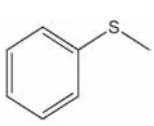
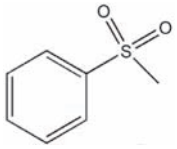
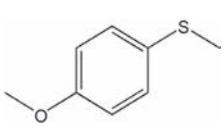
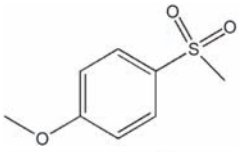
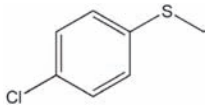
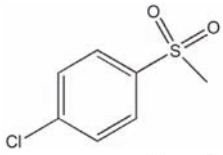
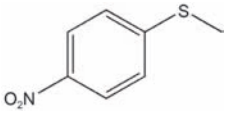
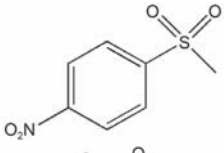
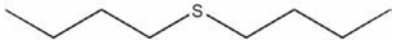
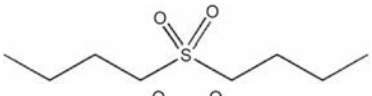
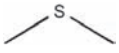
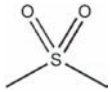
Table 2 Selective oxidation of various sulfides to sulfoxides catalysed by **1**

条目	硫醚底物	产物亚砜	转化率(%)	选择性(%)[b)]
1			98.5	97.5
2			96.5	97.5
3			94.5	98.2
4			87.4	98.5
5			92.2	95.5
6			98.7	83.5
7			–[c)]	84.5

a) 反应条件: 硫醚(0.25 mmol, 1 equiv.), **1**(8.0 μmol, 3.2 mol%), H_2O_2(1.2 equiv.), 乙腈(1 mL), 45℃, 4 h; b) 副产物砜通过GC-MS测定; c) GC不适应于分析沸点过低的化合物

表 3　化合物 1 催化的多种硫醚氧化为砜的反应[a)]

Table 3　Selective oxidation of various sulfides to sulfones catalysed by **1**

条目	硫醚底物	产物砜	转化率(%)	选择性(%)
1			>99	97.5
2			>99	97.0
3			>99	96.5
4			>99	95.5
5			98.5	95.5
6			–[b)]	93.0

a) 反应条件: 硫醚(0.25 mmol, 1 equiv.), **1**(8.0 μmol, 3.2 mol%), H_2O_2(2.5 equiv.), 乙腈(1 mL), 60℃, 6 h; b) GC不适应于分析沸点过低的化合物

反应条件, 发现通过提高氧化剂用量和反应温度及反应时间, 甲基苯基硫醚和不同取代基的单芳基硫醚(表3, 条目第1~4)以及二正丁基硫醚和二甲基硫醚(表3, 条目第5, 6)都有很好的转化率以及对应产物砜的选择性, 说明利用化合物**1**做催化剂同样适用于硫醚氧化制备砜的反应. 因化学战剂模拟物CEES氧化产物砜也有较大的毒性, 失去了化学战剂降解的意义, 所以硫醚氧化制备砜的反应没有考察CEES氧化催化.

3　结论

本文以中性的六核钒氧簇$V^{IV}_2V^{V}_4O_{14}(eIM)_8$为钒源, 在有机碱存在下制备了无机-有机杂化的铜钒酸盐化合物. 利用XSRD, FT-IR, XPRD以及元素分析等对其结构进行了表征, 进一步考察了其硫醚氧化反应的催化性能. 结果表明, 在以H_2O_2为氧化剂的条件下, 化合物$Cu_2(eIM)_6[V_4O_{12}]$(**1**)中的钒酸盐多阴离子簇和铜配合物的阳离子两组分之间的协同作用, 使其成为高活性和高选择性的非均相氧化催化剂. 而在相同的氧化剂H_2O_2存在下, 通过控制催化反应条件, 我们能以较好的收率和普适性由硫醚氧化分别制备亚砜和砜. 作为非均相催化剂, 化合物**1**能重复利用, 催化活性没有明显的降低, 其经过3个循环后甲基苯基硫醚的转化率依然能达到96.5%. 后续的工作中我们将继续探索以中性的钒氧簇来制备高催化活性和高稳定性的过渡金属钒酸盐化合物的合成策略, 并进一步拓展到其他催化模型反应.

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补充材料

图 S1 化合物 **1** 的“之”字形一维链和二维平面网状超分子结构
图 S2 化合物 **1** 的 TG 图

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Summary for "无机-有机杂化铜钒酸盐 $Cu_2(eIM)_6[V_4O_{12}]$的合成及其硫醚氧化催化性能"

Synthesis and catalytic property of inorganic-organic hybrid copper vanadate $Cu_2(eIM)_6[V_4O_{12}]$ in selective oxidation of sulfides

Jikun Li[1*], Chuanping Wei[1] & Changwen Hu[2*]

[1] *College of Chemistry and Chemical Engineering, Taishan University, Tai'an 271021, China;*
[2] *Key Laboratory of Cluster Science of Ministry of Education, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, China*
* Corresponding authors, E-mail: lijk0212@163.com; cwhu@bit.edu.cn

Polyoxometallates (POMs) a re familiar inorganic building blocks for their rich structural diversities and potential applications in many fields, such as catalysis, magnetism, and energy, etc. As an important subclass of POMs, vanadates are a promising candidate to construct POMs-based hybrid materials due to their unprecedented structural diversity, mixed valency, and variable coordination geometries. Inorganic-organic hybrid vanadates with first-row transition metals show very rich structural diversities. Further, the hybrid vanadates are expected to exhibit improved properties by the synergetic interaction between the metal-organic subunits and the vanadium oxide. Thus, it is essential but remains challenging to control the synthesis of inorganic-organic hybrid vanadates rationally. Recently, our group reported several examples of inorganic-organic hybrid vanadates by controlling the synthetic reaction conditions and further explored their catalytic properties in the oxidation of sulfides, alcohols and olefin, etc.

In order to continue our research in the controlling synthesis and catalytic properties of inorganic-organic hybrid vanadates, here we synthesized a hybrid copper vanadate $Cu_2(eIM)_6[V_4O_{12}]$ (**1**). In the synthetic procesure, a neutral V6 cluster $V^{IV}_2V^{V}_4O_{14}(eIM)_8$ (eIM=1-ethylimidazole) which was reported in our earlier research, was selected as vanadium source and reacted with $Cu(OAc)_2{\cdot}H_2O$ in the presence of triethylamine by rationally controlling the reaction conditions. Compound **1** was fully characterzized by single-crystal X-ray diffraction (SXRD) and powder X-ray diffraction (PXRD) analyses, FT-IR spectroscopy and element analyses, etc. SXRD analyse shows that the molecular struture of **1** contains a $[V_4O_{12}]^{4-}$ anion cluster and two types of copper complex cation, $Cu[(eIM)_2]^{2+}$ and $Cu[(eIM)_4]^{2+}$. All the $[V_4O_{12}]^{4-}$ anion clusters were further connected to a two-dimensional (2D) plane network supramolecular structure by four- and six-coordinated copper complexes cations with the eIM ligands. Two types of coordination modes existing in the same tructure is rare in complexes of inorganic-organic hybrid vanadates.

Selective oxidation of organic compounds, such as sulfides, alcoholes, aromatic and aliphatic hydrocarbons, etc., is one of the most vital transformations for upgrading raw starting materials into high value added products. Vanadium-containing materials show excellent catalytic performance in selective oxidation of these compounds. Given the importance of sulfoxides and sulfones as intermediates of biologic molecules, chiral auxiliaries and oxo-transfer reagents, the high selective oxidation of sulfides to obtain these compounds is more desirable. As a green oxidant, H_2O_2 offers significant enviromental and economic benefits over traditional stoichiometric oxidants. First, we selected the oxidation of methyl phenyl sulfide as a model reaction to evaluate the catalytic activities of compound **1**. We evaluated the influencing factors of the ammount of catalyst and oxidant, the reaction temperature and time. Under the optimized conditions, the conversion of methyl phenyl sulfide and the selectivity to corresponding sulfoxide up to 98.5% and 97.5%, respectively. Other aromatic sulfides were also examined and no obvious decrease of the catalytic activity was observed when electron donor or acceptor groups with less steric hindrance were introduced in the monophenyl sulfides (conversion from 87.4% to 96.5%; selectivity toward corresponding sulfoxides from 97.5% to 98.5%). When the reaction conditions were applied to aliphatic sulfides including *n*-butyl sulfide, 2-chloroethyl ethyl sulfide and dimethyl sulfide, the high conversion (from 92.2% to 98.7%) and selectivity toward corresponding sulfoxides (from 83.5% to 95.5%) were also abtained. We also probed the role of each active center of compound **1** and found that the cooperation between copper complex cations and vanadate anions played some synergistic role in the sulfonation process, which can improve the catalytic performance. As a heterogeneous catalyst, **1** was also selected to examine the long-term stability and after at least 3 runs still maintained its activity without significant changes in its structure which characterized by FT-IR spectra and PXRD analyses, respectively. It is worth pointing out that by controlling the catalytic reaction conditions and using the same oxidant, we can prepare sulfones by various sulfides oxidation with excellent conversion and selectivity up to >99% and 97.5%, respectively.

inorganic-organic hybrid, copper vanadates, heterogeneous catalyse, sulfides oxidation

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