过渡金属为中心的多酸基晶态框架材料的制备与性能

兰青¹, 靳素娟¹, 张志明^{2*}

1. 南阳师范学院化学与制药工程学院, 南阳 473061;

2. 天津理工大学, 新能源材料与低碳技术研究院, 天津 300384

* 联系人, E-mail: zmzhang@email.tjut.edu.cn

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摘要 多酸由于具有良好的电子储存和氧化还原能力, 使其具有优异的催化与光/电致变色性能, 在清洁、绿色环保的高效催化剂开发领域具有重要的潜在前景. 然而, 由于多酸阴离子本身带有负电荷, 在催化过程中易于团聚失活, 且具有较低的比表面积. 因此, 将多酸引入到结构明确、具有可设计修饰孔道与较高孔隙率的晶态多孔材料中显得尤为迫切. 过渡金属为中心的多酸由于过渡金属引入, 不仅能够调控其电荷数目, 而且可以优化其能带结构, 被认为是设计合成结构明确多孔框架材料的理想构筑单元. 此类晶态材料有望应用于单分子磁体, 光/电催化水分解, 脱硫等领域. 本文系统总结了以过渡金属为中心的多酸基晶态框架材料的研究进展, 并提出了该领域所面临的挑战和机遇.

关键词 过渡金属, 多酸, 框架材料, 催化, 光催化

多金属氧酸盐(简称多酸)是一类具有纳米尺寸、结构明确的过渡金属氧簇, 表现出良好的热稳定性、酸碱稳定性和良好的氧化还原能力^[1]. 前期研究中, 多酸化学家主要集中于以主族元素(P, Si, As, B, S等)为中心的多金属氧酸盐的研究. 取得了丰硕的研究成果. 此类多酸材料在催化、光电磁材料、荧光等领域具有十分广泛的潜在应用前景^[2]. 例如, 王训课题组^[3]利用Keggin型多酸 $[\text{PW}_{12}\text{O}_{40}]^{3-}$ 和表面活性剂组装形成线型管状结构的复合材料, 表现出良好的催化脱硫性能. 胡长文课题组^[4]报道了基于双盖帽型多钼酸盐和四核多钒酸盐的新型双阴离子化合物 $\text{H}_{13}[(\text{CH}_3)_4\text{N}]_{12}[\text{PNb}_{12}\text{O}_{40}(\text{V}^{\text{V}}\text{O})_2(\text{V}^{\text{IV}}\text{O}_{12})_2]\cdot 22\text{H}_2\text{O}$, 具有良好的水解神经毒剂模拟剂的催化性能. 在这些多酸结构中, 主族杂原子多与氧原子形成四配位构型四面体单元, 为多金属氧簇配原子提供聚合中心.

众所周知, 通常过渡金属离子的配位构型是六配位八面体构型, 将其作为杂原子引入到多酸结构中需要将六配位八面体构型转化为四配位四面体构型, 往往需要较高的能量. 因此, 过渡金属离子作为中心杂原子的多酸研究相对较少^[5,6]. 近年来, 研究者采用水热合成方法设计与合成了以四配位构型的过渡金属为中心杂原子的杂多酸, 在单分子磁体、水分解等领域取得了一定的研究进展^[7-11]. Mialane课题组^[7]报道了以铁离子为中心的Keggin型缺位多酸衍生的多酸基单分子磁体 $[(\text{Fe}_4\text{W}_9\text{O}_{34}(\text{H}_2\text{O}))_2(\text{FeW}_6\text{O}_{26})]^{19-}$ 和 $[\text{Fe}_4(\text{H}_2\text{O})_2(\text{FeW}_9\text{O}_{34})_2]^{10-}$. 丁勇课题组^[8]采用含有混价Co(III)和Co(II)离子的Keggin型多酸 $\text{K}_7[\text{Co}^{\text{III}}\text{Co}^{\text{II}}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]\cdot 15\text{H}_2\text{O}$ 作为水氧化催化剂, 研究表明其在可见光照射下具有较好的光催化产氧性能. Lv等人^[12]报道了纯无机、均相的、以钒原子为中心的多

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酸基水氧化催化剂 $\text{Na}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{VW}_9\text{O}_{34})_2]\cdot 35\text{H}_2\text{O}$, 在以 $[\text{Ru}(\text{bpy})_3]^{2+}$ 为光敏剂和过硫酸盐为牺牲剂条件下, $\text{Na}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{VW}_9\text{O}_{34})_2]\cdot 35\text{H}_2\text{O}$ 的产氧效率相比于同构的 $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$ 得到较大提高, 揭示出钒原子中心对此类多酸光催化活性有着显著的影响。

多酸由于具有良好的电子储存和氧化还原能力, 使其具有优异的催化与光/电致变色性能, 在清洁、高效、绿色环保催化剂的开发领域具有重要的潜在前景。然而, 在实际应用过程中, 多酸基材料在均相体系中表现出较好的溶解度、难以分离回收且易于团聚, 而在非均相体系中往往具有较低的比表面积等问题极大地限制了其工业催化应用。发展负载型多酸催化剂是实现其工业催化应用的一种有效途径。传统方法采用静电吸附法或焙烧法负载。静电吸附法负载的催化剂由于多酸与载体间作用力小而稳定性较差, 多酸簇合物仍存在易流失的问题。焙烧法负载是一个高温煅烧过程, 在该过程中易于导致多酸分子结构的破坏, 进一步用于实际催化过程往往反应选择性较差。以上策略的局限性导致此类催化材料无法满足工业催化的需求。因此, 构建结构明确、稳定、高催化活性的多酸基多孔非均相催化剂是将多酸应用于工业催化的关键技术难题^[13-15]。金属有机框架(MOF)材料结构明确且具有多孔性, 可以定向设计合成, 引起多酸研究者的广泛兴趣。前期研究发现, 多酸在合成框架材料过程中可以充当连接体或模板剂, 在酸催化、氧化还原催化、光催化水分解等领域具有潜在的应用前景^[16-18]。人们将多酸与框架材料复合构筑多孔晶态材料, 不仅能够提高催化剂的比表面积, 暴露更多的多酸催化位点, 而且易于回收重复利用。最近, 研究发现功能性过渡金属元素也可以充当中心杂原子, 形成具有明确结构的多酸, 过渡金属杂原子的引入能够有效调节多酸的能带结构, 使具有较好的催化活性^[19]。进一步, 利用过渡金属为中心的多酸作为客体或构筑单元构筑了一系列金属有机框架材料, 在光催化、电催化以及荧光等领域取得了较好的进展。本文对以过渡金属为中心的多酸构筑的金属有机框架材料进行详细的总结。

1 基于1:12系列(Keggin和Silverton型)多酸基框架材料

高度对称的1:12系列Keggin型多酸是多酸的经

典结构之一, 在催化、磁性、荧光、医药等领域展示出尤为出色的应用前景。以Keggin型多酸为基本建筑单元的框架材料层出不穷^[20]。然而, 前期研究大多侧重于利用p区非金属元素为杂原子的多酸为构筑单元^[21]。过渡金属为中心的多酸基有机无机杂化材料的研究也获得了一定的进展, 为过渡金属基框架材料的发展奠定了基础^[22-26]。2007年, 牛景杨课题组^[23]报道了基于 $[\text{CuW}_{12}\text{O}_{40}]^{6-}$ 的杂化化合物 $[\text{Cu}(2,2'\text{-bpy})_3]_2\text{H}_4[\text{CuW}_{12}\text{O}_{40}]\cdot 6\text{H}_2\text{O}(2,2'\text{-bpy}, 2,2'\text{-联吡啶})$ 。王恩波课题组^[24]报道了基于 $[\text{FeW}_{12}\text{O}_{40}]^{5-}$ 的纯无机框架材料 $\text{Fe}(\text{H}_2\text{O})_6\text{H}[\text{Na}_6\text{FeW}_{12}\text{O}_{40}]\cdot 44\text{H}_2\text{O}$, 具有A和B孔的结构特征。2018年, Das课题组^[25]将饱和Keggin型多酸 $[\text{CoW}_{12}\text{O}_{40}]^{6-}$ 封装进ZIF-8框架中, 构筑了高效水氧化电催化剂, 实现了饱和型多酸的电催化产氧(图1)。 $[\text{H}_6\text{CoW}_{12}\text{O}_{40}]\text{@ZIF-8}$ 循环1000次仍能表现出稳定的水氧化性能。该催化剂的转化率(TOF)为 $10.8 \text{ mol O}_2 (\text{mol Co})^{-1} \text{ s}^{-1}$, 在中性溶液中具有高效的电催化水氧化活性。宋宇飞课题组^[26]采用多孔泡沫镍作为基底, 将 $[\text{PW}_{12}\text{O}_{40}]^{3-}$ 分散在多孔的商用泡沫镍中, 水热条件下实现了多金属氧簇的高效转化, 获得分散在多孔材料中的过渡金属为中心的Silverton型多酸 $\text{Co}_{6.8}\text{Ni}_{1.2}\text{W}_{12}\text{O}_{40}(\text{OH})_4(\text{H}_2\text{O})_8$ 。研究表明其在碱性(pH 13)条件下具有较好的电催化析氧催化性能。

最近, 人们研究发现过渡金属钒原子由于存在V(III), V(IV), V(V) 3种价态与多种配位构型(如: 四

图1 (网络版彩色)将 $[\text{CoW}_{12}\text{O}_{40}]^{6-}$ 多酸封装进ZIF-8 MOF中构筑高效水氧化电催化剂^[25]

Figure 1 (Color online) POM was encapsulated in ZIF-8 for construction of high performance electrocatalyst for water oxidation^[25]

配位的四面体、五配位的四方锥或扭曲的三角双锥、六配位的扭曲八面体或四方双锥),使得金属钒原子被广泛地用于构筑结构多样的多金属氧簇^[27].以往研究表明钒离子中心不仅能够作为中心杂原子构筑稳定结构的多酸,还可以作为修饰单元获得衍生结构的多酸.此外,过渡金属钒的引入能进一步优化多酸基框架材料与复合材料的催化性能.

2001年,王恩波课题组^[28]报道了以钒原子为中心的双钒盖帽的 α -Keggin型钒钼酸盐 $\{\text{Mo}_8\text{V}_7\text{O}_{42}\}$,此类多阴离子簇通过V-O-V连接模式连接成为一维链状结构.2002年,卢灿忠课题组^[29]通过水热法合成了以顺磁性稀土阳离子 Gd^{3+} 原子为杂原子的Silerton型多酸,每个多阴离子与6个 Gd^{3+} 离子配位形成具有孔道的三维结构.2009年,林深课题组^[30]在水热条件下利用 $[\text{VO}_2\text{Ag}(\text{phen})_3]_2$ 金属-有机单元修饰12-钒钨酸盐 $[\text{VW}_{12}\text{O}_{40}]$ 构筑了金属-有机杂化材料 $[\text{VW}_{12}\text{O}_{40}][\text{VO}_2\text{Ag}(\text{phen})_3]_2$,此类材料展现出较好的催化降解罗丹明B的性能.2010年,王恩波课题组^[31]合成了2例钒原子为中心的钒钼混配型多酸 $[\text{VMo}_8\text{V}_4\text{O}_{40}(\text{VO})_2]$,进一步被金属有机基团连接成哑铃型单元.进一步利用分子间氢键作用构筑成三维超分子框架,光催化研究表明该有机-无机杂化材料具有良好的光催化降解罗丹明B的性能.前期研究中主要利用过渡金属原子为中心的多酸构筑了一维、二维或三维超分子框架结构,而利用此类多阴离子构筑共价键连接的三维框架材料仍然是一项挑战性的研究工作.

2013年,王恩波与张志明课题组^[32]合作报道了基于饱和Keggin型多酸 $[\text{VW}_{12}\text{O}_{40}]$ 的三维金属有机框架材料 $[\text{Ni}(\text{bix})_2][\text{VW}_{12}\text{O}_{40}] \cdot (\text{H}_2\text{bix}) \cdot \text{H}_2\text{O}$ ($\text{VW}_{12}\text{-1}$, bix, 1,4-二(咪唑-1-基甲基)苯,图2),不仅具有良好的光催化降解有机染料的性能,还可以稳定存在于酸碱溶液以及多种常见有机溶剂中.随后,通过改变反应条件获得首例以钒原子为中心的双钒氧单元(VO^{IV}_5)盖帽的Keggin型多酸 $[\text{V}^{\text{IV}}\text{W}^{\text{VI}}_{10}\text{V}^{\text{V}}_2\text{O}_{40}(\text{V}^{\text{IV}}\text{O})_2]$,通过金属镍离子链接成为一维链状结构 $[\text{Ni}_4\text{V}^{\text{IV}}\text{W}^{\text{VI}}_{10}\text{WV}_2\text{O}_{40}(\text{V}^{\text{IV}}\text{O})_2](\text{L}, 1,4\text{-二(咪唑-1-亚甲基)苯})$,其中镍离子被4个有机配体配位修饰而稳定存在^[33].一维链之间通过互锁作用形成类拉链状的三维超分子结构.研究表明该化合物不仅可以有效地光催化降解有机污染物,而且在水溶液中表现出对阳离子型染料具有选择性光催化活性.

2018年,姚爽课题组与本课题组^[34]合作合

图2 (网络版彩色)化合物 $\text{VW}_{12}\text{-1}$ 结构图. (a) 化合物 $\text{VW}_{12}\text{-1}$ 中二维 $[\text{Ni}(\text{bix})_2]_n^{2+}$ 层的结构; (b) 化合物 $\text{VW}_{12}\text{-1}$ 中二维 $[\text{Ni}(\text{bix})_2]_n^{2+}$ 层与 $[\text{VW}_{12}\text{O}_{40}]$ 多酸配位模式; (c) 化合物 $\text{VW}_{12}\text{-1}$ 三维结构示意图; (d) 化合物 $\text{VW}_{12}\text{-1}$ 沿 b 轴的三维结构^[32]

Figure 2 (Color online) The structure of $\text{VW}_{12}\text{-1}$. (a) 2D $[\text{Ni}(\text{bix})_2]_n^{2+}$ layer; (b) linking modes between 2D $[\text{Ni}(\text{bix})_2]_n^{2+}$ layer and the POMs; (c) schematic representation of the 3D layered structure; (d) 3D structure along the b axis^[32]

成了由1,2,4-三氮唑和镍形成的二维金属有机层,在该二维结构中,有机配体与金属阳离子之间通过配位连接模式构筑了金属-有机冠醚类结构类型.该金属-有机冠可用于捕获 $[\text{Ni}(\text{H}_2\text{O})_2]^{2+}$ 阳离子基团,所捕获 $[\text{Ni}(\text{H}_2\text{O})_2]^{2+}$ 基团可与V金属中心的 $[\text{VW}_{12}\text{O}_{40}]$ 阴离子利用分子间氢键作用构筑成三维超分子框架材料 $\{\text{H}_4[\text{Ni}(\pi\text{-H}_2\text{O})_2]_2[\text{Ni}(\text{rt-H}_2\text{O})_2]_8\text{Ni}_4(\text{Tri})_{24}\} \cdot [\text{VIVW}_{12}\text{O}_{40}]_2 \cdot 24\text{H}_2\text{O}(\text{Tri}, 1,2,4\text{-三氮唑})$.有趣的是,进一步将饱和Keggin型多酸 $[\text{VW}_{12}\text{O}_{40}]$ 替换为双VO基团盖帽型多金属氧簇 $[\text{VW}_{10}\text{V}_2\text{O}_{40}]$,通过增长多金属氧簇的长度与减小其位阻效应成功将二维金属有机层通过配位键连接形成三维框架材料 $\{\text{H}[\text{Ni}(\pi\text{-O})_2]_2[\text{Ni}(\text{rt-H}_2\text{O})_2]_8\text{Ni}_4(\text{Tri})_{24}\}[\text{V}^{\text{IV}}\text{W}_{10}\text{V}^{\text{V}}_2\text{O}_{40}\text{V}_2][\text{V}^{\text{IV}}\text{W}_9\text{V}_3\text{O}_{40}\text{V}^{\text{IV}}_2] \cdot 24\text{H}_2\text{O}$.此外,还研究了这两种化合物的电化学行为和电催化性能,它们可作为双功能电催化剂,在中性水溶液中实现了电催化还原 H_2O_2 和电催化氧化亚硝酸盐.

常见的以过渡金属钒原子为中心的Keggin型多酸主要是多钨酸盐和多钼酸盐.最近,在多钨酸盐领域也成功获得了数例以过渡金属钒为中心的Keggin型多酸.2011年,胡长文课题组^[35]报道了以钒原子为中心的双钒盖帽的Keggin型多酸 $\{\text{VNb}_{12}\text{O}_{40}(\text{VO})_2\}$.2014年,本课题组与王新龙课题组^[36]报道了以钒原子为中心双钨盖帽的Keggin型 $\{\text{VNb}_{14}\}$ 多酸簇,通过钠离子和钾离子连接成为三维网络,具有一维孔道结构,并研究了其光催化产氢气性能.2014年,王恩波课题组^[37]报道了以钒原子为中心的钒钼酸盐,并

研究其抗肿瘤活性。

2 Anderson型多酸基框架材料

Anderson型多酸作为多酸化学中一个重要的家族成员之一,由6个 MoO_6 (或 WO_6)八面体围绕中心金属-氧八面体组成.与经典的Keggin或Dawson-型多酸相比,Anderson-型多酸表现出迷人的平面结构.每个Mo(或W)原子都有2个末端氧原子,使得它们具有高的反应活性,易于与过渡金属离子配位.另外,Anderson型多酸的富氧表面展示出不同的配位模式,导致形成各种各样的新奇结构,受到了研究者的青睐.目前报道的Anderson型多酸中,可以作为中心杂原子的元素较多,主要有过渡金属以及主族元素 Al^{3+} , Ga^{3+} , Te^{6+} , I^{7+} 等^[38].以主族元素为中心的Anderson型多酸化合物已经得到了广泛研究,近期以过渡金属为中心的Anderson型多酸基框架材料获得了新的进展.

2005年,王恩波课题组^[39]报道了基于 $[\text{CrMo}_6\text{H}_6\text{O}_{24}]$ 通过稀土金属离子(La^{3+})链接形成一维链状结构.随后,他们又以 $[\text{CrMo}_6\text{H}_6\text{O}_{24}]$ 为建筑单元与稀土元素(La和Ce)组装构筑了2例三维开放框架材料,沿 a 轴和 b 轴孔道的尺寸分别为 $10.0 \text{ \AA} \times 8.5 \text{ \AA}$ 和 $10.7 \text{ \AA} \times 6.2 \text{ \AA}$,游离的客体分子填充在孔道内.2007年,许林课题组^[40]利用草酸根和铜离子组成的双核配合物,进一步连接 $[\text{Cr}(\text{OH})_7\text{Mo}_6\text{O}_{17}]$ 多酸分子簇形成一维链状结构,通过氢键进而形成三维超分子网络框架.2011年,An等人^[41]利用 $[\text{CrMo}_6\text{H}_6\text{O}_{24}]$ 与锰和钠组装形成二维网络,通过氢键连接成沿 a 轴方向具有 $11.8 \text{ \AA} \times 7.7 \text{ \AA}$ 的孔道三维超分子结构.2014年,Wang等人^[42]报道了2例基于 $[\text{CrMo}_6(\text{OH})_6\text{O}_{18}]$ 的三维多酸基金属有机框架材料.这2例化合物在紫外光、可见光、太阳光照射下表现出优异的光催化降解亚甲基蓝的性质.2015年,Wang等人^[43]采用水热法合成了2例基于 $[\text{CrMo}_6(\text{OH})_6\text{O}_{18}]$ 的金属有机化合物 $\text{H}\{\text{CuL}_{0.5}^1[\text{CrMo}_6(\text{OH})_6\text{O}_{18}](\text{H}_2\text{O})\} \cdot 0.5\text{L}^1(\text{CrMo}_6-1)$ 和 $\{\text{Cu}_2(\text{L}_2)_2[\text{CrMo}_6(\text{OH})_5\text{O}_{19}](\text{H}_2\text{O})_2\} \cdot 2\text{H}_2\text{O}(\text{CrMo}_6-2)$ (L^1 , N,N' -二(3-吡啶甲酰胺)-1,2-乙烷; L^2 , N,N' -二(3-吡啶甲酰胺)-1,3-丙烷).化合物 CrMo_6-1 是由一维Cu- CrMo_6 无机链组成,进而通过有机配体连接成为一维梯状的链.化合物 CrMo_6-2 是一例三维多酸基金属有机框架材料,展现出 $\{4^{12}.6^3\}$ 拓扑类型.

2017年,Gong等人^[44]报道了以 $[\text{CrMo}_6(\text{OH})_6\text{O}_{18}]$

阴离子柱撑 $[\text{Cu}_5(1,4\text{-ttb})(\text{H}_2\text{O})_8](\text{ttb}, 1\text{-三氮唑-4-四氮唑苯})$ 二维金属有机层形成的三维框架结构 $[\text{Cu}_5(1,4\text{-ttb})_4(\text{CrMo}_6(\text{OH})_6\text{O}_{18})(\text{H}_2\text{O})_8] \cdot 10\text{H}_2\text{O}$ (图3).磁化率测试表明该化合物中存在着反铁磁性相互作用,光催化表明该化合物对亚甲基蓝、盐酸副玫瑰苯胺(副品红)和罗丹明B具有良好的光催化降解作用.

最近,杨国昱课题组^[45]选取2-羟基甲基-2-(4-吡啶)-1,3-丙二醇配体通过与Anderson型多酸中心金属离子配位,实现对Anderson型多酸的修饰,形成长度为 1.47 nm 的建筑单元 $(\text{TBA})_3[\text{MnMo}_6\text{O}_{18}\text{L}_2] \cdot 2\text{CH}_3\text{CN}(\text{MnMo}_6-1)$.在该结构中,3个羟基氧原子可以和中心杂原子锰离子配位形成多酸基多齿配体,其中吡啶上的氮原子进一步与额外的过渡金属离子配位形成三维框架材料 $(\text{TBA})_6[\text{Cu}_4\text{I}_4][\text{MnMo}_6\text{O}_{18}\text{L}_2]_2 \cdot 2\text{DMA}(\text{MnMo}_6-2)$ 和 $(\text{TBA})_6[\text{Cu}_2\text{I}_2][\text{MnMo}_6\text{O}_{18}(\text{L}_2)_2] \cdot 4\text{DEF}(\text{MnMo}_6-3)$ (TBA , n -四丁基铵根离子;DEF, N,N -二乙基甲酰胺;DMA, N,N -二甲基乙酰胺)(图4).结构分析表明,在化合物 MnMo_6-2 中,1个 $[\text{MnMo}_6\text{O}_{18}\text{L}_2]^{3-}$ 建筑单元与2个 Cu_4I_4 簇相连,1个 Cu_4I_4 与4个 $[\text{MnMo}_6\text{O}_{18}\text{L}_2]^{3-}$ 建筑单元相连,形成三维具有金刚石拓扑的阴离子簇基有机框架材料.由于具有较大尺寸的孔道,形成了三重互穿结构,最终结构在 c 轴上具有 $1.01 \text{ nm} \times 1.01 \text{ nm}$ 不规则的孔道,该化合物的孔隙率高达69.4%,高于许多沸石材料.在化合物 MnMo_6-3 中,每个 Cu_2I_2 簇与4个 $[\text{MnMo}_6\text{O}_{18}\text{L}_2]^{3-}$ 建筑单元相连,形成二维簇-有机框架.相邻两层之间的距离是 $4.877 \text{ \AA}$,层与层之间稍微有所位移,导致沿 a 轴具有 $2.30 \text{ nm} \times 2.45 \text{ nm}$ 的孔道.化合物 MnMo_6-3 的空隙率高达71.4%,并对它们的催化、光谱行为和磁学性能进行了研究.

图3 (网络版彩色)化合物 $[\text{Cu}_5(1,4\text{-ttb})_4(\text{CrMo}_6(\text{OH})_6\text{O}_{18})(\text{H}_2\text{O})_8] \cdot 10\text{H}_2\text{O}$ 的三维结构^[44]

Figure 3 (Color online) View of the 3D structure of $[\text{Cu}_5(1,4\text{-ttb})_4(\text{CrMo}_6(\text{OH})_6\text{O}_{18})(\text{H}_2\text{O})_8] \cdot 10\text{H}_2\text{O}$ ^[44]

图4 (网络版彩色)化合物三维结构. (a) 化合物MnMo₆-2的三维金属-有机框架(沿c轴); (b) 化合物MnMo₆-3中二维层面板的三维堆叠方式, 沿a轴有一维孔道^[45]

Figure 4 (Color online) View of the three-dimensional (3D) structure. (a) View of the 3D cluster organic framework of MnMo₆-2 along the *c* axis; (b) view of the 3D stacking style of two-dimensional (2D) layers in MnMo₆-3, showing one-dimensional (1D) channels along the *a* axis^[45]

3 Waugh型多酸基框架材料

Waugh多酸[MnMo₉O₃₂]本身具有手性特征, 但都是以消旋形式存在. 自从1966年发现以来, 实现此类多酸分子簇的手性拆分一直备受关注^[46]. 直到2007年, 王恩波课题组^[47]利用过渡金属离子配位修饰策略构筑成三维框架材料, 使得同手性多酸分子簇在晶态框架矩阵中的均一排列, 实现了有效的手性拆分. 在该过程中, 以手性多酸[MnMo₉O₃₂]为基本建筑块与Zn²⁺离子组装, 形成具有三维网络的手性多酸化合物L-(Zn(H₂O)₃)₃[MnMo₉O₃₂]·4H₂O(L-1)和D-(Zn(H₂O)₃)₃[MnMo₉O₃₂]·4H₂O(D-1). 其中, Zn²⁺呈现出变形的四方锥配位环境, 每个Zn²⁺与3个水分子和2个[MnMo₉O₃₂]的端氧配位. Zn²⁺将同手性的[MnMo₉O₃₂]阴离子簇连成了具有 α -Po拓扑的三维孔道结构, 孔道大小约为12.3 Å×9.3 Å(图5). 由于孔道的存在, 2个三维网络相互穿插, 形成三维互穿结构. 随后该课题组通过选取不同种类金属离子合成了一系列基于[MnMo₉O₃₂]的化合物. 通过对这一系列化合物的结构、手性传递情况及分子间作用力等详细研究, 探讨了手性多阴离子自发拆分影响因素、固体中多阴离子手性传递影响因素等.

同时, 为了研究手性多酸化合物的自发拆分、手性识别和传递的规律, 王恩波课题组^[48]进一步以Waugh型多阴离子[MnMo₉O₃₂]⁶⁻为模型, 通过改变[MnMo₉O₃₂]⁶⁻间连接单元, 调控多阴离子间作用力, 实现了[MnMo₉O₃₂]⁶⁻从外消旋化合物经外消旋固体溶液到纯手性材料的调变. 此外, 通过对晶体中

图5 (网络版彩色)化合物L-1的三维框架结构^[47]

Figure 5 (Color online) The 3D framework structure of L-1^[47]

不同连接单元的调控, 实现了同手性 [MnMo₉O₃₂]⁶⁻阴离子簇相互作用, 构筑成一维、二维、三维手性框架材料. 从而证实了手性多阴离子自发拆分的存在^[49], 实验表明该类多维手性多酸化合物是一种优良的光催化剂和气致变色材料.

最近, Chen等人^[50]以[CoMo₆O₂₄]³⁻为原料合成出Waugh型[CoMo₉O₃₂]⁶⁻簇, 以氢键相连构筑成三维超分子结构, 研究表明这种n-型半导体材料表现出良好的热和电化学稳定性, 是一种在太阳能利用领域具有应用前景的光敏剂材料.

4 Evans-Showell型多酸基框架材料

Evans-Showell型多酸[Co₂Mo₁₀H₄O₃₈]⁶⁻含有10个钼金属中心与2个过渡金属钴离子中心. 在[Co₂Mo₁₀

$\text{H}_4\text{O}_{38}]^{6-}$ 中,每个钼中心拥有2个端氧原子,使得其易于与金属离子配位形成多维结构.且由于过渡金属钼离子中心的引入,已经被证明是一种高活性的可见光水氧化催化剂^[51].以 $[\text{Co}_2\text{Mo}_{10}\text{H}_4\text{O}_{38}]^{6-}$ 为构筑单元设计合成多维框架结构成为了研究热点.

2015年,An等人^[52]报道了基于 $[\text{Co}_2\text{Mo}_{10}\text{H}_4\text{O}_{38}]^{6-}$ 和稀土阳离子在不同温度下构筑的4例化合物 $[\text{Ln}(\text{H}_2\text{O})_7][\text{Ln}(\text{H}_2\text{O})_5][\text{Co}_2\text{Mo}_{10}\text{H}_4\text{O}_{38}]\cdot 5\text{H}_2\text{O}$ (Ln=Gd, Co₂-1; Tb, Co₂-2), $(\text{NH}_4)_3[\text{Ln}(\text{H}_2\text{O})_6][\text{Co}_2\text{Mo}_{10}\text{H}_4\text{O}_{38}]\cdot 6\text{H}_2\text{O}$ (Ln=Gd, Co₂-3; Tb, Co₂-4),并利用元素分析、红外和拉曼光谱、粉末衍射、热重和单晶X射线衍射分析对化合物的结构与组成进行了表征.化合物Co₂-1和Co₂-2分别由Gd³⁺和Tb³⁺与 $[\text{Co}_2\text{Mo}_{10}\text{H}_4\text{O}_{38}]^{6-}$ 连接形成三维框架材料,拥有一维之字形孔道,是首例基于 $[\text{Co}_2\text{Mo}_{10}\text{H}_4\text{O}_{38}]^{6-}$ 的三维框架结构.有趣的是,稳定的三维微孔化合物展现出对水和甲醇的选择性吸附性能,并在可见光照射下能够催化降解有机染料分子.当反应温度降低到室温(25℃)时,获得了2例手性化合物Co₂-3和Co₂-4.化合物Co₂-3和Co₂-4由 $[\text{Co}_2\text{Mo}_{10}\text{H}_4\text{O}_{38}]^{6-}$ 和 $[\text{Ln}(\text{H}_2\text{O})_6]^{3+}$ 组成,结晶于P₂₁手性空间群.2016年,Fei等人^[53]报道了4例基于锌-有机配位聚合物和 $[\text{Co}_2\text{Mo}_{10}\text{H}_4\text{O}_{38}]^{6-}$ 构筑的有机无机杂化材料,均展示出一维链状结构,可以作为硅腈化反应的Lewis酸异相催化剂.随后又报道了6例基于 $[\text{Co}_2\text{Mo}_{10}\text{H}_4\text{O}_{38}]^{6-}$ 多阴离子的化合物 $(4\text{-H}_2\text{pya})_6[\text{Co}_2\text{Mo}_{10}\text{H}_4\text{O}_{38}]\cdot 10\text{H}_2\text{O}$ (Co₂-5, 4-Hpya, 3-(4-吡啶基)丙烯酸)和 $(4\text{-H}_2\text{pya})_4[\text{M}(\text{H}_2\text{O})_6][\text{Co}_2\text{Mo}_{10}\text{H}_4\text{O}_{38}]\cdot 5\text{H}_2\text{O}$ (M=Co, Co₂-6; Ni, Co₂-7; Cu, Co₂-8; Zn, Co₂-9; Cd, Co₂-10).化合物Co₂-5由质子化4-H₂pya分子和孤立的 $[\text{Co}_2\text{Mo}_{10}\text{H}_4\text{O}_{38}]^{6-}$ 组成,结晶于中心对称的P-1空间群^[54].在制备化合物Co₂-5的过程中,加入不同的金属离子能够获得同构的化合物Co₂-6~Co₂-10,它们是通过自发拆分结晶于P₁手性空间群. $[\text{Co}_2\text{Mo}_{10}\text{H}_4\text{O}_{38}]^{6-}$ 多阴离子中的端氧原子通过氢键与 $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ 阳离子单元和质子化的4-H₂pya配体形成三维超分子手性框架.化合物Co₂-6~Co₂-10是目前基于 $[\text{Co}_2\text{Mo}_{10}\text{H}_4\text{O}_{38}]^{6-}$ 多阴离子的手性无机-有机杂化化合物,并研究了它们的二阶非线性光学性能.随后,又报道了4例基于 $[\text{Co}_2\text{Mo}_{10}\text{H}_4\text{O}_{38}]^{6-}$ 多阴离子和Zn-有机配合物单元构成的有机无机杂化材料,并作为路易斯酸催化剂研究其硅腈化反应催化性能.2017年,采用同样的方法合成了4例基于 $[\text{Co}_2\text{Mo}_{10}\text{H}_4\text{O}_{38}]^{6-}$ 多阴离子和Cu-有机配合物

单元的无机有机杂化化合物 $(\text{en})[\text{Cu}_3(\text{ptz})_4(\text{H}_2\text{O})_4][\text{Co}_2\text{Mo}_{10}\text{H}_4\text{O}_{38}]\cdot 24\text{H}_2\text{O}$ ^[55].结构分析表明三维Cu-ptz作为主体, $[\text{Co}_2\text{Mo}_{10}\text{H}_4\text{O}_{38}]^{6-}$ 作为客体分子,形成三维主体-客体框架,是首例以 $[\text{Co}_2\text{Mo}_{10}\text{H}_4\text{O}_{38}]^{6-}$ 为客体分子的主体-客体框架化合物,并对其催化氧化脱硫和醇氧化等性能进行研究.

5 杂多钒酸盐基框架材料

与杂多钨酸盐和杂多钼酸盐相比,杂多钒酸盐的研究相对较少.前期研究中,杂多钒酸盐集中于利用主族元素(如: P, S, Cl, As等)为杂原子构筑结构多样的多钒酸盐^[56].通过长期探索,以过渡金属为中心的杂多钒酸盐及由其构筑的框架材料取得了较大的研究进展.Flynn和Pope^[57]报道了1:13杂多阴离子 $\text{MV}_{13}\text{O}_{38}^{7-}$ (M=Mn, Ni)设计与合成,此类化合物在抗菌、抗肿瘤活性与催化活性的研究相继开展起来^[58].2006年,刘术侠课题组^[59]报道了 $[\text{MV}_{13}\text{O}_{38}]^{7-}$ (M=Mn, Ni)与稀土阳离子 Ln^{3+} (Ln=La, Ce, 或 Pr)反应,获得5例同构化合物 $[\text{Ln}_6(\text{H}_2\text{O})_{25}(\text{MV}_{12}\text{O}_{38})(\text{HMV}_{13}\text{O}_{38})]\cdot n\text{H}_2\text{O}$ (V-1: Ln, La; M, Mn; $n \approx 31$; V-2: Ln, Ce; M, Mn; $n \approx 29$; V-3: Ln, Pr; M, Mn; $n \approx 31$; V-4: Ln, La; M, Ni; $n \approx 28$; V-5: Ln, Pr; M, Ni; $n \approx 33$).结构分析表明,该系列化合物中含有2种不同的多钒酸盐簇 MnV_{13} 和 MnV_{12} ,这2种簇通过稀土离子连接形成二维层状框架材料, MnV_{12} 是由 MnV_{13} 多酸簇在反应过程中转化形成.Li等人^[60]通过阳离子交换实现 $\text{MnV}_{11}\text{O}_{32}$ 到 $\text{MnV}_{12}\text{O}_{34}$ 的转化,通过单晶结构测定和冷喷雾质谱测试得到证明.

2013年,Lan等人^[61]报道了一系列由不同过渡金属离子和 $[\text{MnV}_{13}\text{O}_{38}]^{7-}$ 构筑的扩展结构化合物 $\{\text{M}_2(\text{H}_2\text{O})_{10}(\text{MnV}_{13}\text{O}_{38})\}$ (M=Co²⁺, Mn²⁺和Ni²⁺),并对化合物进行电化学和磁性表征.随后,他们利用具有催化活性的 $[\text{MnV}_{13}\text{O}_{38}]^{7-}$ 作为节点,具有多配位数的稀土阳离子(Ln^{3+})作为连接体,合成了3例多酸基纯无机框架化合物 $\text{H}[\text{La}(\text{H}_2\text{O})_4]_2[\text{MnV}_{13}\text{O}_{38}]\cdot 9\text{NMP}\cdot 17\text{H}_2\text{O}$ (V-6), $\text{H}[\text{Ce}(\text{H}_2\text{O})_4]_2[\text{MnV}_{13}\text{O}_{38}]\cdot 9\text{NMP}\cdot 17\text{H}_2\text{O}$ (V-7)和 $\text{H}[\text{La}(\text{H}_2\text{O})_4]_2[\text{MnV}_{13}\text{O}_{38}]\cdot 8\text{NMP}\cdot 9\text{H}_2\text{O}$ (V-8, NMP, N-甲基吡咯烷酮)(图6)^[62].结构分析表明,V-6与V-7是同构的,在不同方向都具有通道,通道之间是相交的且沿着6个方向伸展,最大的通道尺寸达到了21.47 Å×10.65 Å.然而在V-8中,相交的通道沿着3个方向伸展,通道的尺寸最大为21.54 Å×13.76 Å.对V-7进

行了吸附实验研究, 结果表明该化合物允许尺寸较小的水分子和甲醇分子自由地进入孔道, 而尺寸较大的乙醇分子不能进入. 因而利用此类材料的选择吸附性能, 实现对生物乙醇的净化. 催化实验研究结果表明, 将V-7作为异相催化剂, 对部分噻吩类硫化物的氧化具有良好的催化活性, 例如二苯并噻吩在催化反应3 h后, 转化率高达99.5%. 紧接着, Liu等人^[63]设计与合成了基于 $[\text{MnV}_{13}\text{O}_{38}]^{7-}$ 的系列有机无机稀土衍生物 $\text{H}[\{\text{La}_2(\text{DMF})_5(\text{H}_2\text{O})_4\}\{\text{MnV}_{13}\text{O}_{38}\}]\cdot\text{DMF}\cdot 5\text{H}_2\text{O}$ (V-9), $\text{H}[\{\text{Ce}_2(\text{DMF})_2(\text{H}_2\text{O})_7\}\{\text{MnV}_{13}\text{O}_{38}\}]\cdot 0.5\text{DMF}\cdot 5.5\text{H}_2\text{O}$ (V-10), $\text{H}_2[\{\text{K}(\text{H}_2\text{O})_2\}_2\{\text{Nd}(\text{DMF})(\text{H}_2\text{O})_3\}\{\text{MnV}_{13}\text{O}_{38}\}]\cdot 5\text{H}_2\text{O}$ (V-11), $\text{H}[\{\text{Ln}_2(\text{C}_6\text{H}_5\text{NO}_2)_3(\text{H}_2\text{O})_6\}\{\text{MnV}_{13}\text{O}_{38}\}]\cdot \text{C}_6\text{H}_5\text{NO}_2\cdot 10\text{H}_2\text{O}$ (Ln=La, V-12; Ce, V-13), $\text{H}_{2.5}[\{\text{Pr}(\text{C}_6\text{H}_5\text{NO}_2)(\text{H}_2\text{O})_{3.5}\}\{\text{Pr}_{0.5}(\text{H}_2\text{O})_2\}\{\text{MnV}_{13}\text{O}_{38}\}]\cdot 0.5\text{C}_6\text{H}_5\text{NO}_2\cdot 10\text{H}_2\text{O}$ (V-14, DMF=*N,N*-二甲基甲酰胺; $\text{C}_6\text{H}_5\text{NO}_2$ =异烟酸). 结构分析表明, V-9和V-10是一维链状结构, V-11是具有孔道的三维开放框架结构, V-12~V-14是三维超分子结构. 磁性研究表明, 该系列化合物中存在着反铁磁性相互作用. 2015年, Hill教授课题组^[64]以 $[\text{MnV}_{13}\text{O}_{38}]^{7-}$ 为起始原料, 在酸性条件下转化为 MnV_{14} 单元, 通过 K^+ 离子构筑成为二维框架材料, 具有有效催化降解类芥子气2-氯乙基乙基硫醚性能, 显示出在空气净化与化学战剂分解领域具有潜在应用前景.

6 结论与展望

在过去几年里, 研究者成功利用过渡金属为中心的杂多酸构筑了系列框架材料. 在合成过程中, 多

图6 (网络版彩色)化合物V-6和V-8的三维框架结构和拓扑图^[62]

Figure 6 (Color online) 3D framework and topological representation of compounds V-6 and V-8^[62]

酸能够作为构筑单元均匀分布在框架材料中, 不仅提高了框架材料的稳定性还赋予其优异的催化性能, 在光催化污水处理、燃油脱硫、分解化学战剂与水分解制备清洁能源等领域具有潜在的应用价值. 目前, 过渡金属为中心的杂多酸主要是杂多钨酸盐和杂多钼酸盐, 而杂多钒酸盐和杂多铌酸的研究明显不足. 过渡金属为中心的杂多酸由于在多酸中引入新的过渡元素能够调控多酸的能带结构, 在光电领域展示出巨大的潜在应用前景, 越来越引起人们的研究兴趣. 以此类多金属氧簇作为构筑单元组装具有优异催化性能的光/电催化剂已成为国际热点研究领域之一.

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Summary for “过渡金属为中心的多酸基晶态框架材料的制备与性能”

Synthesis and functionality of transition metal-centered polyoxometalate-based crystalline framework materials

Qing Lan¹, Sujuan Jin¹ & Zhiming Zhang^{2*}

¹ School of Chemistry & Pharmaceutical Engineering, Nanyang Normal University, Nanyang 473061, China;

² Institute of New Energy Materials & Low Carbon Technology, Tianjin University of Technology, Tianjin 300384, China

* Corresponding author, E-mail: zmzhang@email.tjut.edu.cn

Polyoxometalates, a class of discrete nanoscale molecular metal-oxo clusters, have excellent catalytic and photoelectric/electrochromic properties due to their excellent electronic storage and redox capacity. They possess of plenty of potential applications as efficient catalysts in the development of clean and green fuels. However, polyoxometalates are easy to agglomerate and deactivate in the catalytic process, and possess of low specific surface area. Therefore, it is extremely urgent to introduce polyoxometalates into crystalline porous materials with well-defined structure, modifiable channels and high porosity. The introduction of transition metal into polyoxometalates can not only regulate their charge number, but also optimize their band structure. As well known, polyoxometalates, as one kind of unique metal oxide cluster, have been considered as promising secondary building units for construction of porous frameworks because of their adjustable compositions, variable topologies and oxygen-rich surface as well as their diverse physical and chemical properties. Recently, more and more attention has been paid to introducing polyoxometalates into frameworks to functionalize porous frameworks materials. So, these transition metal-centered polyoxometalates should be ideal building units for the design and synthesis of porous crystalline framework materials. These crystalline materials are expected to be used in the fields of single-molecule magnets, photocatalytic water splitting, desulfurization and so on.

This review is directed to cover the main advances on the development of transition metal-centered polyoxometalate-based framework materials. In the past several decades, researchers have synthesized 1:12 Keggin type and Silverton type polyoxometalate, Anderson type polyoxometalate Waugh type polyoxometalate, Evans-Showell type polyoxometalate and heteropolyvanadate-based framework materials by hydrothermal method and conventional aqueous solution method. The water oxidation and photocatalytic degradation of organic pollutants of the framework materials were detailly studied. For example, the Keggin anion $[\text{CoW}_{12}\text{O}_{40}]^{6-}$ turned into an efficient and robust electrocatalyst upon its confinement in the well-defined void space of metal-organic framework (ZIF-8). In the electrocatalytic process, the $[\text{H}_6\text{CoW}_{12}\text{O}_{40}]/\text{ZIF-8}$ composite crystalline framework materials is very stable for water oxidation that could retain its initial activity even after 1000 catalytic cycles. The catalyst has a turnover frequency (TOF) of 10.8 mol O_2 (mol Co) $^{-1}\text{s}^{-1}$, one of the highest TOFs for electrocatalytic oxygen evolution at neutral pH.

Further, the POM-based crystalline framework materials were used for oxidative desulfurization and the decomposition of chemical warfare agent. In these fields, the porous frameworks with catalytic active manganese(IV)-containing heteropolyvanadate $[\text{MnV}_{13}\text{O}_{38}]^{7-}$ as nodes and rare earth ions as linking units have been successfully prepared. These multifunctional polyoxometalate-based porous framework materials exhibit selective adsorption behavior and remarkable catalytic activity as heterogeneous catalysts for the oxidation of sulfides. A novel manganese(IV)-containing symmetrical heteropolyvanadate $\text{K}_7[\text{MnV}_{13}\text{O}_{38}] \cdot 18\text{H}_2\text{O}$ to $\text{K}_4\text{Li}_2[\text{MnV}_{14}\text{O}_{40}] \cdot 21\text{H}_2\text{O}$ was also prepared, which is an deficient catalyst for the oxidation of 2-chloroethyl ethyl sulfide with tert-butyl hydroperoxide oxidizing agent. In this catalytic process, a TON of 40 is achieved in 8 h, showing potential application toward air decontamination technology. The results show that the transition metal-centered polyoxometalate-based crystalline framework materials possess of many functionalities, especially as excellent catalysts. In this paper, the research progress of crystalline framework materials constructed from transition metal-centered polyoxometalates is systematically summarized, and the challenges and opportunities in this field are also presented.

transition metal, polyoxometalate, framework materials, catalysis, photocatalysis

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