



柠檬酸法制备复氧化物材料的配位结构化学

陈全亮, 陈茂龙, 毛少瑜, 周朝晖*

固体表面物理化学国家重点实验室; 厦门大学化学化工学院, 厦门 361005

*通讯作者, E-mail: zhzhou@xmu.edu.cn

收稿日期: 2010-12-30; 接受日期: 2011-02-12

doi: 10.1360/032010-951

摘要 柠檬酸法在复氧化物材料制备中占有重要地位, 它具有分散均匀、制备温度低、产物粒径小的特点. 以特定组成和结构的柠檬酸络合物为前驱体, 直接分解可得到纯度较高的复氧化物, 从中可以了解复氧化物的形成过程. 本文从配位结构化学的角度, 评述以钛、钒、钼和钨柠檬酸络合物为前驱体制备复氧化物材料的研究进展.

关键词
柠檬酸
复氧化物
Pechini 法
柠檬酸法

1 引言

复氧化物在无机材料中占有重要的地位^[1], 它被广泛应用于催化^[2]、陶瓷材料^[3,4]、超导材料^[5]、磁性材料^[6]、光学材料^[7,8]等方面. 常见制备复氧化物的方法包括机械混合、金属盐浸渍法和水热法等^[9~12]. 近年来柠檬酸法越来越受到关注^[13~20], 以 Elsevier 出版期刊、美国专利和中国专利为检索资源, 每年以柠檬酸法制备复氧化物材料的文献报道近千篇. 柠檬酸法的优点主要有分散均匀、制备温度低、产物粒径小, 这些特点使柠檬酸法在复氧化物材料制备中占有重要地位.

柠檬酸是最大宗的有机酸产品, 我国年产量九十万吨, 80% 出口, 占世界总产量的 60%. 对于柠檬酸制备法, 目前多数复氧化物材料多采用过渡金属、稀土或碱土金属盐按计量投料, 再加入柠檬酸、乙二醇等溶解, 热分解得到复氧化物. 制备过程不了解混合物溶液中可能形成多种产物(包括络合物)的组成, 也不分离和表征其中的柠檬酸络合物. 这样所得到的复氧化物的物相组成变化范围较大, 重现性难控制, 而且常有明显的杂质存在. 因此, 以组成和结构

确定的柠檬酸络合物为前驱体, 直接分解即可能得到组成确定和纯度较高的复氧化物, 也能更好地了解柠檬酸法的特点. 应用柠檬酸法制备的复氧化物种类很多, 本文着重介绍以钛、钒、钼和钨为基的柠檬酸络合物前驱体的研究进展, 探讨它们在溶液中的组成与结构的变化, 以便深入了解复氧化物的形成过程和本质, 为更好地用柠檬酸法制备复氧化物材料提供理论依据和指导.

2 柠檬酸法制备钛基复氧化物

钛基复氧化物有着卓越的物理、化学和光学性能, 目前研究较多的钛基复氧化物如 MTiO_3 ($M = \text{Ca}^{[21]}$, $\text{Sr}^{[22]}$, $\text{Ba}^{[23]}$ 或 $\text{Pb}^{[24]}$), $\text{M}_2\text{Ti}_2\text{O}_7$ ($M = \text{La}$ 或 $\text{Y}^{[25]}$) 和 $\text{BaTi}_n\text{O}_{2n+1}$ ($n = 2-5$). 柠檬酸法制备钛基复氧化物历史已久, 1966 年, Pechini 利用柠檬酸、异丙醇钛和氯化钡反应, 生成柠檬酸钛钡前驱体, 由于柠檬酸钛钡溶于热水, 故可以利用重结晶的方法进一步纯化柠檬酸钛钡, 最后在 690 °C 热分解制得钛酸钡, 在这个专利里, Pechini 初步确定柠檬酸钛钡(BTC)的化学式为: $\text{BaO} \cdot \text{TiO}_2 \cdot 3\text{H}_2\text{cit} \cdot 6\text{H}_2\text{O}$ (柠檬酸

$C_6H_8O_7 = H_4cit$, 原专利有误)^[26]. Hennings^[27]研究小组利用红外光谱、拉曼光谱、粉末衍射和光电子能谱等手段研究了柠檬酸钛钡热分解制备钛酸钡的过程, 提出了柠檬酸钛钡热分解生成钛酸钡的基本步骤. 在这个分解过程中, 柠檬酸钛钡热分解生成钛酸钡 经过三个阶段(图 1): (1) 柠檬酸钛钡脱去结晶水和配位水生成无水的柠檬酸钛钡; (2) 无水柠檬酸钛钡分解形成中间相; (3) 中间相进一步分解形成钛酸钡.

Pérez-Maqueda^[28]和 Ward 研究小组^[29]以柠檬酸钛钡为前驱体, 通过不同的实验方法, 制备了不同形貌的钛酸钡材料; Pérez-Maqueda 认为不同的热处理条件可以控制钛酸钡的微结构, 他们通过两个步骤制备了针状的钛酸钡: (1) 用修饰的 Pechini 方法合成针状的柠檬酸钛钡前驱体; (2) 前驱体在反应温度可控制的条件下热分解生成钛酸钡; Ward 研究小组利用气溶胶高温裂解在 800 °C 制备出球型的钛酸钡. 也有文献对柠檬酸法制备钛酸钡粉体进行了综述^[30]. 我们^[31]制备了柠檬酸过氧钛络合物 $Ba_2(NH_4)_2[Ti_4(O_2)_4(Hcit)_2(cit)_2] \cdot 10H_2O$ (图 2), 该化合物在 800 °C 空气中进行灼烧, 产物通过 XRD 表征表明生成了 $BaTi_2O_5$ 纯相. 并通过控制不同外界阳离子分离得到组成和结构明确的络合物 $(NH_4)_2[Ti(H_2cit)_3] \cdot 3H_2O$, $(NH_4)_5[Fe(H_2O)_6][Ti(H_2cit)_3(Hcit)_3Ti] \cdot 3H_2O$, $Ba_2[Ti(H_2cit)(Hcit)_2] \cdot 8H_2O$ 和 $Ba_3(NH_4)_7[Ti(cit)_3H_3(cit)_3Ti] \cdot 15H_2O$. 其中 $Ba_2[Ti(H_2cit)(Hcit)_2] \cdot 8H_2O$ 在 1000 °C

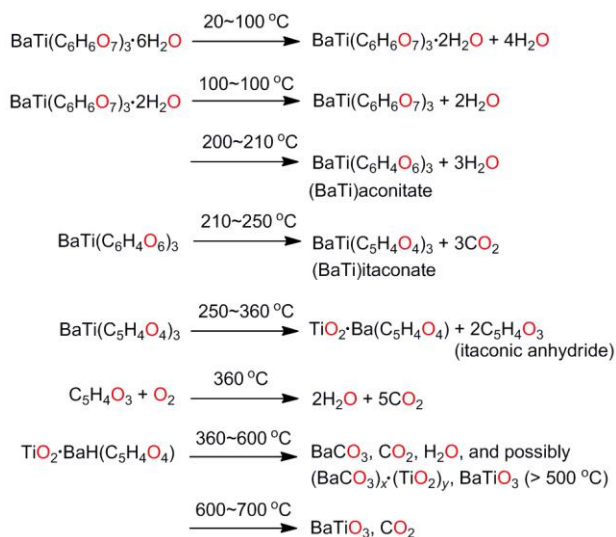


图 1 柠檬酸钛钡热分解生成钛酸钡的基本步骤^[27]

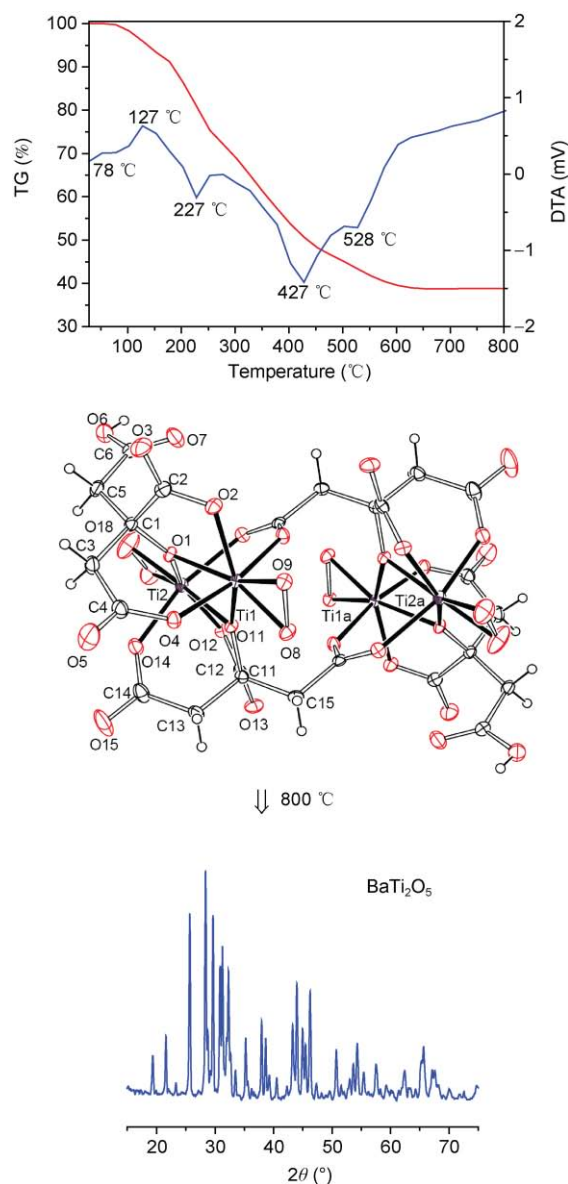


图 2 $Ba_2(NH_4)_2[Ti_4(O_2)_4(Hcit)_2(cit)_2] \cdot 10H_2O$ 的差热热重和阴离子结构图, 及其在 800 °C 空气中灼烧 2 h 热分解得到的 $BaTi_2O_5$ 的 XRD 图^[31]

热分解可以得到 Ba_2TiO_4 纯相^[32].

柠檬酸是多元羟基羧酸, 它通过去质子 α -羟氧基、 α -羧基与钛离子配位后, β -羧基上质子的多少可以通过调节溶液的 pH 值来调节, 这样就产生了带不同电荷的柠檬酸钛阴离子结构, 从而控制复氧化物的组成. 图 3 列出了柠檬酸钛阴离子在 pH 影响下的转换反应, 该转化反应可用于在不同 pH 值条件下分离得到不同质子化的柠檬酸钛络合物. 柠檬酸钛在

水溶液中也通过阳离子交换发生相互转换, 图4列出了具有代表性的不同外界阳离子柠檬酸钛络合物的合成和转换示意图. 从图表中可以看出, 尽管有着相同电荷的柠檬酸钛阴离子结构, 但是不同阳离子形成的柠檬酸钛络合物稳定的 pH 范围不同, 表明外界阳离子在构筑前驱体也起着重要的作用^[32]. 另外, 从不同 pH 值条件下的柠檬酸钛络合物的结构表征结果说明, 在柠檬酸钛络合物中, 柠檬酸主要通过去质子的 α -烷氧基和 α -羧基与钛离子配位, 形成五员螯环; 同时, 柠檬酸还通过去质子的 α -烷氧基和 α -羧基与钡离子配位, 形成六元螯环.

3 柠檬酸法制备钒基复氧化物

对钒基复氧化物, 程课题组^[33]报道了用柠檬酸法制备 $\text{Mg}_3(\text{VO}_4)_2$ 纳米颗粒, 实验表明该颗粒在环己烷氧化成环己烯反应中显示了良好的催化性能. Kakihana 等^[34]利用柠檬酸过氧钒为前驱体制备了 $\text{YVO}_4 \cdot \text{Eu}$ 荧光体材料. 吴课题组^[35]报道了用柠檬酸法制备了 $\text{Li}_{1+x}\text{V}_3\text{O}_8$ 化合物, 这种材料被认为可在充电的电池阴极材料上应用.

与金属钛相似, 钒和柠檬酸形成的络合物类型较多, 这些络合物可以作为制备钒基复氧化物的前驱体. 由于钒存在着多种价态, 以及柠檬酸配位模式的多样化, 导致钒和柠檬酸体系在溶液中的存在形式复杂. 柠檬酸钒在溶液中存在的物种不仅和它们本身的反应浓度比有关, 还和溶液的酸碱性密切相关. 许多柠檬酸钒的络合物已经被从溶液中分离并

表征了结构, 1995 年我们和 MIT 的研究组几乎同时分离得到了柠檬酸钒 $\text{K}_2[\text{VO}_2(\text{cit})]_2 \cdot 4\text{H}_2\text{O}$ ^[36, 37]; 在中性溶液中, 我们分离了含柠檬酸钒(V)酰四价和六价阴离子络合物 $\text{Na}_2\text{K}_2[\text{VO}_2(\text{Hcit})]_2 \cdot 9\text{H}_2\text{O}$ 和 $\text{K}_2(\text{NH}_4)_4[\text{VO}_2(\text{cit})]_2 \cdot 6\text{H}_2\text{O}$; 及其还原产物 $\text{Na}_4[\text{VO}(\text{cit})]_2 \cdot 6\text{H}_2\text{O}$ ^[38, 39]; 后续文献上报道了一系列钒(V/IV)柠檬酸络合物, 这些络合物的阳离子主要以钠、铵和钾盐为主, 如钒(V)柠檬酸络合物: $(\text{NH}_4)_4[\text{V}_2\text{O}_4(\text{Hcit})_2] \cdot 4\text{H}_2\text{O}$ ^[40], $\text{K}_4[\text{V}_2\text{O}_4(\text{H}_2\text{cit})_2] \cdot 5.6\text{H}_2\text{O}$ ^[41]; 钒(IV)柠檬酸络合物: $\text{K}_3[\text{V}_2\text{O}_2(\text{cit})(\text{Hcit})] \cdot 7\text{H}_2\text{O}$ ^[42], $\text{K}_4[\text{V}_2\text{O}_2(\text{cit})_2] \cdot 6\text{H}_2\text{O}$ ^[43]和 $\text{Na}_2\text{K}_2[\text{V}_2\text{O}_2(\text{cit})_2] \cdot 6\text{H}_2\text{O}$ ^[44].

柠檬酸钒物种之间存在着相互转化, 包括四价柠檬酸钒和五价柠檬酸钒络合物之间的转化. 2002 年 Salifoglou^[45]课题组研究了双核柠檬酸钒(IV/V)物种 $\text{K}_2[\text{V}_2\text{O}_4(\text{H}_2\text{cit})_2] \cdot 4\text{H}_2\text{O}$, $\text{K}_4[\text{V}_2\text{O}_4(\text{Hcit})_2] \cdot 5.6\text{H}_2\text{O}$, $\text{K}_2[\text{V}_2\text{O}_2(\text{O}_2)_2(\text{H}_2\text{cit})_2] \cdot 2\text{H}_2\text{O}$, $\text{K}_4[\text{V}_2\text{O}_2(\text{cit})_2] \cdot 6\text{H}_2\text{O}$, $\text{K}_3[\text{V}_2\text{O}_2(\text{cit})(\text{Hcit})] \cdot 7\text{H}_2\text{O}$, $(\text{NH}_4)_4[\text{V}_2\text{O}_2(\text{cit})_2] \cdot 2\text{H}_2\text{O}$ 和 $(\text{NH}_4)_6[\text{V}_2\text{O}_4(\text{cit})_2] \cdot 6\text{H}_2\text{O}$ 在溶液中的相互转化, 这些转化是通过钒的氧化还原过程进行的. 在研究反应转化时, 作者引入了过氧化氢, 认为钒(V/VI)和过氧化氢的反应摩尔比是影响不同价态柠檬酸钒物种转

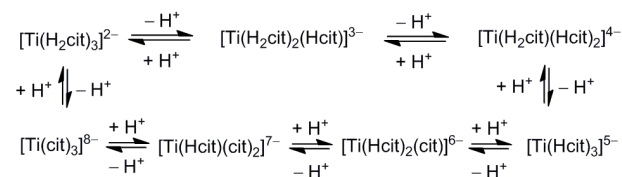


图3 结构表征的柠檬酸钛阴离子之间的转换^[32]

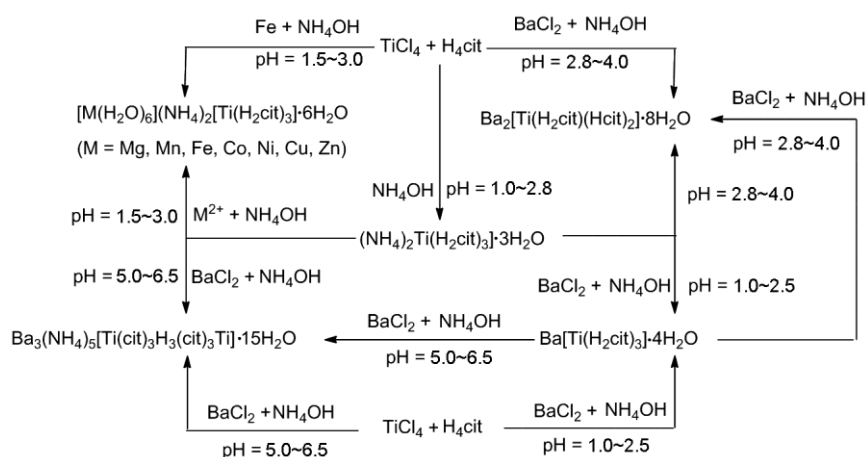


图4 钛柠檬酸络合物的合成和转化^[32]

化的关键因素之一. 另外, 作者通过红外光谱和结构解析, 对不同结构模式的双核钒(IV/V)进行了化学关联.

除了研究不同价态钒的柠檬酸钒的络合物, 不同阳离子的柠檬酸钒络合物也受到人们的关注. Salifoglou 等^[46]分离了不同阳离子的化合物 $M_2[V_2O_4(H_2cit)_2] \cdot nH_2O$ ($M^+ = Na^+, NH_4^+, n = 2; Me_4N^+, K^+, n = 4$). 虽然这些化合物有不同的阳离子, 但它们的阴离子结构并不发生变化, 阴离子结构中都含有 V_2O_2 单元(图 5), V_2O_2 单元钒的价态都为正五价. 在过氧化氢存在下, 分离得到的络合物 $M_2[V_2O_2(O_2)_2(Hcit)_2] \cdot 2H_2O$ ($M = K^+, NH_4^+$) 钒的配位数为七配位.

4 柠檬酸法制钼、钨基复氧化物

钼、钨基复氧化物在催化反应有着广泛的应用, 在均相催化反应中, 钼、钨基复氧化物在溶液中能活化过氧化氢, 显示了独特的催化性能, 如烯烃的环氧化、醇的氧化以及烯烃断键形成羧酸等^[47~50]. 在钼、钨基化合物掺杂 Bi, Fe, Co, Mn, Ce 等金属或者其他的杂配体能够提高它们的催化性能或者提高它们的选择性. 王等^[51]用柠檬酸、乙二酸和硫酸制备具有微球结构的 MoO_2 ; Rocha 等^[52]用柠檬酸法制备 La_2MoO_6 , La_2MoO_6 复氧化物是类似介孔粉末, 同时具有高的表面能.

作为钼基复氧化物的前驱体, 柠檬酸钼络合物种类比较丰富. 现已报道的不同钼(VI)与柠檬酸比的络合物, 包括 1:1、1:2 和 2:1 (Mo: cit 摩尔比)这三种类型. 摩尔比为 1:1 的络合物有 $K[(MoO_2)_2(OH)(H_2cit)_2] \cdot 4H_2O$ ^[53], $[MoO_2(H_2cit)(bpy)] \cdot H_2O$ ^[54], $K_6[(MoO_2)_2-$

$O(cit)_2] \cdot 5H_2O$ ^[55], $K_2Na_4[(MoO_2)_2O(cit)_2] \cdot 5H_2O$ ^[56], $K_6[(MoO_2)_2O(cit)_2] \cdot 2H_2O$ ^[57], $K_4[MoO_3(cit)] \cdot 2H_2O$ ^[58] (图 6); 摩尔比为 1:2 的络合物如 $Na_2[MoO_2(H_2cit)_2] \cdot 3H_2O$ ^[58], $K_2[MoO_2(H_2cit)_2] \cdot 3H_2O$ ^[59]; 摩尔比为 2:1 的络合物有 $K_4[(MoO_2)_4O_3(Hcit)_2] \cdot 6H_2O$ ^[60], $Me_3N(CH_2)_6NMe_3]_2[(MoO_2)_4O_3(Hcit)_2] \cdot 12H_2O$ ^[61]. 柠檬酸钼络合物的分离主要受到柠檬酸和钼酸盐不同摩尔比与溶液的 pH 影响. 在这些络合物中, 柠檬酸以多齿配位模式通过 α -烷氧基、 α -羧基和(或) β -羧基与钼原子配位, 中心金属常常处在畸变的八面体 MoO_6 构型, 这与其他 α -羟基羧酸(苹果酸、柠草酸)和钼的配位模式相似^[62, 63].

在过氧化氢的参与下, 柠檬酸钼体系变得更加的复杂^[64]. 与没有过氧化氢参与的反应相似, 溶液的 pH 值影响着产物的生成. 钼柠檬酸的过氧物种的合成转化如图 7 所示, 在 pH 7~9 的范围内, 先得到红色的溶液, 这种红色的中间产物被认为是不稳定的 $[Mo(O_2)_4]^{2-}$ ^[65], 然后转化到最终产物 $K_4[MoO(O_2)_2(cit)] \cdot 4H_2O$. 在 pH 2~6 的范围内, 得到产物 $K_5[MoO(O_2)_2(Hcit)H(Hcit)(O_2)_2OMo] \cdot 6H_2O$; 由于在相同的 pH 范围内, 在加入相同比例的柠檬酸后, $K_2[Mo_2O_3(O_2)_4(H_2O)_2] \cdot 4H_2O$ 可以直接转化为络合物 $K_5[MoO(O_2)_2(Hcit)H(Hcit)(O_2)_2OMo] \cdot 6H_2O$, 由此认为 $K_2[Mo_2O_3(O_2)_4(H_2O)_2] \cdot 4H_2O$ 是此反应的中间产物. 在更为酸性的条件下, 得到 $K_2[MoO(O_2)_2(H_2cit)] \cdot 3H_2O \cdot 0.5H_2O_2$.

单核的柠檬酸钼络合物 $K_4[MoO_3(cit)] \cdot 2H_2O$ 在 pH 8.0~8.5、含有钼酸钾和柠檬酸的溶液中制得^[66]. 络合物 $K_4[MoO(O_2)_2(cit)] \cdot 4H_2O$ 、 $K_5[MoO(O_2)_2(Hcit)H(Hcit)(O_2)_2OMo] \cdot 6H_2O$ 还可以通过过氧化氢氧化该

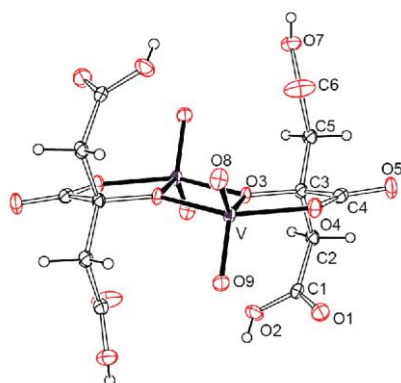


图 5 阴离子 $[V_2O_4(H_2cit)_2]^{2-}$ 的结构图^[46]

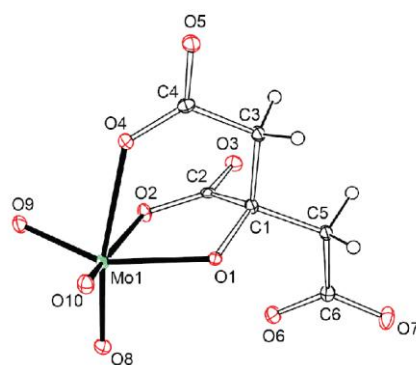
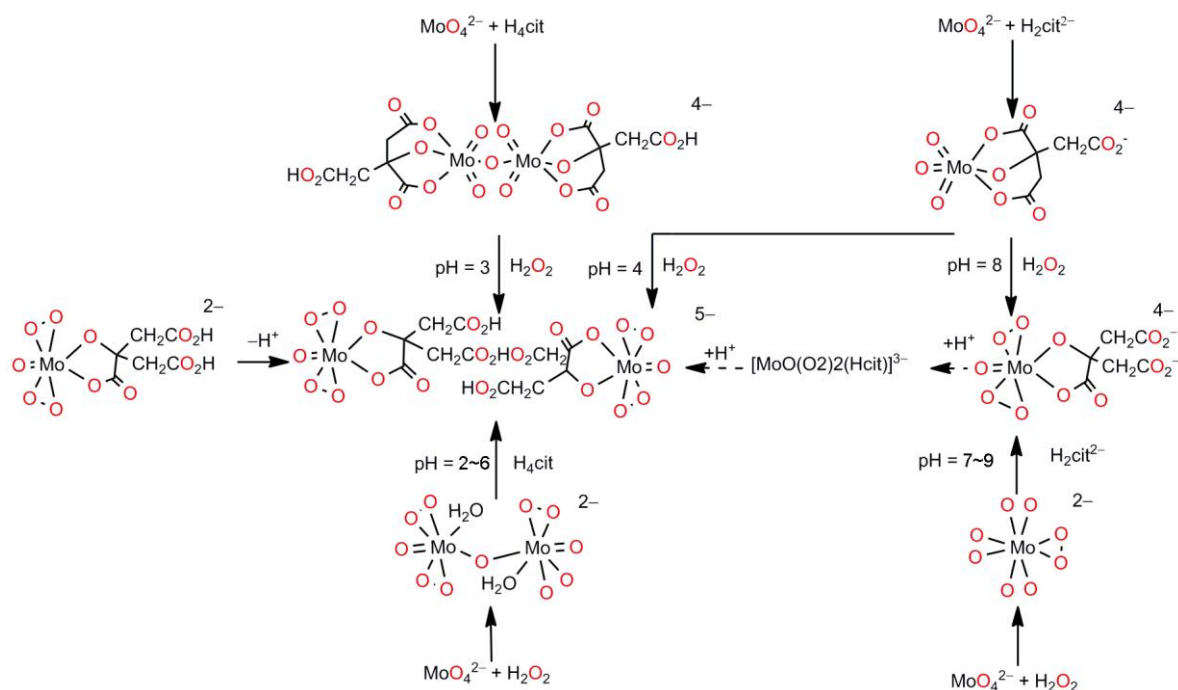


图 6 化合物 $K_4[MoO_3(cit)] \cdot 2H_2O$ 的阴离子结构图

图 7 过氧柠檬酸钼络合物的合成和转化^[65]

络合物制备. 溶液的 pH 值直接控制了这个转化反应的反应产物: 在 pH 8 时得到络合物 $\text{K}_4[\text{MoO}(\text{O}_2)_2(\text{cit})] \cdot 4\text{H}_2\text{O}$, 在 pH 4 时得到双核络合物 $\text{K}_5[\text{MoO}(\text{O}_2)_2(\text{Hcit})\text{H}(\text{Hcit})(\text{O}_2)_2\text{OMo}] \cdot 6\text{H}_2\text{O}$. 另外, 双核柠檬酸钼络合物 $\text{K}_4[(\text{MoO}_2)_2(\text{Hcit})] \cdot 4\text{H}_2\text{O}$ 在 pH 为 3 时可以被过氧化氢氧化, 得到产物 $\text{K}_5[\text{MoO}(\text{O}_2)_2(\text{Hcit})\text{H}(\text{Hcit})(\text{O}_2)_2\text{OMo}] \cdot 6\text{H}_2\text{O}$. 在这两个不含过氧的单核或双核的柠檬酸钼络合物中, 柠檬酸作为三齿配体和钼配位, 这些转化反应说明柠檬酸在过氧存在下由三齿配位的方式转化为更为稳定的二齿配位, 即柠檬酸配体的 β -羧基与钼的配位能力较弱, 在过氧存在下被取代.

在这些过氧物种中, 应该还存在一种柠檬酸配体质子化的中间物种 $[\text{MoO}(\text{O}_2)_2(\text{Hcit})]^{3-}$, 而实际上络合物 $\text{K}_4[\text{MoO}(\text{O}_2)_2(\text{cit})] \cdot 4\text{H}_2\text{O}$ 快速地形成更稳定的络合物 $\text{K}_5[\text{MoO}(\text{O}_2)_2(\text{Hcit})\text{H}(\text{Hcit})(\text{O}_2)_2\text{OMo}] \cdot 6\text{H}_2\text{O}$, 因此分离不到此物种. 物种 $[\text{MoO}(\text{O}_2)_2(\text{H}_2\text{cit})]^{2-}$ 在 pH 2~6 的条件下, 也可以转化形成 $\text{K}_5[\text{MoO}(\text{O}_2)_2(\text{Hcit})\text{H}(\text{Hcit})(\text{O}_2)_2\text{OMo}] \cdot 6\text{H}_2\text{O}$, 这个事实说明了络合物 $\text{K}_5[\text{MoO}(\text{O}_2)_2(\text{Hcit})\text{H}(\text{Hcit})(\text{O}_2)_2\text{OMo}] \cdot 6\text{H}_2\text{O}$ 很稳定.

与柠檬酸钼络合物相比, 柠檬酸钨络合物报道较少. 1993 年 Lopis 等发表了双核柠檬酸钨络合物

$\text{Na}_6[\text{W}_2\text{O}_5(\text{cit})_2] \cdot 10\text{H}_2\text{O}$ 的分离和表征^[67]. 本课题组先后合成并分离得到了单核和双核络合物 $\text{Na}_2[\text{WO}_2(\text{H}_2\text{cit})_2] \cdot 3\text{H}_2\text{O}$ ^[68], $\text{Na}_4\text{K}_2[\text{W}_2\text{O}_5(\text{cit})_2] \cdot 11\text{H}_2\text{O}$ ^[68], $\text{K}_4[\text{WO}_3(\text{cit})] \cdot 2\text{H}_2\text{O}$, $\text{NaK}_3[\text{W}_2\text{O}_5(\text{Hcit})_2] \cdot 4\text{H}_2\text{O}$, $(\text{Hphen})_3[\text{WO}_2\text{H}(\text{Hcit})_2] \cdot 6\text{H}_2\text{O}$ ^[69]. 由于钨形成的过氧络合物稳定性差, 目前报道的过氧柠檬酸钨络合物也很少^[70].

钨柠檬酸体系在溶液中同样多物种并存, 在溶液中, 单核柠檬酸钨被认为可能存在的主要物种有 $[\text{WO}_3(\text{cit})(\text{OH}_2)]^{4-}$, $[\text{WO}_3(\text{Hcit})(\text{OH}_2)]^{3-}$, $[\text{WO}_3(\text{H}_2\text{cit})(\text{OH}_2)]^{2-}$, $[\text{WO}_2(\text{H}_2\text{cit})(\text{OH})(\text{OH}_2)]^{-}$, $[\text{WO}_2(\text{H}_2\text{cit})_2]^{2-}$, 双核钨物种有 $[\text{W}_2\text{O}_5(\text{cit})_2(\text{OH}_2)_2]^{6-}$, $[\text{W}_2\text{O}_5(\text{Hcit})(\text{cit})(\text{OH}_2)_2]^{5-}$, $[\text{W}_2\text{O}_6(\text{Hcit})(\text{OH}_2)_2]^{3-}$, 以及它们不同的质子化产物. 这些物种在溶液中的转化主要与钨和柠檬酸的摩尔比以及溶液酸碱性关系较大. 目前分离得到的柠檬酸钨络合物主要有 2:2, 1:2, 1:1(钨:柠檬酸)的柠檬酸钨络合物. 本课题组^[69]分离得到的化合物 $\text{K}_4[\text{WO}_3(\text{cit})] \cdot 2\text{H}_2\text{O}$, $\text{NaK}_3[\text{W}_2\text{O}_5(\text{Hcit})_2] \cdot 4\text{H}_2\text{O}$, $(\text{Hphen})_3[\text{WO}_2\text{H}(\text{Hcit})_2] \cdot 6\text{H}_2\text{O}$ 进一步支持了柠檬酸钨不同物种在溶液中的转化(图 8).

5 结束语与展望

通过以上四种金属柠檬酸络合物前驱体的讨论

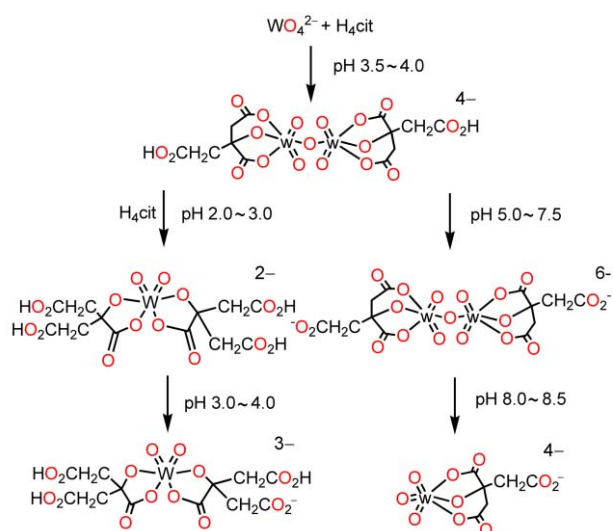


图8 单核和双核柠檬酸钨的合成和转化^[69]

表明, 柠檬酸络合物的类型很多, 这主要是由柠檬酸

本身配位多齿配位模式的多样性和金属离子在溶液中的多种存在形式引起的。除此之外, 金属价态的变化和其他添加剂的引入也导致金属络合物前驱体种类的多样化。在分离这些金属柠檬酸络合物时, 柠檬酸和金属的反应摩尔比、溶液的 pH 值、外界离子和其他混合溶剂的加入直接影响产物的分离。在过氧化氢的参与下, 过氧柠檬酸络合物是溶液的主要物种。由此可见, 反应条件控制对柠檬酸法制备复氧化物材料的重要性, 它直接影响分离得到的金属柠檬酸络合物前驱体种类。在实际应用中, 溶液中单核、双核、多核络合物和柠檬酸配位聚合物形成; 多组分条件下的混配络合物、多金属形成的共混络合物和掺杂体系中复合物形成; 强酸性反应体系的物种变化等条件的选择, 对于减少柠檬酸的用量、避免前驱体的物相分离、形成合适的溶胶、降低热解温度, 包括后续热分解过程的研究都是值得探索和研究的课题。

致谢 感谢审稿专家提出的宝贵意见, 感谢厦门大学蔡启瑞教授长期以来对本工作的支持和帮助。感谢国家自然科学基金项目(21073150)和国家重点基础研究发展计划(973 计划)(2010CB732303)的资助。

参考文献

- 1 Fernandez-Garcia M, Martinez-Arias A, Hanson JC, Rodriguez JA. Nanostructured oxides in chemistry: Characterization and properties. *Chem Rev*, 2004, 104: 4063–4104
- 2 Davis RJ, Liu ZF. Titania-silica: A model binary oxide catalyst system. *Chem Mater*, 1997, 9: 2311–2324
- 3 Lee KS, Jung KI, Heo YS, Kim TW, Jung YG, Paik U. Thermal and mechanical properties of sintered bodies and EB-PVD layers of Y_2O_3 added $\text{Gd}_2\text{Zr}_2\text{O}_7$ ceramics for thermal barrier coatings. *J Alloys Compd*, 2010, 507: 448–455
- 4 Gene HH. Ferroelectric ceramics: History and technology. *J Am Ceram Soc*, 1999, 82: 797–818
- 5 Shin JF, Hussey L, Orera A, Slater PR. Enhancement of the conductivity of $\text{Ba}_2\text{In}_2\text{O}_5$ through phosphate doping. *Chem Commun*, 2010, 46: 4613–4615
- 6 Srivastava M, Ojha AK, Chaubey S, Singh J. *In situ* synthesis of magnetic ($\text{NiFe}_2\text{O}_4/\text{CuO}/\text{FeO}$) nanocomposites. *J Solid State Chem*, 2010, 183: 2667–2674
- 7 Linsebigler AL, Lu G, Yates JT. Photocatalysis on TiO_2 surfaces: Principles, mechanisms, and selected results. *Chem Rev*, 1995, 95: 735–758
- 8 Peña MA, Fierro JLG. Chemical structures and performance of perovskite oxides. *Chem Rev*, 2001, 101: 1981–1987
- 9 Chen LY, Shen YM, Bai JF. Large-scale synthesis of uniform spinel ferrite nanoparticles from hydrothermal decomposition of trinuclear heterometallic oxo-centered acetate clusters. *Mater Lett*, 2009, 63: 1099–1101
- 10 Chen LY, Zhao CL, Bai JF. Gel-hydrothermal preparation of hollow CoFe_2O_4 nanospheres and their properties. *Chem Lett*, 2009, 38: 276–277
- 11 Chen LY, Dai H, Shen YM, Bai JF. Size-controlled synthesis and magnetic properties of NiFe_2O_4 hollow nanospheres via a gel-assisted hydrothermal route. *J Alloys Compd*, 2010, 491: L33–L38
- 12 Chen LY, Zhao CL, Zhou Y, Peng H, Zheng YY. Controlled synthesis of Fe_3O_4 nanosheets via one-step pyrolysis of EDTA ferric sodium salt. *J Alloys Compd*, 2010, 504: L46–L50
- 13 Alifanti M, Florea M, Parvulescu VI. Ceria-based oxides as supports for LaCoO_3 perovskite; catalysts for total oxidation of VOC. *Appl Catal B: Environ*, 2007, 70: 400–405

- 14 Xia ZG, Sun JF, Du HY, Chen DM, Sun JY. Luminescence properties of double-perovskite $\text{Sr}_2\text{Ca}_{1-2x}\text{Eu}_x\text{Na}_x\text{MoO}_6$ red-emitting phosphors prepared by the citric acid-assisted sol-gel method. *J Mater Sci*, 2010, 45: 1553–1559
- 15 Kazuya T, Yoshinori S, Toshihiko O. Sorption and oxidation of tetravalent plutonium on Mn oxide in the presence of citric acid. *Chem Lett*, 2009, 38: 1032–1033
- 16 Bruno A, Idriss A, Agustin BL, Avelina GG. Probing the surface of ceria-zirconia catalysts using NO_x adsorption/desorption: A first step toward the investigation of crystallite heterogeneity. *J Phys Chem C*, 2010, 114: 13300–13312
- 17 Cho S, Jang JW, Jung SH, Lee BR, Oh E, Lee KH. Precursor effects of citric acid and citrates on ZnO crystal formation. *Langmuir*, 2009, 25: 3825–3831
- 18 Nomura A, Shin S, Mehdi OO, Kauffmann JM. Preparation, characterization, and application of an enzyme-immobilized magnetic microreactor for flow injection analysis. *Anal Chem*, 2004, 76: 5498–5502
- 19 华斌, 孔永红, 卢凤双, 张建福, 蒲健, 李箭. MnCo_2O_4 的电性能及其对 SUS 430 金属连接体的改性. 科学通报, 2010, 55: 1055–1062
- 20 白守礼, 刘志勇, 石冰洁, 马丽景, 杨鹏程, 李殿卿, 陈霭璠. 氧化镁表面修饰稀土催化材料的制备和气敏性能. 中国科学 B 辑: 化学, 2009, 39: 1603–1609
- 21 Pan YX, Su Q, Xu HF, Chen TH, Ge WK, Yang CL, Wu MM. Synthesis and red luminescence of Pr^{3+} -doped CaTiO_3 nanophosphor from polymer precursor. *J Solid State Chem*, 2003, 174: 69–73
- 22 Kakihana M, Okubo T, Arima M, Nakamura Y, Yashima M, Yoshimura M. Polymerized complex route to the synthesis of pure SrTiO_3 at reduced temperatures: Implication for formation of Sr-Ti heterometallic citric acid complex. *J Sol-Gel Sci Technol*, 1998, 12: 95–109
- 23 Arima M, Kakihana M, Nakamura Y, Yashima M, Yoshimura M. Polymerized complex route to barium titanate powders using barium-titanium mixed-metal citric acid complex. *J Am Ceram Soc*, 1996, 79: 2847–2856
- 24 Kakihana M, Okubo T, Arima M, Uchiyama O, Yashima M, Yoshimura M, Nakamura Y. Polymerized complex synthesis of perovskite lead titanate at reduced temperatures: Possible formation of heterometallic (Pb, Ti)-citric acid complex. *Chem Mater*, 1997, 9: 451–456
- 25 Kakihana M, Milanova MM, Arima M, Okubo T, Yashima M, Yoshimura M. Polymerized complex route to synthesis of pure $\text{Y}_2\text{Ti}_2\text{O}_7$ at 750°C using yttrium-titanium mixed-metal citric acid complex. *J Am Ceram Soc*, 1996, 79: 1673–1676
- 26 Pechini MP. Barium titanium citrate, barium titanate and processes for producing same. US Patent, No. 3231328, 1966
- 27 Hennings D, Mayr W. Thermal decomposition of (Ba, Ti) citrates into barium titanate. *J Solid State Chem*, 1978, 26: 329–338
- 28 Pérez-Maqueda LA, Diáñez MJ, Gotor FJ, Sayagués MJ, Real C, Criado JM. Synthesis of needle-like BaTiO_3 particles from the thermal decomposition of a citrate precursor under sample controlled reaction temperature conditions. *J Mater Chem*, 2003, 13: 2234–2241
- 29 Guo WP, Datye AK, Ward TL. Synthesis of barium titanate powders by aerosol pyrolysis of a Pechini-type precursor solution. *J Mater Chem*, 2005, 15: 470–477
- 30 Kakihana M, Yoshimura M. Synthesis and characteristics of complex multicomponent oxides prepared by polymer complex method. *Bull Chem Soc Jpn*, 1999, 72: 1427–1443
- 31 Deng YF, Zhou ZH, Wan HL, Tsai KR. Ammonium barium citrate peroxotitanate(IV) $\text{Ba}_2(\text{NH}_4)_2[\text{Ti}_4(\text{O}_2)_4(\text{Hcit})_2(\text{cit})_2]\cdot 10\text{H}_2\text{O}$: A molecular precursor of stoichiometric BaTi_2O_5 . *Inorg Chem Comm*, 2004, 7: 169–172
- 32 Deng YF, Zhou ZH, Wan HL. pH-Dependent isolations and spectroscopic, structural, and thermal studies of titanium citrate complexes. *Inorg Chem*, 2004, 43: 6266–6273
- 33 Jin M, Cheng ZM, Gao YL, Fang XC. Oxidative dehydrogenation of cyclohexane with $\text{Mg}_3(\text{VO}_4)_2$ synthesized by the citrate process. *Mater Lett*, 2009, 63: 2055–2058
- 34 Kaowphong S, Petrykin V, Thongtem S, Kakihana M. Synthesis of nanocrystalline YVO_4 : Eu red emission phosphor with high fluorescence intensity by hydrothermal method using original vanadium-peroxo-citrate complex. *J Ceram Soc Jpn*, 2009, 117: 273–276
- 35 Wu ZJ, Zhao XB, Tu J, Cao GS, Tu JP, Zhu TJ. Synthesis of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ by citrate sol-gel route at low temperature. *J Alloys Compd*, 2005, 403: 345–348
- 36 Zhou ZH, Yan WB, Wan HL, Tsai KR, Wang JZ, Hu SZ. Metal-hydroxycarboxylate interactions: Syntheses and structures of $\text{K}_2[\text{VO}_2(\text{C}_6\text{H}_6\text{O}_7)]_2\cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2[\text{VO}_2(\text{C}_6\text{H}_6\text{O}_7)]_2\cdot 2\text{H}_2\text{O}$. *J Chem Crystallogr*, 1995, 25: 807–811
- 37 Wright DW, Humiston PA, Orme-Johnson WH, Davis WM. A unique coordination mode for citrate and a transition metal $\text{K}_2[\text{VO}_2(\text{C}_6\text{H}_6\text{O}_7)]_2\cdot 4\text{H}_2\text{O}$. *Inorg Chem*, 1995, 34: 4194–4197
- 38 Zhou ZH, Wan HL, Hu SZ, Tsai KR. Syntheses and structures of the potassium-ammonium dioxocitratovanadate(V) and sodium oxocitratovanadate(IV) dimers. *Inorg Chim Acta*, 1995, 237: 193–197
- 39 Zhou ZH, Zhang H, Jiang YQ, Lin DH, Wan HL, Tsai KR. Complexation between vanadium(V) and citrate: Spectroscopic and structural characterization of a dinuclear vanadium(V) complex. *Trans Metal Chem*, 1999, 24: 605–609

- 40 Kaliva M, Raptopoulou CP, Terzis A, Salifoglou A. Systematic studies on pH-dependent transformations of dinuclear vanadium(V)-citrate complexes in aqueous solutions. A perspective relevance to aqueous vanadium(V)-citrate speciation. *J Inorg Biochem*, 2003, 93:161–173
- 41 Kaliva M, Giannadaki T, Salifoglou A, Raptopoulou CP, Terzis A. A new dinuclear vanadium(V)-citrate complex from aqueous solutions. Synthetic, structural, spectroscopic, and pH-dependent studies in relevance to aqueous vanadium(V)-citrate speciation. *Inorg Chem*, 2002, 41: 3850–3858
- 42 Tsaramyrsi M, Kaliva M, Salifoglou A, Raptopoulou CP, Terzis A, Tangoulis V, Giapintzakis J. Vanadium(IV)-citrate complex interconversions in aqueous solution. A pH-dependent synthetic, structural, spectroscopic, and magnetic study. *Inorg Chem*, 2001, 40: 5772–5779
- 43 Velayutham M, Verghese B, Suramianian S. Magneto-structural correlation studies of a ferromagnetically coupled dinuclear vanadium(IV) complex. Single-crystal EPR study. *Inorg Chem*, 1998, 37: 1336–1340
- 44 Zhou ZH, Wan HL, Hu SZ, Tsai KR. Synthesis and structure of sodium-potassium oxocitratovanadium(IV) dimer. *Chinese J Struct Chem*, 1995, 14: 37–341
- 45 Kaliva M, Kyriakakis E, Salifoglou A. Reactivity investigation of dinuclear vanadium(IV) citrate complexes in aqueous solutions. A closer look into aqueous vanadiumcitrate interconversions. *Inorg Chem*, 2002, 41: 7015–7023
- 46 Tsaramyrsi M, Kavousanaki D, Raptopoulou CP, Terzis A, Salifoglou A. Systematic synthesis, structural characterization, and reactivity studies of vanadium(V)-citrate anions $[\text{VO}_2(\text{C}_6\text{H}_5\text{O}_7)]^{2-}$, isolated from aqueous solutions in the presence of different cations. *Inorg Chim Acta*, 2001, 320: 47–59
- 47 Gharah N, Chakraborty S, Mukherjee AK, Bhattacharyya R. Oxoperoxo molybdenum(VI)- and tungsten(VI)-complexes with 1-(2'-hydroxyphenyl) ethanone oxime: Synthesis, structure and catalytic uses in the oxidation of olefins, alcohols, sulfides and amines using H_2O_2 as a terminal oxidant. *Inorg Chim Acta*, 2009, 362: 1089–1100
- 48 Herbert M, Montilla F, Moyano R, Pastor A, Alvarez E, Galindo A. Olefin epoxidations in the ionic liquid $[\text{C}_4\text{mim}][\text{PF}_6]$ catalysed by oxodiperoxomolybdenum species *in situ* generated from molybdenum trioxide and urea-hydrogen peroxide: The synthesis and molecular structure of $[\text{Mo}(\text{O})(\text{O}_2)_2(4\text{-MepyO})_2]\cdot\text{H}_2\text{O}$. *Polyhedron*, 2009, 28: 3929–3934
- 49 Maiti SK, Malik KMA, Gupta S, Chakraborty S, Ganguli AK, Mukherjee AK, Bhattacharyya R. Oxo- and oxoperoxo-molybdenum(VI) complexes with aryl hydroxamates: Synthesis, structure, and catalytic uses in highly efficient, selective, and ecologically benign peroxidic epoxidation of olefins. *Inorg Chem*, 2006, 45:9843–9857
- 50 Maiti SK, Dinda S, Bhattacharyya R. Unmatched efficiency and selectivity in the epoxidation of olefins with oxo-diperoxomolybdenum(VI) complexes as catalysts and hydrogen peroxide as terminal oxidant. *Tetrahedron Lett*, 2008, 49: 6205–6208
- 51 Wang ST, An CH, Zhang YG, Zhang Z, Qian YT. Ethanothermal reduction to MoO_2 microspheres via modified Pechini method. *J Cryst Growth*, 2006, 293: 209–215
- 52 Rocha RA, Muccillo ENS. Characterization of La_2MoO_6 prepared by the cation complexation technique. *J Alloys Compd*, 2005, 400: 83–87
- 53 Zhou ZH, Chen CY, Cao ZX, Tsai KR, Chow YL. N-Heterocycle chelated oxomolybdenum(VI and V) complexes with bidentate citrate. *Dalton Trans*, 2008, 2475–2479
- 54 Zhou ZH, Deng YF, Cao ZX, Zhang RH, Chow YL. Dimeric dioxomolybdenum(VI) and oxomolybdenum(V) complexes with citrate at very low pH and neutral conditions. *Inorg Chem*, 2005, 44: 6912–6914
- 55 Zhou XH, Xing YH, Xu JQ, Li DM, Wang RZ, Liu SQ, Zeng QX, Huang XY. Molybdenum(VI)-oxygen complex containing citrate ligand: Synthesis and characterization of $\text{K}_6[(\text{MoO}_2)_2\text{O}(\text{cit})_2]\cdot 5\text{H}_2\text{O}$. *Solid State Sci*, 1999, 189–198
- 56 Zhou ZH, Wan HL, Tsai KR. Molybdenum(VI) complex with citric acid: Synthesis and structural characterization of 1:1 ratio citrato molybdate $\text{K}_2\text{Na}_4[(\text{MoO}_2)_2\text{O}(\text{cit})_2]\cdot 5\text{H}_2\text{O}$. *Polyhedron*, 1997, 16: 75–79
- 57 Xing YH, Xu JQ, Sun HR, Li DM, Wang RZ, Wang TG, Bu WM, Ye L, Yang GD, Fan YG. Hexapotassium μ -oxo-bis[(citrate)-dioxomolybdate] dehydrate. *Acta Crystallogr C*, 1998, 54: 1615–1616
- 58 Zhou ZH, Wan HL, Tsai KR. Bidentate citrate with free terminal carboxyl groups, syntheses and characterization of citrato oxomolybdate(VI) and oxotungstate(VI), $\Delta/\Lambda\text{-Na}_2[\text{MO}_2(\text{H}_2\text{cit})_2]\cdot 3\text{H}_2\text{O}$ (M = Mo or W). *J Chem Soc Dalton Trans*, 1999, 4289–4290
- 59 Jiang YQ, Zhao H, Fang ZM, Wan HL, Xiong M, Zhou ZH. Preparations of pure alkaline earth molybdate phases from single molecular precursors. *Chem Res Chinese Univ*, 2004, 20: 675–680
- 60 Alcock NW, Dudek M, Gryboś R, Hodorowicz E, Kanas A, Samotus A. Complexation between molybdenum(VI) and citrate-structural characterization of a tetrameric complex, $\text{K}_4[(\text{MoO}_2)_4\text{O}_3(\text{cit})_2]\cdot 6\text{H}_2\text{O}$. *J Chem Soc Dalton Trans*, 1990, 707–711
- 61 Nassimbeni LR, Niven ML, Cruywagen JJ, Heyns JBB. Complexation between molybdenum(VI) and citrate: Crystal and molecular structure of $[\text{Mo}_4\text{O}_{11}(\text{citrate})_2](\text{Me}_3\text{N}(\text{CH}_2)_6\text{NMe}_3)_2\cdot 12\text{H}_2\text{O}$. *J Crystallogr Spectrosc Res*, 1987, 17: 373–382

- 62 Knobler CB, Wilson AJ, Hider RN, Jensen IW, Penfold BR, Robinson WT, Wilkins CJ. Molybdenum(VI) complexes with malic acid: Their inter-relationships, and the crystal structure of dicesium bis[(*S*)-malato(2-)]-*cis*-dioxomolybdate(VI)-water(1/1). *J Chem Soc Dalton Trans*, 1983, 1299–1303
- 63 Zhou ZH, Yan WB, Wan HL, Tsai KR. Synthesis and characterization of homochiral polymeric *S*-malato molybdate(VI): Toward the potentially stereospecific formation and absolute configuration of iron-molybdenum cofactor in nitrogenase. *J Inorg Biochem*, 2002, 90: 137–143
- 64 Zhou ZH, Hou SY, Wan HL. Peroxomolybdate(VI)-citrate and -malate complex interconversions by pH-dependence. Synthetic, structural and spectroscopic studies. *Dalton Trans*, 2004, 1393–1399
- 65 Stomberg R. Studies on peroxomolybdates V. The crystal structure of tetramminezinc(II) tetraperoxomolybdate(VI), $[\text{Zn}(\text{NH}_3)_4][\text{Mo}(\text{O}_2)_4]$. *Acta Chem Scand*, 1969, 23: 2755–2763
- 66 Zhou ZH, Wan HL, Tsai KR. Syntheses and spectroscopic and structural characterization of molybdenum(VI) citrato monomeric raceme and dimer, $\text{K}_4[\text{MoO}_3(\text{cit})]\cdot 2\text{H}_2\text{O}$ and $\text{K}_4[(\text{MoO}_2)_2\text{O}(\text{Hcit})_2]\cdot 4\text{H}_2\text{O}$. *Inorg Chem*, 2000, 39: 59–64
- 67 Llopis E, Ramírez JA, Doménech A, Cervilla A. Tungsten(VI) complexes with citric acid (H_4cit). Structural characterisation of $\text{Na}_6[\{\text{WO}_2(\text{cit})_2\text{O}\}\cdot 10\text{H}_2\text{O}]$. *J Chem Soc Dalton Trans*, 1993, 1121–1124
- 68 Wang G, Zhou ZH, Zhang H, Ye JL, Wan HL. Synthesis, spectroscopic properties and structural characterization of sodium potassium citrato oxotungstate(VI) dimer. *Chinese J Struct Chem*, 2000, 19: 181–186
- 69 Zhang H, Zhao H, Jiang YQ, Hou SY, Zhou ZH, Wan HL. pH- and mol-ratio dependent tungsten(VI)-citrate speciation from aqueous solutions: syntheses, spectroscopic properties and crystal structures. *Inorg Chim Acta*, 2003, 351: 311–318
- 70 Hou SY, Zhou ZH, Lin TR, Wan HL. Peroxotungstates and their citrate and tartrate derivatives. *Eur J Inorg Chem*, 2006, 1670–1677

Progress in coordinated structural chemistry to citrate process

CHEN QuanLiang, CHEN MaoLong, MAO ShaoYu & ZHOU ZhaoHui

State Key Laboratory of Physical Chemistry of Solid Surfaces; College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

Abstract: Citrate method is one of the popular processes for the synthesis of mixed oxide. This is due to the advantages of its homogeneous, low decomposed temperature, and resulted small particle sizes. Citrate complexes are considered as the molecular precursors for the mixed oxides by thermal decomposition, which may show different compositions and structures. The mixed oxides can be used as catalysts and the other materials by citrate process. In the present paper, recent progress of Ti, V, Mo and W citrate complexes as precursors for the preparation of mixed oxides is reviewed.

Keywords: citric acid, mixed oxides, Pechini method, citrate method