非均相 Schiff 碱铬 (III) 配合物催化环己烯环氧化性能的研究

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摘要: 将 3 种典型的氨基酸-水杨醛 Schiff 碱铬 (III) 配合物固载于介孔 MCM-41 上, 制得非均相 Schiff 碱铬配合物, 用傅里叶变换红外光谱、紫外-可见光谱、X 射线固体粉末衍射、N₂ 吸附和元素分析对其结构进行了表征, 并以 30% H₂O₂ 为氧化剂, 考察该配合物对环己烯环氧化反应的催化性能。结果表明, 均相配合物非均相化后, 其催化活性明显提高。在较优的反应条件下, 环己烯转化率可达 52.6%, 环氧环己烷选择性为 73.5%, 且该非均相催化剂重复使用 6 次后, 仍保持较高的催化活性。

关键词: 非均相; 氨基酸; Schiff 碱; 环己烯; 环氧化

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Preparation of Immobilized Chromium Schiff Base Complexes and Their Catalytic Performance for Cyclohexene Epoxidation

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Abstract: Three typical amino acid Schiff base chromium(III) complexes immobilized on MCM-41 were prepared and characterized by various physico-chemical methods such as Fourier transform infrared spectroscopy, ultraviolet-visible spectroscopy, X-ray powder diffraction, N₂ sorption, and elemental analysis. The obtained immobilized complexes were effective catalysts for the epoxidation of cyclohexene with 30% hydrogen peroxide and they exhibited significantly enhanced catalytic performance compared with their corresponding homogeneous analogues. Under optimal reaction conditions the highest conversion of cyclohexene was 52.6% with 73.5% epoxide selectivity. In addition, the catalytic activity was retained after recycling 6 times.

Key words: immobilized; amino acid; Schiff base complex; cyclohexene; epoxidation

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环氧环己烷分子中存在活泼的环氧基团, 可直接开环制己二醇、己二酸; 也可经醇解、氨解、水解制邻甲氧基环己醇、邻氨基环己醇、1,2-环己二醇;

还可与 CO₂ 反应制聚碳酸酯, 与二羧酸反应制不饱和和聚酯等。因此它是重要的有机中间体^[1,2]。最常见的环氧环己烷制备方法是环己烯环氧化法。但由于

环己烯分子中有 1 个不饱和 C=C 双键和 4 个活性 α -H, 故其氧化反应的选择性较差. 因此, 设计清洁、高效的催化氧化体系以提高目标产物的选择性, 成为环己烯环氧化研究中亟待解决的难题.

烯烃环氧化催化体系众多^[2,3], 其中过渡金属 Schiff 碱配合物因反应条件温和、反应速率高而广受关注. 尤其是氨基酸-水杨醛 Schiff 碱金属配合物, 作为维生素 B₆ 催化氨基酸酶反应的模拟体系引起了人们的普遍重视, 并在不对称合成和环氧化反应中显示出较好的催化性能^[4-6]. 然而均相催化剂不可避免地存在产物分离和催化剂重复使用等问题, 因此研制高效的非均相催化剂, 特别是将已知高活性的均相催化剂非均相化, 成为一个广泛的研究领域^[7]. 为此, 本文合成了三种典型的氨基酸水杨醛 Schiff 碱铬配合物, 并通过弹性的氨基丙基偶联基团将其固载于具有规则介孔孔道结构的 MCM-41 分子筛上. 再用于环己烯环氧化反应中, 详细地考察了该非均相催化剂的催化性能和重复使用性能.

1 实验部分

1.1 催化剂的制备

MCM-41 和 3-氨基三乙氧基硅烷修饰的 MCM-41 (记作: APTES-MCM-41) 分别按文献[8]和[9]合成.

均相铬配合物按文献[10]合成. 具体实验步骤: 将 20 mmol 丙氨酸、甘氨酸或苯丙氨酸溶于 30 ml 去离子水中, 再在搅拌条件下缓慢滴加有 20 mmol 水杨醛的 30 ml 无水乙醇液, 于 80 °C 回流 3 h. 接着用适量 NaOH 调节溶液成中性, 再滴加溶有 20 mmol CrCl₃·6H₂O 的 30 ml 无水乙醇液, 搅拌回流 6 h 后, 混合物冷却至室温, 滤出绿色沉淀物, 在无水乙醇中重结晶, 即得丙氨酸、甘氨酸或苯丙氨酸水杨醛 Schiff 碱铬配合物, 记作: Cr(Sal-Ala)(Cr(Sal-Gly) 或 Cr(Sal-Phe)). 元素分析 (%), Cr(Sal-Ala) (C₁₀H₉NO₃CrCl) 实测值 (计算值): C, 43.05 (43.09); H, 3.22(3.23); N, 5.00(5.03); Cr, 18.6(18.67); N: Cr (摩尔比) = 1.01:1.00; Cr(Sal-Gly) (C₉H₇NO₃CrCl) 实测值 (计算值): C, 40.85(40.83); H, 2.66(2.65); N, 5.31(5.29); Cr, 19.7(19.66); N:Cr (摩尔比) = 1.00:1.00; Cr(Sal-Phe)(C₁₆H₁₃NO₃CrCl) 实测值 (计算值): C, 54.15(54.16); H, 3.65(3.67); N, 3.95(3.95); Cr,

14.7(14.67); N:Cr (摩尔比) = 0.99: 1.00.

由于中心离子 Cr 的配位不饱和性, 均相配合物可以通过与 APTES-MCM-41 上氨基 N 配位而固载到载体上^[11]. 典型的实验操作: 将 4 等份 1 g APTES-MCM-41 加入含有 1.5 g Cr(Sal-Ala) (Cr(Sal-Gly) 或 Cr(Sal-Phe)) 的 100 ml 甲苯溶液中, N₂ 保护下搅拌回流 10 h. 冷却至室温, 减压抽滤, 所得的固体样品用体积比为 1:1 的无水乙醇和乙腈索氏抽提 24 h, 以脱除吸附在载体表面的均相铬配合物. 将样品在 60 °C 下真空干燥过夜, 得淡绿色粉末, 即得非均相丙氨酸 (甘氨酸或苯丙氨酸) 水杨醛 Schiff 碱铬配合物, 记作 Cr(Sal-Ala)-MCM-41 (Cr(Sal-Gly)-MCM-41 或 Cr(Sal-Phe)-MCM-41), 经 ICP 测定 Cr 含量为 2.05% (2.12% 或 1.98%).

图式 1 非均相铬配合物的结构示意图

Scheme 1. Structural representation of the heterogenized chromium complexes.

1.2 催化剂的表征

催化剂样品的 X 射线衍射 (XRD) 谱在 Rigaku D/max-rA 型 XRD 仪上测定. 样品的比表面积和孔径采用 ASP-2000 型自动物理吸附仪测定, 在 -196 °C 下进行 N₂ 吸附. 样品的 C, H 和 N 含量通过 Vario EL 型元素分析仪测定. 样品的 Cr 含量在 ARL-3520 型电感耦合等离子体原子发射光谱 (ICP-AES) 仪上测定. 样品的红外光谱用 Nicolet Magna 550-II 型红外光谱仪测定, KBr 压片法. 样品的紫外-可见光谱 (UV-Vis) 用 Shimadzu UV-2101PC 型紫外-可见光谱仪测定.

1.3 催化氧化反应

向 100 ml 带有聚四氟内衬的不锈钢反应釜中加入 2.05 g (25 mmol) 环己烯、10 ml 溶剂和 0.25 g 非均相催化剂或 0.5 mol% 的均相催化剂 (相对于环

己烯), 室温下磁力搅拌 10 min, 然后在 5 min 内把温度升至指定温度, 再加入所需量的 30% H_2O_2 . 反应进行一段时间后, 冷却、过滤出催化剂. 滤液用上海海欣色谱有限公司的 GC-920 型气相色谱仪分析 (N_2 作为载气 (5 ml/min), FID 检测器, HP-5 毛细管柱). 碘量法测定 H_2O_2 的利用率. 经 GC-MS、GC-IR 分析并与标准谱比较, 反应产物为: 环氧环己烷 (I), 2-环己烯基-1-醇 (II), 2-环己烯基-1-酮 (III), 2-环己烯基-1-过氧化氢 (IV) 和己二酸 (V)(见图示 2).

图式 2 环己烯氧化反应过程的示意图

Scheme 2. Possible process for the oxidation of cyclohexene.

2 结果与讨论

2.1 催化剂的光谱分析结果

均相铬配合物的 FT-IR 和 UV-Vis 谱见图 1, 其中 FT-IR 特征峰指认见表 1. 可以看出, 均相配合物中都出现了氨基酸 Schiff 碱配合物的特征峰, 且与文献[12~14]类似, 证明合成产物即为目标铬配合物. 当均相配合物固载于载体上后, 部分均相铬配合物的吸收峰被较强的分子筛骨架振动峰所覆盖, 但上述的特征峰均清晰可见 (见图 1 和表 1), 说明非均相化过程较为成功. 当然, 非均相配合物特征峰强度有所降低, 这主要是铬配合物固载量较低的缘故.

均相配合物的 UV-Vis 谱的特征峰指认也列于表 1 中. 可以看出, 均相配合物的谱中均出现了两个特征吸收峰, 前者归属于配合物中的电荷转移吸收, 后者归属于配合物中金属的 $d-d$ 跃迁^[15]. 与 FT-IR 谱类似, 均相配合物固载于载体上后, 虽然特

图 1 铬配合物样品的 FT-IR 和 UV-Vis 谱

Fig. 1. FT-IR (a) and UV-Vis (b) spectra of the chromium complexes. (1) Cr(Sal-Ala); (2) Cr(Sal-Ala)-MCM-41.

征峰强度有所降低, 但峰位置基本没变 (见图 1 和表 1), 这进一步证实合成产物即为目标配合物.

2.2 催化剂的物相结构

图 2 为各非均相铬配合物样品的 XRD 谱. 可以看出, 非均相配合物在 $2^\circ \sim 3^\circ$ 处都出现了一个单峰, 对应于六方晶胞单元的 (100) 面衍射, 说明非均相配合物仍保持母体 MCM-41 的结构有序性. 但并未出现母体中两个弱的 (110) 和 (200) 衍射峰, 这主要由于载体表面固载了有机基团而导致局部有序性的降低^[16].

图 3 为各非均相铬配合物样品的低温 N_2 吸附-脱附等温线. 可以看出, 表面修饰前后样品等温线

表 1 不同铬配合物的 FT-IR 和 UV-Vis 谱特征峰数据

Table 1 Data from FT-IR and UV-Vis spectra of the chromium complexes

Sample	FT-IR (cm^{-1})							UV-Vis (nm)	
	$\nu_{\text{C=N}}$	$\nu_{\text{as(COO}^-)}$	$\nu_{\text{s(COO}^-)}$	$\nu_{\text{Ph-O}}$	$\nu_{\text{Cr-O}}^{\text{a}}$	$\nu_{\text{Cr-O}}^{\text{b}}$	$\nu_{\text{Cr-N}}$	$p-\pi^*$	$d-d$
Cr(Sal-Ala)	1621	1570	1400	1332	661	612	463	382	600
Cr(Sal-Ala)-MCM-41	1620	1570	1400	1332	661	612	463	383	600
Cr(Sal-Gly)	1625	1610	1398	1330	545	470	395	390	600
Cr(Sal-Gly)-MCM-41	1625	1610	1398	1330	545	470	395	391	600
Cr(Sal-Phe)	1620	1592	1390	1341	550	470	495	375	580
Cr(Sal-Phe)-MCM-41	1620	1591	1390	1340	550	470	495	375	581

^aPhenolic oxygen; ^bCarboxylic oxygen.

图 2 不同非均相铬配合物的 XRD 谱

Fig. 2. XRD patterns of the immobilized chromium complexes. (1) Cr(Sal-Ala)-MCM-41; (2) Cr(Sal-Gly)-MCM-41; (3) Cr(Sal-Phe)-MCM-41.

图 3 不同非均相铬配合物的低温 N₂ 吸附-脱附等温线

Fig. 3. N₂ adsorption-desorption isotherms of the immobilized chromium complexes. (1) Cr(Sal-Ala)-MCM-41; (2) Cr(Sal-Gly)-MCM-41; (3) Cr(Sal-Phe)-MCM-41.

均呈现出典型的 IV 型, 表明母体 MCM-41 的介孔结构并没有因为有机基团的修饰而被破坏^[17], 但固载后, 样品比表面积有所下降 (表 2), 主要是介孔分子筛内壁固载了有机基团所致^[18].

2.3 催化剂的催化性能

2.3.1 不同 Schiff 碱铬配合物的催化性能

表 3 为各配合物催化环己烯氧化反应的性能。可以看出, 不使用催化剂时, 仅有少量的环氧化物生成 (<5%); 以均相配合物为催化剂时, 环己烯转化率最高为 28.3%, 环氧环己烷选择性为 37.2%; 而以非均相铬配合物为催化剂时, 反应性能均高于其对应

表 2 不同非均相铬配合物样品的物相参数

Table 2 Textural properties of the immobilized chromium complexes

Sample	BET surface area (m ² /g)	Pore volume ^a (cm ³ /g)	Average pore size ^a (nm)
MCM-41	1050	0.72	2.76
Cr(Sal-Ala)-MCM-41	650	0.30	2.27
Cr(Sal-Gly)-MCM-41	657	0.31	2.30
Cr(Sal-Phe)-MCM-41	632	0.28	2.22

^aCalculated by the BJH method from the desorption isotherm.

表 3 不同铬配合物样品的催化性能

Table 3 Catalytic performance of the different chromium complexes

Sample	Cyclohexene conversion (%)	Selectivity (%)				
		I	II	III	IV	V
Blank	3.0	2.5	30.2	45.5	19.2	2.6
Cr(Sal-Ala)	26.5	32.5	19.1	29.8	17.0	1.6
Cr(Sal-Gly)	25.8	30.5	20.4	29.1	18.3	1.7
Cr(Sal-Phe)	28.3	37.2	21.1	25.2	16.5	0
Cr(Sal-Ala)-MCM-41	52.6	73.5	7.7	11.2	7.0	0.6
Cr(Sal-Gly)-MCM-41	50.2	67.8	9.3	13.9	8.7	0.3
Cr(Sal-Phe)-MCM-41	43.5	68.2	9.1	12.5	8.5	1.7

Reaction conditions: cyclohexene 30 mmol, H₂O₂ 25 mmol, heterogenised catalyst 0.25 g or 0.5 mol% of homogeneous complex (relative to cyclohexene), CH₂ClCH₂Cl 10 ml, 60 °C, 6 h.

的均相配合物, 与文献[19~23]结果类似。一方面, 在均相 Schiff 碱配合物的催化体系中, 单位体积内活性组分的浓度较高, 易形成非活性的聚合物; 当均相配合物固载于载体上后, 高比表面积的载体使活性组分分散而浓度降低, 则形成非活性聚合物的机会减少, 因此催化性能提高^[19~22]。另一方面, 载体的引入改变了活性中心周围的局部环境, 进而影响反应物、中间产物和生成物在活性中心周围的局部浓度, 也导致非均相配合物的催化性能提高^[23]。

还可以看出, 三个非均相配合物催化性能高低顺序为: Cr(Sal-Ala)-MCM-41> Cr(Sal-Gly)-MCM-41> Cr(Sal-Phe)-MCM-41。当以 Cr(Sal-Ala)-MCM-41 为催化剂时, 环己烯转化率最高可达 52.6%, 此时环氧环己烷选择性为 73.5%。鉴于三个非均相配合物的活性配合物固载量、分散度、表面极性和疏水性没有明显差别, 因此它们催化性能的差异可能与其配体结构有关。Cr(Sal-Phe)-MCM-41 的催化性能最差, 可能是由于较大的苯基不利于反应物与活性中心间的接触所致。Cr(Sal-Ala)-MCM-41 表现出了比 Cr(Sal-Gly)-MCM-41 更高的催化性能, 说明 Cr(Sal-Ala)-MCM-41 中 Schiff 碱配体相对较高的给

电子能力有利于氧化反应的进行。

2.3.2 反应条件对非均相配合物催化性能的影响

以催化性能最好的 Cr(Sal-Ala)-MCM-41 为催化剂, 详细考察了反应条件对催化剂性能的影响。表 4 为不同溶剂对非均相铬配合物样品的催化性能的影响。可以看出, 在无溶剂时, 仅有 4.6% 的环己烯被氧化; 加入溶剂后, 非均相配合物的催化性能明显提高, 其中以 1,2-二氯乙烷为溶剂时, 催化性能最佳, 环己烯转化率最高可达 52.6%, 环氧环己烷选择性为 73.5%。

表 4 溶剂对非均相配合物的催化性能的影响

Table 4 Effect of solvents on the catalytic performance of the immobilized complexes

Solvent	Cyclohexene conversion (%)	Selectivity (%)				
		I	II	III	IV	V
None	4.6	7.3	27.5	41.0	18.2	6.0
CH ₃ OH	36.2	55.7	12.7	19.1	11.5	1.0
CH ₃ CN	47.5	51.3	13.8	21.5	12.9	0.5
CH ₂ Cl ₂	45.1	57.2	12.2	19.0	10.7	0.9
ClCH ₂ CH ₂ Cl	52.6	73.5	7.7	11.2	7.0	0.6

Reaction conditions: cyclohexene 30 mmol, H₂O₂ 25 mmol, catalyst 0.25 g, solvent 10 ml, 60 °C, 6 h.

图 4 为环己烯与 H₂O₂ 的摩尔比、 $n(\text{C}_6\text{H}_{10})/n(\text{H}_2\text{O}_2)$ 、催化剂用量、反应温度和反应时间对非均相配合物催化性能的影响。首先, 在催化剂用量 0.25 g, 60 °C 的条件下反应 6 h, 考察了 $n(\text{C}_6\text{H}_{10})/n(\text{H}_2\text{O}_2)$ 对反应性能的影响。由图 4(a) 可见, 当 $n(\text{C}_6\text{H}_{10})/n(\text{H}_2\text{O}_2)$ 为 0.5 时, 虽然环己烯转化率较高, 但环氧环己烷选择性很低, 产物以烯丙基氧化副产物为主。随着 $n(\text{C}_6\text{H}_{10})/n(\text{H}_2\text{O}_2)$ 的增加, 环己烯转化

率先下降后上升, 而环氧环己烷的选择性则是先上升后下降。以环氧环己烷选择性为基准, $n(\text{C}_6\text{H}_{10})/n(\text{H}_2\text{O}_2)$ 为 1.2 时最理想。

接着在 $n(\text{C}_6\text{H}_{10})/n(\text{H}_2\text{O}_2)$ 为 1.2, 60 °C 的条件下反应 6 h, 考察了催化剂用量对催化剂性能的影响。由图 4(b) 可见, 随着催化剂量的增加, 环己烯转化率逐渐上升。环氧环己烷选择性至 0.25 g 时达最大值, 进一步增加催化剂用量, 环氧环己烷选择性下降, 这可能由于过量的催化剂促进了副反应的进行。

在 $n(\text{C}_6\text{H}_{10})/n(\text{H}_2\text{O}_2) = 1.2$, 催化剂用量 0.25 g, 反应 6 h 条件下, 考察了反应温度对催化剂性能的影响。由图 4(c) 可知, 在反应温度从 30 °C 升至 60 °C 时, 环己烯转化率显著升高。这可能由于该反应是在多相催化体系下进行, 反应温度升高则有利于反应物与催化剂间的接触, 从而使环己烯转化率升高。然而继续升高温度, 环己烯转化率增加不大, 但环氧环己烷选择性大幅度下降, 说明相对于环己烯环氧化过程而言, 过高反应温度下副反应易于发生。

在上述实验基础上, 进一步考察了反应时间对反应性能的影响。可以看出, 反应 6 h 时, 产物选择性最高。继续延长反应时间对环己烯转化率影响不大, 但环氧环己烷选择性急速下降, 说明过长的反应时间使得生成的环氧化物进一步生成副产物。综上所述, 该非均相催化剂对环己烯环氧化反应的适宜条件应为: $n(\text{C}_6\text{H}_{10})/n(\text{H}_2\text{O}_2) = 1.2$, 催化剂用量 0.25 g, CH₂ClCH₂Cl 10 ml, 于 60 °C 下反应 6 h。

表 5 为添加剂对非均相配合物催化性能的影响。可以看出, 添加剂对非均相配合物在环己烯环氧化反应中的催化性能影响很大。添加少量 Na-

图 4 反应条件对非均相配合物催化性能的影响

Fig. 4. Effects of condition parameters on the catalytic performance of the immobilized complexes. (1) Cyclohexene conversion; (2) Epoxide selectivity. Reaction conditions: cyclohexene 30 mmol, CH₂ClCH₂Cl 10 ml.

表 5 添加剂对非均相配合物催化性能的影响
Table 5 Effect of additives on the catalytic performance of the immobilized complexes

Additive	H ₂ O ₂ efficiency ^a (mol %)	Conversion (%)	Selectivity (%)				
			I	II	III	IV	V
blank	92.5	52.6	73.5	7.7	11.2	7.0	0.6
2 mmol NaHSO ₄	93.8	57.0	61.2	10.9	18.5	9.0	0.4
4 mmol NaHSO ₄	94.5	60.5	53.3	14.0	20.1	11.7	0.9
10 mmol NaHSO ₄	89.0	45.2	38.7	17.5	25.3	14.6	3.9
2 mmol Pyridine	90.3	48.0	65.5	9.7	14.3	8.6	1.9
10 mmol Pyridine	87.5	45.6	60.1	10.9	18.0	9.7	1.3
2 mmol 1-methylimidazole	91.7	51.5	72.7	6.5	11.8	7.2	1.8
10 mmol 1-methylimidazole	92.8	52.9	72.5	7.6	12.3	7.0	0.6

^aEfficiency of H₂O₂ = (moles of H₂O₂ converted to the products/moles of H₂O₂ consumed) × 100.
Reaction conditions: cyclohexene 30 mmol, H₂O₂ 25 mmol, catalyst 0.25 g, CH₂ClCH₂Cl 10 ml, 60 °C, 6 h.

HSO₄ 后, H₂O₂ 利用率和环己烯转化率升高, 但产物中环氧化物含量降低, 环己烯醇和环己烯酮的含量增加, 这说明弱酸性条件下催化剂活性提高, 有利于烯丙基氧化反应的进行. 然而, 当酸性过强时, 环己烯转化率降低, 这可能是由于酸性太强导致 Schiff 碱配合物分解所致. 当加入吡啶后, H₂O₂ 利用率、环己烯转化率和对环氧化物选择性均下降, 说明碱性条件下仅促进了 H₂O₂ 的无效分解, 而对环氧化反应不利. 加入 1-甲基咪唑供电子配体后, 环己烯转化率和环氧化物的选择性都未见明显变化, 可见, 轴向配体对配合物的催化性能没有显著影响.

2.3.3 非均相配合物在环己烯环氧化体系中的稳定性

在上述适宜反应条件下, 考察了非均相催化剂的重复使用性能. 将使用过的催化剂用溶剂反复清洗, 在 60 °C 真空干燥过夜, 重新用于环己烯氧化反应中. 图 5 为 Cr(Sal-Ala)-MCM-41 的重复使用性能.

图 5 Cr(Sal-Ala)-MCM-41 的重复使用性能
Fig. 5. Catalytic reusability of Cr(Sal-Ala)-MCM-41.

能. 可以看出, 该非均相铬配合物重复使用 6 次后, 仍具有较好的催化性能. 经 ICP 测定该回收的催化剂中 Cr 含量为 2.02%, 说明金属配合物的降解和流失并非是影响催化活性降低的主要原因, 而可能与反应次数的增加而使得扩散限制的增加有关. 可见, 该非均相催化剂在环己烯氧化体系中具有较好的稳定性.

3 结论

合成了三种 MCM-41 固载的非均相氨基酸水杨醛 Schiff 碱铬 (III) 配合物, 在环己烯氧化反应中表现出比其相应非均相催化剂更高的催化性能. 在以 Cr(Sal-Ala)-MCM-41 为催化剂, $n(\text{C}_6\text{H}_{10})/n(\text{H}_2\text{O}_2)$ 为 1.2, 催化剂用量为 0.25 g, 于 60 °C 反应 6 h 时, 环己烯转化率最高可达 52.6%, 环氧环己烷选择性为 73.5%; 且该催化剂至少可重复使用 6 次. 若进一步优化配合物催化剂的结构、组成, 将会提高其非均相催化剂选择性. 本文对研发高效的非均相催化剂提供一定的参考.

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英 译 文

English Text

Cyclohexene epoxide is an important organic intermediate because of its active epoxide group. It can be easily converted into hexanediol and adipic acid by direct ring opening; into *o*-methoxy cyclohexanol, *o*-amino cyclohexanol, 1,2-cyclohexanediol by alcoholysis, aminolysis and hydrolysis, respectively; into polycarbonate by reaction with CO₂ or into unsaturated polyesters by reaction with dicarboxylic acids etc. These compounds are widely used in the field of medicine, pesticides, paints, resins or surface active agents etc. [1,2]. Conversion to cyclohexene epoxide

is usually done by the epoxidation of cyclohexene, however, the selectivity is very low because of the presence of unsaturated C=C and four active α -H's in the cyclohexene molecule. Therefore, there is an urgent need to develop a clean and effective catalytic oxidation system for the epoxidation of cyclohexene to improve the selectivity of the desired product.

Many methods have been used for the conversion of alkenes to epoxides [2,3] and the most notable method is transition metal Schiff base complex-catalyzed oxidations because of their mild reaction conditions and quick reaction rates. Amino acid Schiff base complexes that resemble the vitamin B6 amino acid catalytic enzyme have attracted a large amount of attention and they have excellent catalytic performance for asymmetric synthesis and epoxidation [4–6]. However, these homogeneous complexes suffer from poor catalyst recovery and difficult product separation. Thus, over the past decade much effort has been put into the development of active heterogeneous complexes especially the heterogenization of the known efficient homogeneous complexes [7]. Therefore, in our investigation, three typical amino acid Schiff base complexes were prepared and then immobilized onto MCM-41 containing regular mesoporous pores by flexible aminopropyl linkers. The obtained immobilized catalysts were used for the epoxidation of cyclohexene and their catalytic performance and stabilities were investigated extensively.

1 Experimental

1.1 Catalyst preparation

Pure siliceous MCM-41 was synthesized as previously described [8]. Aminopropyl functionalized MCM-41 (APTES-MCM-41) were prepared as given in the literature [9].

The synthetic procedures used for the homogeneous chromium complexes were similar to those reported previously [10]. Typically, 20 mmol alanine (glycine or phenylalanine) was suspended in 30 ml deionized water. Then 20 mmol salicylaldehyde dissolved in 30 ml absolute ethanol was added dropwise with vigorous stirring of the suspension. After refluxing for 3 h at 80 °C the mixture was neutralized with an appropriate amount of NaOH to a pH close to 7. A solution of 20 mmol CrCl₃·6H₂O in 30 ml ethanol was added dropwise to the above-mentioned mixture. After further refluxing for 6 h the solid was cooled to room temperature, filtered, and recrystallized in absolute ethanol. The obtained green precipitates were the desired homogeneous complex alanine (glycine or phenylalanine)-salicylaldehyde Schiff base chromium (III) complexes and these were denoted

Cr(Sal-Ala) ((Cr(Sal-Gly) or Cr(Sal-Phe)). Elemental analysis (%), Cr(Sal-Ala), $C_{10}H_9NO_3CrCl$, measured value(calculated value): C, 43.05(43.09); H, 3.22(3.23); N, 5.00(5.03); Cr, 18.6(18.67); N/Cr molar ratio = 1.01:1.00. Cr(Sal-Gly), $C_9H_7NO_3CrCl$: C, 40.85(40.83); H, 2.66(2.65); N, 5.31(5.29); Cr, 19.7(19.66); N/Cr molar ratio = 1.00:1.00. Cr(Sal-Phe), $C_{16}H_{13}NO_3CrCl$: C, 54.15(54.16); H, 3.65(3.67); N, 3.95(3.95); Cr, 14.7(14.67); N/Cr molar ratio = 0.99:1.00.

Since the chromium center in the homogeneous complex was either five- or six-coordinate, the immobilization of the homogeneous complex onto MCM-41 was readily achieved by the coordination of chromium to the amino nitrogen of APTES-MCM-41 by simple addition or by ligand substitution reactions [11]. Typically, 1 g of freshly dried APTES-MCM-41 was added to a solution of 1.5 g as-prepared homogeneous complex in 100 ml dry toluene. The mixture was vigorously stirred under reflux and under the protection of N_2 for 10 h. The resulting suspension was then cooled to room temperature and filtered through a Buchner funnel. The collected powder was washed overnight in a Soxhlet extractor using equivalent amounts of alcohol and acetonitrile as a solvent to remove the homogeneous complexes that were adsorbed on the surface of the support and then the solid was dried at 60 °C in air overnight. The obtained green samples were the expected immobilized complex alanine (glycine or phenylalanine)-salicylaldehyde Schiff base chromium (III) complexes and these were denoted Cr(Sal-Ala)-MCM-41 (Cr(Sal-Gly)-MCM-41 or Cr(Sal-Phe)-MCM-41).

1.2 Catalyst characterization

Powder X-ray diffraction (XRD) experiments were performed at room temperature on a Rigaku D/Max-rA instrument. The specific surface area and average pore diameter were measured by N_2 adsorption-desorption at -196 °C using a Micromeritics ASAP-2000 instrument (Norcross, Georgia). The carbon, hydrogen, and nitrogen content of the samples were determined using a Vario EL analyzer. The chromium content was measured by inductively coupled plasma (ICP) emission spectroscopy (ARL-3520). FT-IR spectra of the samples were recorded using KBr disks at room temperature on a Nicolet Magna 550-II spectrophotometer. UV-Vis absorption spectra were recorded on a Shimadzu UV-2101PC spectrophotometer.

1.3 Catalytic reaction

The oxidation of cyclohexene was carried out in a 100 ml Teflon-lined and magnetically stirred autoclave. In a typical experiment, a mixture of 0.25 g heterogenized catalyst or 0.5

mol% homogeneous complex (relative to cyclohexene), 25 mmol cyclohexene, and 10 ml solvent was stirred for about 10 min. The autoclave was adjusted to the desired temperature within 5 min and then the corresponding amount of 30% H_2O_2 was introduced. After the reaction ran for the desired time the products were cooled and filtered to separate them from the catalyst and they were analyzed using a gas chromatograph (GC-920, Haixin Chromatography Co., Ltd, Shanghai) with a capillary HP-5 column, a FID detector, and N_2 as the carrier gas (5 ml/min). H_2O_2 consumption was determined after the reactions by an iodometric titration. An analysis of the reaction mixture by GC-MS and GC-IR, and a comparison with standard spectra revealed the presence of five products: cyclohexene epoxide (I), 2-cyclohexene-1-ol (II), 2-cyclohexene-1-one (III), 2-cyclohexene-1-hydrogen peroxide (IV), and adipic acid (V) under the conditions used (see Scheme 2).

2 Results and discussion

2.1 Spectroscopic characterization of the catalysts

The important diagnostic bands from the spectroscopic characterization were assigned (Fig. 1) and the band positions are listed in Table 1. Characteristic bands indicating the successful preparation of the amino acid Schiff base complexes were all present in the FT-IR spectra of all three homogeneous complexes (Fig. 1 and Table 1), and the band positions agree well with published data [12–14]. This confirmed that the obtained samples were the desired homogeneous complexes. In the FT-IR spectra of the immobilized complexes, apart from the bands in the overlapping regions of the silica backbone, the other bands of the homogeneous complexes were all clearly present (Fig. 1 and Table 1) indicating the successful immobilization of the homogeneous complexes onto MCM-41. However, compared with their corresponding homogeneous complexes the intensity of the characteristic bands of the immobilized complexes decreased. This is mainly attributed to the low loading of chromium complexes.

The UV-Vis spectra of the homogeneous complexes all displayed two typical peaks; the former could be assigned to metal-ligand bands and the latter is associated with a $d-d$ transition [15] (Fig. 1 and Table 1). This also implies the successful preparation of homogeneous complexes. The UV-Vis spectra of the three immobilized materials were quite similar to the spectra of their corresponding homogeneous analogues (Fig. 1 and Table 1), further confirming that the immobilized complexes depicted in Scheme 1 were all successfully prepared.

2.2 Phase structures of the catalysts

The powder XRD patterns of the three immobilized complexes all showed one single peak at 2θ angles around 2° – 3° (Fig. 2). This peak could be attributed to the (100) plane of the hexagonal unit cell indicating that the structural ordering of the parent MCM-41 channel remains intact after the immobilization of chromium complexes. However, the higher angle peaks associated with the (110) and (200) reflections that are present in their parent samples no longer appeared because of the decrease in local order as previously mentioned by Lim et al. [16].

N_2 adsorption-desorption isotherms of the three immobilized complexes all correspond to the type IV IUPAC classification suggesting that the mesoporous structures of the support survived the immobilization of organic groups [17]. However, the immobilized materials all exhibited a decrease in surface area and pore size by comparison with their parent samples (Table 2), which might be due to the attachment of organic moieties onto the walls of the support [18].

2.3 Catalytic performance

2.3.1 Catalytic performance of the different chromium Schiff base complexes

The catalytic performance of the different chromium complexes for the epoxidation of cyclohexene are listed in Table 3. Only a small amount of epoxide (<5%) was produced in the absence of a catalyst. With homogeneous complexes as catalysts the best cyclohexene conversion and epoxide selectivity increased slightly to 28.3% and 37.2%, respectively. However, when the reaction was performed over immobilized Schiff base complexes the catalytic performance was found to significantly improve and similar phenomena have also been reported previously [19–23]. Such obviously enhanced catalytic performance, on the one hand, could be attributed to the dispersion effect of the supports. Compared with active sites in homogeneous systems the dispersed active sites in the immobilized complexes showed a lower probability of forming inactive μ -oxo dimers or other polymeric species. Therefore, the immobilized complexes gave far better catalytic performance [19–22]. On the other hand, the introduction of the support modified the local environment of the active sites and changed the local concentrations of the reactant and the product around the active sites, which might also contribute to the enhanced catalytic performance of the immobilized complexes [23].

The results in Table 3 also show that the catalytic performance of the immobilized complexes with different Schiff base ligands decrease in the following order: Cr(Sal-Ala)-MCM-41 > Cr(Sal-Gly)-MCM-41 > Cr(Sal-Phe)-MCM-41. The optimal cyclohexene conversion was 52.6% while the epoxide selectivity was 73.5% over

Cr(Sal-Ala)-MCM-41. Considering that the three immobilized complexes exhibited a similar loading and dispersion of active complexes, surface polarity, and hydrophobicity, the significant differences in their catalytic performance could be reasonably attributed to their different ligand structures. Cr(Sal-Phe)-MCM-41 gave the worst catalytic performance especially epoxide selectivity. This was probably because of the large phenyl ligand that resulted in a significant diffusion limitation and thus inhibited the accessibility of the reactants to the active sites. Cr(Sal-Ala)-MCM-41 gave much better catalytic performance than Cr(Sal-Gly)-MCM-41 indicating that the relatively higher π -donating ability of the ligand in Cr(Sal-Ala)-MCM-41 was responsible for its improved epoxidation behavior.

2.3.2 Effect of reaction conditions on the catalytic performance of the immobilized complexes

To obtain the best catalytic results the effect of condition parameters on the catalytic performance of Cr(Sal-Ala)-MCM-41, which was the most active catalyst among all the immobilized materials investigated. The effect of the solvent on the catalytic performance of the immobilized complexes is given in Table 4. The results reveal that only a small amount of cyclohexene (<5%) was oxidized without solvent. In the presence of solvents the catalytic performance improved significantly and the best cyclohexene conversion was 52.6% with a 73.5% selectivity toward epoxide when using 1,2-dichloroethane as a solvent.

Figure 4 gives the effect of oxidant and catalyst dosage as well as the reaction time and temperature on the catalytic performance of the immobilized complexes. First, the effect of the C_6H_{10}/H_2O_2 molar ratio on the reaction results was investigated when the reaction ran for 6 h at 60 °C with a catalyst dose of 0.25 g (Fig. 4(a)). The catalyst gave much higher cyclohexene conversion but lower epoxide selectivity with a C_6H_{10}/H_2O_2 molar ratio of 0.5 and here cyclohexene was mainly converted into allylic oxidation by-products. With an increase in the C_6H_{10}/H_2O_2 molar ratio, cyclohexene conversion initially decreased and then increased while epoxide selectivity initially increased and then decreased. On the basis of epoxide yield the optimum C_6H_{10}/H_2O_2 molar ratio was 1.2.

The effect of the amount of catalyst on the catalytic performance was investigated at 60 °C over 6 h with a C_6H_{10}/H_2O_2 molar ratio of 1.2 (Fig. 4(b)). At the beginning of the reaction cyclohexene conversion and epoxide selectivity both increased with an increase in the amount of catalyst until 0.25 g. However, with a further increase in the amount of catalyst the selectivity toward epoxide decreased remarkably probably because of the excessive catalyst promoted side reactions.

The effect of reaction temperature on the reaction results was also investigated using 0.25 g of catalyst over 6 h with a C_6H_{10}/H_2O_2 molar ratio of 1.2 (Fig. 4(c)). The cyclohexene conversion was found to increase significantly when the reaction temperature increased from 30 to 60 °C. This might be attributed to the increased contact probability between the reactants and the catalysts with the increased temperature in the heterogeneous catalytic system. However, with a further increase in the reaction temperature the cyclohexene conversion only increased slightly while the epoxide selectivity decreased sharply. This indicates that too high a temperature benefited side reactions.

On the basis of the above-mentioned experiment the effect of reaction time on the reaction was further investigated at 60 °C using 0.25 g of catalyst and a C_6H_{10}/H_2O_2 molar ratio of 1.2 (Fig. 4(d)). The results reveal that the epoxidation reaction reached equilibrium when the reaction ran for 6 h. A further increase in the reaction time only slightly influenced cyclohexene conversion and the epoxide selectivity decreased rapidly indicating that too long reaction time could increase the probability of forming by-products. In conclusion, when the reaction ran for 6 h at 60 °C with 0.25 g of catalyst, 10 ml solvent, and a C_6H_{10}/H_2O_2 molar ratio of 1.2 the best yield of epoxide was obtained.

The effect of additives on the catalytic performance of the immobilized complexes is given in Table 5. The additives had a remarkable influence on the catalytic performance of the immobilized catalysts for the epoxidation of cyclohexene. After adding a small amount of $NaHSO_4$, the H_2O_2 efficiency and cyclohexene conversion improved while the epoxide content decreased and the 2-cyclohexene-1-ol and 2-cyclohexene-1-one contents increased in the product mixtures. This suggests that the weak acid environment benefited the allylic oxidation of cyclohexene by improving the catalytic activity of the immobilized complexes. However, the cyclohexene conversion and epoxide selectivity both decreased under strong acid conditions because of the probable decomposition of the Schiff base complexes. With pyridine as an additive the H_2O_2 efficiency, the cyclohexene conversion and the epoxide selectivity all decreased indicating that basic conditions did not favor epoxidation because of the unproductive decomposition of H_2O_2 to O_2 . Upon the addition of the electron donating 1-methylimidazole no significant change in the catalytic

performance of the immobilized complexes was found implying that the axial ligand had a negligible effect on catalytic performance.

2.3.3 Stability of the immobilized complexes for the epoxidation of cyclohexene

A further investigation into the stability of $Cr(Sal-Ala)-MCM-41$ was also carried out under the optimum reaction conditions. After the first catalytic run the immobilized catalyst was separated from the reaction solution, washed several times with solvent to remove any physisorbed molecules, dried at 60 °C overnight and then reused in another five catalytic runs. The catalyst was still active during the sixth run (Fig. 5). ICP measurement results revealed that the recovered catalyst almost had the same chromium content as the fresh catalyst (Cr, 2.02%), indicating that the degradation and leaching of metal complexes was not the main reason for the decreased catalytic performance of the immobilized catalysts. This decrease in catalytic performance might be related to an increase in the diffusion limitation with an increase in the number of cycles. Thus, the immobilized complexes are highly stable in the present catalytic oxidation system.

3 Conclusions

Three immobilized amino acid Schiff base complexes were prepared and showed promising catalytic performance towards the epoxidation of cyclohexene with 30% H_2O_2 . The introduction of mesoporous MCM-41 resulted in the immobilized complexes giving far better catalytic performance than their homogeneous analogues. The best cyclohexene conversion was 52.6% with 73.5% selectivity toward epoxide over $Cr(Sal-Ala)-MCM-41$ when the reaction was run at 60 °C for 6 h with 0.25 g of catalyst and a C_6H_{10}/H_2O_2 molar ratio of 1.2. We believe that more efficient immobilized catalysts for the epoxidation of cyclohexene can be prepared by modifying their structures and compositions, which will result in more applications. This work is of significance for the design of highly effective heterogeneous catalysts.

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