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水滑石负载Au纳米粒子的制备及其催化醇氧化反应

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摘要: 采用离子交换法和$NaBH_4$还原法制备了Mg-Al-水滑石(LDH)负载的Au纳米粒子(Au/LDH)催化剂. X射线衍射和透射电镜结果表明, Au粒子较均匀地分散在水滑石表面, 载体仍保持层状结构. 在温和的反应条件下, Au/LDH对一系列醇的氧化反应表现出优异的催化性能, 如在室温常压下进行分子O_2氧化1-苯基乙醇的反应, 底物转化率和苯乙酮选择性都接近100%, 而且催化剂经过多次循环使用后, 其活性未见下降. 可见, Au/LDH催化剂在醇氧化反应中具有良好的应用前景.

关键词: 金; 纳米粒子; 水滑石; 醇; 氧化; 分子氧

中图分类号: O643 **文献标识码**: A

Au Nanoparticles Supported on a Layered Double Hydroxide with Excellent Catalytic Properties for the Aerobic Oxidation of Alcohols

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Abstract: Au nanoparticles supported on Mg-Al-layered double hydroxide (Au/LDH) were successfully prepared by ion-exchange and reduction. XRD patterns and TEM images indicate that the Au nanoparticles are highly dispersed on the LDH support, and that the layered structure remains intact during the preparation process. Interestingly, Au/LDH shows high catalytic activity for the aerobic oxidation of alcohols under mild conditions. For example, the conversion of 1-phenylethanol and selectivity for acetophenone was nearly 100% using molecular oxygen as an oxidant under atmospheric pressure at room temperature. The Au/LDH composite exhibits high catalytic stability during these reactions, and therefore, it has great potential for industrial application.

Key words: gold; nanoparticle; layered double hydroxide; alcohol; oxidation; molecular oxygen

醇选择氧化为对应的醛或酮反应在工业和医药中应用广泛[1~3]; 传统方法中采用的次氯酸盐和高锰酸盐等氧化剂成本高而且污染环境[4~6]. 后来, 人们采用过渡金属配合物均相催化剂, 实现了氧气对醇的有效氧化, 但这些均相催化剂的回收再利用困难, 严重地限制了它们在工业上的广泛应用[7~9]. 因此, 开发反应条件温和、高效可再生的“绿色”催化剂备受关注[10]. 近年来, Au催化剂成为醇氧化反应研究的热点之一[11~13]. 研究发现, 小尺寸的Au纳米粒子对醇的选择性氧化具有较高的催化活性[14~16]. 对于负载型Au纳米粒子催化剂, 其活性主要依赖于Au粒子的尺寸、分散度以及载体的类型[17]. 以CeO_2, TiO_2和$Ga_3Al_3O_9$等金属氧化物为载体, 可提高Au纳米粒子催化剂的活性[18~21]. 水滑石(LDH)是层状阴离子型粘土, 具有独特的层状结构, 层间阴离子可交换, 因而在催化方面有着很好的应用前景. 因此, 本文以层状Mg-Al-水滑石为载体制备了Au/LDH催化剂, 并用于一系列醇的选择性氧化反应.

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采用尿素均匀沉淀法制备阴离子柱撑镁铝水滑石[22]. 将 30.76 g 的 $Mg(NO_3)_2·6H_2O$ (AR, 北京化工厂) 和 15 g 的 $Al(NO_3)_3·9H_2O$ (AR, 北京化工厂) 溶于 400 ml 水中, 搅拌下加入 72 g 尿素 (AR, 北京化工厂), 然后加热沸腾至出现白色沉淀, 继续维持沸腾 8 h 后停止加热, 室温静置 12 h, 再用大量蒸馏水洗涤沉淀多次, 可得 LDH 样品. 采用离子交换法和还原法制备 Au/LDH 催化剂. 将 0.22 g 的 $HAuCl_4·4H_2O$ (AR, 上海化学试剂有限公司) 溶于 80 ml 水中, 加入 6 g 的 LDH 样品搅拌过夜后过滤、洗涤. 100 ºC 真空干燥后转移至 50 ml 甲苯 (AR, 北京化工厂, 用 P_2O_5 干燥处理后蒸出) 中, 加入 $NaBH_4$ (AR, 北京化工厂) 搅拌 10 min 后, 加入 15 ml 乙醇搅拌 6 h, 即制得 Au/LDH 催化剂.

通过电感耦合等离子体原子发射光谱 (ICP, Perkin-Elmer 3300DV) 分析得到 Au/LDH 中 Au 的含量为 1.8%. 图 1 为 LDH 和 Au/LDH 样品的 XRD 谱 (Rigaku D/MAX 2550 型 X 射线衍射仪, Cu K_α 射线源, λ = 0.154 06 nm). 由图可以看出, 两个样品的 XRD 谱基本相似, 均为典型的层状结构, 且结晶度较高. 这表明在负载 Au 的过程中, LDH 依然维持了其典型的层状结构. 同时还可以看出, 在 Au/LDH 催化剂上, Au 粒子的衍射峰并不明显, 说明 Au 很好地分散于载体上, 没有发生严重的团聚现象. 这也被 Au/LDH 催化剂的 TEM 照片 (采用日本 JEOL JEM-200CX 型电子显微镜, 电压 300 kV) 所证实 (见图 2(a)). 在 Au/LDH 样品上, Au 粒子尺寸分布大致在 1.0~4.0 nm (见图 2(b)).

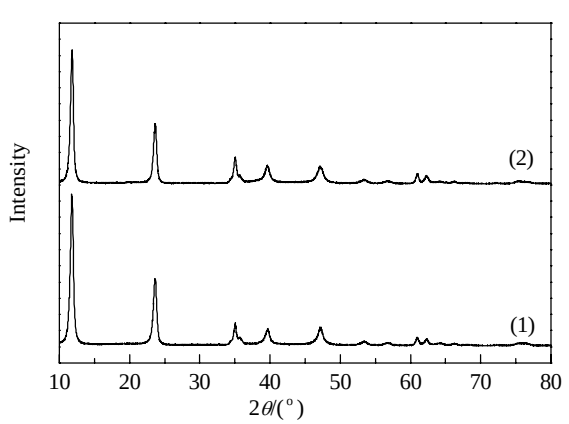


图 1 LDH 和 Au/LDH 样品的 XRD 谱

Fig. 1. XRD patterns of LDH (1) and Au/LDH (2) samples. LDH—Layered double hydroxide.

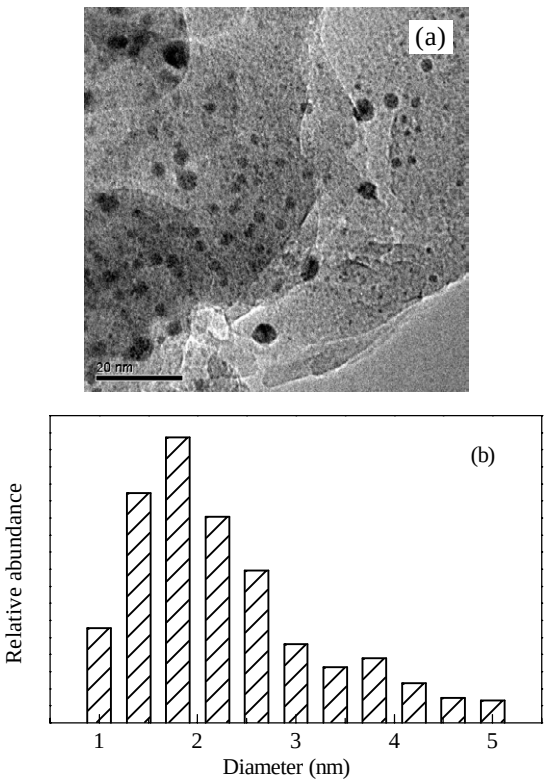


图 2 Au/LDH 样品的 TEM 照片和 Au 粒子粒径分布

Fig. 2. TEM image (a) and Au size distribution (b) of the Au/LDH sample.

图 3 为 Au/LDH 催化剂的 XPS 谱 (Thermo ESCALAB 250 型 X 光电子能谱仪, Al K_α 射线源, 以 C 1*s* 峰出现在 284.9 eV 处来校正). 可以看出, 在 83.2 eV 处出现了归属于 Au $4f_{7/2}$ 的峰, 这表明 Au/LDH 中 Au 是以单质的形式存在.

表 1 列出了以 O_2 为氧化剂, Au/LDH 催化剂对一系列醇氧化反应的催化性能. 可以看出, Au/LDH 催化剂基本对所有的反应物都表现出较高的活性和选

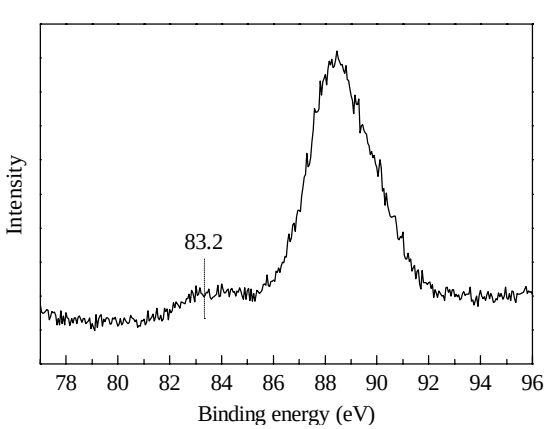
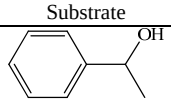
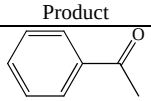
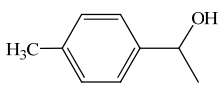
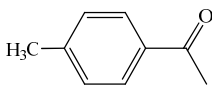
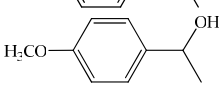
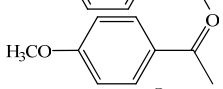
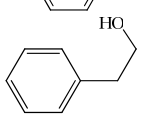
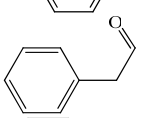
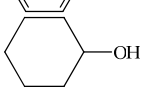
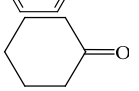
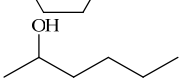
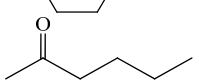
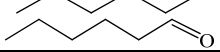


图 3 Au/LDH 催化剂的 XPS 谱

Fig. 3. XPS spectrum of the Au/LDH catalyst.

表 1 Au/LDH 催化剂对醇氧化反应的催化性能

Table 1 Aerobic oxidation of alcohols over the Au/LDH catalyst

Entry	Substrate	Product	Time (h)	Conversion (%)	Selectivity (%)
1[a]			2.0	>99	>99.5
2[b]			12.0	96	>99.5
3[c]			2.0	24	>99.5
4[d]			2.0	4	>99.5
5[e]			2.0	17	>99.5
6[f]			2.0	11	>99.5
7[g]			2.0	39	>99.5
8[h]			2.5	>99	>99.5
9[i]			2.5	97	>99.5
10[a]			2.5	97	>99.5
11[a]			2.0	99	>99.5
12[a]			20.0	79	88.0
13[a]			3.0	67	>99.5
14[b]			24.0	60	>99.5
15[j]			24.0	42	>99.5
16[j]			24.0	<1	—

[a]80 ºC, 1.5 mmol of alcohol, 80 mg of catalyst, 10 ml of toluene as solvent, O_2 bubbling rate 30 ml/min. [b]Room temperature 20 ºC. [c]2.0% Au/TiO_2 prepared as reference [23]. [d]2.0% Au/SiO_2 prepared as reference [23]. [e]3 mmol of CH_3COONa was added. [f]2.0% Au/MgO prepared as reference [23]. [g]2.0% Au/Fe_2O_3 prepared as reference [23]. [h]Recycled 3 times. [i]Recycled 6 times. [j]0.7 mmol of alcohol.

择性. 在 80º C 常压下仅反应 2 h, Au/LDH 催化剂上 1-苯基乙醇可完全转化为苯乙酮 (实验 1). 当以相似 Au 负载量的 Au/TiO_2, Au/SiO_2, Au/MgO 和 Au/Fe_2O_3 为催化剂时, 该反应转化率分别为 24%, 4%, 11% 和 39% (实验 3, 4, 6 和 7), 即使加入额外的无机碱 CH_3COONa, 在 Au/SiO_2 催化剂上 1-苯基乙醇转化率也只有 17% (实验 5), 远远低于 Au/LDH. 需要注意的是, 即使室温下, 反应 12 h 时, 在 Au/LDH 上 1-苯基乙醇转化率仍可达 96%. 对于对甲基-α-苯乙醇和对甲氧基-α-苯乙醇等其他芳香醇, Au/LDH 催化活性也很高, 反应转化率分别为 97% 和 99% (实验 10 和 11). 还可以看出, Au/LDH 对一级醇的催化活性比对二级醇的催化活性要低, 反应 20 h 时, 2-苯基乙醇转化率只有 79%, 苯乙醛选择性也仅为 88.0% (实验 12).

相对于较容易氧化的芳香醇, 脂肪醇氧化一直是该领域的难点. 而以 Au/LDH 为催化剂时, 脂肪醇的氧化活性较高. 在 80 ºC 只需反应 3 h, 环己醇转化率可达 67% (实验 13); 即使在室温, 也可达 60% (实验 14). 与芳香醇一样, 二级脂肪醇的活性依旧高于一级醇的活性. 在相同反应条件下, 2-己醇转化率可达 42%, 而 1-己醇却基本没有转化 (实验 15 和 16).

催化剂的重复使用性是衡量其性能的一个重要指标. Au/LDH 催化剂在重复使用 3 次后, 其活性未见下降 (实验 8); 重复使用 6 次后, 其活性略有下降

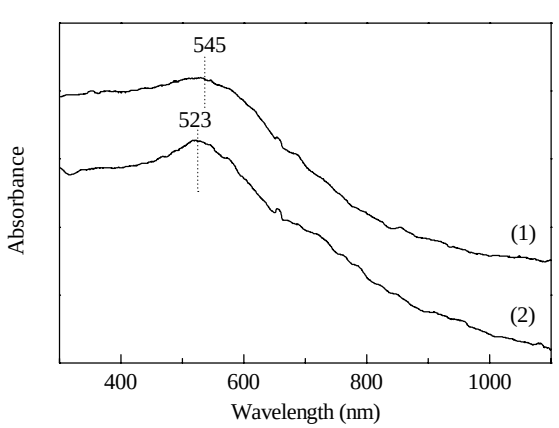


图 4 新鲜 Au/LDH 催化剂和重复使用 6 次后的催化剂的 UV-Vis 谱

Fig. 4. UV-Vis spectra of the as-prepared Au/LDH catalyst (1) and Au/LDH recycled 6 times (2).

(实验 9). 可见, 该催化剂具有较高的稳定性. 与新鲜 Au/LDH 催化剂的紫外谱图相比, 重复使用 6 次之后的样品中 Au 的紫外吸收峰更加尖锐, 并且蓝移 (见图 4), 说明催化剂中 Au 纳米粒子发生了轻微的团聚[24]. 这可能是催化剂活性下降的主要原因. 如果在 1-苯基乙醇催化氧化过程中, 将 Au/LDH 催化剂固体从反应体系分离, 随后的检测结果显示反应停止了, 说明该反应中起催化作用的是纳米 Au 颗粒.

总之, 本文制备了水滑石负载的 Au 纳米粒子催化剂, Au 很好地分散在 LDH 载体上, 它们在醇的氧化反应中表现出优异的催化性能.

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英 译 文

English Text

The selective oxidation of alcohols to their corresponding aldehydes or ketones is of great importance to the fine chemical and pharmaceutical industries [1–3]. Traditionally, the oxidation of alcohols has been carried out using hypochlorite and permanganate as oxidants, which increases the cost and produces plenty of waste [4–6]. A few transition-metal complexes can effectively promote the oxidation of alcohols with molecular oxygen as an oxidant in a homogeneous system. However, these homogeneous transition-metal complex catalysts are not widely used because of the separation and regeneration of the catalysts from the homogeneous system [7–9]. From the point view of green chemistry, developing "green" catalysts with high efficiency and recycling ability under mild reaction conditions is highly desirable [10]. In recent years, Au catalysis has been one of the most important research topics in the oxidation research area [11–13]. One of the exciting findings is that small-size Au nanoparticles are able to promote the oxidation of alcohols [14–16]. Their activity over supported Au nanoparticles highly depends on the Au particle size, dispersion, and the properties of the support [17]. Compared with the inert SiO_2 support, active supports such as CeO_2, TiO_2, and $Ga_3Al_3O_9$ interact with the Au sites resulting in high activities [18–21]. Layered double hydroxides (LDH) are anion clays that are widely used because of their layered structure and anion-exchange ability. In this work, Mg-Al-LDH was used to support the Au nanoparticles (Au/LDH), and we found that Au/LDH is catalytically active for the aerobic oxidation of a series of alcohols.

Mg-Al-LDH was synthesized according to Ref. [22]. As a typical run, 30.76 g of $Mg(NO_3)_2{\cdot}6H_2O$ (AR, Beijing Chem. Co.) and 15 g of $Al(NO_3)_3{\cdot}9H_2O$ (AR, Beijing Chem. Co.) were dissolved in 400 ml of water, followed by the addition of 72 g of urea (AR, Beijing Chem. Co.) while stirring. After heating to boiling point, a white precipitate was formed. After boiling for 8 h and precipitating at room temperature over 12 h, the solid LDH was collected by filtration and washing with water.

Au/LDH was prepared by ion-exchange and $NaBH_4$ reduction. For a typical run, 0.22 g of hydrochloroauric acid ($HAuCl_4{\cdot}4H_2O$, AR, Shanghai Chem. Co.) was dissolved in 80 ml of water, followed by the addition of 6 g of LDH and stirring overnight. After filtration, washing, and drying, the sample was transferred to 50 ml of toluene (AR, Beijing Chem. Co., dried by P_2O_5) followed by the addition of

$NaBH_4$ (AR, Beijing Chem. Co.). After stirring for 10 min, 15 ml of ethanol was added and the mixture was stirred for 6 h. Au/LDH was collected by filtration and washing with ethanol and water.

The Au content of the Au/LDH sample was 1.8% as determined by inductively coupled plasma (ICP, Perkin-Elmer 3300DV) analysis. Figure 1 shows X-ray diffraction (XRD) patterns of LDH and Au/LDH samples (Rigaku D/MAX 2550 diffractometer with Cu K_α radiation, λ = 0.154 06 nm). Both samples show the same diffraction peaks, which are assigned to the typical layered structure with high crystallinity. This indicates that the layered structure of LDH remains intact during the Au loading process. It should be noted that the characteristic peaks of the Au nanoparticles are not present suggesting that the small-size Au nanoparticles are highly dispersed, which is confirmed by TEM (JEM-200CX electron microscope, JEOL, Japan, with an acceleration voltage of 300 kV), as shown in Fig. 2(a). This TEM image gives direct evidence that the Au particle size is distributed between 1.0 and 4.0 nm (Fig. 2(b)).

Figure 3 shows the XPS spectrum of Au/LDH (Thermo ESCALAB 250 with Al K_α radiation, the binding energies were calibrated using the C 1*s* peaks at 284.9 eV), giving a Au $4f_{7/2}$ peak at 83.2 eV, which is attributed to metallic Au nanoparticles.

Table 1 lists the catalytic activities for the aerobic oxidation of various alcohols using molecular oxygen as an oxidant under atmospheric pressure over Au/LDH. Au/LDH is very active for the oxidation of 1-phenylethanol to acetophenone. Upon reacting for 2 h at 80 °C, 1-phenylethanol is completely converted to acetophenone (Table 1, entry 1). Upon reacting for 12 h at room temperature, the conversion is still 96%. In contrast, the Au/TiO_2, Au/SiO_2, Au/MgO, and Au/Fe_2O_3 catalysts with the same Au content exhibit relatively low conversions of 24%, 4%, 11%, and 39%, respectively (Table 1, entries 3, 4, 6, and 7). Even with the presence of additional base (CH_3COONa) in the system, Au/SiO_2 still gives a low conversion of 17% (Table 1, entry 5). For the oxidation of *p*-methyl-α-phenylethanol and *p*-methoxy-α-phenylethanol, Au/LDH gives a high conversion (97% and 99%) and high selectivity (over 99.5%) for the corresponding ketone (Table 1, entries 10 and 11). Interestingly, compared with the secondary aromatic alcohols, the conversion of primary alcohols over Au/LDH was low. For example, 2-phenylethanol gives a 79% conversion and an 88.0% selectivity for phenyl acetaldehyde (Table 1, entry 12).

It is worth noting that Au/LDH has a high activity for the oxidation of aliphatic alcohols. Cyclohexanol can be converted to cyclohexanone with a conversion of 67% in 3 h at 80 ºC (Table 1, entry 13). Even at room temperature the conversion is still only 60% (Table 1, entry 14). Furthermore, the conversion of secondary aliphatic alcohols is higher than that of primary alcohols. For example, 2-hexanol gives a 42% conversion while 1-hexanol is almost inactive under the same conditions (Table 1, entries 15 and 16).

The Au/LDH catalyst exhibits particularly good stability. For example, the conversion is the same (> 99%) after three recycles (Table 1, entry 8). When recycled 6 times, the conversion reduces slightly to 97% (Table 1, entry 9), which is associated with the aggregation of Au nanoparticles, as confirmed by UV-Vis spectroscopy (Fig. 4). The band at 545 nm is assigned to Au nanoparticles and it becomes sharper and shifts to 523 nm after being recycled 6 times. When the Au/LDH catalyst is removed from the system the oxidation stops, which confirms that Au/LDH is active during the oxidation.

In summary, a Au/LDH catalyst was prepared by ion-exchange and reduction and it shows good catalytic properties for the aerobic oxidation of alcohols, which is of potential importance for the production of fine chemicals.

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