

Cu₃P@CuO 纳米片状催化剂用于氨硼烷的高效水解析氢

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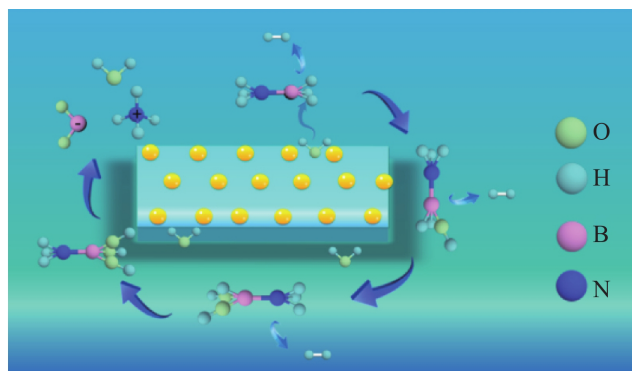
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摘 要: 氨硼烷(AB)作为一种分子量低、含氢量高的优质储氢物质, 若想充分发挥其价值, 开发出针对 AB 水解析氢的低成本、高活性催化剂, 正是推动 AB 水解析氢技术迈向工业化的核心路径。本工作以无水氯化铜为原材料, 在碱性条件下利用溶剂热法制备出氧化铜纳米片(CuO NS)前驱体。在通过低温磷化法, 将 CuO NS 转化成 Cu₃P@CuO 纳米片(Cu₃P@CuO NS)。采用 SEM、TEM、AFM、XRD 和 XPS 表征 Cu₃P@CuO NS 的微观形貌和结构组成, 考察 Cu₃P@CuO NS 催化剂对 AB 析氢反应性能的影响, 并探究不同反应条件下 Cu₃P@CuO NS 催化 AB 析氢反应的析氢速率、转化频率(TOF 值)。结果表明, 当磷化比例为 $m(\text{CuO NS})/m(\text{NaH}_2\text{PO}_2)=1$ 时($m(\text{CuO NS})=m(\text{NaH}_2\text{PO}_2)=0.1\text{ g}$), Cu₃P@CuO NS 表现出优异的催化 AB 活性, TOF 值高达 57.23 min^{-1} , 表观活化能为 44.31 kJ/mol , AB 的水解反应在催化剂用量上遵循伪一级动力学, 在 AB 的用量上则呈现伪零级动力学。对 Cu₃P@CuO NS 所展现出的卓越性能, 可归因于其纳米片结构暴露出的丰富的活性位点。鉴于催化剂的成本极低, Cu₃P@CuO 纳米片催化剂有望取代贵金属催化剂, 成为从 AB 中析氢的理想催化材料。

关键词: 氢能; 铜基催化剂; 氨硼烷; 纳米片

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The Cu₃P@CuO nanosheet catalyst used for the efficient hydrolysis of ammonia borane to produce hydrogen

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Abstract: Ammonia borane (AB) is an excellent hydrogen storage material with low molecular weight and high hydrogen content. To fully unleash its value, the development of low-cost and highly active catalysts for AB hydrolysis hydrogen production is precisely the core path to promote the industrialization of AB hydrolysis hydrogen production technology. This paper used anhydrous copper chloride as raw material, and prepared copper oxide nanosheets (CuO NS) precursor by solvothermal method under alkaline conditions. Through low-temperature phosphating method, CuO NS was converted into $\text{Cu}_3\text{P}@/\text{CuO}$ nanosheets ($\text{Cu}_3\text{P}@/\text{CuO}$ NS). The microstructure and structural composition of $\text{Cu}_3\text{P}@/\text{CuO}$ NS were characterized by SEM, TEM, AFM, XRD and XPS. The effects of as-prepared $\text{Cu}_3\text{P}@/\text{CuO}$ NS for hydrogen evolution reaction (HER) from AB hydrolysis were investigated. Additionally, the hydrogen evolution rate and turnover frequency (TOF value) of $\text{Cu}_3\text{P}@/\text{CuO}$ NS catalyzed AB hydrolysis were explored under different reaction conditions. The results showed that when the phosphating ratio was adjusted to m (CuO NS)/ m (NaH_2PO_2)=1 (m (CuO NS)= m (NaH_2PO_2)=0.1 g), $\text{Cu}_3\text{P}@/\text{CuO}$ NS exhibited the optimal catalytic activity for AB hydrolysis. $\text{Cu}_3\text{P}@/\text{CuO}$ NS exhibited a high turnover frequency (TOF), with a TOF value as high as 57.23 min^{-1} and an apparent activation energy of 44.31 kJ/mol. The hydrolysis of AB followed pseudo-first-order kinetics with respect to the catalyst dosage, while it exhibited pseudo-zero-order kinetics with respect to the AB dosage. The excellent performance exhibited by $\text{Cu}_3\text{P}@/\text{CuO}$ NS could be attributed to the abundant active sites exposed by their nanosheet structure. Given the remarkably low cost of this catalyst, the $\text{Cu}_3\text{P}@/\text{CuO}$ NS catalyst is highly anticipated to serve as a viable substitute for noble metal catalysts. It is poised to emerge as an ideal catalytic material for the hydrogen evolution reaction from AB, leveraging its cost-effectiveness and catalytic efficiency to address the challenges associated with high-cost noble metal-based systems.

Key words: hydrogen energy; copper-based catalyst; ammonia borane; nanosheet

随着化石燃料的过度消耗,由此引起的环境污染和全球能源危机引起了广泛关注。开发清洁、环保和可再生能源是减少对化石燃料依赖、减少温室气体排放的关键^[1-3]。氢被认为是一种理想的能源载体,因其环保性和高能量密度而备受关注。在氢能领域内析氢、储藏、运输、应用等技术方面中,储氢技术仍是一个急需突破的瓶颈^[4-7]。为早日实现氢能的大面积使用,必须解决储氢技术的安全性及高效性突破。与高压压缩和低温液化等物理手段相比较,化学析氢因其安全性、高效性而备受关注^[8-10]。其中,氨硼烷(AB)、水合肼、甲酸等化合物具有较高的化学储氢的能力。AB的分子量低,其含氢量却高达19.6%,成为储氢材料的首选;其次AB在固相、液相中均保持稳定的理化性质,当加以适当催化剂时析氢反应才会发生,当分离催化剂与AB溶液时,析氢反应即刻停止,有利于实现氢气安全、便捷、高效的运输和储藏^[11-15]。

当下对AB水解析氢具有高活性的大多数为贵金属催化剂,例如:Co^[16]、Pt^[17-19]、Ru^[20-22]、Pd^[23-24]等。由于地球矿藏量有限,使用贵金属催化剂的成本过高,限制了氢能被广泛使用。开发一种以非贵金属原料来替代贵金属的催化剂,是实现低成本推广氢能的有效途径,目前,已报道的非贵金属催化剂包括金属氧化物^[25-27]、合金类^[28-29]、

硼化物^[30-32]和金属磷化物^[33-35]。其中,过渡金属磷化物(TMPs),例如CoP、FeP、Ni₂P和Cu₃P等因其优异的催化活性备受关注,有望成为贵金属催化剂的替代品^[36]。TMP晶体由三角棱形几何体构成,独特的晶体结构使其在表面产生更多可协调的不饱和原子,明显提升了催化活性,在析氢反应中,P本身持有的负电荷可以捕获质子转化为活性位点,因此,可以通过增加P的浓度来增加活性位点数量;但当P过量时,金属作为氢化物的接收-反应中心,其占比会减少,催化剂的反应活性也会降低。Dang等^[37]制备了Cu/Cu₃P纳米阵列催化剂,通过两步合成策略实现,包括水热合成Cu/CuO纳米阵列前体和Ar气氛下进行低温磷化处理。所制备的Cu/Cu₃P纳米阵列作为电催化剂,在化学产氢反应中表现出优异的催化性能和耐久性。Wang等^[38]通过水热法合成了Cu₃P纳米片,并使用红磷代替有毒的PH₃作为磷源,构建出一种具有特殊结构的Z-scheme Cu₃P/TiO₂异质结。在异质界面形成后,金属磷化物晶格的周期性被破坏,导致局部电子结构发生变化。物种间的电子相互作用重新分配了它们各自状态的电子密度。研究表明,P的掺杂可作为一种有效的研究思路,以提升催化剂对AB水解制氢的反应活性。

本工作通过在碱性条件下合成CuO NS前驱体,将CuO NS前驱体与次磷酸钠分别研磨放置于

刚玉舟两端,在管式炉内以 3 K/min 的升温速率升至 573 K,并在该温度下保持 2 h。在低温磷化的过程中, NaH_2PO_2 分解为 PH_3 ,与表面 CuO 反应形成具有多重暴露区域的凸起结构,形成 $\text{Cu}_3\text{P}@/\text{CuO}$ NS。在光照条件下测试 $\text{Cu}_3\text{P}@/\text{CuO}$ NS 催化剂催化 AB 水解析氢的性能。

1 实验部分

1.1 实验仪器

CuO 、 $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ 、 NaOH 、氨硼烷(NH_3BH_3)、 NaH_2PO_2 , AR, 上海阿拉丁生化科技股份有限公司;实验用水为去离子水,自制。

Dimension Icon 型原子力显微镜(AFM)、D8 Advance 型 X 射线衍射仪(XRD),德国 Bruker 公司;Regulus 8100 型扫描电子显微镜(SEM),日本 Hitachi 公司;Talos F200X G2 型透射电子显微镜(TEM),美国 FEI 公司;K-Alpha 型 X 射线光电子能谱仪(XPS),美国 Thermo Fisher Scientific 公司。

1.2 CuO NS 的制备

在典型的 CuO NS 合成中, CuO NS 是用水热法合成的,如以往文献报道的^[39]。具体合成过程如下:将 NaOH 水溶液(50.0 mL, 6 mol/L)倒入 $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ 溶液(50.0 mL, 0.1 mol/L)中。将所得溶液保持在室温下,搅拌 0.5 h。将悬浮液转移到 100 mL 特氟隆内衬的高压釜中,在 373 K 下保持 720 min,自然冷却到室温。所得样品 CuO NS 通过离心、乙醇洗涤和干燥直接获得。

1.3 $\text{Cu}_3\text{P}@/\text{CuO}$ NS 的制备

采用简单的低温磷化途径制备了 $\text{Cu}_3\text{P}@/\text{CuO}$ NS。在典型的制备过程中,将 0.10 g CuO NS、0.10 g NaH_2PO_2 在砂浆中研磨形成细粉。在 573 K 下煅烧 2 h 得到 $\text{Cu}_3\text{P}@/\text{CuO}$ NS 固体,加热速率为 3 K/min。

1.4 转化频率(TOF)

转化频率(Turnover Frequency, TOF)作为评估多相催化体系本征活性的核心动力学参数,其定义为单位时间单位活性位点(或单位质量/摩尔催化剂)所转化的底物物质的量。通过式(1)所示的数学关系式精确计算 TOF 值,该计算模型通过标准化数据处理流程,确保不同催化剂体系间的 TOF 值具有严格可比性。

$$\text{TOF} = \frac{n_{\text{H}_2}}{n_{\text{catalyst}} \times t} \quad (1)$$

式中: n_{H_2} 为 H_2 产生的摩尔数,催化剂中所用金属的摩尔量为 n_{catalyst} ,反应时间为 t 。

2 结果与讨论

图 1(a) 和 (b) 为不同尺寸下的扫描电子显微镜图像(SEM),用于分析催化剂的微观形貌。从图 1(a) 中可观测到,催化剂整体呈片状结构,有部分呈片状堆积状态。从图 1(b) 中观测到催化剂表面分布直径大小不一的表面凸起,经后续 XRD 和 AFM 分析可知,该凸起为磷化过程中在 CuO NS 表面生成的 Cu_3P NS 颗粒。图 1(c) 和 (d) 为不同尺寸下的透射电子显微镜图像,均显示出明显的片状结构。综上所述,所制备的催化剂呈现片状结构。

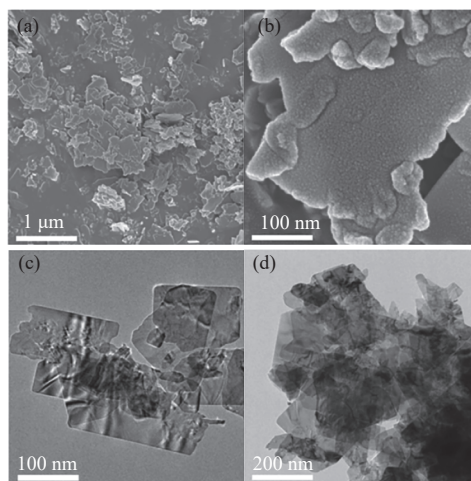


图 1 (a)、(b) $\text{Cu}_3\text{P}@/\text{CuO}$ NS 催化剂的 SEM 图像; (c)、(d) $\text{Cu}_3\text{P}@/\text{CuO}$ NS 催化剂的 TEM 图像

Fig. 1 (a), (b) SEM images of $\text{Cu}_3\text{P}@/\text{CuO}$ NS catalyst; (c), (d) TEM images of $\text{Cu}_3\text{P}@/\text{CuO}$ NS catalyst

图 2(a)–(d) 分别为前驱体 CuO NS 和 $\text{Cu}_3\text{P}@/\text{CuO}$ NS 的原子力显微镜图像(AFM)。从图 2(a) 和 (b) 中可以观测到前驱体 CuO NS 为很明显的片状结构,整体厚度为 2.8 nm;而图 2(c) 和 (d) 则显示出均匀分布的凸起点,凸起整体厚度为 2.0 nm。结合图 1(b) 和 (c) 可以表明, $\text{Cu}_3\text{P}@/\text{CuO}$ NS 催化剂整体呈片状,片状结构源自前驱体 CuO NS 的片状支撑,片状表面有均匀分布的凸起结构,源自磷化过程中生成的 Cu_3P 。图 2(e) 为 $\text{Cu}_3\text{P}@/\text{CuO}$ NS 的 X 射线衍射谱图(XRD),图中 41.9° 、 45.5° 、 48.4° 和 53.9° 分别对应 Cu_3P 的 (112)、(022)、(211) 和 (300) 晶面,而 41.9° 、 45.3° 、 45.8° 和 57.3° 则分别对应 CuO 的 (-111)、(111)、(200) 和 (-202) 晶面,验证了催化剂中的主要组成成分为片状的 CuO 基底和表面凸起的 Cu_3P 。图 2(f) 为从 TEM 图像中分析所得的晶格条纹数据,图中晶格条纹间距为 0.22 和 0.19 nm 的分别为 Cu_3P 的 (022) 和 (112) 晶

面, 而晶格间距为 0.20 和 0.21 nm 的则对应 CuO 的(-111)和(111)晶面, 进一步验证了催化剂的结构为片状表面覆有凸起, 主要组成成分为 CuO 和 Cu_3P ^[39-40]。

通过 X 射线光电能谱(XPS)对 $\text{Cu}_3\text{P}@/\text{CuO}$ NS 催化剂的元素组成及价态进行了表征, 结果如图 3(a) 和 (b) 所示。

从图 3(a) 的 XPS 全谱谱图中可以检测到 $\text{Cu}_3\text{P}@$

CuO NS 催化剂中共含 C、O、Cu、P 四种化学元素。图 3(b) 为前驱体 CuO NS 和 $\text{Cu}_3\text{P}@/\text{CuO}$ NS 催化剂中 Cu 元素价态的对比 XPS 谱图。图中展示了 $\text{Cu}_3\text{P}@/\text{CuO}$ NS 催化剂的 Cu 2p 光谱。其中, 两个明显的峰分别位于约 952.58 和 932.48 eV 处, 对应于 $\text{Cu}_3\text{P}@/\text{CuO}$ NS 催化剂中 Cu-P 键的 Cu $2p_{1/2}$ 和 Cu $2p_{3/2}$ 两种 Cu 物种^[39]。

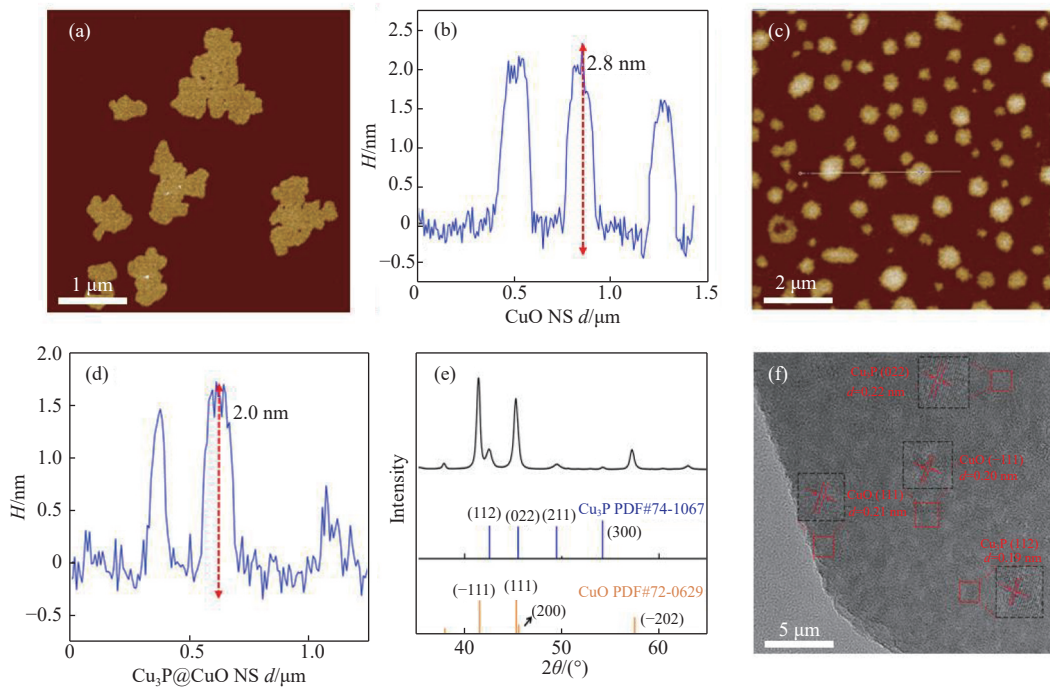


图 2 (a)、(c) CuO NS 和 $\text{Cu}_3\text{P}@/\text{CuO}$ NS 催化剂的 AFM 图像; (b)、(d) CuO NS 和 $\text{Cu}_3\text{P}@/\text{CuO}$ NS 催化剂的 AFM 厚度值; (e) $\text{Cu}_3\text{P}@/\text{CuO}$ NS 催化剂的 XRD 谱图; (f) $\text{Cu}_3\text{P}@/\text{CuO}$ NS 催化剂的 TEM 图像

Fig. 2 (a), (c) AFM images of CuO NS and $\text{Cu}_3\text{P}@/\text{CuO}$ NS catalysts; (b), (d) AFM thickness values of CuO NS and $\text{Cu}_3\text{P}@/\text{CuO}$ NS catalysts; (e) XRD patterns of $\text{Cu}_3\text{P}@/\text{CuO}$ NS catalyst; (f) TEM image of $\text{Cu}_3\text{P}@/\text{CuO}$ NS catalyst

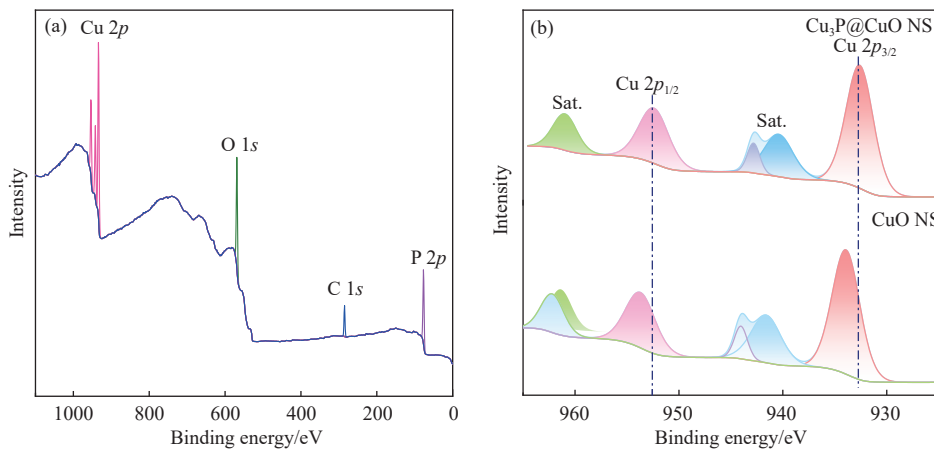


图 3 (a) $\text{Cu}_3\text{P}@/\text{CuO}$ NS 催化剂的 XPS 全谱谱图; (b) CuO NS 和 $\text{Cu}_3\text{P}@/\text{CuO}$ NS 催化剂的 XPS 谱图

Fig. 3 (a) The XPS survey spectrum of $\text{Cu}_3\text{P}@/\text{CuO}$ nanosheet catalyst; (b) The XPS comparison diagrams of CuO NS and $\text{Cu}_3\text{P}@/\text{CuO}$ NS catalysts

相较于 CuO NS, 这些峰显示出正向位移的趋势。原因归根于 Cu 物种向磷原子转移了较多的价电子。以 961.08、942.78 和 940.48 eV 为中心的附加峰可归因于 Cu 物种的卫星峰^[41]。

反应温度对催化剂的性能有很大影响, 因此, 通过调控析氢反应过程中的温度测试了催化性能。从图 4(a) 中可以看出, 温度的升高会有效加速氢气的生成, 同时温度的升高会加速水分子和离子的移动, 更有利于氢气的生成。图 4(b) 是根据阿伦尼乌斯方程和氢气的生成速率生成的速率直方图, 可以计算出反应的活化能为 44.31 kJ/mol ($R^2=0.99$), 此时活性组分 Cu_3P 的含量为 0.078 mmol,

通过式(1)计算得出转化频率(TOF)为 57.23 min^{-1} , 当继续增加 NaH_2PO_2 在磷化过程中的使用量, 催化剂中过量 P 的强吸电子作用过度, 会导致金属组分对氨硼烷分子的吸附能力减弱, 催化剂的反应活性也会降低。总的来说, $\text{Cu}_3\text{P}@/\text{CuO}$ NS 催化剂的催化性能优于大部分非贵金属催化剂(表 1)。

图 5(a) 显示在添加了不同催化剂用量时, 生成的氢气速率。随着催化剂的使用量的增加, 氢气生成速率明显加快。在一定范围内, 增加催化剂的用量可通过为 AB 析氢提供更多的活性结合位点来提高产氢速率。

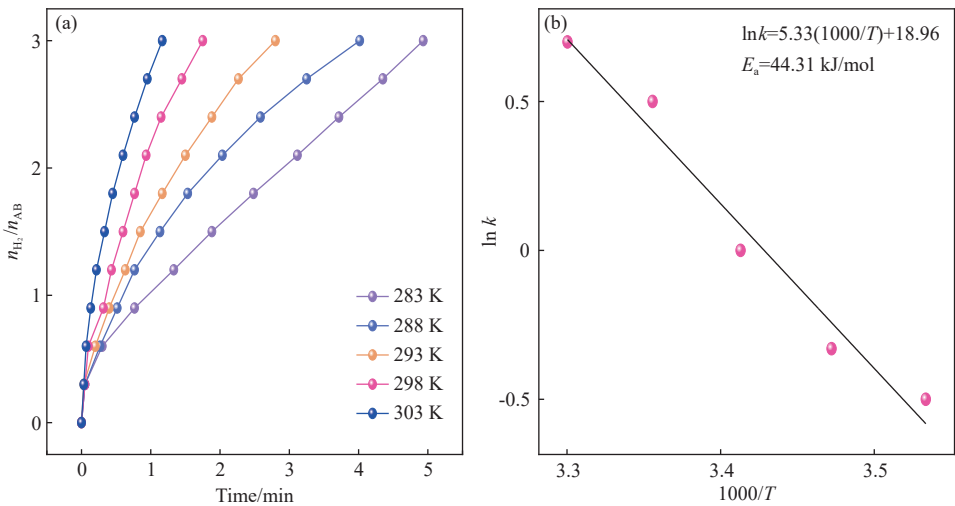


图 4 (a)反应温度与反应体系析氢速率的关系; (b)阿伦尼乌斯图和速率直方图
Fig. 4 (a) The relationship between reaction temperature and the hydrogen evolution rate of the reaction system;
(b) Arrhenius plot and rate histogram

表 1 文献中报道的各种催化剂的 TOF(转化频率)和活化能

Table 1 The comparison of TOF and activation energy of various catalysts reported in the literature				
Catalyst	Temperature/K	TOF/min ⁻¹	$E_a/(\text{kJ}\cdot\text{mol}^{-1})$	Ref.
$\text{Cu}_3\text{P}@/\text{CuO}$ NS	298	57.23	44.31	this work
Ni/BN	298	1.03	61.1	[42]
NiO/CeO ₂	298	1.7	25	[43]
Ni _{1.2} Fe _{0.8} @CN-G	298	23.25	38.24	[44]
Ni ₂ P	298	39.1	44.6	[45]
Co/CTF	298	42.3	42.7	[46]
Ni NPs/C	298	8.8	28	[47]
Cu _{0.49} Co _{0.51} /C	298	28.7	51.9	[48]
Ni NPs@3D-(N)GFs	298	41.7	—	[49]
hcp-CuNi/C samples	298	22.64	29.92	[50]
Co@Co ₂ Mo ₃ O ₈	298	17.28	51.8	[51]
Multishelled Co-P	298	23.5	38.7	[52]
Co ₃ B-CoP/h-BN	298	27.5	51.8	[53]
Cu _{0.5} Ni _{0.5} /CMK-1	298	54.8	—	[54]

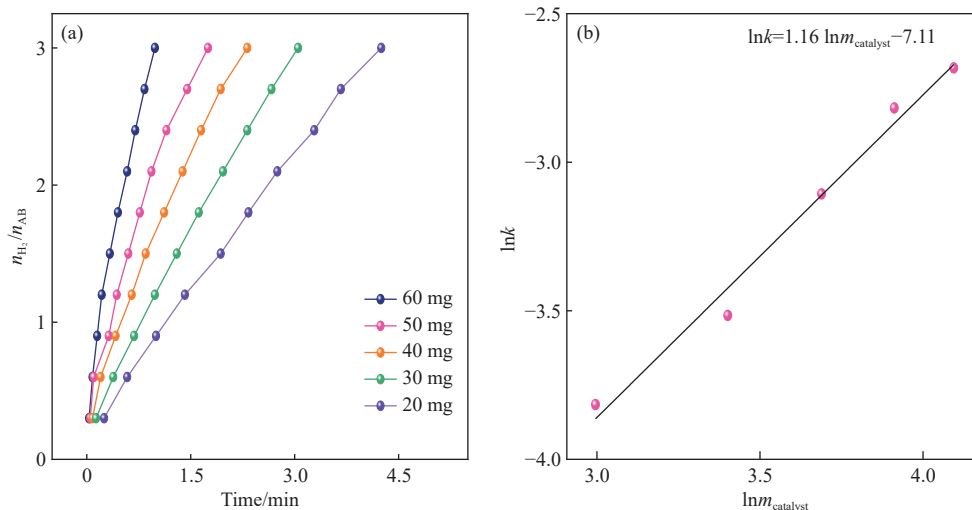


图 5 (a) 催化剂与反应体系析氢速率的关系; (b) $\text{Cu}_3\text{P}@/\text{CuO}$ NS 使用量与 AB 析氢速率的对数
Fig. 5 (a) The relationship between catalyst and hydrogen evolution rate in the reaction system; (b) The logarithmic curve of the content of $\text{Cu}_3\text{P}@/\text{CuO}$ NS versus the hydrogen evolution rate of AB

然而, 催化剂用量的过度增加会导致活性位点相对于需求出现过饱和现象, 进而使得产氢速率仅能获得少许改善。图 5(b) $\text{Cu}_3\text{P}@/\text{CuO}$ NS 的使用量与氢气生成速率的对数曲线, 拟合曲线的斜率为 1.16 ($R^2=0.99$) 表明 AB 析氢速率对于催化剂的使用量是一级反应, 在一定范围内增加催化剂的使用量可以显著提高析氢速率。

如图 6(a) 和 (b) 所示, 氢气的产生量与 AB 的浓度呈现正相关, 在温度恒定为 298 K 时, 氢气析

出速率基本上保持一致。将 AB 浓度与 AB 析氢速率两者的对数进行线性拟合, 得到的斜率为 0.29 ($R^2=0.98$), 结合图 5 数据进行分析可得, AB 析氢速率遵循一级反应动力学, 与 AB 浓度无直接联系。因此, AB 析氢的动力学方程可描述如下:

$$r = k(n_{\text{AB}})^{0.29} \times (m_{\text{catalyst}})^{1.16} \approx k(n_{\text{AB}})^0 \times (m_{\text{catalyst}})^1 = k(m_{\text{catalyst}}) \quad (2)$$

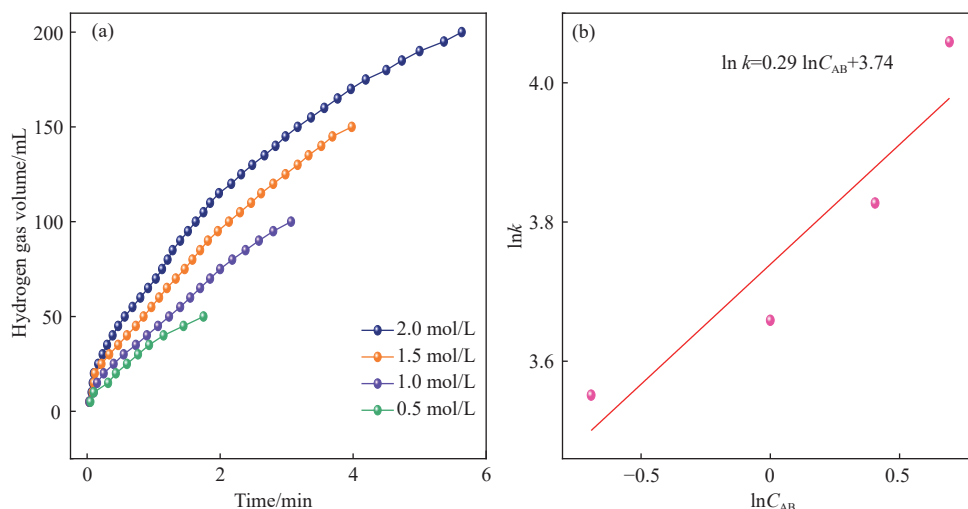


图 6 (a) AB 浓度与反应体系析氢速率的关系; (b) AB 浓度与 AB 析氢速率的对数曲线
Fig. 6 (a) The relationship between AB concentration and hydrogen evolution rate in the reaction system; (b) Logarithmic curve of AB concentration versus hydrogen evolution rate of AB

3 结 论

本研究合成了片状结构的 $\text{Cu}_3\text{P}@/\text{CuO}$ NS 催化剂, 并将其运用于 AB 析氢。在碱性环境下, 通

过水热法合成了 CuO NS 前驱体, 再将所得的 CuO NS 前驱体与 NaH_2PO_2 在管式炉中进行低温吹扫磷化, 磷化温度为 573 K, 磷化时长为 2 h。得益于

其片状的结构, 并且吹扫磷化的过程中生成的 Cu_3P 物种以小颗粒的形态覆盖在 CuO 上, 提高了活性位点的暴露, 因此, 生成的 $\text{Cu}_3\text{P}@/\text{CuO}$ NS 催化剂在 298 K 的反应温度和光照条件下, 表现出优异的析氢效果, TOF 值高达 57.23 min^{-1} , 活化能为 44.31 kJ/mol 。该催化剂较其他非贵金属催化剂表现出优异的催化效果, 同时因为该催化剂中无贵金属成分, 使得该催化剂的成本低廉, 为过渡金属磷化物的制备并运用于 AB 的大面积工业化提供一种新的思路和策略。

利益冲突声明

作者声明没有利益冲突。

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