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# 铜催化的端基炔偶联反应的研究进展

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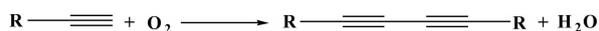
(内蒙古师范大学 化学与环境科学学院 内蒙古自治区绿色催化重点实验室, 内蒙古 呼和浩特 010022)

关键词: 端基炔; 偶联; 铜催化

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二乙炔类聚合物是一类以1,3-丁二炔为主要聚合单体的重要聚合物,应用于有机发光器件<sup>[1]</sup>、太阳能电池<sup>[2]</sup>、磁性材料<sup>[3]</sup>、光纤传导<sup>[4]</sup>、分子传感器<sup>[5]</sup>、药物<sup>[6]</sup>等领域. 中间体二炔化合物是构建分子的基本模块之一<sup>[7]</sup>,不仅是有机合成的重要中间体,也是天然产物和生理活性化合物的基本骨架. 其中1,3-共轭二炔用途最为广泛,应用于超分子化学、聚合物化学、天然产物、抗菌药物、纳米材料官能团等领域<sup>[6]</sup>.

合成1,3-共轭二炔的主要方法为端基炔自偶联,如下式表示:



Glaser在1869年首次将CuCl用于苯乙炔偶联反应<sup>[8]</sup>,在空气中合成了1,4-二苯基-1,3-丁二炔,该系列反应被称为Glaser偶联反应. 由于反应中需要分离中间产物—苯基炔化铜,因此未得到广泛关注. 1962年, Hay<sup>[9]</sup>将四甲基乙二胺引入CuCl催化系统,利用一锅法避免了中间产物的分离,使更多的研究者投入到一价铜盐催化的Glaser偶联反应的研究<sup>[10-11]</sup>.

21世纪之前,Glaser偶联反应主要以Pd/Cu催化和Cu(I)均相催化体系为主,此后的研究主要集中于寻求更简单、高效的催化剂,由Cu(I)催化体系发展到可稳定存在的Cu(II)催化体系,由均相催化体系发展为多相催化体系. 随着催化剂的不断改进,苛刻的反应条件逐渐被温和的反应过程所取

代. 其他金属催化剂如NiCl<sub>2</sub>·6H<sub>2</sub>O/CuI<sup>[12]</sup>、AuPPh<sub>3</sub>NtF<sub>2</sub><sup>[13-14]</sup>、Fe(acac)<sub>3</sub>/Cu(acac)<sub>2</sub><sup>[15]</sup>、FeCl<sub>3</sub>/CuBr<sup>[16]</sup>也先后用于该偶联反应,但受到反应条件及适用性的限制. 目前应用于Glaser偶联反应的催化剂主要有Pd/Cu、Cu(I)、Cu(II)、CuNPs(纳米铜)催化剂,端基炔偶联反应的相关文献报道主要以苯乙炔偶联生成1,4-二苯基-1,3-丁二炔为反应模型,同时将底物扩展至其他芳香类和脂肪类端基炔. 我们将主要以苯乙炔偶联反应为例,综述不同催化体系中溶剂、添加剂及碱性强弱等对铜催化的端基炔偶联反应的影响.

## 1 Cu(I)助催化作用

Cu(I)盐在端基炔偶联反应的钯催化体系中以助催化剂的角色出现,最常见的为CuI. 表1是以CuI为助催化剂的苯乙炔偶联反应各类钯催化体系,包括均相钯配合物催化体系(编号1~8)、负载型多相钯催化体系(编号9~11). 这些催化体系大多需要加入碱(如Et<sub>3</sub>N、NaOAc)及其它附加物(如Me<sub>3</sub>NO、BrCH<sub>2</sub>COOEt、Ph<sub>3</sub>P),其中碱被认为有助于加快端基炔与CuI生成中间体炔化铜的速率. 与PdCl<sub>2</sub><sup>[17]</sup>相比,Pd(OAc)<sub>2</sub><sup>[18]</sup>催化体系避免了使用附加物,反应时间较短,空气条件下可得到较高产率的二炔. 另外一种无附加物催化剂为环钯的二茂铁亚胺配合物<sup>[19]</sup>,通过比较KOAc、i-Pr<sub>2</sub>EtN、Cs<sub>2</sub>CO<sub>3</sub>3种碱,可得以KOAc为碱时催化效果最好. 多相催化剂Pd/C<sup>[20]</sup>在溶剂DMSO中可直接催化反应,说明弱碱性极性溶剂(如DMF、DMSO)有利于反应的进行.

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表1 催化苯乙炔偶联反应的 Pd/CuI 均相/多相催化体系

Table 1 Homogeneous and heterogeneous Pd/CuI catalytic systems for homocoupling of ethynylbenzene

Entry	Year	Catalyst	Additive	Base	Solvent	Atmosphere	Temp. /°C	Time /h	Yield /%	Ref.
1	2005	PdCl <sub>2</sub>	Me <sub>3</sub> NO	NaOAc	CH <sub>3</sub> CN	N <sub>2</sub>	Room temp.	10	96	17
2	2005	Pd(OAc) <sub>2</sub>	—	DABCO	CH <sub>3</sub> CN	Air	Room temp.	2	100	18
3	2009	Pd(NH <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	TBAB	Et <sub>3</sub> N	H <sub>2</sub> O	Air	Room temp.	6	99	21
4	2002	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	BrCH <sub>2</sub> COOEt	DABCO	THF	Air	Room temp.	2	99	22
5	2005	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	Ph <sub>3</sub> P	Et <sub>3</sub> N	CH <sub>3</sub> CN	O <sub>2</sub>	60	24	80	23
6	2006	NHC-Pd(II)	BnNHCH <sub>2</sub> CH <sub>2</sub> OH	TMEDA	DMF	O <sub>2</sub>	40	12	86	27
7	2005	Amine-Derived PdCl <sub>2</sub> Complex	TBAA	K <sub>2</sub> CO <sub>3</sub>	NMP	Air	110	4	100	28
8	2007	Cyclopalladated ferrocenylimines	—	KOAc	DMF	Air	40	2	96	19
9	2007	Pd/C	—	—	DMSO	O <sub>2</sub>	Room temp.	24	99	20
10	2012	SBA-15@ DABCO-Pd	—	DABCO	CH <sub>3</sub> CN	Air	70	24	94	24
11	2007	PdCl <sub>2</sub> /PS- PEG <sub>400</sub> -PPh <sub>2</sub>	—	SPC	CH <sub>3</sub> CN	Air	Room temp.	8	96	25

TBAA: tetra-*n*-butylammonium acetate; DABCO: 1,4-diaza-bicyclo[2.2.2]octane; DMSO: dimethyl sulfoxide;  
 TBAB: tetra-*n*-butylammonium bromide; TMEDA: tetramethylethylenediamine; SPC: sodium percarbonate;  
 NMP: *n*-methyl-2-pyrrolidone; DMF: *N,N*-dimethylformamide; THF: tetrahydrofuran.

离子型 Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>/CuI 配合物催化体系<sup>[21]</sup>可用于以水为溶剂的端基炔偶联反应,通过萃取分离,可回收使用.与之相比, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>/CuI 催化体系<sup>[22-23]</sup>在合适的溶剂、附加物作用下,反应时间较短,反应温度较低.在碱的作用下,端基炔与 CuI 生成中间体炔化铜,通过转金属化作用形成钯的二炔化合物,进而转化为目标产物 1,3-共轭二炔,同时 Pd(II)被还原为 Pd(0),最后通过氧化剂将 Pd(0)再氧化为 Pd(II)以完成催化剂的循环.

SBA-15 介孔氧化硅<sup>[24]</sup>、PS-PEG<sub>400</sub>-PPh<sub>2</sub> 树脂<sup>[25]</sup>是钯催化剂的有效载体,该系列催化剂可用于端基炔偶联反应,后者使用具有碱与氧化剂双重作用的过碳酸钠<sup>[26]</sup>,使得反应时间缩短,但由于搅拌过程中易发生钯流失或聚合物矩阵被破坏,影响催化剂的寿命.

在 Pd/Cu 催化体系中,炔化铜的生成是反应机

理中的关键步骤,因此作为助催化剂, CuI 是必不可少的.与均相体系相比,虽然多相催化体系的催化剂可回收再利用,但钯组分负载困难,反应条件苛刻.

## 2 Cu(I) 催化体系

由于 Pd-Cu 催化体系成本昂贵,所以更多的研究者致力于 Glaser 首创的 Cu(I) 催化体系的研究.表 2 所示为 CuI (编号 1~5)、CuCl (编号 6~11) 和 Cu(I) 负载型多相催化剂(编号 12~16)的苯乙炔偶联反应催化性能的一些结果.由表可知,在均相体系中 CuCl 催化效果优于 CuI,附加物在 Cu(I) 催化体系中主要作为碱或氧化剂,分别起到加快端基炔去质子化速率和完成催化循环的作用.催化体系中加入强氧化剂 I<sub>2</sub><sup>[29]</sup>、PhI(OAc)<sub>2</sub>(DIB)<sup>[30]</sup>,可在相同条件下有效缩短反应时间.

表2 催化苯乙炔偶联反应的 Cu(I) 均相/多相催化体系

Table 2 Homogeneous and heterogeneous Cu(I) catalytic systems for homocoupling of ethynylbenzene

Entry	Year	Catalyst	Additive	Base	Solvent	Atmosphere	Temp. /°C	Time /h	Yield /%	TON	TOF /h <sup>-1</sup>	Ref.
1	2006	CuI (5 mol%)	—	—	[bmim]OH	Air	Room temp.	1.5	98	19.6	13.1	33
2	2011	CuI (5 mol%)	Et <sub>3</sub> N	TMEDA	Acetone	Air	Room temp.	20	91	18.2	0.9	44
3	2008	CuI (1 mol%)	I <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	DMF	Air	80	3	99	99.0	33.0	29
4	2011	CuI (5 mol%)	KF-Al <sub>2</sub> O <sub>3</sub>	NaOAc	DMF	Air	90	30	97	19.4	0.6	45
5	2011	CuI (5 mol%)	KF-Al <sub>2</sub> O <sub>3</sub>	DABCO	—	Air	Room temp.	0.17	99	19.8	118.8	35
6	2003	CuCl (0.2 mol%)	—	TMEDA	[bmim]PF <sub>6</sub>	O <sub>2</sub>	Room temp.	4.5	95	475.0	105.5	34
7	2008	CuCl (1 mol%)	PhI(OAc) <sub>2</sub>	Et <sub>3</sub> N	CH <sub>3</sub> CN	Air	Room temp.	0.17	83	83	498	30
8	2009	CuCl (2 mol%)	DBU	TMEDA	CH <sub>3</sub> CN	O <sub>2</sub>	Room temp.	18	99	49.5	2.7	46
9	2010	CuCl (2 mol%)	—	(CH <sub>2</sub> ) <sub>5</sub> NH	PhCH <sub>3</sub>	Air	60	5	96	48	9.6	47
10	2011	CuCl (5 mol%)	—	—	DMSO	Air	90	7	96	19.2	2.7	31
11	2011	CuCl (10 mol%)	—	TMEDA	CF <sub>3</sub> CH <sub>2</sub> CF <sub>2</sub> - CH <sub>3</sub>	O <sub>2</sub>	Room temp.	1	93	9.3	9.3	32
12	2009	Cu(I)-USY (30 mol%)	—	—	DMSO	Air	110	15	98	3.2	0.22	36
13	2012	MCM-41-2N-CuI (1 mol%)	—	(CH <sub>2</sub> ) <sub>5</sub> NH	CH <sub>2</sub> Cl <sub>2</sub>	Air	25	2	94	94	47	38
14	2012	A-21 · CuI (5 mol%)	—	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> -NH <sub>2</sub>	—	Air	Room temp.	0.17	97	19.4	116.4	41
15	2013	SBA-15@ amine-Cu (5 mol%)	—	—	Piperidine	Air	Room temp.	4	100	20	5	42
16	2013	CuI-TEDETA /SBA-15 (3 mol%)	—	—	DMSO	O <sub>2</sub> (1 atm)	50	6	99	33	5.5	43

## 2.1 Cu(I) 均相催化体系

溶剂对 Cu(I) 均相催化体系具有很大的影响. CuCl 在弱碱性极性溶剂二甲基亚砷中可实现无碱端基炔偶联反应<sup>[31]</sup>. 五氟丁烷因其具有较高的溶氧能力, 作为苯乙炔偶联反应的溶剂, 可有效缩短反应时间<sup>[32]</sup>. Ranu 课题组将疏水性的离子液体作为反应溶剂, 易于催化剂的回收及产物分离, 推测机理可能为离子液体 [bmIm] OH 可以活化端基炔去质子化形成阴离子, 然后与 CuI 生成 Cu(II) 的双环炔化物. 因此离子液体可以充当反应媒介及碱的双重角色, 有效缩短反应时间<sup>[33-34]</sup>. 此外, 除了常规的加热反应之外, 以 CuI/KF-Al<sub>2</sub>O<sub>3</sub> 为催化剂在球磨机中进行苯乙炔偶联反应<sup>[35]</sup>, 只需 10 min, 转化频率可达 118.8 h<sup>-1</sup>.

## 2.2 Cu(I) 多相催化体系

多相催化剂的寿命是评定催化剂优劣的标准之一, 负载型催化剂活性中心的固定一直是研究者面临的重大挑战性工作. Louis 课题组<sup>[36]</sup>将 Cu(I)-USY 沸石用于无碱条件的 Glaser 型反应, 通过实验证实反应过程中无铜流失. 此外, 他们发现沸石孔径越大、Si/Al 比越高、Cu(I) 的浓度越大, 产率越高<sup>[37]</sup>. MCM-41-2N-CuI 分子筛<sup>[38]</sup>催化剂因其具有大的比表面积, 规则孔结构<sup>[39-40]</sup>, 利于铜的分散, 具有较高的催化活性, 且重复使用 10 次时产率仍保持在 96% ~ 93%. A-21 · CuI 琥珀石催化剂<sup>[41]</sup>中铜负载较稳定, 催化苯乙炔偶联反应只需 10 min, 使用 5 次后没有明显的铜流失, 且产率在 96% ~ 84% 之间. 近期, 以分子筛 SBA-15 为载体的 Cu(I) 催化剂均可在无碱的绿色温和条件下实现端基炔偶联反应<sup>[42-43]</sup>, 且与 Cu(I)-USY 沸石催化剂<sup>[36]</sup>相比, 负载量较小.

与 Cu(I) 均相催化体系相比, 负载型 Cu(I) 多相催化体系催化剂寿命长, 体系中无需加入配体, 甚至有些可在无碱条件下催化反应. 多个报道证明, 载体的比表面积越大, 活性组分铜负载越均匀, 其催化性能越好. 与 Pd/Cu 催化反应机理不同, 无论是 Cu(I) 均相催化体系还是多相催化体系, 催化过程首先生成炔基阴离子, 转而生成为铜的二炔化合物, 最后还原消除, 得到二炔化合物.

## 3 Cu(II) 催化体系

虽然负载型 Cu(I) 催化剂的出现改善了催化剂的寿命情况, 但 Cu(I) 催化剂易被氧化且价格相对

昂贵, 因此更为绿色廉价的 Cu(II) 催化剂是近年来的研究热点之一. 如表 3 所示, 反应均不需要附加物的加入. Cu(II) 均相催化体系主要以铜盐为主 (编号 1 ~ 6), Cu(II) 多相催化体系 (编号 7 ~ 13) 主要以水滑石、无溶剂铜盐及 Cu(OH)<sub>x</sub> 系列催化剂为主. Cu(OH)<sub>x</sub> 系列催化剂<sup>[48-49]</sup>因其本身具有强碱性, 足以激发反应, 所以不需要额外加碱.

### 3.1 Cu(II) 均相催化体系

应用于端基炔偶联的 2 价铜盐催化剂主要有 CuSO<sub>4</sub><sup>[50]</sup>、CuCl<sub>2</sub><sup>[51-52]</sup>、CuBr<sub>2</sub><sup>[53]</sup>、Cu(OAc)<sub>2</sub><sup>[54]</sup>. CuSO<sub>4</sub> 可在水溶液中起催化作用, 虽然水溶液中反应绿色环保, 但是相比于有机溶剂中反应速率慢, 反应时间长. CuCl<sub>2</sub> 为催化剂时需要加入碱, 电化学研究结果表明, 当以 1,8-二氮杂二环-双环(5,4,0)-7-十一烯(DBU)为碱时, 其与 CuCl<sub>2</sub> 形成的配合物中存在 Cu<sup>2+</sup>/Cu<sup>+</sup> 氧化还原对, 可以促进催化循环<sup>[55]</sup>. 自由基抑制剂 2,2,6,6-四甲基哌啶氧化物(TEMPO) 的加入并未影响反应的正常进行, 说明该催化体系中端基炔偶联并不遵循自由基反应历程. Cu(OAc)<sub>2</sub> 中的 OAc<sup>-</sup> 可以发挥碱的作用<sup>[56]</sup>, 使得 DMSO 为溶剂的 Cu(OAc)<sub>2</sub> 催化体系不需要任何附加物和额外碱的加入, 整个过程中水是唯一副产物, 催化体系简单高效<sup>[54]</sup>. 端基炔和 Cu(OAc)<sub>2</sub> 形成炔铜中间体, 通过氧化, 形成偶联产物和水, 再生 Cu(OAc)<sub>2</sub>.

硅钨酸盐的双铜取代物 TBA<sub>4</sub> [γ-H<sub>2</sub>SiW<sub>10</sub>O<sub>36</sub>Cu<sub>2</sub>(μ-1,1-N<sub>3</sub>)<sub>2</sub>] 可用于催化氧化反应, 包括端基炔氧化偶联反应<sup>[57-58]</sup>. 通过跟踪反应液的紫外可见光谱可知, 反应过程中伴随着 Cu<sup>2+</sup> 的 d-d 跃迁引起的 700 nm 处的吸收峰减弱, 说明 Cu<sup>2+</sup> 被还原为 Cu<sup>+</sup>. 通入 O<sub>2</sub> 之后, 吸收峰又再现, 这说明 Cu<sup>+</sup> 很容易被氧化为 Cu<sup>2+</sup>, 完成催化剂的循环过程<sup>[59]</sup>.

### 3.2 Cu(II) 多相催化体系

水滑石具有表面酸碱性, 所以常常被用作催化剂或载体. Cu-Mg-Al<sup>[60]</sup> 和 Cu-Al 水滑石<sup>[61]</sup> 被先后用于苯乙炔偶联反应, 后者回收使用 9 次, 产物的产率保持在 88% ~ 76%. 继负载型催化剂之后, 2 价铜盐也可用于无溶剂端基炔偶联反应, 如 CuCl<sub>2</sub><sup>[62-64]</sup>、Cu(OAc)<sub>2</sub><sup>[65]</sup> 等, 其中微波反应的效果最佳.

Mizuno 课题组<sup>[48]</sup>将 Cu(OH)<sub>x</sub>/TiO<sub>2</sub> 催化剂用于无额外碱条件下的端基炔偶联反应中, 但仅研究

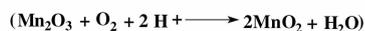
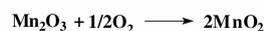
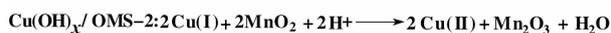
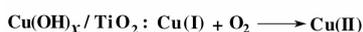
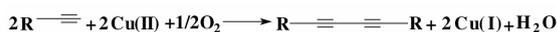
表 3 催化苯乙炔偶联反应的 Cu(II) 均相/多相催化体系

Table 3 Homogeneous and heterogeneous Cu(II) catalytic systems for homocoupling of ethynylbenzene

Entry	Year	Catalyst	Base	Solvent	Atmosphere	Temp. /°C	Time /h	Yield /%	TON	TOF /h <sup>-1</sup>	Ref.
1	2011	CuSO <sub>4</sub> · 5H <sub>2</sub> O (5 mol%)	KOAc	H <sub>2</sub> O	Air	120	24	99	20	0.825	50
2	2011	CuCl <sub>2</sub> (10 mol%)	DBU	THF	Air	Room temp.	24	92	9.2	0.4	51
3	2011	CuCl <sub>2</sub> (10 mol%)	NaOAc	PEG-1000	CO <sub>2</sub> , O <sub>2</sub>	120	3	99	9.9	3.3	52
4	2013	CuBr <sub>2</sub> (20 mol%)	Pyrrolidine	CH <sub>2</sub> Cl <sub>2</sub>	Air	Room temp.	12	99	4.8	0.4	53
5	2011	Cu(OAc) <sub>2</sub> (10 mol%)	—	DMSO	Air	90	10	90	9.0	0.9	54
6	2008	TBA <sub>4</sub> [γ-H <sub>2</sub> SiW <sub>10</sub> O <sub>36</sub> - Cu <sub>2</sub> (m-1,1-N <sub>3</sub> ) <sub>2</sub> ] (0.2 mol%)	—	PhCN	O <sub>2</sub> (1 atm)	60	18	93	465	25.8	58
7	1995	Cu-Mg-Al LDH (1.3 mol%)	NaOH	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> -OH	O <sub>2</sub> (20atm)	60	1	66	50.8	50.8	60
8	2007	Cu-Al LDH (110 mol%)	TMEDA	MeCN	O <sub>2</sub>	25	4	89	0.9	0.2	61
9	2010	CuCl <sub>2</sub> (3 mol%)	Et <sub>3</sub> N	—	Air	60	6	99	33	5.5	62
10	2002	Cu(OAc) <sub>2</sub> · H <sub>2</sub> O/KF /Al <sub>2</sub> O <sub>3</sub> (20 mol%)	O(CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> -NH	—	Air	Room temp.	3	96	4.8	1.6	64
11	2009	Cu(OH) <sub>x</sub> /TiO <sub>2</sub> (5 mol%)	—	PhCH <sub>3</sub>	O <sub>2</sub> (1atm)	110	0.5	90	18	36	48
12	2011	Cu(OH) <sub>x</sub> /KMn <sub>8</sub> O <sub>16</sub> (1 mol%)	—	PhCH <sub>3</sub>	O <sub>2</sub> (1atm)	110	0.17	90	90	540	49
13	2012	[Cu(TMEDA)(OH)]Cl (5 mol%)	TMEDA	SILP	Air	Room temp.	72	95	19	0.04	67

了以碳氢化合物为基础的端基炔为反应底物的偶联反应. 随后, 他们用锰的氧化物为基础的八面体分子网(OMS-2)<sup>[49]</sup>代替 TiO<sub>2</sub> 载体, 反应时间缩短至 10 min, 催化剂回收使用 14 次, 产物的产率仍可高达 90%. 从机理上研究表明, TiO<sub>2</sub> 仅为载体, 催化剂循环过程中起到氧化作用的是 O<sub>2</sub>, 而 OMS-2 还

扮演着电子传输者的角色, 反应过程如下:



负载型离子液体(SILP)催化剂是在离子液体薄膜上形成的一种多相催化剂<sup>[66]</sup>, Cu/Si/bmmim(OTf)系列催化剂<sup>[67]</sup>成功实现了端基炔的偶联,可以回收使用至少4次而活性没有明显下降,但是反应时间太长,且底物范围覆盖面太窄.

Cu(II)催化体系中,首先端基炔与Cu(II)生成炔铜化合物,随后经过还原消除释放Cu(I),得到二炔化合物,最后氧化剂将Cu(I)再氧化为Cu(II),完成催化循环.因为Cu(I)的再氧化是反应中的控速步骤,直接影响着催化剂的效率,所以氧化剂在反应中扮演着极为重要的角色.从反应时间、转化数、转化频率等方面对比,Cu(II)多相催化体系明显优于均相体系,尤其是碱性铜基催化剂,倍受研究者的关注.

## 4 纳米铜催化体系

近年来,金属纳米粒子因其独特的电子供给能力应用于C-C偶联反应中<sup>[68-70]</sup>.铜纳米粒子应用于端基炔偶联反应有两种存在形式:非负载型和负载型,如表4所示.2009年,纳米铜(CuNPs)首次被报道用于催化端基炔偶联反应<sup>[71]</sup>,但加热易聚集,暴露在空气中不稳定,难以确定活性组分铜的价态(编号1).CuNPs/TiO<sub>2</sub>催化剂<sup>[72]</sup>经过简单的过滤洗涤,可重复利用3次(产率:99%~89%),但催化剂负载铜的利用率仍有待提高(编号2).此外,将铜纳米粒子负载于具有大比表面积的硅纳米管上,用于微波反应<sup>[73]</sup>,可有效缩短反应时间(编号3).经证实,前驱体金属盐的阴离子半径越小,纳米铜的粒径越均匀,催化剂活性越好.

表4 催化苯乙炔偶联反应的CuNPs多相催化体系

Table 4 Heterogeneous CuNPs catalytic systems for homocoupling of ethynylbenzene

Entry	Year	Catalyst	Base	Solvent	Atmosphere	Temp. /°C	Time /h	Yield /%	TON	TOF /h <sup>-1</sup>	Ref.
1	2009	Cu(0)NPs (400 mol%)	Na <sub>2</sub> CO <sub>3</sub>	THF	N <sub>2</sub>	60	6	90	0.2	0.04	71
2	2011	CuNPs/TiO <sub>2</sub> (1 mol%)	C <sub>4</sub> H <sub>9</sub> NO	THF	Air	65	6	95	95	16	72
3	2010	Cu-MINT (6 mol%)	DABCO	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CH <sub>3</sub>	Air	160	0.5	68	11	23	73

## 5 结语与展望

端基炔偶联反应的研究已有一百多年的历史,研究者们一直致力于寻求高效、廉价的绿色催化剂.以CuI为助剂的Pd催化体系因其昂贵的成本及钯流失逐渐被Cu(I)、Cu(II)、CuNPs催化体系所取代.Cu(I)催化剂不稳定,铜的固定困难,反应条件苛刻.CuNPs制备过程中铜的利用率低,反应温度较高,铜的有效价态及反应机理尚未确定.相比较而言,Cu(II)催化体系更为绿色、高效,尤其Cu(OAc)<sub>2</sub>催化体系可以实现无碱条件下的反应.碱在端基炔反应中起着关键性的作用,可加快端基炔去质子化,提高反应速率,所以不加碱时,体系中溶剂和催化剂的碱性至关重要.多相催化剂的优势在于较高的回收使用率,特别是负载型Cu(II)多

相催化剂,金属负载量较低,反应条件温和,拥有较高的TOF,倍受研究者的关注,将成为今后端基炔偶联催化剂的发展趋势.此外,不同种类的端基炔的交叉偶联反应,将是未来研究的侧重点.随着光催化的日益发展,加之铜催化剂的光催化性能,我们推测该反应的驱动源可能由光来取代热,该领域是研究者面临的又一项重大的挑战.

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