溶胶凝胶法制备的 Cu/SiO₂ 催化剂及其催化草酸二甲酯加氢反应

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摘要: 采用溶胶凝胶法制备了用于草酸二甲酯加氢合成乙二醇的 Cu/SiO₂ 催化剂, 在优化的反应条件下, 当催化剂中 Cu 含量为 15%~25% 时, 草酸二甲酯转化率和乙二醇选择性分别达到 99.9% 和 95.0%。通过 N₂ 吸附-脱附、透射电镜、X 射线衍射、氢气程序升温还原、N₂O 滴定法和 X 射线光电子能谱等手段对各 Cu/SiO₂ 催化剂进行了表征。结果表明, 在相同反应条件下, 随着 Cu 含量增加, 硅胶对活性物种的包裹作用和 Cu 物种间的团聚作用对催化剂活性影响较大, 当 Cu 含量 ≤ 10% 时, 硅胶对 Cu 物种的包裹作用强烈, 是影响催化剂活性的主要因素; 当 Cu 含量 > 10% 时, 催化剂表面 Cu 物种间的团聚作用变得突出, 成为影响催化剂活性的主要因素, 二者的消长对催化剂表面结构、活性物种的形态和化学环境的影响很大, 并最终影响催化剂的性能。

关键词: 溶胶凝胶法; 草酸二甲酯; 加氢; 铜; 二氧化硅; 乙二醇; 包裹作用; 团聚作用

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Cu/SiO₂ Catalysts Prepared by the Sol-Gel Method for Hydrogenation of Dimethyl Oxalate to Ethylene Glycol

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Abstract: A series of Cu/SiO₂ catalysts for the hydrogenation of dimethyl oxalate to ethylene glycol were prepared by the sol-gel method. Under optimized hydrogenation conditions, dimethyl oxalate conversion and ethylene glycol selectivity were found to reach 99.9% and 95.0%, respectively, upon varying the copper loading between 15% and 25%. The prepared catalysts were characterized by N₂-physisorption, transmission electron microscopy, X-ray diffraction, H₂-temperature-programmed reduction, N₂O titration, and X-ray photoelectron spectroscopy. The results show that when the copper loading was increased under the same experimental conditions the factors that mostly affect the activities of the catalysts prepared by the sol-gel method are encapsulation and agglomeration. The encapsulation of silica is strong and it becomes the major factor when $w(\text{Cu}) \leq 10\%$ while agglomeration among the copper species on the catalyst surface becomes more serious and is a major factor when $w(\text{Cu}) > 10\%$. These two factors influence the surface structure, the morphology of the copper species, and the chemicals surroundings the catalysts and as a result the performance of the catalysts is affected too.

Key words: sol-gel method; dimethyl oxalate; hydrogenation; copper; silica; ethylene glycol; encapsulation; agglomeration

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乙二醇 (EG) 是一种重要的有机化工原料, 目前工业上主要以乙烯为原料的石油路线来制得. 随着石油资源的日益减少, 开发利用我国丰富的煤炭和天然气资源具有重要的战略和经济意义. 现有的煤经合成气制乙二醇的工艺路线可分为直接法和间接法. 直接法需高温高压和贵金属催化剂, 离工业化生产尚远; 间接法是先由 CO 氧化偶联制得草酸二酯, 草酸二酯再经催化加氢制得乙二醇^[1~4], 该方法反应条件温和, 具有大规模工业应用的前景. 中国科学院福建物质结构研究所经过 20 多年的研究, 开发出有自主知识产权的“煤制乙二醇”系列核心催化剂及其全套工艺技术. 万吨级工业“煤制乙二醇”技术于 2009 年 3 月通过了由中科院组织的鉴定, 20 万吨级“煤制乙二醇”工业示范装置也在内蒙古通辽建成.

亚铬酸铜催化剂具有高效催化草酸二酯加氢合成乙二醇的性能, 但在制备过程中产生含铬的废液废渣, 对环境造成危害, 从而限制了它的应用. 因此, 急需研究环境友好、高效的酯加氢催化剂. Cu/SiO₂ 催化剂在草酸二酯加氢中表现出较高的催化性能^[5~7], 目前主要采用硅胶浸渍法、沉淀沉积法、离子交换法以及硅酸酯溶胶凝胶法制备^[5~10]. 其中硅酸酯溶胶凝胶法使 Cu 物种有效地与离子氧化物网络结合在一起, 从而具有很高的稳定性和很高的金属分散度, Cu 含量可达到 10%, 但活性物种易被离子氧化物网络所包裹, 从而导致催化剂性能降低^[11~14].

目前, 基于硅酸酯溶胶凝胶法制备的 Cu/SiO₂ 催化剂中 Cu 含量一般不超过 10%, 且在草酸二酯加氢反应中的催化性能鲜见报道. 因此, 本文采用溶胶凝胶法制备一系列不同 Cu 含量的 Cu/SiO₂ 催化剂, 并用于草酸二甲酯的催化加氢反应中, 系统地表征了催化剂的物化性质, 探讨了 Cu 含量对催化剂活性影响的内在因素.

1 实验部分

1.1 催化剂的制备

将硝酸铜 (AR, 上海国药公司) 溶解在一定量的蒸馏水中, 再加入正硅酸四乙酯 (TEOS, AR, 上海国药公司) 和乙醇 (AR, 上海国药公司) 搅拌, 并置于 50 °C 的水浴中反应 6 h 形成溶胶凝胶^[11,15]. 将所得

凝胶老化、烘干和焙烧还原即得 Cu/SiO₂ 催化剂. 投料中的铜含量分别为 5%, 10%, 15%, 20%, 25%, 30%, 和 40%, 由 $w(\text{Cu}) = w_{\text{Cu}} / (w_{\text{Cu}} + w_{\text{SiO}_2})$ 式算得. 其中, w_{Cu} 为实际投入的硝酸铜折算成金属铜的质量, w_{SiO_2} 为实际投入的正硅酸四乙酯折算成 SiO₂ 的质量.

1.2 催化剂的表征

样品比表面积用 Micromeritics Tristar 3020 型吸附仪测定, 样品在 150 °C 时抽空预处理 2 h, 以氮气为吸附质, 在液氮温度下进行吸附, 比表面积采用 BET 方法得到, 介孔的孔体积和孔径分布利用 BJH 方法计算, 微孔孔体积根据 t -plot 方法计算.

透射电镜 (TEM) 照片由日本 JEM-2010 型透射电镜摄取, 配有 Gatan-794MSC CCD 相机系统、Gatan-676TV 系统以及 OXFORD-INCA 超薄窗口能谱系统.

X 射线粉末衍射 (XRD) 在 Rigaku Rotaflex D/Max-C 型转靶 X 射线粉末衍射仪上进行, Cu 靶, 工作电流 30 mA, 工作电压 40 kV, 石墨单色器, 测角仪采用连续扫描方式, 扫描速度 3°/min, 扫描范围 $2\theta = 10^\circ \sim 80^\circ$.

程序升温还原 (H₂-TPR) 实验在 Micromeritics AutoChemII 2920 型化学吸附仪 (接英格海德质谱仪 QIC 20) 上进行, 催化剂用量 50 mg (20~40 目). 实验前催化剂先于 100 °C 用 5% H₂-95% Ar 混合气处理 60 min, 待样品温度降至室温且基线平稳后, 以 10 °C/min 进行程序升温, TCD 记录耗氢量.

X 射线光电子能谱 (XPS) 和 X 射线引起的俄歇电子能谱 (XAES) 在 VG MultiLab 2000 谱仪上进行, Mg K α 辐射源, 以表面污染碳的 C 1s 结合能 (284.6 eV) 为内标校正其它元素的结合能.

N₂O 滴定法测定金属 Cu 表面积实验装置同 TPR, 在 350 °C 用 H₂ 还原催化剂 2 h, 降温到 60 °C 后, 通 0.5 h 的 N₂O 将催化剂上的 Cu⁰ 氧化成 Cu⁺, 再在 300 °C 下采用 H₂ 脉冲技术还原 Cu⁺, 通过测定耗氢量算得活性 Cu 的数量. 计算时假设两个表面 Cu 原子消耗一分子 N₂O, Cu 表面原子密度为 $1.46 \times 10^{19} / \text{m}^2$.

催化剂中实际 Cu 含量由等离子体发射光谱法 (ICP) 测定, 仪器为 Jobin Yvon 公司 Ultima2 型等离子发射光谱仪.

1.3 催化剂的评价

草酸二甲酯加氢反应在连续流动气固相不锈钢反应器(内径 14 mm, 长 490 mm)中进行. 催化剂(20~40 目)用量 5.6 g, 催化剂床层高度约为 70 mm, 上下装填瓷环. 催化剂先在 1.0 MPa 下用 500 ml/min H₂, 以 1 °C/min 从室温升至 250 °C, 保持 5 h, 然后降温到 220 °C, 再将 H₂ 压力升至 2.0 MPa, 进行反应, 5 h 后记录活性数据. 草酸二甲酯溶于甲醇配制成浓度为 0.2 g/ml 的溶液, 由高压计量泵计量并打入汽化器, 草酸二甲酯液时空速(LHSV)为 0.2~0.5 h⁻¹, 氢酯比为 50~80 (mol/mol).

2 结果与讨论

2.1 催化剂的织构和物相

不同 Cu 含量的 Cu/SiO₂ 样品的织构性质见表 1. 可以看出, 随着铜含量的增加, 催化剂比表面积开始有所上升, 至 10% 时, 逐渐下降; 当 Cu 含量为 25%~30% 时, 催化剂比表面积降至 400 m²/g 左右, 至 40% 时, 降至 273 m²/g. 还可以看出, 随着铜含量的增加, 催化剂的孔体积和孔径先增加, 至 15% 和 25% 时, 样品的孔体积和平均孔径分别达到最大, 为 0.43 cm³/g 和 4.14 nm, 继续增加 Cu 含量, 二者有所下降, 当 Cu 含量为 40% 时, 二者均有所增加.

表 1 不同 Cu 含量的 Cu/SiO₂ 催化剂的物化性质

Table 1 Physical and chemical properties of Cu/SiO₂ catalysts with different Cu contents

Sample	w(Cu) ^b / (wt%)	A _{BET} / (m ² /g)	V _{Por} / (cm ³ /g)	D _{Por} / nm	d _{CuO} ^c / nm	d _{Cu} ^c / nm	A _{Cu} ^d / (m ² /g)
SiO ₂ ^a	—	582	1.13	7.74	—	—	—
5%Cu/SiO ₂	4.3	382	0.20	2.08	—	—	5.5
10%Cu/SiO ₂	6.1	497	0.28	2.24	—	14.0	9.1
15%Cu/SiO ₂	10.0	462	0.43	3.70	22.4	21.7	14.7
20%Cu/SiO ₂	13.4	423	0.42	4.00	25.6	29.8	17.6
25%Cu/SiO ₂	14.2	402	0.42	4.14	31.6	40.3	16.2
30%Cu/SiO ₂	16.3	401	0.38	3.74	24.7	27.7	13.8
40%Cu/SiO ₂	33.3	273	0.51	7.50	32.0	43.7	13.3

^aPrepared by the sol-gel method.

^bDetermined by ICP-AES.

^cCalculated from the XRD data based on the Scherrer equation.

^dCu metal surface area determined by the N₂O titration method.

ICP 测试表明, 除样品 5%Cu/SiO₂ 和 40%Cu/SiO₂ 外, 其他样品中的 Cu 含量远小于理论值, 这表明实际制得的催化剂中可能仍含有一定量的羟基.

研究表明^[16~18], 溶胶凝胶法制备的 Cu/SiO₂ 催

化剂中, Cu 含量低于 10% 时, 铜物种以 Cu²⁺离子的形式高度分散于硅胶网络中, 焙烧后催化剂颜色是绿色, 不存在大的 CuO 晶粒; Cu 含量高于 10% 时, 焙烧后催化剂的颜色由绿到黑绿相间, 再变为黑色, 这可能是 Cu 含量的增加使得载体表面的 CuO 物种浓度增加所致.

图 1 为还原前后各 Cu/SiO₂ 催化剂的 XRD 谱. 可以看出, 各样品均在 2θ = 22.0° 处出现弥散的 SiO₂ 包峰. 当 Cu 含量 ≤ 10% 时, 还原前的 Cu/SiO₂ 催化剂, 未出现明显的 CuO 衍射峰, 还原后的样品仅在 2θ = 43.3° 处出现非常微弱的 Cu⁰ 衍射峰. 对于 10% < Cu 含量 < 30% 的催化剂, 还原前的样品出现明显的 CuO 衍射峰, 且随着铜含量的增加而增强. 相应地, 还原后的样品中 Cu⁰ 衍射峰随着 Cu 含量的增加而增强; 另外在 2θ = 36.5° 处还观察到较弱的宽化的 Cu₂O 衍射峰出现, 且随着 Cu 含量

图 1 还原前后各 Cu/SiO₂ 催化剂的 XRD 谱

Fig. 1. XRD patterns of Cu/SiO₂ catalysts with different Cu contents before (a) and after (b) reduction. (1) 5%Cu/SiO₂; (2) 10%Cu/SiO₂; (3) 15%Cu/SiO₂; (4) 20%Cu/SiO₂; (5) 25%Cu/SiO₂; (6) 30%Cu/SiO₂; (7) 40%Cu/SiO₂.

的增加而增强, 这说明还原后的样品中 Cu 物种有 Cu^0 和 Cu^+ . 由表 1 可见, 随着 Cu 含量的增加, 样品中 CuO 及 Cu^0 的平均粒径增加, 且 Cu^0 平均粒径大于 CuO , 说明在还原过程中 Cu 物种仍有一定程度的团聚. 当 Cu 含量 $\geq 30\%$ 时, 特别是 Cu 含量达到 40% 时, CuO 及 Cu^0 的衍射峰最强, 估算得 CuO 及 Cu^0 的晶粒尺寸均达最大, 分别为 32.0 和 43.7 nm, 可见 Cu 物种间的团聚非常严重. 有趣的是, $30\%\text{Cu}/\text{SiO}_2$ 样品的平均粒径明显小于样品 $20\%\text{Cu}/\text{SiO}_2$ 和 $25\%\text{Cu}/\text{SiO}_2$. $40\%\text{Cu}/\text{SiO}_2$ 样品中实际 Cu 含量与理论值接近, 其孔径也与纯 SiO_2 相当. 这可能是 Cu 含量过高时破坏了硅胶骨架, 造成 Cu 物种与硅胶分离.

综上所述, 当 Cu 含量 $\leq 10\%$ 时, Cu 物种高度分散在载体表面或 CuO 晶粒非常小; 随着 Cu 含量增加, 催化剂表面 CuO 晶粒不断增大, 出现明显的晶相 Cu 衍射峰.

2.2 催化剂的形貌

图 2 是未还原的各 Cu/SiO_2 催化剂的 TEM 照片. 由图可以看出, 当 Cu 含量 $\leq 10\%$ 时, 载体表面的 Cu 物种呈矩阵分布的, 且分散均匀, 其粒径小于 3 nm. 其中, 样品 $5\%\text{Cu}/\text{SiO}_2$ 在放大倍数低的 TEM 照片中未观察到明显的 Cu 物种, 而 $10\%\text{Cu}/\text{SiO}_2$ 样品中的 Cu 物种嵌于硅胶中, 可见 Cu 物种间的团聚并不明显, 而硅胶对 Cu 物种有强烈的包裹.

由 XRD 结果可知, 当 Cu 含量 $>10\%$ 时, 样品出现明显的 CuO 衍射峰, 且随着 Cu 含量增加而增强, 相应的 TEM 图片中难以观察到清晰的 CuO 晶粒, 但可以看到明显的晶格条纹, 如样品 $20\%\text{Cu}/\text{SiO}_2$ 团聚后的晶粒粒径在 $5\sim 20$ nm, 而 $30\%\text{Cu}/\text{SiO}_2$ 和 $40\%\text{Cu}/\text{SiO}_2$ 样品中团聚的 CuO 晶粒超过 20 nm, 可见样品中 CuO 晶粒团聚严重. 由样品的低分辨 TEM 照片可见, 随着 Cu 含量的增加, Cu 物种团聚成不同大小的晶粒, 而且随着 Cu 含量的增加, 相互

图 2 还原前不同 Cu 含量的 Cu/SiO_2 催化剂的 TEM 照片

Fig. 2. TEM images of Cu/SiO_2 catalysts before reduction with different Cu contents. (a) $5\%\text{Cu}/\text{SiO}_2$; (b) $10\%\text{Cu}/\text{SiO}_2$; (c) $15\%\text{Cu}/\text{SiO}_2$; (d) $20\%\text{Cu}/\text{SiO}_2$; (e) $30\%\text{Cu}/\text{SiO}_2$; (f) $40\%\text{Cu}/\text{SiO}_2$.

间的团聚现象越来越明显. 当 Cu 含量 >25% 时, 出现单晶 CuO, 其粒径超过 100 nm, 而且这些单晶 CuO 开始从硅胶中脱落, 其比负载的 CuO 更难被还原.

还可以看出, 虽然 XRD 估算得 30%Cu/SiO₂ 样品的平均粒径小于样品 20%Cu/SiO₂ 和 25%Cu/SiO₂, 但其 Cu 物种间的团聚作用更明显, 且有一定数量单晶 CuO 生成, 这可能会影响它的活性. Lambert 等^[19]认为, 2~3 nm 的 Cu 物种没有反应活性, 而大于 8 nm 的 Cu 物种是 2-丁醇脱氢反应的活性物种.

2.3 H₂-TPR 结果

还原温度的不同可归因于 Cu 物种尺寸、Cu 物种之间及其与载体间的相互作用强度, 以及 Cu 物种的分散度等差异所致. Chen 等^[20]报道, 若还原峰低于 200 °C, 说明存在 [Cu-O-Cu]²⁺, 若存在 260 °C 以上的还原峰, 说明存在晶相 CuO. Carniti 等^[21]采用化学吸附水解法制备了 Cu/SiO₂ 催化剂, 研究发现, 当 Cu 含量 <8% 时, Cu 物种高度分散. Dow 等^[22]研究了 Cu/γ-Al₂O₃ 催化剂, 认为高分散的 Cu 物种是与载体相互作用强的 Cu²⁺物种、与载体作用弱且相互靠近的孤立的 Cu²⁺物种以及小的二维和三维 Cu 簇. Wang 等^[11]认为, 溶胶凝胶法制备的 Cu/SiO₂ 催化剂存在两个还原峰, 分别对应于高分散的 Cu 物种和小晶粒 CuO; 而浸渍法制备的 Cu/SiO₂ 催化剂有三个还原峰, 其中高温还原峰对应的是大的 CuO 晶粒, 且难还原. Yin 等^[23]认为, 在强酸性条件下, Cu²⁺与载体作用较弱, 易形成大的 Cu 物种. Kundakovc 等^[24]认为, Cu 含量低时, 存在与载体间作用很强的高分散的 Cu 物种; 鲁继青等^[18]认为, Cu 含量为 5% 时, 由于形成了难还原的 Si-O-Cu 物种, 使其还原峰出现在 320 和 400 °C.

综上并结合图 3 可以认为, 当 Cu 含量 ≤ 15% 时, 催化剂前驱体中的 Cu 物种呈高分散; 当 Cu 含量 >15% 时, 催化剂前驱体中除了高分散的 Cu 物种外还出现小晶粒的 CuO; 当 Cu 含量 >30% 时, 样品中还存在难还原的大晶粒 CuO.

由图 3 可以看出, 当 Cu 含量为 5% 时, 样品还原峰出现在 225 °C, 这可归属于与载体作用弱且相互靠近的孤立的 Cu(II) 物种以及小的二维和三维 Cu 簇; 同时还在 320~500 °C 出现明显的尾峰, 表明

图 3 不同铜含量的 Cu/SiO₂ 催化剂的 H₂-TPR 谱

Fig. 3. H₂-TPR profiles of Cu/SiO₂ catalysts with different Cu contents. (1) 5%Cu/SiO₂; (2) 10%Cu/SiO₂; (3) 15%Cu/SiO₂; (4) 20%Cu/SiO₂; (5) 25%Cu/SiO₂; (6) 30%Cu/SiO₂; (7) 40%Cu/SiO₂.

硅胶与 Cu 物种之间存在强的相互作用, 即硅胶对 Cu 物种强烈包裹.

当 Cu 含量 = 10% 时, 样品低温还原峰在 214 °C 附近有肩峰, 可归属于一种与载体作用较弱、易于被还原的小晶粒 CuO^[25]. 这也反映出此时 Cu 物种有所团聚, 从而产生一种与载体作用较弱的 CuO.

Chary 等^[26]认为, 随着 Cu 含量的增加, 还原峰出现宽化及峰顶温度偏向高温是由于催化剂表面 CuO 晶粒增多所致. 由图 3 可见, 随着 Cu 含量增加, 低温还原峰峰温明显向高温方向移动, 特别是 Cu 含量为 15% 时, 样品还原峰峰温明显高于 Cu 含量为 20% 的样品. 当 Cu 含量 >15% 时, 高分散的 Cu 物种团聚成较多小晶粒的 CuO, 且随着 Cu 含量的增加还出现晶比较大、甚至是难还原的块状 CuO. 由此可见, 当 Cu 含量 >10% 时, 催化剂表面的 CuO 晶粒间开始发生明显的团聚并不断增强. Zhang 等^[27]发现, 随着 Cu 含量的增加, 孤立的 Cu 离子会发生部分簇合. 硝酸铜易水解显酸性, 随着 Cu 含量的增加, 制备液的 pH 值不断减小, 这也可能促进 Cu 物种团聚成大的难还原的晶相 CuO.

2.4 催化剂表面的化学环境

图 4 为还原后各 Cu/SiO₂ 催化剂的 XPS 谱. 可以看出, Cu 2p_{3/2} 结合能在 934.9~932.6 eV 左右, 且未见 Cu²⁺在 942~944 eV 特征 2p→3d 卫星峰, 表明还原后催化剂中的 Cu 物种主要以 Cu⁰/Cu⁺的形式

图4 还原后不同 Cu 含量的 Cu/SiO₂ 催化剂的 XPS 谱

Fig. 4. XPS spectra of Cu/SiO₂ catalysts with different Cu contents after reduction. (1) 5%Cu/SiO₂; (2) 10%Cu/SiO₂; (3) 15%Cu/SiO₂; (4) 20%Cu/SiO₂; (5) 25%Cu/SiO₂; (6) 30%Cu/SiO₂; (7) 40%Cu/SiO₂.

存在^[28,29]. 由于 Cu⁰ 和 Cu⁺ 的结合能相近, 因此需要用修正的俄歇参数 (α') 来确定, 通常 Cu⁰ 和 Cu⁺ 对应的 α' 值为 1851.0 和 1849.0 eV^[28]. 图 5 为各 Cu/SiO₂ 催化剂的 XAES, 其分峰得到的结果列于表 2. 可以看到, 还原后催化剂中 Cu 物种以 Cu⁰ 和 Cu⁺ 的形式存在, 其 α' 分别为 1851.0 eV 和 1848.0 eV. Cu⁺ 的 α' 值小于体相表明它与载体之间存在强相互作用. 研究发现^[30], 当 Cu 物种高度分散于载体中或

图5 还原后不同 Cu 含量的 Cu/SiO₂ 催化剂的 XAES 谱

Fig. 5. XAES spectra of Cu/SiO₂ catalysts with different Cu contents after reduction. (1) 5%Cu/SiO₂; (2) 10%Cu/SiO₂; (3) 15%Cu/SiO₂; (4) 20%Cu/SiO₂; (5) 25%Cu/SiO₂; (6) 30%Cu/SiO₂; (7) 40%Cu/SiO₂.

表2 各 Cu/SiO₂ 催化剂还原后 Cu 物种的 LMM XAES 结果

Table 2 Cu species on the reduced Cu/SiO₂ catalysts derived from Cu LMM XAES spectra

Sample	KE (eV)		α' (eV)		$X_{\text{Cu}^+}^{\text{a}}/\%$	$X_{\text{Cu}^0}^{\text{a}}/\%$
	Cu ⁺	Cu ⁰	Cu ⁺	Cu ⁰		
5%Cu/SiO ₂	915.3	918.3	1848.0	1850.9	44.8	55.2
10%Cu/SiO ₂	915.1	918.3	1847.6	1850.8	40.4	59.6
15%Cu/SiO ₂	916.0	918.8	1848.6	1851.4	39.7	60.3
20%Cu/SiO ₂	915.6	918.8	1848.3	1851.5	34.6	65.4
25%Cu/SiO ₂	916.1	918.9	1848.6	1851.5	41.7	58.3
30%Cu/SiO ₂	915.4	918.7	1848.1	1851.3	41.3	58.7
40%Cu/SiO ₂	915.7	919.0	1848.3	1851.6	43.2	56.8

^aIntensity ratio of Cu⁺(or Cu⁰)/(Cu⁺+Cu⁰) by deconvolution of Cu LMM XAES spectra.

与载体发生强烈相互作用时, 其 α' 值可比体相低 2~3 eV.

由图 5 和表 2 可见, Cu⁺/(Cu⁺+Cu⁰) 的比值随着 Cu 含量增加而呈倒火山形, 且 Cu 含量为 5% 和 20% 时, 分别有最大值和最小值. 研究发现^[31,32], 350 °C 时 CuO/SiO₂ 催化剂中与载体作用弱的 CuO 易还原为 Cu⁰, Chen 等^[8]认为, Cu⁺ 比例高意味着 Cu²⁺ 还原受到抑制. 由此可见, Cu 含量低时 Cu⁺/(Cu⁺+Cu⁰) 比值高, 表明了硅胶与 Cu 物种之间存在强烈的相互作用, 因而难还原到 Cu⁰, 而随着 Cu 含量增加, 硅胶对 Cu 物种的包裹作用逐渐减弱; 当 Cu 含量 > 20% 时, Cu⁺/(Cu⁺+Cu⁰) 值又有所增加, 可能是产生了大的甚至块状难还原的单晶 CuO, 表明 Cu 含量高时因 Cu 物种的团聚而使 Cu 物种也难以还原到 Cu⁰.

表面 Cu 的比表面积与表面 Cu 数量有直接关系, 图 6 为各 Cu/SiO₂ 催化剂中金属 Cu 比表面积和分散度. 可以看出, 随着 Cu 含量的增加, 表面 Cu 的比表面积呈火山型变化, 且当 Cu 含量 < 15% 时, 样品表面 Cu 的比表面积远小于其它样品, 表明随着 Cu 含量的增加, 未被硅胶包裹的 Cu 物种数量也增加, 即硅胶对 Cu 物种的包裹没有增强, 反而有减弱的趋势. 当 Cu 含量 > 20% 时, 样品表面 Cu 的比表面积下降是由于 Cu 物种的团聚所致. Yin 等^[33]认为负载在大孔径和高比表面积的六角介孔硅载体 (HMS) 上的 Cu 物种可获得较大的 Cu 表面积, 这有助于提高催化剂的活性.

还可以看到, 催化剂表面 Cu 的分散度随 Cu 含量的增加而有所下降但很缓慢, 但当 Cu 含量 > 20%

图 6 各 Cu/SiO₂ 催化剂中金属 Cu 比表面积和分散度

Fig. 6. Cu metal surface area and Cu dispersion of the Cu/SiO₂ catalysts.

后, 催化剂的 Cu 分散度急剧下降, 表明 Cu 含量的增加使得 Cu 物种的团聚作用不断增强, 至大于 20% 时团聚作用特别严重. 由此可见, Cu 含量在一定范围内增加对活性物种分散度的影响较小, 但却能够削弱硅胶对其的包裹.

2.5 Cu/SiO₂ 催化剂上草酸二甲酯加氢反应的活性

图 7 为各 Cu/SiO₂ 催化剂上草酸二甲酯加氢反应性能. 由图可见, 当催化剂中 Cu 含量 < 15% 时, DMO 转化率、EG 选择性和时空收率都较低, 当 Cu 含量为 15% 时, DMO 转化率达到 99.9%, EG 选择性也达到 95.0%, 时空收率接近 100 g/(L·h), 至 Cu

图 7 不同 Cu 含量 Cu/SiO₂ 催化剂上草酸二甲酯加氢反应性能

Fig. 7. Activities of Cu/SiO₂ catalysts with different Cu contents for DMO hydrogenation reaction. (1) Space-time yield of EG; (2) DMO conversion; (3) EG selectivity. Reaction conditions: 220 °C, 2.0 MPa, H₂/DMO = 80 (mol/mol), LHSV = 0.2 h⁻¹. DMO: dimethyl oxalate; EG: ethylene glycol.

表 3 各 Cu/SiO₂ 催化剂上草酸二甲酯加氢反应的 TOF 值

Table 3 TOF value of Cu/SiO₂ catalysts with different Cu contents for dimethyl oxalate hydrogenation reaction

Sample	TOF _{DMO} ^a (h ⁻¹)	TOF _{EG} ^a (h ⁻¹)
5%Cu/SiO ₂	1.0	0.3
10%Cu/SiO ₂	8.3	3.2
15%Cu/SiO ₂	8.6	8.2
20%Cu/SiO ₂	7.1	6.8
25%Cu/SiO ₂	7.8	7.5
30%Cu/SiO ₂	8.1	3.9
40%Cu/SiO ₂	3.8	0.9

^aCalculated as moles of ester reacted (or EG product) in the initial 1 h per mole of surface copper calculated from the copper dispersion.

含量为 25% 时, 催化剂活性仍有所增加, 但增幅较小. 当 Cu 含量 > 25% 时, 催化剂活性明显下降. 总体而言, 当 Cu 含量为 20% 时较适宜.

由表 3 各 Cu/SiO₂ 催化剂上草酸二甲酯加氢反应的 TOF 值可见, Cu 含量在 15%~25% 时, TOF 值较为接近, Cu 含量为 5% 和 40% 时, 样品 TOF 值特别小.

有关 Cu⁰, Cu⁺ 及 Cu²⁺ 在催化加氢反应中的作用仍没有定论, 但相关文献也进行了一定程度的研究探讨^[8,34~37]. 李振花等^[36]认为, Cu/SiO₂ 中 Cu⁰ 和 Cu⁺ 相对存在, Cu⁺ 决定 DMO 的转化率, Cu⁰ 决定 EG 的选择性; Chen 等^[8]发现, 在 DMO 加氢过程中, Cu⁰ 与 Cu⁺ 的协同作用决定了催化剂的活性. Yin 等^[38]认为高的金属分散度和合适的 Cu⁰/Cu⁺ 均有助于提高催化剂活性. 图 8 为各 Cu/SiO₂ 催化剂上 EG

图 8 各 Cu/SiO₂ 催化剂上 EG 时空收率与 Cu⁰/(Cu⁺+Cu⁰) 的关系

Fig. 8. EG space-time yield and the Cu⁰/(Cu⁺+Cu⁰) ratio as a function Cu contents. Reaction conditions: 220 °C, 2.0 MPa, H₂/DMO = 50 (mol/mol), LHSV = 0.5 h⁻¹.

时空收率与 $\text{Cu}^0/(\text{Cu}^++\text{Cu}^0)$ 的关系. 可以看出, 在较低氢酯比和较高空速下, 催化剂活性和 $\text{Cu}^+/(\text{Cu}^++\text{Cu}^0)$ 比随着 Cu 含量的增加均呈现非常明显的火山型关系, 表明催化剂活性与 Cu^0 和 Cu^+ 相对含量有关, 即 Cu^0 和 Cu^+ 的协同作用也会影响催化剂活性.

由此可见, 样品 20%CuSiO₂ 表现出最佳活性, 是由于硅胶对活性物种的包裹与 Cu 物种间的团聚相互作用改变了催化剂的表面结构, 使得单位质量催化剂表面有较多粒径较小 (约 5~20 nm) 的 CuO 晶粒, 表面 Cu 的比表面积达最大值, 同时这两种相互作用也使 Cu^0/Cu^+ 比达最佳.

3 结论

在溶胶凝胶法制备的催化剂中, 硅胶对活性物种的包裹与 Cu 物种间的团聚相互作用是影响催化剂活性内在因素, 通过调控催化剂中的 Cu 含量, 可以在一定程度上抑制硅胶对活性物种的包裹和 Cu 物种间的团聚, 从而产生较多粒径较小 (约 5~20 nm) 的易被还原的 CuO 晶粒. 本工作和以往工作一个不同之处就是制备了铜含量 >10% 的具较高酯加氢活性的 Cu/SiO₂ 催化剂, 不足之处就是提高铜含量的同时产生较严重的铜物种间的团聚, 导致 Cu 物种分散度下降. 今后将采取适当措施 (如添加一定助剂), 在削弱硅胶对活性物种包裹作用的同时注意减少铜物种间的团聚, 进一步提高表面铜面积, 同时使 Cu^0/Cu^+ 达到最佳比例.

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英 译 文

English Text

As an important chemical material, ethylene glycol (EG) is currently prepared by ethylene oxidation. However, as crude oil resources gradually decrease the development and use of abundant coal and natural gas resources is strategically and economically significant in China. Currently, the synthesis of EG from syngas can be divided into a direct and an indirect synthesis process. The indirect synthesis process requires noble metal catalysts, high reaction temperatures and pressures, and it is far from being industrialized. The direct synthesis process includes the coupling of CO with nitrite esters to form diethyl oxalate followed by the hydrogenation of diethyl oxalate. Interesting work has been done on oxalate hydrogenation [1–4]. Because of the moderate reaction conditions large-scale industrial application is promising. The Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences (CAS) has developed a series of core catalysts for a “coal to ethylene glycol” process and their technology includes independent intellectual property rights obtained from over 20 years of research. The “coal to ethylene glycol” technology with a production capacity of 1 million tons of EG a year passed an appraisal by CAS in March 2009. An industrial demonstration unit with a production capacity of 20 million tons EG in a year has been built in Tongliao, Inner Mongolia, China.

Copper chromite catalysts are highly active catalysts for the synthesis of EG from syngas but the toxicity of Cr severely limits its practical application. Therefore, the research and development of environment friendly and efficient ester hydrogenation catalysts is urgent. Cu/SiO₂ catalysts have shown good activities toward the hydrogenation of dimethyl and diethyl oxalate [5–7], and these have been prepared by methods such as aqueous impregnation, deposition precipitation, ion exchange, and the silicate ester sol-gel method [5–10]. The sol-gel technique offers advantages such as the effective incorporation of the Cu species into the ionic oxide network, and this leads to the formation of a catalyst with a Cu loading of up to 10%. The prepared catalysts exhibit high stability and metal dispersion. However, lower activities are usually observed because of encapsulation in some sol-gel catalysts [11–14].

Based on previous work, the copper loading of the catalysts prepared by the sol-gel technique was found to be less than 10% and reports about the application of these catalysts

to the hydrogenation reaction of dimethyl or diethyl oxalate are rare. Therefore, we prepared a series of catalysts with different copper loadings by the sol-gel technique and used them for the catalytic hydrogenation reaction of dimethyl oxalate. The physical and chemical properties of the Cu/SiO₂ catalysts with the different copper loadings were systematically characterized and we discuss the factors that influence the catalytic activity.

1 Experimental

1.1 Catalyst preparation

Cupric nitrate trihydrate (AR, Shanghai Country Medicine Group) was dissolved in deionized water and then tetraethylorthosilicate (TEOS, AR, Shanghai Country Medicine Group) as well as ethanol (AR, Shanghai Country Medicine Group) were added under stirring. The solution was placed in a 50 °C water bath for 6 h to generate a gel followed by aging, drying, calcination, and reduction to produce the Cu/SiO₂ catalysts. The copper content of the catalysts were 5%, 10%, 15%, 20%, 25%, 30%, and 40%, respectively. The copper loading of the catalysts was calculated using the following equation: $w(\text{Cu}) = w_{\text{Cu}} / (w_{\text{Cu}} + w_{\text{SiO}_2})$, where w_{Cu} is the weight of metallic copper calculated from the amount of cupric nitrate trihydrate actually used; w_{SiO_2} is the weight of SiO₂ calculated from the amount of TEOS actually used.

1.2 Catalyst characterization

The specific surface area and pore volume of the catalysts were determined by nitrogen adsorption using a Micromeritics Tristar 3020. The samples were pretreated at 150 °C for 2 h in vacuum. The specific surface area was obtained based on the BET method. The pore volume of the mesoporous material and its pore size distribution were calculated by the BJH method while the micropore volume was determined by the t -plot method.

Transmission electron microscopy (TEM) images were obtained using a Japan JEM-2010 transmission electron microscope equipped with a Gatan-794MSC CCD camera system, a Gatan-676TV system, and an OXFORD-INCA ultra-thin window EDS system.

X-ray diffraction (XRD) patterns were collected on a Rigaku Rotaflex D/Max-C X-ray diffractometer using Cu K_{α} radiation and the tube voltage was 40 kV while the current was 30 mA. The XRD data were collected between $2\theta = 10^{\circ}$ – 80° at a scan speed of $3^{\circ}/\text{min}$.

H₂-temperature-programmed reduction (H₂-TPR) was carried out using a Micromeritics AutoChemII 2920 (with a Hidden mass spectrometer QIC 20) with 50 mg of a calcined Cu/SiO₂ sample that had been outgassed at 100 °C under 5%

H₂-95% Ar for 60 min. After cooling to room temperature under 5% H₂-95% Ar the sample was heated to 700 °C at a ramping rate of 10 °C/min.

X-ray photoelectron spectroscopy (XPS) and X-ray induced Auger electron spectroscopy (XAES) were obtained using a VG MultiLab 2000 analyzer with a Mg K_α radiation source and the binding energies were referenced to C 1s (284.6 eV).

The metallic Cu surface area was measured using a Micromeritics AutoChemII 2920 and the catalyst was reduced with H₂ at 350 °C over 2 h. Surface oxidation was performed by bringing nitrous oxide (5% N₂O/Ar) into contact with the reduced catalysts at 60 °C for 0.5 h. We assumed that all the surface copper atoms were oxidized from Cu⁰ to Cu⁺. Cu⁺ was then reduced by a pulsed method with H₂ and the consumption of H₂ was determined using a TCD. An adsorption stoichiometry of two Cu atoms per O atom and a Cu surface density of 1.46×10^{19} Cu atom/m² were assumed.

The bulk composition was analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP) and the test was carried out using an Ultima2 plasma emission spectrometer from Jobin Yvon.

1.3 Catalyst testing

Activity tests were carried out in a continuous flow system equipped with a stainless steel fixed-bed tubular reactor (inner diameter and length were 14 mm and 490 mm, respectively). The amount of catalyst (20–40 mesh) used was 5.6 g, the height of the catalyst bed was about 70 mm and both sides of the catalyst bed were packed with porcelain rings. The catalyst was activated in a H₂ atmosphere under the following conditions: pressure 1.0 MPa, flow rate 500 ml/min, temperature 250 °C for 5 h at a ramping rate of 1 °C/min. After cooling to 220 °C, 0.2 g dimethyl oxalate (DMO) in 1 ml methanol and H₂ were fed into the reactor at a H₂/DMO molar ratio of 50–80 under a system pressure of 2.5 MPa. The liquid hourly space velocity (LHSV) of DMO was controlled between 0.2 to 0.5 h⁻¹. The products were condensed and analyzed by gas chromatography after 5 h time on stream.

2 Results and discussion

2.1 Textural properties and crystalline phase of the catalysts

The physicochemical properties of the catalysts with different copper loading are summarized in Table 1. The specific surface areas initially increased with an increase in copper loading and decreased gradually at higher than 10%. The specific surface area of the catalysts decreased to about

400 m²/g and when the copper loading was increased to 40% it decreased to 273 m²/g. The pore volumes and pore diameters all increased initially with an increase in copper loading and the maximum pore volume was 0.43 cm³/g when the copper loading was 15%. The maximum pore size was 4.14 nm when the copper loading was 25% and these values decreased when the copper loading was increased further. Nevertheless, these values increased again when the copper loading was 40%.

The real copper loading, as determined by ICP, was far less than that calculated based on the amount of cupric nitrate trihydrate used apart from the 5%Cu/SiO₂ and 40%Cu/SiO₂ samples and these results imply that the catalysts contained a certain amount of hydroxyl groups.

At a copper loading of less than 10% the catalyst prepared by the sol-gel method was found to be green in the presence of cupric ions Cu²⁺ and these were incorporated into the silica gel matrix and, therefore, no separate CuO phase was formed during calcination [16–18]. When the copper loading was higher than 10%, the color of the catalysts changed from green to black and this shows that the concentration of CuO increased as the copper loading increased.

Figure 1 shows the XRD patterns of the calcined Cu/SiO₂ samples before and after reduction. The peak at $2\theta = 22.0^\circ$ belongs to amorphous silica. For a copper loading lower than 10% the copper oxide signal is absent for the catalysts before reduction and the catalysts after reduction showed a dramatically weakened diffraction peak at $2\theta = 43.3^\circ$. For a copper loading between 10% and 30% the catalysts before reduction show strong diffraction peaks that come from CuO and all the peaks become stronger as the copper loading increases. Accordingly, the diffraction peaks from Cu⁰ become strong as the copper loading increases. In addition, a weak diffraction peak from Cu₂O is present at $2\theta = 36.5^\circ$ and it becomes stronger as the copper loading increases and this indicates that a portion of the copper exists as Cu⁺ after reduction. Table 1 shows that the average diameters of the CuO and Cu⁰ species all increase as the copper loading increases while the diameter of Cu⁰ becomes larger than that of CuO. This indicates that agglomeration of the copper species may take place during the reduction process. When the copper loading is higher than 30%, and especially when raised to 40%, the peaks from CuO and Cu⁰ all strengthen and the average diameters of the CuO and Cu⁰ species, as estimated from the XRD data, reaches 32.0 nm and 43.7 nm, respectively. This also shows that the agglomeration was very serious. The average diameter of CuO in the 30%Cu/SiO₂ sample was obviously less than those of the 20%Cu/SiO₂ and 25%Cu/SiO₂ samples. The copper loading measured by ICP corresponds to the copper loading calculated from the amount of cupric nitrate trihydrate actually used for the 40%Cu/SiO₂ sample. Additionally, the BET results show

that the pore diameter of the 40%Cu/SiO₂ sample corresponds to that of pure SiO₂. It seems that the high copper content resulted in the destruction of the silica gel skeleton leading to the separation of the copper species from silica.

From the above XRD analysis we determined that the copper species on the surface was dispersed very well or that the CuO species was very small when $w(\text{Cu}) \leq 10\%$. The surface CuO diameter increased as the copper loading increased and a peak specific to the copper crystallite phase was found when $w(\text{Cu}) > 10\%$.

2.2 Morphology of the catalysts

TEM images of the catalysts with different copper loadings are shown in Fig. 2. When the copper loading is lower than 10%, small copper particles with diameters of ca. 3 nm were homogeneously dispersed in the silica matrix as shown in the TEM image. In the low magnification TEM image the clear copper species was difficult to find for the 5%Cu/SiO₂ sample and a copper species that was embedded in silica gel was observed for the 10%Cu/SiO₂ sample. This shows that the agglomeration of the copper species was weak while encapsulation by silica was very strong.

XRD results show that a strong CuO diffraction peak was observed when the copper loading was higher than 10% and the peak became stronger as the copper loading was increased. Clear single CuO crystallite particles were difficult to find while a clear lattice stripe was observed especially in the TEM image of the 20%Cu/SiO₂ sample and the average diameter of the CuO crystallite particles was about 5–20 nm while the diameter of the agglomerated CuO crystallites were larger than 20 nm for the 30%Cu/SiO₂ and 40%Cu/SiO₂ samples. This shows that agglomeration in the samples was serious. The agglomerated CuO species of different size are easily observed in the TEM images and agglomeration among the CuO crystallite particles became more obvious as the copper loading increased. Single-crystallite CuO was observed when the copper loading was higher than 25% and its diameter became larger than 100 nm while some of the CuO single-crystallite particles that separated from the silica gel were also observed. We found that the single-crystallite CuO that separated from the silica gel was reduced with more difficulty than the supported CuO phase.

The average diameter of the 30%Cu/SiO₂ sample was less than that of the 20%Cu/SiO₂ and 25%Cu/SiO₂ samples but the agglomeration was more obvious. Moreover, a considerable amount of single-crystallite CuO particles were present in the 30%Cu/SiO₂ sample, which may affect its activity. Lambert et al. [19] reported that large copper particles (> 8 nm) catalyze the reaction and that small copper particles (2–3 nm) are completely inactive during the dehydrogenation of 2-butanol.

2.3 H₂-TPR results

The observed shift in reduction temperature may be because of the different copper particle sizes, the different interactions between the copper oxide and silica, and the different copper oxide dispersions. Chen et al. [20] reported that the lack of reduction peaks at temperatures lower than 200 °C indicated the absence of oxocations [Cu-O-Cu]²⁺ while the lack of peaks at temperatures higher than 260 °C indicated the absence of a copper crystal phase. The $w(\text{Cu}) < 8\%$ catalysts were prepared by the chemisorption-hydrolysis method, which ensured the formation of a unique copper phase that was well dispersed over all the supports [21]. Dow et al. [22] investigated the TPR of supported CuO under hydrogen. For copper oxide supported on $\gamma\text{-Al}_2\text{O}_3$ the highly dispersed copper species include isolated Cu²⁺ ions that strongly interact with the support and isolated Cu²⁺ that weakly interact with the support (cupric ions are in close contact with each other) as well as small two-dimensional clusters or three-dimensional clusters. Wang et al. [11] reported that for a sol-gel catalyst only two peaks were present in the low temperature region. Compared with the impregnation catalyst in the TPR profile this shows that highly dispersed Cu(II) species and small clusters exist in the sol-gel catalyst.

Three TPR peaks were observed in the impregnation catalyst and the strong peak was assigned to the reduction of larger CuO clusters. Yin et al. [23] pointed out that the formation of large CuO crystallites is most probably due to a poor interaction between Cu²⁺ and the surface of the silica support under higher acidity. Kundakovic et al. [24] reported that copper is present as highly dispersed clusters or as isolated copper ions, which could interact strongly with the support at a low copper loading. Lu et al. [18] reported that reduction peaks at 320 and 400 °C were due to the formation of a Si-O-Cu species.

From the above and Fig. 3, the copper species are highly dispersed in the precursor when $w(\text{Cu}) \leq 15\%$, and they are not only highly dispersed the CuO crystallite but small CuO crystallites also exist in the catalysts when $w(\text{Cu}) > 15\%$ while the copper species also include bulk-like CuO when $w(\text{Cu}) > 30\%$.

For $w(\text{Cu}) = 5\%$ the peak at 225 °C is attributed to a weak interaction between isolated copper species, small two-dimensional copper clusters or three-dimensional clusters and the support (cupric ions are in close contact with each other) while the tailing peak at 320–500 °C is attributed to isolated Cu²⁺ ions that strongly interact with the support.

A shoulder peak is present at 214 °C for $w(\text{Cu}) = 10\%$ and it is probably due to the reduction of surface copper, which can be reduced more easily than the bulk copper oxide [25] suggesting that the copper species agglomerates to a

certain degree when $w(\text{Cu}) = 10\%$.

Chary et al. [26] reported that the broadening of the peak and the shifting of the reduction peak toward high temperatures may be due to the increase in crystallinity of CuO with an increase in the copper loading. It is obvious that the low temperature reduction peak shifted to higher temperatures in Fig. 3 especially for $w(\text{Cu}) = 15\%$ and its reduction peak is higher than that for $w(\text{Cu}) = 20\%$. When $w(\text{Cu}) > 15\%$, many CuO crystallites from the agglomeration of the highly dispersed copper species emerge and large CuO crystallites, even bulk-like CuO particles, formed as the copper loading was increased. Therefore, the agglomeration of the surface copper species becomes more obvious and stronger when $w(\text{Cu}) > 10\%$. Zhang et al. [27] found that isolated cupric ions become clustered when the copper loading was increased. Because of cupric nitrate hydrolysis, the pH of the preparation solution decreases as the copper loading increases. This may promote copper species agglomeration.

2.4 Surface chemical states of the catalysts

XPS and X-ray induced Auger spectra (XAES) of the reduced Cu/SiO₂ catalysts are shown in Figs. 4 and 5, respectively. The binding energy of the Cu 2p_{3/2} core level rested between 934.9–932.6 eV and the absence of the characteristic shakeup 2p→3d satellite peaks suggests that the copper species is reduced (Cu⁰ or/and Cu⁺) [28,29]. Because the binding energy values for Cu⁺ and Cu⁰ are almost identical the distinction between these two species on the catalyst surface needs a modified Auger parameter (α'). The α' value at ca. 1851.0 eV is due to Cu⁰ and that at ca. 1849.0 eV to Cu⁺ [28]. The deconvolution of the original Cu LMM peaks was thus carried out and the peak positions as well as their contributions were extracted from the deconvolution and are listed in Table 2. These results indicate that both Cu⁰ and Cu⁺ coexist on the surface of the reduced catalyst. The smaller α' value for Cu⁺ compared with the bulk value is attributed to a strong interaction between Cu⁺ and the support. It has been reported that when copper is in a highly dispersed state and in intimate contact with the supports, α' can range between 2–3 eV lower than the bulk values [30].

Table 2 shows that the change in the Cu⁺/(Cu⁺+Cu⁰) intensity ratio that is derived by fitting the Cu LMM peak with an increase in the copper loading is in inverted volcanic form, and the maximum and minimum are $w(\text{Cu}) = 5\%$ and 20%, respectively. It has also been shown that the CuO species weakly interact with the support and can be readily reduced to Cu⁰ at 350 °C [31,32]. The high Cu⁺/(Cu⁺+Cu⁰) intensity ratio for the reduced Cu/SiO₂ catalysts signifies the retarded Cu²⁺ reduction in the calcined Cu/SiO₂ samples [8]. Therefore, the high Cu⁺/(Cu⁺+Cu⁰) intensity ratio with low copper loading suggests that the encapsulation of silica gel is very

strong and the copper species is reduced to Cu⁰ with difficulty while the encapsulation is less at a higher copper loading. The high Cu⁺/(Cu⁺+Cu⁰) intensity ratio increases when $w(\text{Cu}) > 20\%$, and it is probable that large and even single-crystal CuO was formed and this shows that the agglomeration of the copper species increases the difficulty of copper species reduction to Cu⁰.

The Cu surface area was relative to the amount of Cu on the surface, the Cu metal surface area and the Cu dispersion of the Cu/SiO₂ catalysts, as shown in Fig. 6. Changes in the Cu surface area with an increase in copper loading took on a volcanic shape and the Cu surface area of the $w(\text{Cu}) < 15\%$ sample was far less than that of the others suggesting that the amount of Cu on the surface increases while the encapsulation decreases. The decrease in Cu surface area is due to agglomeration when $w(\text{Cu}) > 20\%$. Yin et al. [33] reported that a large Cu surface enhanced the activities of the catalysts.

Copper species dispersion slowly decreased but when the copper loading was higher than 20%, the copper species dispersion decreased quickly. This shows that agglomeration becomes more serious with an increase in copper loading and the agglomeration was especially serious when the copper loading was higher than 20% and this may decrease the activities of the catalysts. Therefore, the effect of copper loading on dispersion was weak to a certain degree while it could obviously weaken the encapsulation.

2.5 Activities of the Cu/SiO₂ catalysts for the dimethyl oxalate hydrogenation reaction

The results of Cu/SiO₂ catalyst activities with different Cu content for the dimethyl oxalate hydrogenation reaction are shown in Fig. 7. We found that DMO conversion and EG selectivity were all very low when $w(\text{Cu}) < 15\%$. The activity increased sharply when the copper loading was increased to 15%. The conversion of DMO and the selectivity for EG was 99.9% and 95.0%, respectively. The space-time yield was close to 100 g/(L·h). The activities of the catalysts obviously decreased when the copper loading was higher than 25% independent of activities or stability and the 20%Cu/SiO₂ sample was optimal.

Table 3 shows that the TOF values of EG were similar when the copper loading was between 15% and 25% and the TOF values were very low when the copper loading was 5% and 40%.

The role of Cu⁰, Cu⁺, and Cu²⁺ has been reported in the literature but there is still no agreement on the role of the copper species toward catalytic hydrogenation [8,34–37]. Li et al. [36] reported that Cu⁺ was decisive in the conversion of oxalate and that Cu⁰ is responsible for the selectivity for ethylene glycol. Chen et al. [8] reported that a cooperative

effect exists between Cu⁰ and Cu⁺ and that this was responsible for their activities during DMO catalytic hydrogenation.

Yin et al. [38] reported that better dispersion of copper species together with proper ratio of Cu⁰/Cu⁺ made great contributions to the enhanced catalytic performance. Figure 8 presents EG space-time yield and Cu⁰/(Cu⁺+Cu⁰) ratio as a function of Cu content. It showed that the changes of catalytic activities and Cu⁺/(Cu⁺+Cu⁰) ratio with the increase of copper loadings were all volcanic form under lower H₂/DMO and higher LHSV. This suggested that the catalytic performance was relevant to the content of Cu⁰ and Cu⁺, that is, the cooperation of Cu⁰ and Cu⁺ had an effect on the catalytic performance.

Therefore, the relatively large quantity of small CuO crystallites (5–20 nm) on the catalyst surface results from encapsulation and agglomeration and the highest Cu surface area and the most optimal Cu⁰ to Cu⁺ ratio is responsible for the highest hydrogenation activity for the 20%CuSiO₂ sample.

3 Conclusions

The encapsulation of silica and the agglomeration of Cu species can be overcome to a degree by adjusting the copper loading in catalysts prepared by the sol-gel method. This results in a larger number of small CuO crystallites (about 5–20 nm), which are easily reduced. The difference between this and previous work is that the copper loading exceeded 10% and the catalysts prepared by the sol-gel method gave high activities when the copper loading was higher. The shortcoming is that the agglomeration becomes more serious and results in the copper species dispersion decreasing with an increase in copper loading. In future work, we will add additives to weaken the encapsulation and to reduce the amount of agglomeration in the higher copper loading catalysts and the Cu surface area should thus increase. The Cu⁰ to Cu⁺ ratio will also be optimized.

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