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Effect of Zn on catalytic performance of Cu/AC catalysts for oxidative carbonylation of methanol to dimethyl carbonate

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Abstract: Zn-promoted Cu/AC catalysts CuZn/AC were prepared by impregnation method, and the effects of impregnation sequence and Zn loading amount on the catalytic performance of the catalysts for liquid-phase oxidative carbonylation of methanol to dimethyl carbonate (DMC) were investigated. The microstructure and surface property of the catalysts were characterized by XRD, H_2-TPR, CO-TPD, AAS and TEM. The results showed that the catalysts prepared by the co-impregnation method had better dispersion and catalytic performance compared with the separated impregnation method. Adding an appropriate amount of Zn by using co-impregnation method could improve the dispersion of copper species of the CuZn/AC catalysts and increase the Cu0 amount of the reduced catalysts, which contributed to the improvement of catalytic performance. The 10Cu2Zn/AC with Zn of 2% by mass exhibited the best catalytic activity, and the conversion of methanol and the selectivity of DMC were 10.58% and 95.15%, respectively.

Keywords: dimethyl carbonate; Cu/AC catalyst; zinc promoter; oxidative carbonylation; methanol

动态简讯

德国无二氧化碳产生的甲烷裂解制氢技术概念验证

日前德国先进可持续性研究院(IASS)与卡尔斯鲁厄理工学院(KIT) 的研究人员宣布实现了创新的具有成本效益的甲烷裂解制氢技术概念验证,其不产生 CO_2 副产物。由于技术尚未完全成熟,此阶段成本估算是不精确的,然而初步计算表明,在德国的天然气价格下,未考虑炭黑副产品的价值时,氢成本为 1.9~3.3 欧元/kg。

世界上大部分的氢气生产目前基于传统技术,如天然气(甲烷)蒸汽重整(SMR),但在这个过程中会释放出大量的 CO_2。炭黑是高价值的工业大宗商品,该技术得到的副产品炭黑质量高且特别纯,因此可提高甲烷裂解的经济可行性。

在过去的 20 年里, 许多不同的机构进行过甲烷裂解实验,证明了其技术可行性。但这些尝试受到炭堵塞和低转化率等问题的制约。

IASS 和 KIT 的团队建立了一个实验性反应器, 可望证明甲烷裂解的潜力,并克服以前的障碍。新反应器基于液态金属技术。细小的甲烷气泡在充满熔融锡的塔底部注入。当这些气泡上升到液态金属的表面,裂解反应即发生,生成的炭在泡沫表面被分离, 并在反应器顶端作为粉末被沉积。2012 年底到 2015 年春期间,研究人员评估了不同的参数和选项, 如温度、建筑材料和停留时间。最终的设计是一个 1.2m 高、由石英和不锈钢制成的设施,使用纯锡和由石英组成的填充床结构。在 2015 年 4 月最近的实验中,反应器连续操作两周,产出氢气,在 1200°C 下转化率达 78%。创新的反应器可抗腐蚀和避免堵塞,产生的微粒炭粉可以很容易地进行分离,从而可满足工业规模反应器连续操作所需的技术条件。

生产单位氢气的 CO_2 排放, 该技术可与水电解相媲美,并比 SMR 清洁 50%以上。实验结果以及环境和经济评估都指明甲烷裂解可作为清洁的替代方案。　(钱伯章)