2 种催化剂在甲苯燃烧反应中的催化性能

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摘要 利用甲苯有机废气为指标反应, 在常压连续流动反应装置上研究了贵金属和非贵金属峰窝陶瓷整体催化剂的催化性能. 考察了甲苯浓度、氧含量、反应空速及床层线速度对催化剂活性的影响及其耐高温性能. 表明不同条件下贵金属催化剂的活性均优于非贵金属催化剂. 催化剂经 600℃处理 3h 后, 非贵金属催化剂上甲苯有机废气的起燃温度比贵金属催化剂高 50℃. 当催化剂经 900℃处理 3h 后, 甲苯有机废气在贵金属催化剂上的起燃温度与 600℃处理催化剂相比仅提高了 3℃. 而相同处理条件下, 非贵金属催化剂上甲苯有机废气起燃温度却提高了 87℃.

关键词 甲苯有机废气燃烧反应, 蜂窝陶瓷整体催化剂, 热稳定性, 起燃温度.

工业有机废气的消除有直接燃烧和催化燃烧. 前者消耗大量能源, 而且难以达到排放标准, 例如甲苯直接燃烧要达到 800℃左右, 此高温下易生成 NO_x 造成二次污染. 采用催化燃烧方法仅需 220– 300℃即可达到完全燃烧[1, 2]. 因此已广泛用于化工、轻工、机械、喷涂等行业中, 成为有机废气最佳净化技术[3, 4].

本文是利用贵金属和非贵金属 2 种类型的蜂窝陶瓷整体催化剂, 以甲苯工业有机废气为指标反应, 研究了这 2 类催化剂的催化性能及甲苯有机废气在这 2 类催化剂上的反应性能, 以适应工业有机废气中有机废气浓度、空速、氧含量多变的特征, 以满足不同工艺过程对催化燃烧技术的要求.

1 实验部分

1.1 催化剂制备

催化剂载体为堇青石蜂窝陶瓷整体, 62 孔/cm^2, 孔内涂有 Al_2O_3 涂层, 经 900℃焙烧后表面积为 20– 22 m^2/g. 用常规浸渍方法加入活性组分, 于 600℃焙烧 3h, 制备出 Pt、Pd 贵金属催化剂 A 及过渡金属氧化物催化剂 B. 为了考察催化剂耐高温性能, 将 A、B 催化剂分别于 700℃、800℃和 900℃焙烧 3h, 再比较甲苯有机废气的反应性能.

1.2 催化剂活性测试及分析方法

催化剂活性评价采用常压连续流动固定床反应器, 内径 26mm. 反应温度由程序升温仪控制. 催化剂体积为 4.5ml 圆柱体, 进行线速度变化试验时, 催化剂直径在 ϕ22– ϕ10 mm 间变化, 催化剂体积不变. 反应前后甲苯浓度变化用气相色谱分析, 色谱柱为长 1 m, 内径 4 mm 的不锈钢管, 内装有机担体-406, 氢火焰鉴定器. 催化剂比表面积由 BET 法测定.

2 实验结果与讨论

2.1 甲苯浓度对催化剂反应性能影响

在反应空速 $4\times10^4\ h^{-1}$时, 从废气中甲苯浓度变化对 A、B 2 种催化剂性能的影响(图 1)可以看出, 甲苯在贵金属催化剂 A 上起燃温度随着甲苯浓度的增加而迅速下降. 当甲苯浓度大于 6000mg/m^3 时, 下降趋于缓慢, 甲苯起燃温度随浓度变化曲线与甲苯转化> 90%时的温度浓度曲线平行而基本接近. 当甲苯浓度为 2000mg/m^3 时, 起燃温度为 243℃, > 90% 转化时的温度为 249℃, 之间相差 6℃; 当甲苯浓度为 12000mg/m^3 时, 起燃温度为 223℃, > 90%

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转化时的温度为 226℃, 之间仅差 3℃, 即> 90% 转化时的温度仅比 50% 转化温度高 3–6℃. 而在非贵金属催化剂 B 上, 起燃温度仍是随反应气体中甲苯浓度的增加而急剧下降, 但当甲苯浓度～8000 mg/m^3 时出现最低点, 然后随甲苯浓度增加, 起燃温度也缓慢上升. 更值得注意的是, 当甲苯浓度为 2000 mg/m^3 时, 起燃温度为 279℃, > 90% 转化时的温度为 307℃, 二者相差 26℃; 当甲苯浓度大于 6000mg/m^3 时, 起燃温度与> 90% 转化温度随浓度变化趋势相同, 2 条曲线相靠近, 温度相差小于 8℃. 这主要是由于贵金属与非贵金属催化剂上活性中心性质和数目不同所致. 贵金属催化剂上适于甲苯燃烧反应活性中心数特别是低温活性中心数多, 而且活性中心效率高, 因而在较低温度下甲苯就具有较高反应活性, 表现出甲苯具有较低的起燃温度.

非贵金属催化剂 B 上, 由于对甲苯燃烧反应有贡献的活性中心数目低于贵金属催化剂 A, 因而起燃温度高.

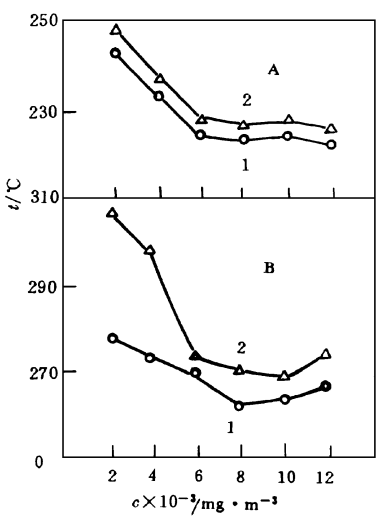

图 1 甲苯浓度对催化剂活性影响
A. 贵金属催化剂 B. 非贵金属催化剂
1. 50% 转化时温度 2. > 90% 转化时温度

2.2 氧含量变化对甲苯氧化性能影响

表 1 中列出了空速 40 000 h^{-1}, 甲苯浓度 8000 mg/m^3 时, 甲苯反应性能与氧含量关系. 由表 1 数据看出, 废气中氧含量由 21% 降至 5.25%, 催化剂 B 上甲苯氧化活性明显下降, 而在催化剂 A 上这一影响不明显, 说明非贵金属催化剂 B 对氧浓度变化的适应性远不如贵金属催化剂 A.

表 1 氧含量对反应的影响

废气中氧浓度/%		21	10.5	5.25
A	50% 转化温度/℃	224	229	227
	90% 转化温度/℃	228	236	240
B	50% 转化温度/℃	262	286	288
	90% 转化温度/℃	271	295	310

2.3 空速对催化剂活性影响

在废气中甲苯浓度为 8000 mg/m^3 条件下, 考察了 2 种催化剂对反应空速变化的适应能力, 实验结果如图 2.

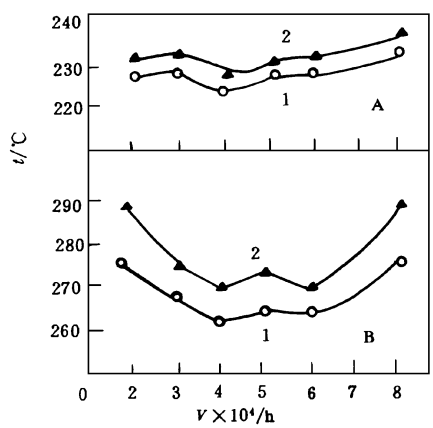

图 2 空速变化对反应的影响
A. 贵金属催化剂 B. 非贵金属催化剂
1. 50% 转化时温度 2. > 90% 转化时温度

由图 2 数据可以看出, 催化剂 A 对空速变化的适应性比催化剂 B 高. 说明只要压降允许的条件下使用少量 A 催化剂可处理大量废气. 非贵金属催化剂 B 由于活性低, 在低空速条件下反应放热量少促使床层升温较慢, 因而表现出在相同转化率时要求比 A 催化剂更高的废气预热温度. 当空速 80 000 h^{-1}时, 在 B 催化剂上物料未达到完全转化而穿透床层, 当要求与 A 相同的转化率时, 其反应温度也应提高. 因此过高或过低的空速对非贵金属催化剂均不适宜. 如将 A、B 2 种催化剂合理组合匹配使用就可弥补单纯使用非贵金属催化剂之不足.

空速变化在 2 种催化剂上所表现出不同的反应特征, 同样也是由于贵金属与非贵金属催化剂上的活性中心的属性所决定.

2.4　催化床中气体线速对反应性能影响

保持催化剂体积不变,变化催化剂柱体直径以改变床层线速度. 在空速 40 000 h^{-1}, 甲苯浓度 8000 mg/m^3 条件下测定 50% 转化的起燃温度及> 90% 转化温度,并计算该温度条件下的催化剂孔道内实际线速度, 结果如表 2. 由表 2 中数据可以看出,在相同空速条件下, 反应床的空塔线速、催化剂孔道中实际反应温度下的线速与反应性能的关系基本是平行的. 最佳线速在 2 种催化剂上基本是一致的. 当空塔线速在 25 cm · s^{-1}或反应状态线速为 80– 100 cm · s^{-1}时, A、B 催化剂上起燃温度或最高转化时

表 2　催化床中线速度对反应的影响

催化剂编　号	空塔线速 /cm · s⁻¹	50% 转化温度/℃	实际线速 /cm · s⁻¹	90% 转化温度/ ℃	实际线速 /cm · s⁻¹
A	13.16	238	47.6	244	48.1
	17.60	230	62.6	237	63.47
	24.89	223	87.3	220	89.06
	32.47	226	114.6	232	116.0
	44.25	227	156.5	232	158.0
	63.69	236	229.7	239	230.6
B	13.16	272	50.7	277	51.2
	17.60	267	67.2	274	68.1
	24.89	262	94.2	272	95.9
	32.47	272	125.1	284	127.9
	44.25	275	171.5	297	178.4
	63.69	287	252.2		

的温度均处于最低值, 即催化剂效率发挥最佳. 非贵金属催化剂耐受高线速的能力不如贵金属催化剂, 因此在催化床设计中其直径与床高比 D/h 应大于贵金属催化剂. 上述实际结果有待在扩大规模装置上进行工程研究.

2.5　催化剂耐热性能考察

将 A、B 2 种催化剂在不同温度下进行焙烧处理, 考察其耐热性能. 甲苯浓度 8000 mg/m^3, 空速 40 000 h^{-1}条件下测得的结果如图 3. 由图 3 中数据可以看出, A 催化剂在 600–900℃温度范围焙烧处理后活性基本不变. 催化剂 B 随焙烧温度的提高起燃温度向高温区移动, 活性下降. 当处理高浓度有机废气时, 有可能使床层升温至 900℃情况下不宜使用非贵金属催化剂.

3　结　语

(1) 贵金属和非贵金属蜂窝陶瓷整体催化剂对于甲苯有机废气均有较好的反应性能, 但非贵金属催化剂对空速、线速的适应能力均不如贵金属催化剂, 对甲苯浓度适用范围较窄. 2 类催化剂当反应状态处于线速 80– 100 cm · s^{-1}时, 其转化效果最佳.

(2) 2 类催化剂耐高温性能相差较大, 在 600– 900℃高温焙烧后, 贵金属催化剂活性基本不变, 非贵金属催化剂活性随焙烧温度的提高活性下降, 当床层升温有可能达到 900℃时, 不适宜单独使用非贵金属催化剂.

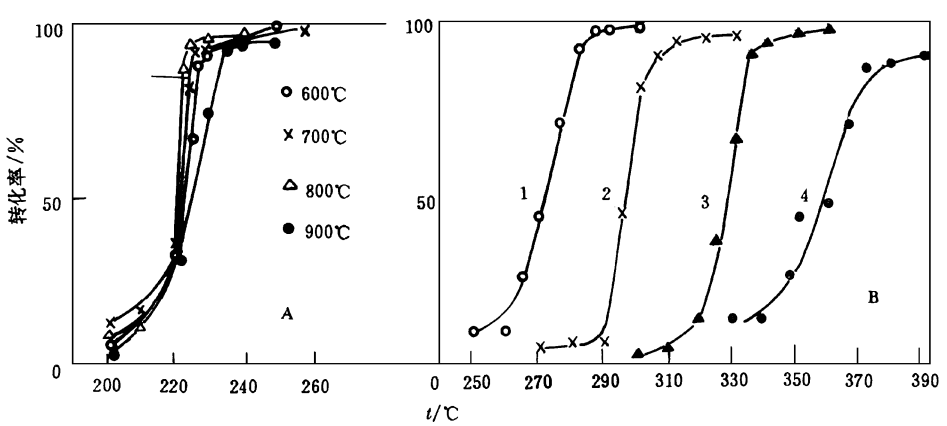

图 3　A、B 2 种催化剂耐热性能比较

A. 贵金属催化剂　B. 非贵金属催化剂　1. 600℃　2. 700℃　3. 800℃　4. 900℃

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The Mn^{2+} removing activity of the filter sand from 2 Chinese Water Plants was analyzed to determine the role of the bacteria in the Mn^{2+} removing Procession. Enumeration of bacteria on PYCM medium showed that there were 10^5-10^6 bacteria per g wet sand and about 40%-50% of the colonies had the ability to oxidize Mn^{2+}. By the in situ enrichment of the bacteria, sterilization and the $HgCl_2$ inhibition of the mature sand, it was found that bacteria were indispensable to the maintenance of the activity of the sand. When the bacterial activity was inhibited, the activity of the sand was reduced to20% of the original one. The remaining activity might be due to the chemical catalysis. Bacteria were the major source of the Mn^{2+} removing activity of the filters.

Key words: groundwater, Mn^{2+}, bacteria, chemical factors, filter sand.

A Study on the Characteristics of the Activated Sludge for Anaerobic Attached Microbial Film Expanded Bed Process. Zhang Jianli and Li Lijian (Dept. of Food Science, Laiyang Agricultural College, Laiyang 265200), Feng Xiaoshan (Dept. of Environ Science, Zhejiang Agricultural University, Hangzhou 310029): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 42-44

The characteristics of activated sludge in the anaerobic attached microbial film expanded bed (AAFEB) reactor were studied. The results showed that there were three consecutive phases in the course of biofilm formation and development, namely, adsorbtion phase, partly coating phase and fully coating phase. In this process, the predominant microorganisms were changed gradually from coccus to filamentous organisms, which caused anaerobic sludge activity increasing. Under the acidification condition, there were a lot of streptococcus and extracellular polymer on the surface of activated sludge, and the sludge activity was low.

Key words: anaerobic attached microbial film expanded bed reactor, anaerobic activated sludge, biofilm.

Catalytic Properties of Two Kind of Catalysts in Toluene Combustion Reaction. Li Shiyao, Li Shulian et al. (Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 45-47

Toluene organic exhausts were regarded as index reaction in evaluating the catalytic performance of honeycomb ceramic monolith catalysts consisting of noble metals and non-noble metals respectively by means of a continuous system with a fixed bed of catalysts. The effect of toluene concentration and oxygen content in the exhaust, space velocity, linear velocity on toluene reaction, and the thermal stability of catalysts were investigated. It is found that the activity of noble metal catalyst is superior than that of non-noble metal catalyst under different conditions. The light-off temperature of toluene exhaust on non-noble metal catalyst is by 50℃ higher than that on noble metal catalyst after catalysts calcine at 600℃ for 3h. Meanwhile, after catalysts calcine at 900℃ for 3h, the light-off temperature of toluene exhaust on noble metal catalyst increases only by 3℃ as compared with the calcination of 600℃ for 3h. But under same condition, the light-off temperature of toluene exhaust on non-noble metal catalyst increases by 87℃.

Key words: combustion reaction of toluene exhaust, honeycomb ceramic monolith catalyst, thermal stability, light-off temperature.

Photochemical Disinfection of Wastewater. Kong Lingren, Chen Xi et al. (Dept. of Environ. Sci. and Eng., Nanjing University, 210093): *Chin. J. Environ. Sci.*, **18**(1), 1997, pp. 48-50

A new method of photochemical disinfection for wastewater from Nanjng city was investigated. By aerating and using methylene blue(MB) as photosinsitizer, the wastewater samples were disinfected under sunlight and a medium pressure mercury lamp separately. The results were as follows: (1) The disinfection of wastewater were remarkably affected by the light sources, light intensity, irradiaded time, MB concentration and dissolved oxygen; (2) The bacteria which were disinfected by UV could be partially photoreactivated under sunlight; (3) The disinfection rate could reach 100% and the bacteria photoreactivation were not appeared when 1 liter of the sample containing 3.1×10^6 bacteria and 2 mg MB were irradiaded by a 300W medium pressure mercury lamp for 4 min; (4) The residual MB in the samples could be removed by bentonite clay. The disinfection mechanisms of UV and photosensitization, the bacteria photoreactivetion and the effects for affecting disinfection were discussed.

Key words: photochemistry, photosinsitization, UV irradiation, disinfection.

Summary of Studies on the Ecology of Lake Donghu. Liu Jiankang and Huang Xiangfei (Institute of Hydrobiology, Chinese Academy of sciences, Wuhan 430072): *Chin. J. Enwiron. Sci.*, **18**(1), 1997, pp. 51-53

Taking the Donghu (in Wuhan), a representative lake of the middle and lower basins of Chang Jiang River as a base, the present project has conducted stationary monitoring and systematic researches on the ecology of Lake Donghu for more than 30 years. Achievements of the studies include the estimation of the budgets for the main nutrients nitrogen and phosphorus of the lake, as well as their distribution and accumulation in