TFJF型燃烧催化剂用于烘漆废气治理的研究*

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摘要　研制了一种贵金属-天然沸石/堇青石蜂窝体(TFJF)型催化剂。通过实验室研究和部分漆包线厂实际使用,考察了TFJF催化剂对漆包线机烘漆废气的治理效果。实验结果表明,对芳烃转化率为98%的温度为180—220℃,甲酚为220—240℃;催化剂可耐800℃以上的高温;实用结果表明,对烘漆废气有良好的净化率,对二甲苯的去除率为97%以上,出口浓渡<50mg/m³,同时还可以回收热能。

关键词　催化剂,贵金属,有机废气,废气净化。

大多数油漆、喷漆所使用的溶剂多为甲苯、苯、二甲苯等芳烃,在烘漆过程中溶剂挥发而污染大气,将废气通过特定的催化剂,使可燃的污染物完全氧化成CO_2和H_2O,这是治理该类污染和回收热能的重要方法之一。我国漆包线生产厂达2000多家,所使用的绝缘漆溶剂除二甲苯外,还含有大量的甲酚(占溶剂总量的40%左右)。由于甲酚味很重,毒性大;同时在烘漆过程中,还会产生一些低分子聚合物,凝结在排气管道中,影响风机的动力。因此从70年代开始,少数生产漆包线厂家就陆续开始采用催化燃烧方法治理烘炉废气。所使用的催化剂主要为70年代开发的Pd/Al_2O_3蜂窝体催化剂,但由于其孔道大,接触效果差,去除率不够理想,而且机械强度差,容易热冷破碎,耐热稳定性不佳,从而影响了它的推广使用。笔者研制的TFJF型催化剂,其蜂窝开孔率极高,接触效果佳,并结合天然丝光沸石与Pt、Pd有特殊作用的特点[1],具有高的破坏氧化活性和耐热稳定性。本文在实验室研究的基础上,研究并考察了该催化剂对漆包线机烘漆废气治理的适应性,以利于其推广使用。

1　实验部分

1.1　催化剂制备

TFJF型催化剂是采用堇青石($Mg_2Al_4Si_5O_{18}$)蜂窝体为骨架,用特殊粘结剂把天然沸石粉(>200目)牢固地粘结在蜂窝体的孔壁上,以此为载体,附载上一定量的Pt、Pd等贵金属及过渡金属、稀土氧化物,选择适当的活化条件活化即成,其部分物理性能见表1。

表1　催化剂的基本特性

外型尺寸(mm)	100×100×40,50×50×40
开孔率(孔数/cm²)	30,42
孔壁厚(mm)	0.2—0.3
孔形	方孔
吸水率(g/L)	230—250
热膨胀系数($℃^{-1}$)	1×10^{-6}—2×10^{-6}
比表面(m^2/g)	—20
强度(MPa)　正压	>13
侧压	>3.5

1.2　催化剂活性测试

在实验室固定床流动反应器(装置详见文献[2])中放置2只$\varphi25\times25\times40$mm小圆柱催化剂,模拟原料气为各种有机物和空气的混合气体,空速为$2\times10^4h^{-1}$,有机物浓度为4—6g/m³。反应前后的有机物通过SQ-204型气相色谱仪氢火焰检测。

1.3　催化剂耐热反应性能

催化剂经不同温度烧结一定时间后,再在相同条件下进行活性测试。

2　实验结果与讨论

2.1　催化剂对各有机废气的起燃温度

在前述的实验条件下,不同气体转化率≥98%所需的进口温度详见表2。结果表明,该催化剂有很高的完全氧化活性,尤其对芳烃在200

* 浙江省科委基金资助项目
收稿日期:1993-09-13

表 2 TFJF 型燃烧催化剂转化 98%废气所需的进口温度

组分	温度(℃)	组分	温度(℃)
苯	220	乙酸丁酯	200—220
甲苯	200	乙酸乙酯	280—300
二甲苯	180	丙酮	260
甲酚	240	环己酮	200
丁醇	140—160	正己烷	280—300
冰醋酸	280—300	石油液化气	300
甲醇	100—120		

℃左右就能完全氧化，对较难氧化的酸、酯、烷烃等在 280—300℃亦能完全被氧化。同时，模拟烘漆废气源(漆包线烘漆废气)二甲苯和甲酚混合进料，考察其在 TFJF 型催化剂上转化率与温度的依赖关系，其结果见图 1。

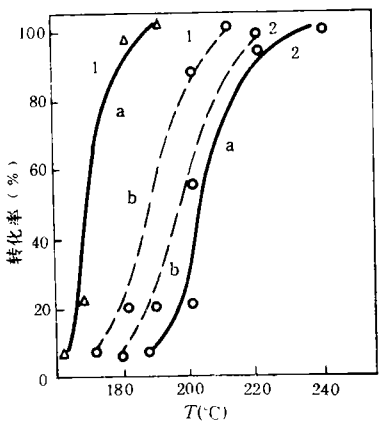

图 1 温度对反应物转化率的影响

a. 二甲苯、甲酚分别进料 b. 二甲苯、甲酚混合进料

1. 二甲苯 2. 甲酚

从图 1 可知，因二甲苯较甲酚容易氧化，而且发热量也大，催化剂一旦起燃后，其表面温度迅速提高，转化率也迅速上升。转化率在 98%以上时温度仅为 180—190℃，即使对较难氧化的甲酚，完全氧化的下限温度也仅为 240℃，而且在与二甲苯混合进料时，完全氧化的下限温度还可下降 20℃左右，说明该催化剂对烘漆废气有良好的燃烧活性。

2.2 催化剂的耐热性能

燃烧催化剂性能不仅需要较低的起燃温度，而且还需要有较好的耐热性。图 2 是催化剂经 800℃、900℃高温灼烧 6h 后的测试结果。

图 2 表明，催化剂经 900℃灼烧后，完全氧化的下限温度仅提高 30—40℃，说明 TFJF 型催化剂有良好的耐热稳定性。同时，还在实验室考察了该催化剂在杭州电工器材厂实际运转了 10000h 以上的催化剂活性，结果见表 3。表 3 表明，TFJF 型催化剂实际运转 800h 后，二甲苯完全氧化的下限温度 240℃，提高 60℃左右，此后在运转到 3000h 后，其活性仍稳定在此范围；其后，由于工艺条件的变化，曾使催化剂冲温到 750℃左右长达 1 个星期，但运转 10000h 后，该催化剂在 320℃下仍能对二甲苯完全氧化，可见催化剂有很好的耐热稳定性。

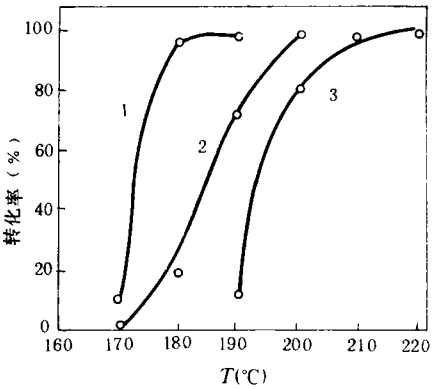

图 2 催化剂的耐热性

1. 新鲜催化剂 2. 800℃灼烧 3. 900℃灼烧

表 3 使用 10000h 前后的活性对比[1)]

实际运转时间(h)	反应温度(℃)	转化率(%)
0	180	98.4
800	240	96.8
	250	99.1
3000	240	90.2
	300	98.4
10800	320	99.2

1) 反应物为二甲苯

2.3 对漆包线机烘漆废气的治理

漆包线生产过程中所使用的绝缘漆是由漆基(聚酯约占 30%—32%)和溶剂(约占 68%—70%)组成，一般每生产 1t 漆包线，需用漆 130—170kg。在烘漆过程中，溶剂完全挥发，废气连续排放，其浓度一般为 2000—8000mg/m³，主要与线径、线速大小以及线头数多少有关，废气排出温度一般为 150—250℃。采用催化燃烧装置，有 2 种技术，其工艺流程见图 3。一种是热风回用技术，也就是利用燃烧反应热以烘干漆包线以及用

以预热进催化床前的废气，是治理该类废气，回收热能的重要方法。但前者节电较为明显，节电效率一般可达 25%—40%。此项技术，在我国进口设备及国产立式漆包机上较为普遍使用。而后者一般应用于国产的卧式漆包机。若生产厂家能允许提高漆包线的收线速度，增加尾气中可燃物的浓度，则节电效果尚可大大增加。

另一种则是废气燃烧后直接排放技术，其设备简单，使用单位可以自己对老设备进行改造，但为了预热进催化床前的废气，往往要增加电耗。若所使用的催化剂活性高，起燃温度低，就可以降低电耗。TFJF 型催化剂现已在国内上百家漆包线生产厂及汽车制造等涂装行业应用。部分漆包线生产厂使用检测结果见表 4。已实际运转半年以上，空速一般为 2—4×10^4h^{-1}，检测对象为二甲笨。

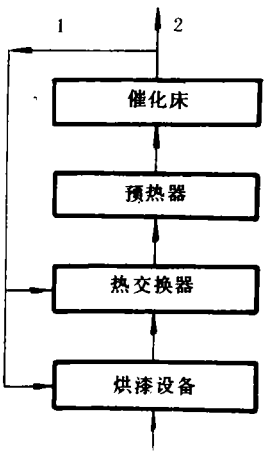

图 3　工艺流程图

1. 热风回用　2. 直接排放

表 4　催化剂燃烧装置的转化率[1)]

催化燃烧装置	使用单位	线径 (mm)	线头数 (个)	预热控制温度 (℃)	燃烧后温度 (℃)	进口浓度 (mg/m^3)	出口浓度 (mg/m^3)	去除率 (%)
热风回用技术	杭州电工器材厂	0.35	40	300(360)[2)]	650	5201	31.2	99.4
	(2 台卧式机)	0.30	38	340 (400)	720	5875	23.5	99.6
	浙江平湖电工厂(卧机)	0.17	36	350(>370)	480--520	1681	45.4	97.3[3)]
	杭州无线电材料厂(立机)	0.72	16	345 (350)	500		21.2	
	郑州电磁线厂(进口)	0.15	39	390	520			
直接排放技术	杭州电工器材厂	0.13	36	360	520	2033	36.6	98.2
	(3 台卧式机)	0.11	36	385	475	1848	29.0	98.4
		0.21	40	350	600	3229	22.6	99.3
	常州无线电材料厂(卧机)	0.15—0.22	40	315—350	500—600			
	江苏吴县电工厂(卧机)	0.42	36	380	650			

1)　多数单位无检测设备，而且有些漆包设备是全封闭的，因而进口浓度无法检测

2)　为燃烧室前的实际温度　3)　为当地环保部门检测数据。

实际使用结果表明，采用 TFJF 型催化剂治理该类废气，除污彻底，对二甲苯的去除率在 97%以上，出口浓度降到 50mg/m^3 以下，达到卫生最高允许浓度 100mg/m^3 以下，而且燃烧后的排放气基本无臭味，说明甲酚也完全去除。表 4 还表明，采用热风回用技术的多数设备，催化床前的实际温度高于预热控制温度，说明当废气预热到一定温度起燃后，废气燃烧就会自热平衡，这样就节约了能源。说明 TFJF 型催化剂用于漆包线机烘漆废气净化是切实可行的，经济合理。

3　结论

(1)TFJF 型催化剂对烃类及其含氧衍生物有良好的燃烧活性，完全氧化的下限温度≤300℃，尤其对烘漆废气中的芳烃有机物，起燃温度低，完全氧化的下限温度仅为 180—220℃；

(2)耐热稳定性能好，可耐 800℃以上高温；

(3)应用于漆包线机烘漆废气的治理，除污彻底，去除率达 97%以上，对高浓度废气在消除污染的同时，还能回收热能。

参考文献

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2　蒋晓源，于庆瑞等. 环境科学. 1992,13(2):44

spheric particle structure to make it excellent in workability. The rubber products in which all calcium carbonate have been replaced with the activated coal ashes have all physical and mechanical properties meeting the requirements, those in which a half of light calcium carbonate have been replaced with the same are also practicable, and those in which less than 1/2 of medium-super carbon black have been replanced with the same can be useful. Due to its grey colour, the activated coal ashes are not suitable to be used in the products with a light or bright colour.

Key words: coal ash, rubber, surface modification.

Study on the Simultaneous Removal of SO_2/NO_x from Flue Cases with Absorption and Catalysis. Sheng Deshu, Zhao Xin et al. (Dept. of Environ. Eng., Hunan University, Changsha 410082): *Chin. J. Environ. Sci.*, **15**(5), 1994, pp. 40—42

Based on the requirements for simultaneous desulfurization and denitrification, a study was carried out on the preparation and reaction processes of the catalysts consisting of CuO as a major active component. The results from activity measurements indicate that the catalyst has the optimum activation temperature of 450 C and the activation time of 2h. Under the conditions of reaction temperature of 400 C, space velocity of $2 \times 10^4 h^{-1}$, $CuSO_4$/CuO ratio by mole of over 1. 46 and Cu/S ratio by mole of over 0. 83, both SO_2 and NO_x can be removed at a rate of over 90%.

Key words: simultaneous desulfurization and denitrification, catalyst, treatment of waste gases.

Study on the Treatment of Wastewater from the Production Process of Jiemycin. Lin shiguang (Center for Environ. Control, Zhongshan (Sun Yetsen) University of Medical Science, Guangzhou 5100631), Luo Guowei et al. (Institute of Environ. Sci., South China Normal University): *Chin. J. Environ. Sci.*, **15**(5), 1994, pp. 43—45

A feasibility study was carried out on the use of the acidic hydrolysis two stage bacteria-added biological contact oxidation/ coagulation process to treat the highly concentrated wastewater from the production process of Jiemycin. The results from this pilot study show that when the influent had a COD concentration in the range of 3500—5000mg/L and a BOD concentration in the range of 1000—1500 mg/L, there were an average COD removal of over 95% and an average BOD removal of over 96%, resulting in an effluent in compliance with the national standards for wastewater discharge under GB8978-88.

Key words: jiemycin wastewater, acidic hydrolysis, bacteria-added biological contact oxidation, coagulation and flocculation, wastewater treatment.

Study on the Role of Sulfuric Acid in the Catalytical Hydrolysis of Black Liquor from Straw Fiber Pulping Process. Yang Runchang et al. (Dept. of Chem. Eng., Xiangtan University 411105): *Chin. J. Environ. Sci.*, **15**(5), 1994, pp. 46—48

Sulfuric acid was found to have a catalytical function in promoting the hydrolysis of black liquor from a reed fiber pulping process. The results from this study show that under the conditions of applied pressure and heating (0. 2 — 0. 6 MPa, 130 — 165 C), sulfuric acid allowed over 99% of lignin in the black liquor to be acid settled, dewatered, carbonized and then separated from the black liquor. More than 62% of theoretical aldehyde content were hydrolyzed, dewatered and then converted to furfural.

Key words: straw fiber pulping, black liquor, sulfuric acid, catalytical hydrolysis, lignin.

Study on the Degradation of Active Bright Red X-3B by Immobilized Purple Non- sulfur Photosynthetic Bacteria. Niu Zhiqing, Wu Guoqing et al. (Dept. of Environ. Eng., Taiyuan University of Technology, Taiyuan 030024): *Chin. J. Environ. Sci.*, **15**(5), 1994, pp. 49—52

The spent dye bath of active Bright Red X-3B was treated by using aggregation and cross linkage immobilized purple non- sulfur photosynthetic bacteria (PSBs). The PSBs and their immobilized cells were compared for some of their performances. It was found that both of the cells had an optimum reaction temperature in the range of 30—40 C, and the immobilized cells had an optimum reaction pH in the broader range of 7. 5 — 9. 4, with a better thermal stability. Cu^{2+} had an inhibitory effect on the enzyme activities of both cells. As compared with the immobilized cells entrapped in sodium alginate, the aggregation and cross linkage immobilized cells had a stronger power of decolorization, a higher activity of enzyme, a longer half lifetime and a more cost-effectiveness, and was simple to operate and easy to be applied on a full-scale.

Key words: purple non- sulfur photosynthetic bacteria, immobilized cells, decolorizing enzyme, active bright red X-3B.

Study on the Use of TFJF Model Combustion Catalyst for the Pollution Control of Waste Gases from stoving Enamel. Zhou Renxian, Fang Heliang et al. (Dept. of Chemistry, Hangzhou University, Hangzhou 310028): *Chin. J. Environ. Sci.*, **15**(5), 1994, pp. 53—55

TFJF Model Catalyst, a noble metal carried over a natural zeolite/ cordierite honeycomb carrier, was developed and examined for its application to the pollution control of the off- gas from the stoving enamel process of enamel covered wires manufacturing. The results show that the temperature for a 98% conversion rate was 180—220 C for aromatic hydrocarbons and 220—240 C for cresylols. The catalyst was resistant to a temperature as high as up to 800 C and had a better effficiency of cleaning up the gaseous wastes from stoving enamel processes. For a highly concentrated

waste gas, energy recovery could be made while the goal of pollution control being achieved.

Key words: catalyst, noble metal, organic waste gases.

Comparison in Vehicular Exhaust Emissions between Hong Kong and Guangzhou Cities. L. Y. Chen (Ph. D) and W. T. Hung (Civil and Structural Eng. Dept. Hong Kong Polytechnic, Hunghom, Hong Kong), Y. Qin (Institute of Environ. Sci., Zhongshan University, Guangzhou 510275): *Chin. J. Environ. Sci.*, **15**(5), 1994, pp. 56—60

The monitoring results of vehicular exhaust emissions in the urban areas of Hong Kong and Guangzhou were discussed. The monitoring exercise was carried out by using automatic gaseous analyser mounted on road side in Hong Kong for four years and for nine days in Guangzhou. The results show that the pollution level at Castle Peak Road of Hong Kong was comparitively lower than that in Guangzhou. The pollution level in Hong Kong satisfied the national air quality standard (Class 2) of China in both years 1988 and 1989. The pollutant concentration along Jefang Middle Road was very high and exceeded the national air quality standard (Class 3). The traffic flow speed and composition were discovered to be the major reasons for the difference in pollutant concentrations in both cities.

Key words: vehicular exhaust emission, combined emission factor, traffic flow speed and composition.

SDS-PAGE Seperation and HPLC- FID Identification of Selenoproteins in Soybean from Enshi Area Having a Higher Level of Selenium in Soil. Xie Shenmeng, Wang Zijian and Peng An (Research Center for Eco- Environmental Sciences, Chinese Academy of Sciences, Beijing 100085): *Chin. J. Environ. Sci.*, **15**(5), 1994, pp. 61—62

Selenoproteins in soybean from Ensh area where selenium in soil was at a higher level were seperated by using sodium dodecyl sulfate-polyacrylamide gel electrophoresis (SDS-PAGE) and then identified by using high performance liquid chromatography with a fluorescent indication detector (HPLC-FID). Of 27 protein or protein subunit bands identified, 13 were found to be selenium species. According to a standard protein kit, their molecular weights were estimated at 58. 3— 60. 3, 52. 5— 53. 7, 46. 8— 50. 1, 29. 5—30. 9, 28. 8, 25. 1— 25. 7, 24. 3, 19. 7—20. 9, 18. 4—18. 6, 16. 8— 17. 9, 16. 1— 16. 2, 15. 2—15. 8 and 14. 3— 14. 8 KDa, respectively.

Key words: SDS-PAGE, HPLC-FID, selenoprotein, speciation.

Acute Toxicity of Organotin Compounds to Benthos. Chen Tian' yi et al. (Dept. of Environ. Sci., Nankai University, Tianjin 300071): *Chin. J. Environ. Sci.*, **15**(5), 1994, pp. 63—64

The acute toxicities of three organotin compounds, i. e., monobutyltin (MBT), dibutyltin (DBT) and tributyltin (TBT), to benthos (Chironomid larvae and tubificids) were reported. The results show that (1) the toxic effects of these compounds in a decreasing order were TBT > DBT > MBT; (2) the median lethal concentration (24h LC_{50}) of TBT to 4 species of benthos was 26. 85 ppb for chironomid larvae (*Chironomus plumosus*), 241. 55 ppb for chironomid larvae (*Chaetocladius sexpapilosus*), 145. 55 ppb for tubificids (*Branchiura sowerbyi*), and 355. 63 ppb for tubificids (*Limnodrilus hoffmesteri*); (3) there was a strong negative correlation between the concentration of TBT and the median lethal time (LT_{50}) for *B. sowerbyi*.

Key words: organotin compounds, benthos, acute toxicity.

Effects of CO_2 on the Grain Compositions of Winter Wheat and Soybean. Gao Suhua and Wang Chun' yi (Chinese Academy of Meteological Sciences, Beijing 100081): *Chin. J. Environ. Sci.*, **15**(5), 1994, pp. 65—66

Winter wheat and soybean crops were treated with different CO_2 concentrations in top-open chambers. The matured grains harvested from the crops were analysed for their compositions by using visible ultraviolet spectrometer, protein analyzer, gas chromatograph, YG-2 fat extractor and automanual nitrometer. The results show that an increased CO_2 concentration can have a positive effect on the contents of both rough protein and rough fat in soybean grain; and as the CO_2 concentration increases, the soybean grain would have an increased level of unsaturated acids and a decreased level of saturated acids. The change in CO_2 concentration had a more complicated effect on the levels of rough protein and lysine in winter wheat grain. In terms of both indicators of rough protein and lysine, a doubled concentration of atmospheric CO_2 had a negative effect on the quality of grains of the present varieties of winter wheat.

Key words: top-open chamber, CO_2 concentration, grain composition, winter wheat, soybean.

Study on the Fluorometric Determination of Beryllium Using Morin. Zhao Zhenhua et al. (Beijing Municipal Research Institute of Environmental Protection, Beijing 100037): *Chin. J. Environ. Sci.*, **15**(5), 1994, pp. 67—70

The fluorometric spectra of beryllium- morin complex were characterized and the graphs of excitation spectrum, emission spectrum and synchronous fluorescence spectrum were given. The synchronous spectrum of beryllium- morin in an alkaline solution had an optimum specific $\Delta\lambda$ of 100nm. A synchronous scanning spectrofluorometry was used to determine beryllium at a level of submicrogram, with a detectable limit of 5 ng/ml Be^{2+}. The results obtained with this method were comparable with those obtained with an atomic absorption spectrophotometric method for air samples and water samples.