Ce-Cr/硅藻土对几种低分子量有机物氧化作用的催化活性研究[*]

罗孟飞　袁贤鑫　陈　敏　仲逸芬

（杭州大学化学系,杭州　310028）

摘要　考察了添加 Al_2O_3 对硅藻土的孔容、平均孔径及比表面的影响．并研究了负载型 Ce-Cr、Ce-Cr-Mn 等复合氧化物催化剂对丙酮、正丁胺、甲苯氧化反应的活性．氧化活性的顺序为：$Ce-Cr-Mn-K \approx Ce-Cr-Mn \approx Ce-Cr >$ $Mn > Cr > Ce$．而且能够抑制正丁胺氧化过程 NO_x 的形成，正丁胺氧化 NO_x 控制能力为：$Ce-Cr-Mn-K > Ce-Cr-Mn > Ce-Cr > Ce$．

关键词　硅藻土,催化剂,氧化活性．

我国硅藻土矿藏资源极为丰富，据报道，1985年探明储量在 4 亿吨以上，仅浙江省就达6000 万吨，原土年产量 5000 吨，基于这个情况，当前大力推广硅藻土在各个领域的应用具有十分重要的意义．硅藻土主要成分为无定形 SiO_2，并含有相当数量的石英、蒙脱石、高岭土和少量有机质等．由于天然硅藻土具有多孔性结构以及耐热、耐酸等特点，所以是催化剂常用的一种载体．但因机械强度较差，目前主要用作固定床催化剂载体．在燃烧催化剂载体方面的应用，国内还未见报道．本文用添 Al_2O_3 的硅藻土为载体,考察了负载 Ce、Cr、Mn 等复合氧化物对丙酮、甲苯、正丁胺的氧化反应性能，其目的在于开拓硅藻土的应用范围．

1　实验部分

1.1　原料

浙江嵊县硅藻土（水洗土）;铝溶胶,浙江温州催化剂厂产品;其它试剂：$Mn(NO_3)_2$（50%液体）、$Cr(NO_3)_3 \cdot 9H_2O$、$Ce(NO_3)_3 \cdot 6H_2O$、KNO_3 均为化学纯．

1.2　硅藻土成型

硅藻土用于燃烧催化剂载体必须重新成型．当硅藻土预先经 H_2SO_4 处理后,尽管加入大量铝溶胶（达 30% Al_2O_3）粘合，发现强度很差，极易粉碎．因此本研究直接用水洗硅藻土，添加铝溶胶粘接成型，120℃烘干，800℃焙烧3h,破碎成 3—5mm．

1.3　催化剂制备

根据配制量称取一定量的活性组分物质，加适量水溶解并调整到硅藻土载体的吸水值，称取规定量的上述载体进行浸渍,强迫吸附,最后于 500℃ 空气氛中活化 2h．催化剂以活性组分元素符号表示．

1.4　催化剂活性评价

评价装置及分析方法见文献[1],反应管内径 20mm,催化剂装量 30ml,空速 $10000h^{-1}$,反应物浓度：丙酮 $6—7g/m^3$;正丁胺 $2—3g/m^3$;甲苯 $4—5g/m^3$．NO、NO_2 用盐酸萘乙二胺比色法测定[2]．

1.5　主要仪器

Carlo Erba 2000 型压汞仪；Carla Erba 自动吸附仪；QCY-602 型电动强度测定仪．

2　结果和讨论

2.1　添铝量对硅藻土物性的影响

由于活性组分直接依附于载体，载体的表面物理性质在很大程度上决定了催化剂的物理

性质，尤其是比表面、孔径、强度。分别添加 0%、3%、6%、12% Al_2O_3 的硅藻土成型，800℃ 焙烧后试样的压汞曲线如图 1 所示。从图 1 孔半径与累积孔容的关系可求得样品的比表面和平均的孔径[3]。结合其它实验数据列于表 1。由表 1 可见，4 个试样的强度、BET 比表面随 Al_2O_3 的增加而增加；而平均孔径、总孔容及压汞比表面却随 Al_2O_3 增加而下降。样品的 X-射线衍射分析表明，随 Al_2O_3 增加，Al_2O_3 衍射线的相对强度没有可觉察的变化，这表示 Al_2O_3 大多以无定形的 Al_2O_3 存在。样品的压汞曲线可见，随 Al_2O_3 量增加，小孔径（37—100 Å）一边曲线上跷势头明显增加，同时 BET 比表面明显增加，这意味着小孔随 Al_2O_3 量的增加而增加，小孔可能来自 Al_2O_3 和 Al_2O_3 进入硅藻土大孔使大孔变小的那部分。因此可通过 Al_2O_3 的添量来调节硅藻土载体的物理性质，以满足实用要求。
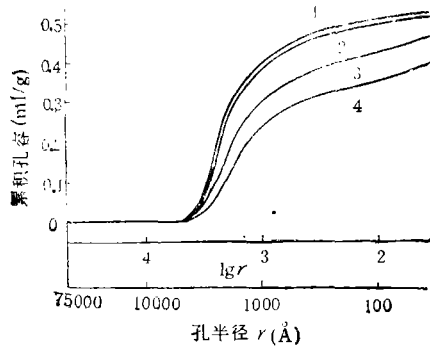

图 1 压汞曲线

1.硅藻土　2. 3% Al_2O_3 硅藻　3. 6%Al_2O_3 硅藻
土　4. 12%Al_2O_3 硅藻土

表 1 试样的基本物性

Al_2O_3 含量 (%)	焙烧温度 (℃)	压汞法（37—75000 Å）			BET 比表面 (m²/g)	吸水率 (ml/100g)	堆密度 (g/ml)	压碎强度 (kg/颗)
		总孔容 (ml/g)	比表面 (m²/g)	平均孔径 (Å)				
0		0.52	21.3	486	20	60	0.53	9*
3		0.51	20.9	410	42	59	0.55	12
6	800	0.46	20.5	403	60	54	0.60	15
12		0.39	20.2	389	70	51	0.62	1o

* 易粉碎

2.2 单组分催化剂的氧化活性

Ce、Cr、Mn 单组分催化剂（载体为 6% Al_2O_3 硅藻土）对丙酮、正丁胺、甲苯的氧化活性见表 2。反应活性以反应物转化率 >98% 的下限反应温度 T_{98} 表示，T_{98} 越低表示活性越高。

表 2 单组分催化剂的氧化活性*

催化剂	T_{98}(℃)		
	丙酮	正丁胺	甲苯
Ce	240	340	360
Cr	300	320	340
Mn	280	280	320

* 活性组分负载量 0.08mol/100g 载体.

由表 2 可见，催化剂上有机物氧化活性次序为：丙酮 > 正丁胺 > 甲苯。催化剂对有机物的氧化活性总体上为：Mn > Cr > Ce。

2.3 活性组分负载量及 Al_2O_3 添加量对催化剂活性的影响

对含氮有机物氧化催化剂的研究[1]表明，Ce-Cr 复合氧化物催化剂，Ce、Cr 在一定比例时有明显的协同催化作用，并表现出较高的氧化活性。本文选择 Ce、Cr 为活性物质，其摩尔比 Ce:Cr = 3:1，考察了 Ce-Cr 负载量及硅藻土的 Al_2O_3 添加量对氧化活性的影响，结果见表 3。由表 3 可见，催化剂氧化活性的次序为：

B = C = D > E > A

表 3 Ce-Cr 催化剂的氧化活性

编 号	催化剂		T_{98}(℃)		
	Ce、Cr 总负载量 (mol/100g)	硅藻土添加 Al_2O_3 量(%)	丙酮	正丁胺	甲苯
A	0.04	6	220	280	350
B	0.08	6	180	220	300
C	0.12	6	180	220	300
D	0.08	3	180	220	300
E	0.08	12	200	240	300

Ce、Cr 的负载量从 0.04mol/100g 增高到 0.08 mol/100g，催化剂活性明显提高，但再增加并无益处。同一负载量（0.08mol/100g）载于不

同含 Al$_2$O$_3$ 量的硅藻土上，催化剂的活性总体上 Al$_2$O$_3$ 含量低时较佳。但从机械强度等物理性质考虑，Al$_2$O$_3$ 添加量 6% 时为最佳，故本文以下均采用 Al$_2$O$_3$ 添加量 6% 的硅藻土载体。

2.4　添加 Mn、K 对 Ce-Cr 催化剂活性的影响

表 4　Mn、K 对 Ce-Cr 催化剂氧化活性的影响

催化剂*	T_{98}(℃)		
	丙酮	正丁胺	甲苯
Ce$_3$Cr$_1$Mn$_0$	180	220	300
Ce$_{67}$Cr$_{23}$Mn$_{10}$	200	220	300
Ce$_{53}$Cr$_{17}$Mn$_{30}$	180	220	280
Ce$_{30}$Cr$_{10}$Mn$_{60}$	200	220	280
Ce$_{53}$Cr$_{17}$Mn$_{30}$K$_{2.5}$	180	220	260
Ce$_{53}$Cr$_{17}$Mn$_{30}$K$_5$	180	230	280
Ce$_{53}$Cr$_{17}$Mn$_{30}$K$_{10}$	180	240	300

* Ce:Cr = 3:1 Ce、Cr、Mn 总负载量 0.08/100g K$_2$O 量按 (Ce、Cr、Mn) 总负载量的百分比计，K$_{2.5}$ 表示 K$_2$O 添加 2.5%。

鉴于氧化锰是重要的氧化还原型催化剂，是过渡金属复合氧化物催化剂的重要组成部分。氧化钾是强碱性物质，掺杂后使催化剂表面酸碱度发生变化，从而改变催化性能。表 4 是 Ce-Cr 催化剂添加 Mn、K 后的氧化性能。由表 4 可见，添 Mn 没有改变 Ce-Cr 催化剂的氧化活性，但在此基础上再添 K，随 K 量增加丙酮活性不变，正丁胺活性呈下降趋势，而少量 K 对甲苯氧化有促进作用。

2.5　控制 NO$_x$ 生成能力

对含氮有机物（如正丁胺）的氧化，氨基的氧化有两种可能，即变成 N$_2$ 或 NO$_x$，作为净化处理，保护环境的要求，希望有控制地氧化到 N$_2$，避免 NO$_x$ 的生成，以免造成二次污染。因此，正丁胺氧化过程 NO$_x$ 控制率是一个重要指标。Ce、Ce$_3$Cr$_1$、Ce$_{53}$Cr$_{17}$Mn$_{30}$、Ce$_5$Cr$_{17}$Mn$_{30}$K$_{2.5}$ 上正丁胺完全氧化时 NO$_x$ 的控制能力见表 5。可见对于含氮有机物，要求催化剂一方面有较高的氧化活性（T_{98} 低），另一方面具有高的控制 NO$_x$ 生成能力。即氧化活性温度（T_{98}）与 NO$_x$

明显生成温度（NO$_x$ 控制率 >90% 的上限温度 T_{90NO_x} 表示）之间要有较大的温度范围（ΔT），我们把 ΔT 的大小用来衡量催化剂 NO$_x$ 控制能力，ΔT 越大表示 NO$_x$ 控制能力越强。由表 5 可见，在 Ce-Cr 上添加 Mn、K 尽管对正丁胺氧化活性没有改善，但 NO$_x$ 控制能力明显提高，其中以 Ce-Cr-Mn-K 4 组分的性能最佳。

表 5　NO$_x$ 控制能力

催化剂	温度(℃)	NO$_x$ 控制率(%)*	T_{98}(℃)	T_{90NO_x}(℃)	ΔT ($T_{90NO_x}-T_{98}$)
Ce	360	90.2	340	360	20
	380	78.1			
Ce$_3$Cr$_1$	260	93.2	220	260	40
	280	83.2			
	350	56.2			
Ce$_{53}$Cr$_{17}$Mn$_{30}$	290	92.5	220	300	80
	300	90.1			
	350	68.7			
Ce$_{53}$Cr$_{17}$Mn$_{30}$K$_{2.5}$	320	92.5	220	340	120
	340	90.3			
	360	78.9			

* 产物中 NO$_x$ 以 NO$_2$ 计

$$NO_x\ 控制率 = \frac{NO_2\ 理论生成量 - 实测量}{NO_2\ 理论生成量} \times 100\%$$

上述结果可见，Ce-Cr-Mn 复合氧化物催化剂对丙酮、正丁胺、甲苯有较高的氧化活性。具有工业应用前景。当然本文仅是初步的探索，对于如何进一步提高催化剂性能及氧化机理的理论问题，还有待于进一步研究，相信硅藻土能在催化燃烧应用领域发挥更大的优势。

3　结论

（1）硅藻土的强度及比表面与 Al$_2$O$_3$ 添加量成正比，而孔容、平均孔径与 Al$_2$O$_3$ 量成反比。

（2）添加 Mn、K 对 Ce-Cr 复合氧化物的氧化活性影响不大，但对正丁胺氧化过程 NO$_x$ 控制能力有明显提高。

参　考　文　献

1　袁贤鑫等. 石油化工. 1990,12: 828
2　国家大气环境质量标准 GB3095-82
3　王祖兴等. 非金属矿. 1989,6: 9

Study on Water Quality Control Plan of Yongjiang River of Zhejiang Province.

Huang Mingrong, He Qiang, Cheng Shengtong, Jing Wenyong et al. (Institute of Environmental Engineering, Tsinghua University, Beijing 100084): *chin. J Environ. Sci.*, 14(1), 1993, pp. 2—6

Yongjiang River flows through Ningbo city, whose flourishing economy makes the river polluted worse and worse. The old industry mixes with the new, and the drainage system in the old district is imperfect. These are the common problems for the coastal cities opening to the outside world. based on the combination of the principles of concentration conttrol for degradable pollutants, and determination of water quality index system according to its real conditions and conprehensive analysis of pollution control scenari, technologies, reception capacity of pollutants of the environment and economic response of the old and new enterprices, a chart of pollution load—capital cost—environmental effect was dratted. It was concluded that Ningbo needs only to invest 190 million Yuan (58% less than the secondary treatment scheme) and remove BOD load 2.5 t/d from leading sources to keep the water quality for Yongjiang River to its 1987 level.

Key words: Yongjiang-river, pollution control, Programme.

The Effect of COD/SO_4^{2-} Ratio on the Anaerobic Digestion of Sulfate Wastewater.

Ding Qiong et al. (Department of Environmental Engineering, Tsinghua University, Beijing 100084): *Chin. J. Environ. Sci.*, 14(1), 1993, pp. 7—12

The effect of COD/SO_4^{2-} ratio on anaerobic digestion of sulfate containing high strength organic wastewater was studied with batch test method. Experimental results show that COD/SO_4^{2-} ratio is an important factor which influences the anaerobic digestion of the wastewater. In this study, when COD/SO_4^{2-} was more than 15, the reduction of sulfates hadlittle or basically no inhibition effect on the anaerobic digestion. When COD/SO_4^{2-} was between 5 to 15, the reduction of sulfates had slight inhibition effect on the anaerobic digestion and the relative methane-producing rate was 79.2% to 94.7%. When COD/SO_4^{2-} was 0.5 to 5, the inhibition effect of sulfate reduction on anaerobic digestion was moderate and the relative methane-producing rate was 61.6% to 79.2% When COD/SO_4^{2-} was below 0.5, the anaerobic digestion would be severely inhibited. Experimental results also show that when COD/SO_4^{2-} was greater than 1, a limear relationship between relative methane-producing rate and COD/SO_4^{2-} ratio existed.

Key words: sulfate reduction, COD/SO_4^{2-} ratio, anaerobic inhibitive, relative methane-producing rate.

Fractionation of TOC in Water from Yinluan Channel.

Shu Tao, Deng Baoshan et al. (Dept. of Urban & Environ. Sci., Peking University, Beijing 100871): *Chin. J. Environ. Sci.*, 14(1), 1993, pp.13—16

Organic compounds in water from Yinluan Channel was fractiona ted into five fractions of solids, hydrophobic compounds, humic substances, anions, and other dissolved hydrophillic compounds by filtration, adsorption on XAD-8 resin at different pH values, and adsorption on anion exchange resin. The total amount of DOC was found to be 4.75 mgC/L, half of which is humic substances. The fractions were characterized by UV spectrometry and over 90% of the UV absorption is attributed to the fraction of humic substances.

Key words: TOC, DOC, fractionation, humic substances; UV spectrometry.

Study on the Catalytic Activity of Ce-Cr/ Diatomite Catalysts for the Oxidation of Several Organic Compounds.

Luo Mengfei, Yuan Xianxin et al. (Dep. of Chemistry, Hangzhou University, Hangzhou 310028); *Chin. J. Environ. Sci.*, 14(1) 1993, pp. 17—19

The influence of addition of alumina on the pore volume, mean pore size and surface area of diatomite was investigated. The activity of Ce-Cr, Ce-Cr-Mn, etc. complex oxide supported catalysts

for the oxidation of acetone, butylamine and to-
luene was studied. The order of oxidation activity
was determined to be: Ce-Cr-Mn-K $\approx$ Ce-Cr-Mn $\approx$
Ce-Cr > Mn > Cr > Ce. The formation of NO_x
in the oxidative reaction of butylamine can be
retarded. The order of NO_x formation retardi-
ng ability of the catalysts was: Ce-Cr-Mn-K
> Ce-Cr-Mn > Ce-Cr > Ce.
Key words : diatomite catalyst, oxidation, alu-
mina.

The Effect of Simutating Acid Rain on the Release of Active Aluminum from Soil.

Fu Liusong, Wu Jiemin et al. (Dep
of Environ. Protection, Zhejiang Agri-Unive-
rsity, Hangzhou 310029):
*Chin. J. Environ.
Sci.*, **14**(1), 1993, pp. 20—24

The effect of simulating acid rain on the re-
lease of active aluminum from a typical acidic soil
of Zhejiang Province was investigated by dymanic
leaching experiments under laboratory conditions.
Results indicate that much of the active Al would
be released from soil if the soil is leached by acid
rain with pH value lower than 4.3 over a long pe-
riod of time: the critical acid rainfall, which
leads the guick release of active Al from soil, is
inversely proportional to the acidity of the acid
rain. Based on the relationship between the cri-
tical acid rainfall and the acidity of the acid rain,
the possible effect of natural acid rain on the relea-
se of active Al from soils can be assessed.
Key words: simulating acid rain, active Al,
Soil.

Study on the Analysis of Aldehydes in Ambient Air.

Li Xiaozhen, Bai Yuhua et
al. (Dept. of Technical Physics, Peking Uni-
versity, Beijing 100871):
*Chin. J. Environ.
Sci.*, **14**(1), 1993, pp. 25—28

Two spectrophotometric methods (MBTH me-
thod and Acetyl Acetone method) for the determi-
nation of formaldehyde (HCHO) and total alde-
hyde (TCHO) have been studied and optimized
for the analysis of the ambient air in Beijing. Re-
sults show that time and temperature of color reac-
tion are the major factors which influence obviou-
sly the completeness of the reaction. To get the
best results, experimental conditions if the reaction

time was changed from 30 min to 80 min at room
temperature for MBTH method and from 120 min
at room temperature to 5 min at 70°C for Acetyl
Acetone method. Other aldehyde is not detected
by Acetyl Acetone method, which is natually spe-
cific for Formaldehyde. Hovewer MBTH method
can be used for the determination of formaldehyde
and other aldehyde as well, and the results were ex-
pressed in the concentration of formaldehyde equi-
valents.
Key words: spectrophotometry, formaldehy-
de, aldehyde.

Granulation Technology of BOF Slough-y Dust in Wet Rotary Kiln.

He Tian-
xiang (Design and Research Institute of
Maanshan Iron and Steel Company, Maanshan
243000):
Chin. J Environ. Sci., **14**(1),
1993, pp. 29—31

Preliminary dehydration, granulation and sin-
tering of vacuum-filter dust containing 40% of wa-
ter can continuously be accomplished in wet rotary
kiln. The product from the kiln is a kind of sin-
tered briquette. This sintered briquette can be
reused in the steelmaking process as slag-forming
material. The fuel consumption of the BOF dust
recycling process is not high and economically ac-
ceptable.
Key words: BOF sloughy dust, granulation,
sintering.

Study on Electrolytic Process for the Treatment of Wastewater Containing Copper Nitrate.

Li Chunhua (Beijing Polytechnic
University, Beijing 100022):
*Chin. J. Envi-
ron. Sci.*, **14**(1), 1993, pp.32—36

This paper deals with the study on condi-
tions and principles of the recovery of
copper from copper-nitrate wastewater by
electrolysis. The change of NO_3^- before and
after electrolytic process and the approach
of raising the limit of current density were
also discussed in the paper. Results show
that, when the concentration of $NO_3^- \leqslant 1.0$
mol/L, the corresponding Cu^{2+} is in the ra-
nge of 3—8g/L, H^+ is in the range of 1.0—
1.2g/L, and the current density for the ele-
ctrolysis is in the range of 1.0—2.0 A/dm^2,