研究简报

在 Pt/Al_2O_3 催化剂上异丁醇完全氧化动力学

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摘要　在 Pt/Al_2O_3 催化剂上用外循环无梯度反应器研究了异丁醇完全氧化动力学．异丁醇完全氧化动力学方程用异丁醇及氧吸附，CO_2 吸附阻碍的 L-H 模型描述．用正交设计法求出动力学方程中的参数．用脉冲法测定了异丁醇、氧及 CO_2 的吸附热．

催化完全氧化是治理废气污染的有效方法，Pt/Al_2O_3 是净化废气较好的催化剂[1,2]．我国 Pt 资源较少，减少 Pt 用量是一个重要的问题．随着石油资源不断减少，用醇代替或部分代替汽油已提到日程上来．醇类车的开发已开过四次国际性的会议[3]，醇类车排出的醇及其部分氧化产物例如醛等的净化问题开始引起注意[3,4]．本文研究了异丁醇深度氧化的动力学，探索 Pt 常用量 1/10 作催化剂的可行性．测定了反应物及 CO_2 产物的吸附热，证实动力学模型及其参数的可靠性．另外，动力学方程是反应器设计及生产优化控制的基础．上述研究工作尚未见前人报导．

一、实验部分

（一）催化剂制备与产物分析

采用竞争吸附法制备催化剂．先用 0.1mol/l 乳酸溶液浸泡 Al_2O_3 8h，130℃ 干燥，再浸渍氯铂酸，烘干，500℃ 灼烧 2h，最后用 H_2 还原．铂含量为 0.01%．

反应产物仅含 CO_2 及 H_2O．CO_2 用邻苯二甲酸二丁酯及 β,β'-氧二丙腈固定液的色谱柱分析；CO，O_2 及 N_2 用 5A 分子筛及活性炭分析，H_2 作载气，热导检测．

（二）异丁醇完全氧化的动力学实验

由于异丁醇完全氧化是强放热反应，为使反应温度恒定，反应中加入 66.7kPa 水蒸汕，将反应热带出．改变催化剂颗粒大小及循环速度的实验证实，用 0.45—0.60mm 直径的催化剂，在本实验的条件下排除内、外扩散的影响，反应在动力学区域进行．动力学研究采用外循环无梯度反应器，其循环比约为 30，满足无梯度反应器的要求[5]．异丁醇完全氧化的动力学实验结果列入表 1，其中 $P_{异}$，P_{O_2} 及 P_{CO_2} 分别为异丁醇，O_2 及 CO_2 的分压，r_{CO_2} 为完全氧化速度，$r_{CO_2(计算)}$ 是根据（5）式计算的反应速度．

（三）异丁醇、O_2 及 CO_2 吸附热的测定

为了确定反应按 L-H 机理动力学模型进行，反应物和产物吸附热参数估计值的可靠性，我们用脉冲法测定了异丁醇、O_2 及 CO_2 的吸附热．脉冲法测定吸附热的原理如下[6]：

$$\ln Vg_i = \theta_i/RT + \Delta s_i/R \tag{1}$$

$$i = 异丁醇、O_2、CO_2$$

其中 Vg_i 为 i 物质的色谱校正比保留体积（cm^3），θ_i 及 Δs_i 为 i 物质的吸附热和吸附熵，R 为气体常数．

V_{g_i} 可从实验上求得：

$$V_{g_i} = \frac{F_{N_2}(t_i - t_{He})}{W} \qquad (2)$$

其中FN_2 为载气 N_2 的流速，t_i 为 i 物的保留时间(秒)，t_{He} 为惰性气体 He 的死时间，W 为催化剂的重量，实验中 $F_{N_2} = 20\text{ml/min}$，$W = 1.00$ 克．根据(2)式求得的 $V_{g_异}$，Vg_{O_2} 及 Vg_{CO_2} 实验值，按(1)式作图 1.2.3. 将实验值按(1)式作最小二乘法，测得异丁醇吸附热

表 1　异丁醇完全氧化动力学实验

反应温度 (℃)	P_{O_2} (kPa)	$P_异$ (kPa)	P_{CO_2} (kPa)	r_{CO_2} $\left(\frac{10^3\text{mol}}{\text{ml}\cdot\text{h}}\right)$	$r_{CO_2(计算)}$ $\left(\frac{10^3\text{mol}}{\text{ml}\cdot\text{h}}\right)$	反应温度 (℃)	P_{O_2} (kPa)	$P_异$ (kPa)	P_{CO_2} (kPa)	r_{CO_2} $\left(\frac{10^3\text{mol}}{\text{ml}\cdot\text{h}}\right)$	$r_{CO_2(计算)}$ $\left(\frac{10^3\text{mol}}{\text{ml}\cdot\text{h}}\right)$
	11.7	1.67	2.34	30.3	29.8		4.19	3.93	0.530	7.00	6.78
	11.6	2.03	2.05	27.1	27.1		5.80	3.90	0.653	8.64	9.38
	11.1	2.50	1.78	23.5	23.3		7.48	4.07	0.827	10.9	11.6
	11.4	3.06	1.63	21.6	21.1		8.98	4.04	0.973	12.9	13.9
320	11.1	3.63	1.39	18.1	18.3	320	10.1	4.21	1.07	14.2	15.5
	10.9	4.38	1.19	15.7	15.7		11.9	4.14	1.35	17.8	17.8
	11.3	5.02	1.07	14.1	14.7		13.3	4.31	1.47	19.4	19.2
	11.0	6.84	1.12	14.8	11.1		14.8	4.24	1.74	23.0	21.4
	4.12	3.93	0.527	6.96	6.67		17.6	4.50	1.57	20.8	24.3
							19.2	4.38	2.02	26.8	26.7
	11.0	2.06	1.93	29.3	30.9		7.08	4.07	0.829	12.6	13.5
	10.8	2.49	1.80	27.3	27.5		8.93	4.00	1.12	17.0	17.1
	11.2	3.09	1.51	22.9	25.2		10.4	4.14	1.33	20.2	19.2
	10.6	3.61	1.44	21.8	21.6		11.6	4.11	1.47	22.3	21.5
340	11.0	4.36	1.28	19.3	19.6	340	13.1	4.26	1.67	25.2	23.4
	10.1	5.00	1.15	17.5	16.3		14.1	4.26	1.68	25.4	25.2
	10.3	8.91	0.972	14.7	10.3		17.0	4.38	2.04	30.9	29.3
	3.99	3.95	0.466	7.06	7.90		18.5	4.25	2.56	38.8	32.2
	4.71	3.91	0.639	9.68	9.34						
	11.7	1.54	1.67	44.7	43.6		5.94	3.95	0.455	12.2	14.1
	11.1	4.49	0.741	19.9	23.5		12.4	4.27	0.849	22.8	27.1
360	11.2	5.11	0.734	19.7	21.6	360	14.2	4.45	0.930	24.9	30.0
	11.1	6.96	0.661	17.7	16.8		15.6	4.40	1.13	30.3	33.0
	10.3	9.03	0.515	13.8	12.6		16.5	4.59	1.19	31.9	33.8
	4.43	3.96	0.413	11.1	10.5		18.5	4.57	1.28	34.2	37.8
	11.3	1.38	2.30	47.7	48.7		4.45	3.95	0.466	12.0	12.5
	11.1	1.81	1.71	44.0	44.9		5.94	3.93	0.552	14.2	16.7
	11.5	2.12	1.71	45.0	43.7		7.41	4.11	0.684	17.6	20.1
	11.2	2.56	1.53	39.2	39.1		8.97	4.08	0.789	20.3	24.3
380	11.8	3.12	1.39	35.6	37.1	380	10.7	4.23	1.01	25.9	28.0
	11.4	3.66	1.22	31.4	32.7		11.6	4.21	1.08	27.8	30.4
	11.1	4.41	1.09	27.9	28.2		12.8	4.38	1.29	33.2	32.5
	10.4	5.02	1.07	27.6	24.2		14.5	4.30	1.50	38.5	37.0
	9.93	6.90	0.892	22.9	18.2		15.4	4.51	1.53	39.2	38.0
							18.7	4.41	1.90	48.9	46.2
	10.2	1.01	1.68	50.5	51.9		4.98	3.93	0.537	16.1	16.3
400	11.4	1.72	2.07	62.0	52.5	400	7.44	4.09	0.733	22.0	23.6

续表 1

反应温度 (℃)	P_{O_2} (kPa)	$P_异$ (kPa)	P_{CO_2} (kPa)	r_{CO_2} $\left(\frac{10^3 mol}{ml \cdot h}\right)$	$r_{CO_2(计算)}$ $\left(\frac{10^3 mol}{ml \cdot h}\right)$	反应温度 (℃)	P_{O_2} (kPa)	$P_异$ (kPa)	P_{CO_2} (kPa)	r_{CO_2} $\left(\frac{10^3 mol}{ml \cdot h}\right)$	$r_{CO_2(计算)}$ $\left(\frac{10^3 mol}{ml \cdot h}\right)$
	11.9	2.06	1.94	58.2	51.7		8.49	4.05	0.891	26.7	27.0
	11.5	2.50	1.79	53.4	46.4		9.96	4.21	1.06	31.8	30.7
400	11.4	3.06	1.64	48.9	41.8	400	11.7	4.18	1.18	35.4	36.0
	9.82	3.63	1.36	40.8	33.0		12.6	4.38	1.19	35.8	37.5
	9.99	4.36	1.29	38.6	30.0		14.1	4.30	1.51	45.2	42.2
	10.8	5.01	1.12	33.4	29.6		15.7	3.89	1.58	47.4	49.6

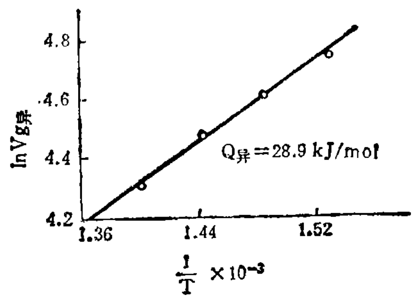

图 1　$\ln Vg_异$与$1/T$ 的关系

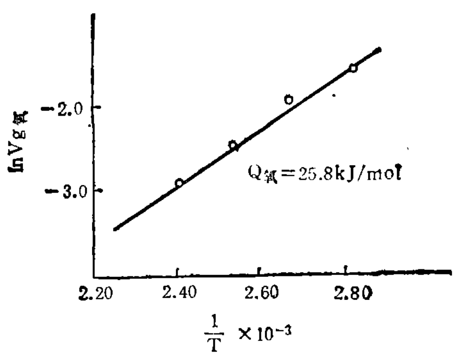

图 2　$\ln Vg_{O_2}$ 与$1/T$ 的关系

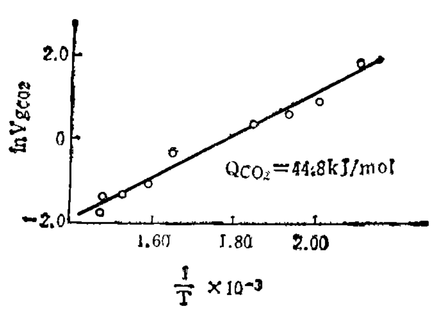

图 3　$\ln Vg_{CO_2}$ 与$1/T$ 的关系

$\theta_异 = 28.9$kJ/mol，氧吸附热 $\theta_{O_2} = 25.8$kJ/mol，CO_2 吸附热 $\theta_{CO_2} = 44.8$kJ/mol。

二、实验结果的讨论

改变催化剂颗粒大小及循环速度证实，0.45—0.60mm 催化剂在本实验条件下排除了内、外扩散的影响。由吸附热实验可知反应可用异丁醇及 O_2 吸附，CO_2 吸附阻碍的 L-H 动力学模型描述。若吸附服从 Langmuir 等温吸附式，则动力学方程为

$$r_{CO_2} = \frac{k b_异 b_{O_2} P_异 P_{O_2}}{(1 + b_异 P_异 + b_{O_2} P_{O_2} + b_{CO_2} P_{CO_2})^2} \quad (3)$$

其中 k 为反应速度常数；$b_异$，b_{O_2} 及 b_{CO_2} 分别为异丁醇、O_2 及 CO_2 的吸附系数。根据 k 与温度的 Arrhenius 方程，$b_异$、b_{O_2} 及 b_{CO_2} 与温度的 Clausius-Clapeyron 方程，由 (3) 式可得

$$r_{CO_2} = (k_0 e^{-E/RT} b_{0异} e^{\theta_异/RT} b_{0_{O_2}} e^{\theta_{O_2}/RT} P_异 P_{O_2}) / (1 + b_{0异} e^{\theta_异/RT} P_异 + b_{0_{O_2}} e^{\theta_{O_2}/RT} P_{O_2} + b_{0_{CO_2}} e^{\theta_{CO_2}/RT} P_{CO_2})^2 \quad (4)$$

其中 E 为反应活化能；k_0 为 Arrhenius 方程的幂前因子；$b_{0异}$、$b_{0_{O_2}}$、$b_{0_{CO_2}}$ 为相应的 Clausius-Clapeyron 方程的幂前因子。(4)式为 8 个参数非线性方程，用一般的线性或非线性最小二乘法，因法方程组的病态[7]，难于求出动力学方程中的参数。我们用正交设计法求上述复杂动力学方程中的参数[8]。我们选用 $L_{49}(7^8)$正交设计表[9]，对 8 个参数，7 个水平进行参数选优，最后求得的参数值如下：

$k_O = 1.66 \times 10^4 (mol/ml \cdot h)$, $E = 35.7kJ/mol$, $b_{O_{异}} = 1.38 \times 10^{-2} (kPa^{-1})$, $\theta_{异} = 25.0kJ/mol$, $b_{O_{O_2}} = 1.00 \times 10^{-4} (kPa^{-1})$, $\theta_{O_2} = 24.7 kJ/mol$, $b_{O_{CO_2}} = 1.34 \times 10^{-5} (kPa^{-1})$, $\theta_{CO_2} = 43.8kJ/mol$. 将上述参数值代入(4)式可得

$$r_{CO_2} = (1.66 \times 10^4 e^{-35700/RT} \times 1.38 \times 10^{-2} e^{25000/RT} \times 1.00 \times 10^{-4} e^{24700/RT} \times P_{异} P_{O_2}) / (1 + 1.38 \times 10^{-2} e^{25000/RT} P_{异} + 1.00 \times 10^{-4} e^{24700/RT} P_{O_2} + 1.34 \times 10^{-5} e^{43800/RT} P_{CO_2})^2 \tag{5}$$

将表 1 中 83 组实验值按(5)得出$r_{CO_2(计算)}$值列表1. 83组 r_{CO_2}与$r_{CO_2(计算)}$的相对误差平均值为 7.52%，说明(5)式较好地符合实验结果. 另外，用脉冲法测得异丁醇、O_2及CO_2吸附热分别为 28.9kJ/mol, 25.8kJ/mol, 44.8kJ/mol, 与用正交设计法估计值 25.0kJ/mol, 24.7kJ/mol, 43.8kJ/mol 是一致的. 异丁醇完全氧化动力学研究工作尚未见文献报道. (5) 式完全氧化复杂反应动力学方程在环保催化动力学方程中也是不多见的.

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臭氧对倒挂金钟和蚕豆呼吸作用的影响

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摘要　在较低浓度臭氧作用下，植物的呼吸受到刺激，在一定时间内，这种影响不易消除；在高浓度臭氧作用下，植物的呼吸受到抑制，在一定时间内保持相对稳定，以后逐渐恢复. 分析讨论了臭氧影响植物呼吸变化的机理.

有关臭氧(O_3)对植物呼吸作用影响的研究早在 50 年代就开始了. 最早 Erikson 和 Wedding (1956) 研究了臭氧-己烯对柠檬叶片光合作用和呼吸作用的影响. 同年 Todd 重复了这一实验. 两年后他又采用红外气体分析仪测量了被 O_3 化己烯处理的斑豆叶和柑桔叶对 CO_2 的吸收[1]. 此后，Macdowall (1965) 专题研究了 O_3 对烟草叶呼吸作用的影响，特别观察了线粒体呼吸作用的变化及其变化机理[2]. Pell 和 Brennan (1973) 讨论了受 O_3 伤害的斑豆叶呼吸、光合、三磷酸腺苷等的关系[3]. 近些年来，还有人研究 O_3 对菜豆根呼吸的影响，以及 O_3 对杂交杨叶片暗呼吸的影响等. 但这些研究结果很不一致. 都没有对 O_3 影响呼吸能否恢复等问题作出回答，然而这些问题对防护 O_3 伤害植物和研究 O_3 伤害机理都有参考价值，有必要继续深入研究.

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Abstracts

Research on Catalytic Oxidation of Organic Vapors by Unheated Stream. Liu Qicai et al. (Department of Environmental Engineering, Tsinghua University, Beijing): *Chin. J. Environ. Sci.*, **11**(2), 1990, pp. 2

This paper focuses on the process and mechanism of catalytic oxidation of xylene vapor by unheated stream. The results demonstrate that the process of catalytic oxidation by unheated stream is possible, and the reaction may be maintained by reaction heat without auxiliary heat required at the xylene concentration of 16.71 g/m^3 and the volumetric velocity of 7083 h^{-1}. The main factor affecting the catalytic oxidation is the temperature of catalyst bed, and the reaction can be realized at a low temperature (about 513k) of inlet stream containing orgainc vapor by the concentration of 1—16.71 g/m^3. Comparing with the process by heated inlet stream, the catalytic oxidation process by unheated stream is characterized by relatively lower temperature of catalyst bed and the outlet stream, less time and less power required for starting the system, and easily controlling the temperature of the catalyst bed.

The Effect of Indoor Heating with a Coal Range on 1-Hydroxypyrene in Urihe. Zhao Zhenhua, Quan Wenyi, Tian Dehai (Beijing Municipal Research Institute of Environmental Protection): *Chin. J. Environ. Sci.*, **11**(2), 1990, pp. 8

The changes of 1-hydroxypyrene in urine of the same households have been observed in the periods of heating with coal ranges or central heating or non-heating. The urinary 1-hydroxypyrene of several groups of people has been detected as an index. The results of statistic analysis shown that its level in the persons of indoor heating with coal ranges is higher than that of central heating or that in non-heating period. So the results demonstrate that indoor air pollution of polynuclear aromatic hydrocarbons(PAHs) is serious in the households with burning coal. It is suggested that urinary 1-hydroxypyrene can be used as a specific sensitive index for human exposure to genotoxic PAHs from burning coal.

Carbon Reserves in the Sea Area of the Zhujiang River Estuary. Han Wuying, Cai Yanya, Rong Ronggui (South China Sea Institute of Oceanology, Academia Sinica, Guanzhou): *Chin. J. Environ. Sci.*, **11**(2), 1990. pp. 12

The amount of carbon in the sea region of the Zhujiang River Estuary has been calculated with the practically surveyed data, of which are divided into four carbon reseves: hydrosphere, nonliving particle, biosphere and sediment. The carbon amount of each reserve is as follows: hydrosphere reserve is about 300×10^6 kg; nonliving particle about 11×10^6 kg; biosphere reserve about 3×10^6 kg and sediment one about 698×10^6 kg. In the paper, some problems on distribution of different speciation of carbon in the region have also been discussed.

Effects of Refuse Compost from Urban Sources on Wheat-Growth and Soil. Zhang Yanyi, Guo Dehui, Fang Ting (Hubei University, Wuhan), Fan Man (Wuhan Institute of Environmental Hygiene): *Chin. J. Environ. Sci.*, **11**(2), 1990, pp. 17

Urban refuse composts utilized as fertilizer has been studied on growth of wheat and soil by using pot-cultivated experiments. The results show that organic matter in soil increased, soil acidity and viscidity decreased, and growth of wheat was significantly promoted. However, the content of some heavy metals increased slightly in wheat grains.

The Linear Graphic Method for Determining Longitudinal Dispersive Coefficient of the Streams by Tracer Test. Guo Jianqing, Wen Ji (Institute of Farmland Irrigation, Ministry of Water Conservancy): *Chin. J. Environ. Sci.*, **11**(2), 1990, pp. 24

The aim of this work is to decribe that linear graphic method or linear repression method can be used to calculate longitudinal dispersive coefficient of flows in a river and its main current velocity.

The Kinetics of Complete Oxidation of Iso-Butyl Alcohol on Pt/Al_2O_3 Catalyst. Yu Qiquan, Jin Yun, Yang Zechang (Department of Chemistry, Peking University, Beijing): *Chin. J. Environ. Sci.*, **11**(2), 1990, pp. 28

The kinetics of complete oxidation of iso-butyl alcohol on Pt/Al_2O_3 catalyst has been investigated by the external recirculation gradientless reactor. It is described by the L-H model of adsorption of iso-butyl alcohol and oxygen with inhibition of carbon dioxide. The parameters of the kinetics equation are estimated by the method of orthogonal design. The adsorption heat of iso-butyl alcohol, oxygen and carbon dioxide have been determined by the pulse method.

The Effects of Ozone on Respiration of the Plants *Fuchsia hybrida* Voss. and *Vicia faba* L.