Ru/Al_2O_3 催化剂对 CO_2 加氢转化的研究*

赵瑞兰　彭美生　马玉梅　张凤武

（中国科学院生态环境研究中心，北京　100085）

摘要　给出了在 Ru/Al_2O_3 催化剂上采用不同的反应条件对 CO_2 转化率及 CH_4 生成率的影响。反应温度低于 350℃时，CO_2 的转化率大于 95%，CH_4 的生成率约为 45%—79%。空速的改变对 CO_2 的转化率及水的生成率无显著影响，即空速在 5000—10000 h^{-1}内波动不大。但对 CH_4 的生成率影响明显，在 7000—9000 h^{-1}间有一波谷；CO 的生成量在 5000—9000 h^{-1}变化不大，在 10000 h^{-1}有较大增加。富 H_2 时，对 CO_2 转化生成 CH_4 有利，最佳生成率可达 98%。

关键词　CO_2，催化剂，催化加氢，甲烷。

采用催化加氢方法转化 CO_2，为 CO_2 的利用提供了途径[1,2]。Gupta 等[3]报道了 γ-射线作用下 Ru 催化剂对 CO_2 转化的催化活性，Darid[4]研究了不同制备条件的 Ru 催化剂对 CO 的转化性能。以 CO_2 为原料合成天然气是开发新能源的途径之一。从长远观点看，从燃烧尾气中回收 CO_2 转化为 CH_4 具有重要意义。国内 Ru/Al_2O_3 催化剂应用于 CO_2 催化加氢转化为 CH_4 的研究鲜见报道。本文研究了 Ru/Al_2O_3 催化剂在不同反应条件下对 CO_2 转化性能。

1　实验

1.1　催化剂制备

采用常规的浸渍法。载体为活性 γ-Al_2O_3（浙江温州氧化铝厂），粒径 2—3 mm，活性组分钌。称取一定量的钌盐（$RuCl_3 \cdot 3H_2O$，上海依粒厂）溶解在去离子水里。将干燥过的 γ-Al_2O_3 浸没在 Ru 盐溶液中，室温下放置 24 h 后烘烤，同时不断搅拌直至小球能自由滚动再放入烘箱中，110℃干燥，冷却后放入干燥器。该催化剂使用前需在 H_2 气氛下 400—550℃恒温 4 h 进行还原。

1.2　催化剂性能评价

催化剂用量 3.6 ml，为了便于控制反应床的温度混入了 3.6 ml 的 Al_2O_3 小球，反应在常压下进行。反应装置流程如图 1。

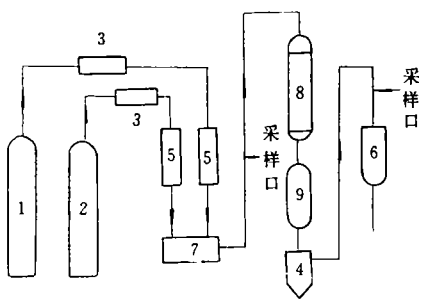

图 1　CO_2 催化加氢反应装置流程图

1、2. CO_2，H_2 气源　3. 净化管　4. 气、水分离器　5、6. 流量计　7. 混合器　8. 反应器　9. 冷却管

1.3　分析

反应产物 CH_4，CO 及反应前后的 CO_2 用 SP-2307 气相色谱仪（北京分析仪器厂），经催化转化后用 FID 测定。分离柱为填有上试 601 碳分子筛的不锈钢柱；反应前后的 H_2 用 104 气相色谱仪（上海分析仪器厂）TCD 测定，分离柱为填有 601 碳分子筛的聚四氟乙烯柱。

2　结果与讨论

2.1　起动温度

表 1 给出了不同空速下 Ru 催化剂的起动

* 863 高技术项目
收稿日期：1995-07-15

温度。表1表明，随着空速的增大，起动温度降低。空速为1200 h^{-1}时85℃就可以起动，在该温度下，向反应床通入CO_2、H_2后9 s钟就有水产生。

表1 不同空速下催化剂的起动温度

空速 (h^{-1})	进气量 (ml)	炉温 (℃)	反应床温 (℃)	起动温度 (℃)	起动时间[1] (s)
5000	300	300	200	200	27
7000	420	300	180	180	
10000	600	300	105	105	12
12000	720	100	85	85	9

1) 通入CO_2、H_2气后至产生水所需时间

2.2 反应温度对CO_2转化率和CH_4生成率的影响

图2给出了反应气CO_2：H_2为1：4时，3种不同空速条件下CO_2的转化率和CH_4生成率。图2表明，随着反应温度的升高，CO_2的转化率下降。3种空速的变化趋势大致相同。空速7000 h^{-1}时，CO_2的转化率高于其它2种空速。CH_4的生成率随温度变化趋势与CO_2转化率不大相同，空速为5000 h^{-1}和10000 h^{-1}时在460℃附近均有一峰值。CH_4的生成率(按尾气中CH_4的生成量和进气中CO_2量计算而得)在上述条件下为45%—79%。

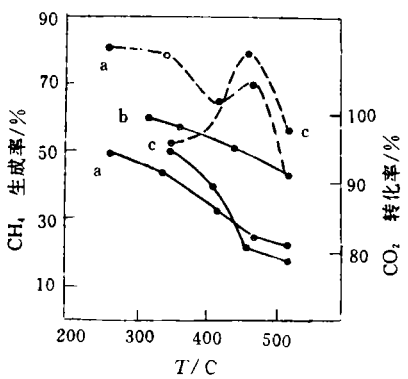

图2 反应温度对CO_2转化率，CH_4生成率的影响

a. 5000 h^{-1} b. 7000 h^{-1} c. 10000 h^{-1}

实线为CO_2转化率，虚线为CH_4生成率

表2给出了在以上试验条件下，生成的CO在尾气中的浓度。从表2可以看出随着反应温度的升高、空速的增大，CO的生成量增大。

表2 不同温度下CO_2转化中CO的生成量

空速 (h^{-1})	进气 总量 (ml)	进气 CO_2含量 (%)	反应温度 (℃)	排气(干) 总量 (ml)	排气(干) CO含量 ($\times10^{-6}$)
5000	300	20.6	260	70	50
	300	20.6	340	74	100
	300	20.3	420	88	1400
	300	20.3	470	110	5600
	300	20.1	520	137	6700
7000	420	20.0	315	95	80
	420	19.4	360	101	100
	420	19.3	440	130	900
	420	19.7	520	184	8000
10000	600	21.3	350	169	160
	600	21.0	410	198	1600
	600	20.6	460	238	2080
	600	19.9	520	303	25000
	684	15.2	520	384	14000

2.3 空速对CO_2转化率和CH_4生成率的影响

图3给出了相同的CO_2和H_2比(1：4)、相同的反应温度(360℃)在不同的空速下CO_2的转化率，H_2O、CH_4的生成率及尾气中CO含量的4条曲线。从图3可以看出，当CO_2：H_2和反应温度不变时CO_2的转化率，H_2O的生成率随空速的变化不明显(<10%)。但甲烷的生成率与空速变化关系密切。自5000 h^{-1}至10000 h^{-1}形成一波谷，在7000 h^{-1}处有一最低值。在该试验条件下，得到的CO曲线表明空速为5000—9000 h^{-1}之间，CO的生成量基本相同，

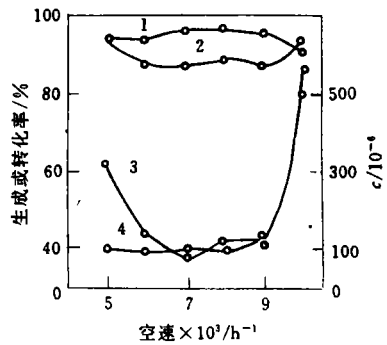

图3 空速对CO_2的转化率、CH_4、H_2O的生成率及CO生成量的影响

1. CO_2转化率 2. H_2O生成率

3. CH_4生成率 4. 尾气中CO含量

只在 10000 h^{-1}时有较大增加。经色谱(PID)测定，尾气中除 CO_2、CO、CH_4 还出现了 4 个不同的色谱峰。David[5]的工作报道了 Ru 催化剂对 CO 加氢反应时有多碳化物生成，这与笔者的测定是吻合的。

2.4 进气 CO_2 ∶ H_2 值对 CO_2 的影响

CO_2 加氢反应：

$$CO_2 + 4H_2 \xrightarrow{Ru/Al_2O_3} CH_4 + 2H_2O + 180\ kJ\uparrow$$

1 mol 的 CO_2 完全反应需 4 mol 的 H_2。图 4 给出了 CO_2 ∶ H_2=1 ∶ 5、1 ∶ 4、1 ∶ 1.8 时 CO_2 的转化率和 CH_4 的生成率。从图 4 可以看出，随 CO_2 ∶ H_2 值降低，CO_2 转化率、CH_4 生成率均降低。尤其缺 H_2 条件下更为明显。富 H_2 条件下反应温度在 280—340℃范围内，CH_4 的生成率与 CO_2 转化率相近。此时可获得 CO_2 催化加氢转化为 CH_4 的最佳产率。

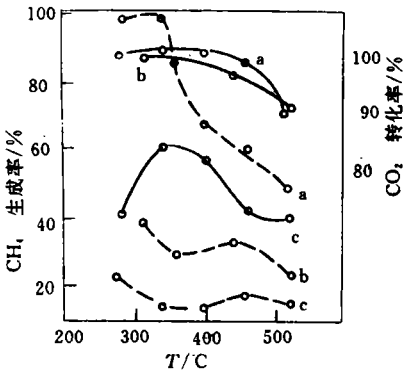

图 4　不同的 CO_2 ∶ H_2 值对 CO_2 转化率及 CH_4 生成率的影响

a. CO_2 ∶ H_2=1 ∶ 5　b. CO_2 ∶ H_2=1 ∶ 4　c. CO_2 ∶ H_2=1 ∶ 1.8

实线为 CO_2 转化率，虚线为 CH_4 生产率

3 结论

(1) 采用 Ru/Al_2O_3 催化剂对 CO_2 进行加氢转化，可以有效地将其转化为 CH_4 和 CO。

(2) 从 CH_4 的生成率考虑，反应温度选择 450—470℃，空速选择 10000 h^{-1}可获得满意的产率。

(3) CO_2 催化加氢反应为放热反应，在高空速下不但催化剂的起动温度低，而且反应过程中能源消耗少，并能获得较高 CH_4 产量。因此选择较高空速(试验值为 10000 h^{-1})为好。

致谢　胡克源研究员对改进 Ru/Al_2O_3 催化剂的性能提供了指导性建议，特此表示谢意。

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将土壤各相态汞含量以及土壤中总汞含量，大气气温值，对土壤挥发性汞释放通量的对数值进行多元逐步回归分析，得出回归方程如下：

$$\ln y = 52.096 + 0.500\ln C - 14632.356/T \quad (4)$$

复相关系数：R=0.8792

式中，C：土壤中汞的总含量；y：通量回归值；T：大气绝对温度(单位为 K)。

从回归方程可以看出，土壤挥发性汞释放通量只与土壤总汞含量相关，而与土壤中单一相态的汞不相关。

致谢　在本文写作中得到谢鸿森教授、洪业汤教授和余志成教授的指导，谨致谢意。

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Study on the Catalytically Hydrogenated Conversion of CO_2 Using Ru/Al_2O_3 Catalyst. Zhao Ruilan et al. (Research Center for Eco-Environmental Sciences, Academy of Sciences, Beijing 100085): *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 23—25

In this paper the catalytically hydrogenated conversion of CO_2 was studied using Ru/Al_2O_3 catalyst, the influence of different reaction conditions, such as reaction temperature (260—520℃, 5000—10000 h^{-1}) and CO_2/H_2 ratio in inlet gas, on CO_2 conversion efficiency and CH_4 formation were reported. At reaction temperature higher than 350℃ the CO_2 conversion efficiency was over 95%. and CH_4 formation rate was about 45%—79%. There was no significant influence on CO_2 conversion efficiency and H_2O formation when the space velocity from 5000 h^{-1} to 10000 h^{-1}. However, for the CH_4 formation efficiency there was a trough at the space velocity of 7000—9000 h^{-1}. The CO formation changed a little at space velocity of 5000—9000 h^{-1}, but it increased a lot at 10000 h^{-1}. The higher CH_4 formation efficiency was obtained when there existed excess of H_2. The highest CH_4 formation efficiency obtained was 98%.

Key words: carbon dioxide, catalyst, catalytically hydrogenated, methane.

Monitoring on The Concentration of Atmospheric Methane of A Rice Cropping Region in Beijing Area. Cui Ping et al. (Chinese Research Academy of Environmental Sciences, Beijing 100012): *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 26—28

Monitoring on methane concentration in the atmosphere in the rice cropping region was carried out between Oct. 1991 and Nov. 1993. Results indicated that the average concentration of methane of the two testing years in the local region were 1.16 and 1.17 μg/L respectively. The variation of methane concentrations showed a strong seasonal pattern. The concentration and concentration deviation were high in summer and low in winter. During rice vegetation period, the methane concentrations were closely related with the variation of methane emission rates from rice paddies indicating rice paddies is one of the most important methane sources of the region. Running analysis showed that the average increasing rate of atmospheric methane in the region was 0.2%, much lower than some previous reports.

Key words: methane, rice, monitoring, Beijing area.

A simulation Study on the Accumulation of Added Rare Earth Elements in Aquatic Ecosystem. Chen Zhaoxi et al. (Dept. of Chem. Eng., East China Institute of Metallurgy, Maanshan 243002): *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 29—31

The accumulation and distribution coefficients of added rare earth elements (RE) in various parts of simulated aquatic ecosystem were investigated. The results showed that concentrations of added RE in bottom mud and water bodies varied smoothly and in *Lemna minor* and *Cyprinus carpio* varied extremely with the time in the period of experiment. Distribution coefficients of added RE in bottom mud were higher than 96%, in *Lemna minnor*, were range of 0.26—1.61%, in water, were range of 0.54%—0.91%; and in carp were less than 0.035%, but almost on linear increment in the period of experiment. Bioconcentration of added RE in carp was also discussed.

Key words: aquatic ecosystem, accumulation, rare earth elements, bioconcentation.

The Quantum Chemistry Studies of the biradical Mechanism of Destroying Ozone in the Atmosphere. Sun Huabin et al. (Institute of Military Medicine, Jinan Command, Jinan 250014): *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 32—34

The reaction mechanisms of the singlet biradicals NH, CH_2, CCl_2 with ozone in the atmosphere have been studied using RHF method of quantum chemistry. The geometries of the reactants, intermediates and products of the above reactions are optimized with the gradient technique at the 3-21G level, their energies have been calculated at the 6-31G or 6-21G level. The structure data of all species have been obtained. The calculated results show that there are two stages in the above reactions, the reactions of the biradicals with ozone take place first to form the stable intermediates, then the intermediates are decomposed by illuminating to the stable molecules HNO, H_2CO and Cl_2CO etc., respectively. In terms of dynamics two reactions in two stages belong to the types $[\pi_{4s}+W_{2s}]$ and $[\pi_{2s}+\pi_{2s}]$, respectively, and they are permited thermodynamically. In this study, a method to investigate complicated reaction based on the combining thermodynamics with Woodward-Hoffmann approach without calculation of transition state was attempted to provide by authors.

Key words: biradical, loss of ozone, reaction mechanism.

The Structure and Toxicity Relationship Study for Nitroaromatics to *Scenedesmus obliquus*. Lu Guanghua et al. (Dept. of Environ. Sci., Northeast Normal Univ., Changchun 130024): *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 35—36

E_{LUMO}, E_{HOMO}, $\Delta(\Delta H_f)$, μ and $Q_{\cdot NO_2}$ of 18 nitroaromatic compounds were calculated using the quantum chemical method MNDO. The quantitative structure-activity relationships (QSAR) were developed using the five quantum chemical descriptors for the acute toxicity of nitroaromatics to *Scenedesmus obliquus*. Through step-wise regression analysis, one best equation contained three variables was obtained: $-\log EC_{50}=2.92-0.077\Delta(\Delta H_f)+0.08\mu+0.28E_{HOMO}$, $n=18$, $r=0.961$, $S=0.173$. The equaiton was used to estimate the toxicity of the studied compounds, and the toxic effect was discussed.

Key words: structure, toxicity, nitroaromatics, *Scenedesmus obliquus*.

Effects of Rare-Earth Elements on Growth and Reproduction of *Chlorella pyrenoides*. Hu Qinhai et al. (Dept. of Environ. Sci., Zhejiang Agricultural University, Hangzhou 310029): *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 37—38

It was studied that effects of rare-earth elements (La, Ce, Pr, Nd and their mixture) on growth and reproduction of *Chlorella pyrenoides*. The results showed that effects of rare-earth elements on growth and reproduction of *Chlorella pyrenoides* were not apparent under lower concentration (2 mg/L), but it was inhibited as the concen-