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Rh/SiO_2 催化剂上甲烷部分氧化制合成气的反应机理

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摘要 采用原位 Raman 光谱技术, 在原料气中的 O2 未完全耗尽的条件下, 对 CH4 部分氧化制合成气反应的 Rh/SiO2 催化剂床层前部贵金属物种的化学态以及由 CH4 解离所生成的碳物种进行了表征. 在此基础上采用脉冲反应和同位素示踪技术, 比较了 CH4 的部分氧化及其与 H2O 和 CO2 的重整等反应对催化剂床层氧化区内 CO 和 H2 生成的相对贡献, 并将实验结果与 Raman 光谱表征结果进行了关联. 结果表明, 在 600 ° C 下将还原后的 4% Rh/SiO2 催化剂切入 CH4:O2:Ar = 2:1:45 原料气, 催化剂床层前部未检测到铑氧化物的 Raman 谱峰, 但可清晰检测到源于 CH4 解离的碳物种; 在 700 ° C 和接触时间小于 1 ms 的条件下, 催化剂床层的氧化区内已有大量 CO 和 H2 生成, 在相同的实验条件下, CH4 与 H2O 或 CO2 重整反应对氧化区内合成气生成的贡献则很小; 以 CH4:16O2:H218O:He = 2:1:2:95 为原料气的同位素示踪实验结果表明, 在原料气中 16O2 未完全耗尽的情况下, 反应产物中 C16O 的含量占 CO 生成总量的 92.3%, 表明 CO 主要来自 CH4 的部分氧化反应. 上述结果均表明, 在 O2 存在下 Rh/SiO2 催化剂上 CO 和 H2 可以通过 CH4 直接解离和部分氧化机理生成.

关键词: 铑 甲烷部分氧化 合成气 脉冲反应 原位拉曼光谱 同位素示踪

Abstract: The partial oxidation of methane (POM) for the production of synthesis gas over Rh/SiO_2 catalyst was investigated by in situ Raman spectroscopy characterization, continuous flowing and pulse reaction evaluation focusing on the reaction mechanism of synthesis gas formation in the oxidation zone, i.e., the catalyst zone where O_2 is still available in gas phase. It was found that when a flow of $CH_4:O_2:Ar = 2:1:45$ at 600 ° C was passed through the pre-reduced 4% Rh/SiO_2 catalyst, no bands associated with rhodium oxide could be detected on the catalyst by Raman spectroscopy. While Raman bands related to carbon species that originated from methane dissociation could be detected at the catalyst oxidation zone under working conditions. The results of pulse reaction of POM as well as steam reforming and CO_2 reforming of methane at 700 ° C with a contact time less than 1 ms over the catalyst indicate that the formation of CO and H_2 is mainly resulted from the direct partial oxidation of CH_4 while the steam reforming and CO_2 reforming reactions play only a minor role in the oxidation zone of the catalyst bed. The pulse reaction with an isotopic gas mixture of $CH_4:{}^{16}O_2:H_2{}^{18}O:He = 2:1:2:95$ over the Rh/SiO_2 catalyst further indicated that the $C^{16}O$ percentage was higher than 92% of the total CO produced in the reaction. Based on these results, the conclusion, that the major reaction responsible for synthesis gas formation in the oxidation zone of Rh/SiO_2 catalyst bed is the pyrolysis of methane on reduced rhodium sites to form hydrogen and carbon adspecies followed by the coupling of two surface hydrogen atoms to H_2 and partial oxidation of surface carbon species to CO, is suggested.

Keywords: rhodium, partial oxidation of methane, synthesis gas, pulse reaction, in situ Raman spectroscopy, isotope tracing

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[1] Rostrup-Nielsen J R. Catal Toady, 1993, 18: 305

[2] Ashcroft A T, Vheetham A K, Green M L H, Vernon P D F. Natute, 1991, 352: 225

[3] Hickman D A, Schmidt L D. Science, 1993, 259: 343

[4] York A P E, Xiao T C, Green M L H. Top Catal, 2003, 22: 345

[5] 陈永东, 陈耀强, 梅大江, 张丽娟, 董文萍, 曹红岩, 陈宏, 龚茂初. 催化学报 (Chen Y D, Chen Y Q, Mei D J, Zhang L J, Dong W P, Cao H Y, Chen H, Gong M Ch. Chin J Catal), 2008, 29: 477

[6] 鲁辉, 佟建华, 楚文玲, 杨维慎, 林励吾. 催化学报 (Lu H, Tong J H, Chu W L, Yang W Sh, Lin L W. Chin J Catal), 2005, 26: 683

[7] Prettre M, Eichner C, Perrin M. Trans Faraday Soc, 1946, 42: 335

[8] Hickman D A, Schmidt L D. J Catal, 1992, 138: 267

[9] Hu Y H, Ruckenstein E. Adv Catal, 2004, 48: 297

[10] Ji H, Feng D, He Y. J Nat Gas Chem, 2010, 19: 575

[11] Lodeng R, Bjorgum E, Enger B C, Eilertsen J L, Holmen A, Krogh B, Boe I A, Ronnekleiv M, Rytter E. Top Catal, 2011, 54: 873

[12] Dissanayake D, Rosynek M P, Kharas K C C, Lunsford J H. J Catal, 1991, 132: 117

[13] Buyevskaya O V, Wolf D, Baerns M. Catal Lett, 1994, 29: 249

[14] Mallens E P J, Hoebink J H B J, Marin G B. J Catal, 1997, 167: 43

[15] Hofstad K H, Hoebink J H B J, Holmen A, Marin G B. Catal Toady, 1998, 40: 157

[16] Fathi M, Monnet F, Schuurman Y, Holmen A, Mirodatos C. J Catal, 2000, 190: 439

[17] Wang D, Dewaele O, de Groote A M, Froment G F. J Catal, 1996, 159: 418

[18] Weng W Z, Yan Q G, Luo C R, Liao Y Y, Wan H L. Catal Lett, 2001, 74: 37

[19] Weng W Z, Chen M S, Wan H L. Chem Rec, 2002, 2: 102

[20] Chin Y H, Iglesia E. J Phys Chem C, 2011, 115: 17845

[21] Chin Y H, Buda C, Neurock M, Iglesia E. J Am Chem Soc, 2011, 133: 15958

[22] Chin Y H, Buda C, Neurock M, Iglesia E. J Catal, 2011, 283: 10

[23] Weng W Z, Pei X Q, Li J M, Luo C R, Liu Y, Lin H Q, Huang C J, Wan H L. Catal Today, 2006, 117: 53

[24] Tolia A A, Smiley R J, Delgass W N, Takoudis C G, Weaver M J. J Catal, 1994, 150: 56

[25] Guerrero-Ruiz A, Ferreira-Aparicio P, Bachiller-Baeza M B, Rodriguez-Ramos I. Catal Toady, 1998, 46: 99

[26] Tsuji H, Shishido T, Okamura A, Gao Y Z, Hattori H, Kita H. J Chem Soc, Faraday Trans, 1994, 90: 803

[27] Guerrero-Ruiz A, Rodriguez-Ramos I. Heterogeneous Hydrocarbon Oxidation. Madrid: ACS Symposium Series, 1996. 347

[28] Tsuji H, Okamura-Yoshida A, Shishido T, Hattori H. Langmuir, 2003, 19: 8793

[1] 陈维苗, 丁云杰, 宋宪根, 朱何俊, 严丽, 王涛.助剂促进的 Rh-Fe/Al_2O_3 催化剂上 CO 加氢制乙醇反应性能[J]. 催化学报, 2012,33(6): 1007-1013

[2] 裴彦鹏, 丁云杰, 臧娟, 宋宪根, 董文达, 朱何俊, 王涛, 陈维苗.Li 助剂对 Co/AC 催化剂上 CO 加氢制直链混合伯醇反应性能的影响[J]. 催化学报, 2012,33(5): 8 812

[3] 曾艳, 王艳华, 徐贻成, 宋颖, 赵家骐, 蒋景阳, 金子林.温控离子液体/有机两相体系中纳米 Rh 催化烯烃氢甲酰化反应[J]. 催化学报, 2012,33(3): 402-406

[4] 李霞, 杨霞珍, 唐浩东, 刘化章.载体对合成气制甲烷镍基催化剂性能的影响[J]. 催化学报, 2011,32(8): 1400-1404