催化学报 » 2011, Vol. 32 » Issue (6) :970-977 DOI: 10.1016/S1872-2067(10)60218-5

研究论文



# Zn 掺杂的 LaCoO3 钙钛矿用于乙醇水蒸气重整制氢反应

马飞, 储伟*, 黄利宏, 余晓鹏, 吴永永

四川大学化工学院, 四川成都 610065

MA Fei, CHU Wei*, HUANG Lihong, YU Xiaopeng, WU Yongyong

Department of Chemical Engineering, Sichuan University, Chengdu 610065, Sichuan, China





摘要 利用一步柠檬酸络合法合成了钙钛矿 $LaCo_{1-x}Zn_xO_3$ (x = 0, 0.05, 0.1, 0.2, 0.3 and 0.5), 并将其用于乙醇水蒸气重整反应. 利用 X 射线衍射、程序升温还原和 X 射线光电子能谱对催化剂进行了表征. 结果表明, Zn 的加入不利于形成 $LaCo_{1-x}Zn_xO_3$ 钙钛矿结构, 当 x ≥ 0.1 时产生了一些分离相. 新鲜 LaCo0.9Zn0.1O3 催化剂中意外发现存在 $Co_3O_4$ 相, 这有利于催化剂反应性能的提高. 反应后的催化剂结构发生变化, 形成了 $La_2O_2CO_3$, 而该物质有利于积炭的消除和甲烷的重整.

关键词: 一步柠檬酸络合法 钙钛矿 多样纳米核 锌 乙醇 蒸气重整 积炭

Abstract: Nanostructured $LaCo_{1-x}Zn_xO_3$ (x = 0, 0.05, 0.1, 0.2, 0.3 and 0.5) perovskites were synthesized by a one-step citric acid-complexing method for hydrogen production by the steam reforming of ethanol. For comparison, 8% CoO/ZnO and 8% CoO/$La_2O_3$ were prepared by impregnation and evaluated. The catalyst samples were characterized by X-ray diffraction, temperature-programmed reduction, and X-ray photoelectron spectroscopy. The results indicated that zinc did not favor the formation of the $LaCo_{1-x}Zn_xO_3$ perovskite and the structures of the substituted samples were stronger than that of $LaCoO_3$. Some segregation was observed for x ≥ 0.1. The reactivity of the studied samples was sensitive to the zinc content and lower substitution values were found to be better. An unexpected phase ($Co_3O_4$) appeared in the fresh $LaCo_{0.9}Zn_{0.1}O_3$ sample. The presence of the $Co_3O_4$ phase increased the reactivity toward hydrogen production by the steam reforming of ethanol. The presence of $La_2O_2CO_3$ is responsible for the low carbon deposition and the $CH_4$ selectivity in the aged samples.

Keywords: one-step citric acid-complexing method, perovskite, multiple nanosized-cores, zinc, ethanol, steam reforming, carbon deposition

收稿日期: 2011-01-25; 出版日期: 2011-04-02

引用本文:

马飞, 储伟, 黄利宏等 .Zn 掺杂的 LaCoO3 钙钛矿用于乙醇水蒸气重整制氢反应[J] 催化学报, 2011,V32(6): 970-977

MA Fei, CHU Wei, HUANG Li-Hong etc .Steam Reforming of Ethanol over Zn-Doped $LaCoO_3$ Perovskite Nanocatalysts[J] Chinese Journal of Catalysis, 2011,V32(6): 970-977

链接本文:

http://www.chxb.cn/CN/10.1016/S1872-2067(10)60218-5 或 http://www.chxb.cn/CN/Y2011/V32/I6/970



[1] izcaíno A J, Carrero A, Calles J A. Catal Today, 2009, 146: 63

[2] ishtika I, Alexandera A, Dattaa R, Geana D. Int J Hydrogen Energy, 2000, 25: 31

[3] oannides T. J Power Sources, 2001, 92: 17

[4] ossi C C R S, Alonso C G, Antunes O A C, Guirardello R, Cardozo-Filho L. Int J Hydrogen Energy, 2009, 34: 323

[5] hang L F, Liu J, Li W, Guo G L, Zhang J L. J Natur Gas Chem, 2009, 18: 55

[6] ereira E B, Homsa N, Martí S, Fierro J L G, de la Piscina P R. J Catal, 2008, 257: 206

[7] ang H, Ye J L, Liu Y, Li Y D, Qin Y N. Catal Today, 2007, 129: 305

[8] irot A, Epron F, Descorme C, Duprez D. Appl Catal B, 2008, 79: 17

[9] ai W J, Wang F G, Zhan E S, Van Veen A C, Mirodatos C, Shen W J. J Catal, 2008, 257: 96

[10] Zhang B C, Tang X L, Li Y, Cai W J, Xu Y D, Shen W J. Catal Commun, 2006, 7: 367

[11] Profeti L P R, Ticianelli E A, Assaf E M. J Power Sources, 2008, 175: 482

[12] Vizcaíno A J, Carrero A, Calles J A. Int J Hydrogen Energy, 2007, 32: 1450
[13] Frusteri F, Freni S, Spadaro L, Chiodo V, Bonura G, Donato S, Cavallaro S. Catal Commun, 2004, 5: 611
[14] 王红, 刘鹏翔, 刘源, 秦永宁. 催化学报 (Wang H, Liu P X, Liu Y, Qin Y N. Chin J Catal), 2006, 27: 976
[15] Llorca J, de la Piscina P R, Dalmon J A, Sales J, Homs N. Appl Catal B, 2003, 43: 355
[16] Llorca J, Homs N, Sales J, Fierro J L G, de la Piscina P R. J Catal, 2004, 222: 470
[17] Guil J M, Homs N, Llorca J, de la Piscina P R. J Phys Chem B, 2005, 109: 10813
[18] Fatsikostas A N, Kondarides D I, Verykios X E. Catal Today, 2002, 75: 145
[19] Song H, Ozkan U S. J Catal, 2009, 261: 66
[20] Song H, Ozkan U S. J Phys Chem A, 2010, 114: 3796
[21] Lin S S Y, Daimon H, Ha S Y. Appl Catal A, 2009, 366: 252
[22] Tsipouriari V A, Verykios X E. J Catal, 1999, 187: 85
[23] Chen H Q, Yu H, Peng F, Yang G X, Wang H J, Yang J, Tang Y. Chem Eng J, 2010, 160: 333
[24] Chen H Q, Yu H, Peng F, Wang H J, Yang J, Pan M Q. J Catal, 2010, 269: 281
[25] de Lima S M, da Silva A M, da Costa L O O, Assaf J M, Jacobsc G, Davis B H, Mattos L V, Noronha F B. Appl Catal A, 2010, 377: 181
[26] Chen S Q, Liu Y. Int J Hydrogen Energy, 2009, 34: 4735
[27] Chen S Q, Wang H, Liu Y. Int J Hydrogen Energy, 2009, 34: 7995
[28] Bedel L, Roger A C, Estournes C, Kiennemann A. Catal To-day, 2003, 85: 207
[29] Bedel L, Roger A C, Rehspringer J L , Zimmermann Y, Kien-nemann A. J Catal, 2005, 235: 279
[30] Tien-Thao N, Alamdari H, Zahedi-Niaki M H, Kaliaguine S. Appl Catal A, 2006, 311: 204
[31] Huang L, Bassir M, Kaliaguine S. Appl Surf Sci, 2005, 243: 360
[32] Khalil M S. Mater Sci Eng A, 2003, 352: 64
[33] Rao G V S, Rao C N R, Ferraro J R. Appl Spectrosc, 1970, 24: 436
[34] Salavati-Niasari M, Davar F, Mazaheri M, Shaterian M. J Magn Magn Mater, 2008, 320: 575
[35] Salavati-Niasari M, Khansari A, Davar F, Salavati-Niasari M, Khansari A, Davar F. Inorg Chim Acta, 2009, 362: 4937
[36] Worayingyong A, Kangvansura P, Ausadasuk S, Praserthdam P. Colloids Surf A, 2008, 315: 217
[37] Royer S, BérubéF, Kaliaguine S. Appl Catal A, 2005, 282: 273
[38] Guo Q, Liu Y. Appl Catal B, 2008, 82: 19
[39] Navarro R M, Alvarez-Galvan M C, Villoria J A, González- Jiménez I D, Rosa F, Fierro J L G. Appl Catal B, 2007, 73: 247
[40] Natile M M, Ugel E, Maccato C, Glisenti A. Appl Catal A, 2007, 72: 351
[41] Khassin A A, Yurieva T M, Kaichev V V, Bukhtiyarov V I, Budneva A A, Paukshtis E A, Parmon V N. J Mol Catal A, 2001, 175: 189
[42] Barbero B P, de Gamboa J A, Cadus L E. Appl Catal B, 2006, 65: 21
[43] Wang Y G, Ren J W, Wang Y Q, Zhang F Y, Liu X H, Guo Y, Lu G Z. J Phys Chem C, 2008, 112: 15293
[44] Taguchi H, Kido H, Tabata K. Phys B, 2004, 344: 271
[45] Llorca J, Dalmon J A, de la Piscin P, Homs N. Appl Catal A, 2003, 243: 261
[46] Llorca J, Homs N, de la Piscina P R. J Catal, 2004, 227: 556
[47] Kwak B S, Kim J, Kang M. Int J Hydrogen Energy, 2010, 35: 11829
[48] Casanovas A, Roig M, de Leitenburg C, Trovarelli A, Llorca J. Int J Hydrogen Energy, 2010, 35: 7690
[49] Karim A M, Su Y, Sun J, Yang C, Strohm J J, King D L, Wang Y. Appl Catal A, 2010, 96: 441
[50] Valderrama G, Kiennemann A, Goldwasser M R. Catal Today, 2008, 133: 142
[51] Hyman M P, Vohs J M. Surf Sci, 2011, 605: 383

[1] 倪晔, 张蓓花, 孙志浩.采用通透性处理的安大略假丝酵母全细胞高效合成 (*R*)-2-氯-1-(3-氯苯基)乙醇[J]. 催化学报, 2012,33(4): 681-687
[2] 孙海杰, 潘雅洁, 王红霞, 董英英, 刘仲毅, 刘寿长.二乙醇胺作添加剂 Ru-Zn 催化剂上苯选择加氢制环己烯[J]. 催化学报, 2012,33(4): 610-620