催化学报 » 2011, Vol. 32 » Issue (12) :1803-1811 DOI: 10.1016/S1872-2067(10)60269-0

研究论文

铈改性钛基层柱粘土负载锰催化剂上低温 NH3 选择性催化还原 NO

沈伯雄 1,*, 姚燕 1, 马宏卿 1, 刘亭 2

1南开大学环境科学与工程学院, 天津 300071; 2中国石化青岛安全工程研究院, 山东青岛 266071

SHEN Boxiong1,*, YAO Yan1, MA Hongqing1, LIU Ting2

1College of Environmental Science and Engineering, Nankai University, Tianjin 300071, China; 2Sinopec Research Institute of Safety Engineering, Qingdao 266071, Shandong, China

摘要 采用离子交换法制备了钛基层柱粘土 (TiO2-PILC), 并应用浸渍法将 Mn 负载于其上制得不同 Mn 含量的 xMn/ TiO2-PILCs 催化剂, 考察了催化剂低温 NH3 选择性催化还原 NO (NH3-SCR) 活性, 研究了添加 Ce 对 8%Mn/TiO2-PILC 催化剂活性及其抗水蒸气抗 SO2 特性的影响. 结果发现, TiO2-PILC 负载的锰基催化剂具有良好的抗水蒸气性能, 但在水蒸气和 SO2 共存时失活严重. Ce 的添加对催化剂活性以及抗 SO2 能力均有所提高, 其中 8%Mn-2%Ce/TiO2-PILC 在 200 oC 时 NO 去除率达到 95%, 同时 SO2 失活速率明显比其他催化剂低. 采用 N2 吸附-脱附、X 射线衍射、NH3 程序升温脱附、H2 程序升温还原和 X 射线光电子能谱等技术对催化剂结构和性质进行了表征. 结果表明, 所制备催化剂具有丰富的中孔结构和较大的比表面积; Ce 的添加使 Mn 在催化剂表面分散性更好, 提高了催化剂表面酸性和催化剂氧化还原性能, 从而使其活性和抗硫性能增加.

关键词: 低温选择性催化还原 钛基层柱粘土 氧化锰 氧化铈 中毒

Abstract: Titania-pillared clays (TiO2-PILC) were synthesized by ion exchange and manganese was introduced as the active phase. The catalytic behavior of the xMn/TiO2-PILC catalysts was studied for the low-temperature selective catalytic reduction (SCR) of NO with NH3. A series of Ce-doped 8%Mn-yCe/TiO2-PILC catalysts were prepared and evaluated for their performance in the low-temperature SCR of NO with NH3, their resistance to water vapor (H2O), and their resistance to sulfur dioxide (SO2). It was found that the NO conversion properties of the 8%Mn/TiO2-PILC catalysts could be significantly improved by adding Ce and all the catalysts gave high resistance to H2O but were sensitive to SO2. The catalyst with a Ce loading of 2% gave 95% NO conversion at 220 ° C and exhibited a moderate SO2-poisoning resistance compared with the other catalysts. X-ray diffraction, N2 adsorption-desorption, temperature-programmed desorption of NH3, X-ray photoelectron spectroscopy, and temperature-programmed reduction of H2 were used to characterize the properties of the catalysts. The addi-tion of Ce improved the diffusion of Mn on the surfaces of the catalysts, which enhanced the surface acidity and improved the reduction properties of the catalysts and these were the main influencing factors for the low-temperature SCR.

Keywords: low-temperature selective catalytic reduction, titania-pillared interlayered clay, manganese oxide, cerium, poisoning

收稿日期: 2011-07-25; 出版日期: 2011-09-14

引用本文:
沈伯雄, 姚燕, 马宏卿等 .铈改性钛基层柱粘土负载锰催化剂上低温 NH3 选择性催化还原 NO[J] 催化学报, 2011,V32(12): 1803-1811

SHEN Bo-Xiong, YAO Yan, MA Hong-Qing etc .Ceria Modified MnO_x/TiO_2-Pillared Clays Catalysts for Selective Catalytic Reduction of NO with NH_3 at Low Temperature[J] Chinese Journal of Catalysis, 2011,V32(12): 1803-1811

链接本文:
http://www.chxb.cn/CN/10.1016/S1872-2067(10)60269-0 或 http://www.chxb.cn/CN/Y2011/V32/I12/1803

[1] ong R Q, Yang R T. Appl Catal B, 2000, 24:13

[2] iu F D, He H. J Phys Chem C, 2010, 114: 16929

[3] ong R Q, Yang R T. J Catal, 1999, 188: 332

[4] i G Sh, Yang R T, Chang R. Appl Catal B, 2004, 51: 93

[5] mirniotis P G, Peňa D A, Uphade B S. Angew Chem, Int Ed, 2001, 40: 2479 3.0.CO;2-7 target="_blank">

[6] i G Sh, Yang R T, Chang R. Catal Lett, 2003, 87: 67

[7] ang X L, Hao J M, Yi H H, Li J H. Catal Today, 2007, 126: 406
[8] ong R Q, Yang R T, Chang R. Chem Commun, 2002: 452
[9] iu F D, He H, Ding Y, Zhang C B. Appl Catal B, 2009, 93: 194
[10] Kang M, Park E D, Kim J M, Yie J E. Catal Today, 2006, 111: 236
[11] Eigenmann F, Maciejewski M, Baiker A. Appl Catal B, 2006, 62: 311
[12] 邱春天, 林涛, 张秋林, 徐海迪, 陈耀强, 龚茂初. 催化学报 (Qiu Ch T, Lin T, Zhang Q L, Xu H D, Chen Y Q, Gong M Ch. Chin J Catal), 2011, 32: 1227
[13] 林涛, 李伟, 龚茂初, 喻瑶, 杜波, 陈耀强. 物理化学学报 (Lin T, Li W, Gong M Ch, Yu Y, Du B, Chen Y Q. Acta Phys-Chim Sin), 2007, 23: 1851
[14] Wu Z B, Jin R B, Liu Y, Wang H Q. Catal Commun, 2008, 9: 2217
[15] Wu Z B, Jin R B, Wang H Q, Liu Y. Catal Commun, 2009, 10: 935
[16] Marban G, Fuertes A B. Appl Catal B, 2001, 34: 55
[17] Jiang B Q, Liu Y, Wu Z B. J Hazard Mater, 2009, 162: 1249
[18] Smirniotis P G, Sreekanth P M, Penaand D A, Jenkins R G. Ind Eng Chem Res, 2006, 45: 6436
[19] Peña D A, Uphade B S, Smirniotis P G. J Catal, 2004, 221: 421
[20] Jin R B, Liu Y, Wu Z B, Wang H Q, Gu T T. Chemosphere, 2010, 78: 1160
[21] Vaccari A. Catal Today, 1998, 41: 53
[22] Yang R T, Chen J P, E. Kikkinides S, Cheng L S, Cichanowicz J E. Ind Eng Chem Res, 1992, 31: 1440
[23] Cheng L S, Yang R T, Cheny N. J Catal, 1996, 164: 70
[24] Chmielarz L, Kustrowski P, Zbroja M, Rafalska-?asocha A, Dudek B, Dziembaj R. Appl Catal B, 2003, 45: 103
[25] Chmielarz L, Dziembaj R, Grzybek T, Klinik J, ?ojewski T, Olszewska D, Wegrzyn A. Catal Lett, 2000, 70: 51
[26] Shen B X, Liu T, Zhao N, Yang X Y, Deng L D. J Environ Sci, 2010, 22: 1447
[27] Wu Z B, Jiang B Q, Liu Y, Zhao W R, Guan B H. J Hazard Mater, 2007, 145: 488
[28] Long R Q, Yang R T. Appl Catal B, 2000, 27: 87
[29] Carija G, Kameshima Y, Okada K, Madhusoodana C D. Appl Catal B, 2007, 73: 60
[30] Yang R T, Tharappiwattananon N, Long R Q. Appl Catal B, 1998, 19: 289
[31] Chmielarz L, Kustrowski P, Zbroja M, ?asocha W, Dziembaj R. Catal Today, 2004, 90: 43
[32] Jagtap N, Ramaswamy V. Appl Clay Sci, 2006, 33: 89
[33] Long R Q, Yang R T. Catal Lett, 1999, 59: 39
[34] Qi G Sh, Yang R T. Appl Catal B, 2003, 44: 217
[35] Chmielarz L, Kustrowski P, Zbroja M, Knap B G, Datka J, Dziembaj R. Appl Catal B, 2004, 53: 47
[36] Kijlstra W S, Brands D S, Poels E K, Bliek A. J Catal, 1997, 171: 208
[37] Gu T T, Liu Y, Weng X L, Wang H Q, Wu Z B. Catal Commun, 2010, 12: 310
[38] Arena F, Trunfio G, Negro J, Fazio B, Spadaro L. Chem Mater, 2007, 19: 2269
[39] Tang X F, Li Y G, Huang X M, Xu Y D, Zhu H Q, Wang J G, Shen W J. Appl Catal B, 2006, 62: 265
[40] Delimaris D, Ioannides T. Appl Catal B, 2008, 84: 303
[41] Tang X F, Chen J L, Huang X M, Xu Y D, Shen W J. Appl Catal B, 2008, 81: 115
[42] 林涛, 张秋林, 李伟, 龚茂初, 幸怡汛, 陈耀强. 物理化学学报(Lin T, Zhang Q L, Li W, Gong M Ch, Xing Y X, Chen Y Q. Acta Phys-Chim Sin), 2008, 24: 1127
[43] Trovarelli A. Catal Rev Sci Eng, 1996, 38: 439
[44] Shen B X, Liu T, Yang X Y, Zhao N. Environ Eng Sci, 2011, 28: 291
[45] Jin R B, Liu Y, Wu Z B, Wang H Q, Gu T T. Catal Today, 2010, 153: 84

[1] 孙明娟, 邹国军, 许珊, 王晓来.前驱体 $CeOHCO_3$ 的结构对产物 CeO_2 催化性能的影响[J]. 催化学报, 2012,33(8): 1318-1325
[2] 高旭锋, 谌春林, 任士远, 张建, 苏党生.氧化铈的结构对其热稳定性及催化丙烷氧化脱氢反应性能的影响[J]. 催化学报, 2012,33(7): 1069-1074
[3] 张慧丽, 任丽会, 陆安慧, 李文翠.$Au/CeO_2/SiO_2$ 催化CO 低温氧化反应过程中CeO_2 的作用[J]. 催化学报, 2012,33(7): 1125-1132

[4] 单文娟, 杨利花, 马娜, 杨佳丽.K/CeO_2催化剂上碳黑催化燃烧性能及稳定性[J]. 催化学报, 2012,33(6): 970-976
[5] 郭荷芹, 李德宝, 陈从标, 范志宏, 孙予罕.V_2O_5/CeO_2 催化剂上甲醇氧化一步法合成二甲氧基甲烷[J]. 催化学报, 2012,33(5): 813-818
[6] 赵德志, 丁天英, 李小松, 刘景林, 石川, 朱爱民.室温 MnO_x 上 O_3 氧化脱除空气中甲醛[J]. 催化学报, 2012,33(3): 396-401
[7] 方星, 陈崇启, 林性贻*, 佘育生, 詹瑛瑛, 郑起.La_2O_3 对 CuO/CeO_2 水煤气变换反应催化剂微观结构及催化性能的影响[J]. 催化学报, 2012,33(3): 425-431
[8] 林建新, 张留明, 王自庆, 王榕, 魏可镁.Pr 掺杂对 Ru/CeO_2 催化剂结构和氨合成性能的影响[J]. 催化学报, 2012,33(3): 536-542
[9] 庞潇健, 陈亚中, 代瑞旗, 崔鹏.柠檬酸络合法制备的 Co/CeO_2 催化剂上中温乙醇水蒸气重整性能[J]. 催化学报, 2012,33(2): 281-289
[10] 朱艺, 潘浩, 陈山虎, 王世丹, 赵明, 龚茂初, 陈耀强.MnO_x 负载量对 $MnO_x/Ce_{0.7}Zr_{0.2}La_{0.1}O_2$-$Al_2O_3$ 催化剂上碳烟燃烧性能的影响[J]. 催化学报, 2012,33(12): 1965-1973
[11] 刘冰, 徐恒泳, 张泽会.程序升温表面反应技术研究氧化铈上 H_2S 的吸附和转化[J]. 催化学报, 2012,33(10): 1631-1635
[12] 钟富兰, 钟喻娇, 肖益鸿, 蔡国辉, 郑勇, 魏可镁.Pt/CeO_2-ZrO_2-La_2O_3 柴油车尾气氧化催化剂活性及抗硫性能[J]. 催化学报, 2011,32(9): 1469-1476
[13] 单文娟, 刘畅, 郭红娟, 杨利华, 王晓楠, 冯兆池.0, 1, 3 维 CeO_2 的可控制备及 CuO/CeO_2 催化剂上 CO 氧化反应[J]. 催化学报, 2011,32(8): 1336-1341
[14] 杨文, 储伟, 江成发, 文婕, 孙文晶.CeO_2 助 Ni/MgO 催化剂用于化学气相沉积法制备多壁碳纳米管[J]. 催化学报, 2011,32(8): 1323-1328
[15] 邱春天, 林涛, 张秋林, 徐海迪, 陈耀强, 龚茂初.改性 ZrO_2-MnO_2 基整体式催化剂上 NH_3 选择性催化还原 NO[J]. 催化学报, 2011,32(7): 1227-1233