[1]代 陈,刘志铭,谢建榕,等.一种煤基合成气制合成天然气用Sc2O3促进Ni-ZrO2高效新型甲烷化催化剂[J].厦门大学学报(自然科学版),2013,52(05):650.[doi:10.6043/j.issn.0438-0479.2013.05.013]

DAI Chen,LIU Zhi-ming,XIE Jian-rong,et al.A Highly Efficient Sc2O3-promoted Ni-ZrO2 Catalyst for Methanation of Coal-based Syngas to Produce Synthetic Natural Gas[J].Journal of Xiamen University(Natural Science),2013,52(05):650.0479.2013.05.013]

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一种煤基合成气制合成天然气用Sc_2O_3促进Ni-ZrO_2化剂(PDF)

分享到:

《厦门大学学报（自然科学版）》[ISSN:0438-0479/CN:35-1070/N] 卷: 52卷 期数: 2013年05期
页码: 650 栏目: 出版日期: 2013-08-15

Title: A Highly Efficient Sc_2O_3-promoted Ni-ZrO_2 Catalyst for Methanation of Coal-based Syngas to Produce Synthetic Natural Gas

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关键词: Ni-ZrO_2催化剂; Sc_2O_3-促进Ni-ZrO_2催化剂; CO/CO_2共甲烷化; 合成天然气

Keywords: Ni-ZrO_2 catalyst; Sc_2O_3-doped Ni-ZrO_2 catalyst; CO/CO_2 co-methanation; SNG

分类号: O 643.36

DOI: 10.6043/j.issn.0438-0479.2013.05.013

文献标志码: -

摘要: 用Sc_2O_3作为促进剂,研发出一种Sc_2O_3掺杂的高效新型Ni-ZrO_2基催化剂,该催化剂对CO和CO_2共甲烷化制合成天然气(SNG)显示出高的活性和优异的热稳定性.在组成经优化的$Ni_6Zr_3Sc_1$催化剂上,0.1 MPa,573 K,$V(H_2):V(CO):V(CO_2):V(N_2)$=75:15:5:5,出口空速GHSV=40 000 mL/(h • g)的反应条件下,在反应开始之后的20～332 h的反应过程中,CO和CO_2的转化率一直分别保持在100%和85%的高水平,产物甲烷的选择性一直保持在100%.耐热试验结果显示,在973 K下经历24 h甲烷化反应、而后降至573 K的$Ni_6Zr_3Sc_1$催化剂试样上,(CO+CO_2)的总转化率仍能稳定地保持在80.2%的水平; 而不含Sc_2O_3的原基质催化剂(Ni_6Zr_4)在经历相同耐热试验过程之后的(CO+CO_2)总转化率骤降至2.7%,暗示其因烧结而失活.催化剂的表征结果证实,可观量的Sc^{3+}溶解入ZrO_2晶格导致具有c-ZrO_2结构的单一c-(Zr-Sc)O_y相的生成并使其稳定化,这类c-(Zr-Sc)O_y相与$Ni_6Zr_3Sc_1$催化剂的高活性,尤其与优良的热稳定性,密切相关.

Abstract: A type of highly efficient Ni-ZrO_2 catalysts doped with Sc_2O_3 for co-methanation of CO and CO_2 was developed,and displayed high activity and excellent thermal stability.Over a $Ni_6Zr_3Sc_1$ catalyst under the reaction conditions of 0.1 MPa,573 K,$V(H_2)$:V(CO):$V(CO_2)$:$V(N_2)$=75:15:5:5,GHSV=40 000 mL/(h • g)(outlet),the observed conversion of CO and CO_2 maintained continuously at high levels of 100% and 85%,respectively,during 20-332 h after the reaction started,with the corresponding selectivity of CH_4 product being 100%.The results of heat-resisting test showed that,over the $Ni_6Zr_3Sc_1$ catalyst after undergoing 24 h of the methanation operation at 973 K followed by going down to 573 K,the total conversion of($CO+CO_2$)still maintained stable at the level of 80.2%,whereas that of the Sc_2O_3-free Ni_6Zr_4 catalyst after undergoing the same heat-resisting test fell to 2.7%,implying that it was deactivated due to sintering.The results of the catalyst characterization demonstrated that solution of a considerable amount of Sc^{3+} in the ZrO_2 lattice resulted in the formation of(Zr-Sc)O_y composite oxide with simple *c*-ZrO_2 phase-structure,which was closely associated with the high activity,especially the extremely high thermal stability,of the $Ni_6Zr_3Sc_1$ catalyst.

参考文献/References:

[1] Kopyscinski J,Schildhauer T J,Biollaz S M A.Production of synthetic natural gas from coal and dry biomass:a technology review from 1950 to 2009[J].Fuel,2010,89(8):1763-1783.
[2] Rostrup-Nielsen J R,Pedersen K,Sehested J.High temperature methanation sintering and structure sensitivity[J].Appl Catal A:Gen,2007,330(1):134-138.
[3] van Heek K H.Progress of coal science in the 20th century[J].Fuel,2000,79(1):1-26.
[4] Nagase S,Takami S,Hirayama A,et al.Development of a high efficiency substitute natural gas production process [J].Catal Today,1998,45(1/2/3/4):393-397.
[5] Hayhoe K,Kheshgi H S,Jai A,et al.Substitution of natural gas for coal:climatic effect of utility sector emissions [J].Climatic Change,2002,54(1):107-139.
[6] 杨伯伦,李星星,伊春海,等.合成天然气技术进展[J].化工进展,2011,30(1):110-116.
[7] 赵钢炜,肖云汉,王钰.煤制天然气工艺技术和催化剂影响因素的分析探讨[J].陶瓷,2009(11):21-26.
[8] 路霞,陈世恒,王万丽,等.CO甲烷化Ni基催化剂的研究进展[J].石油化工,2010,39(3):340-345.
[9] 赵利军,蔺华林.基于甲烷化机理的催化剂设计与甲烷化研究新领域[J].神华科技,2011,9(1):87-91.
[10] PANalytical.XRD data bank attached to X' Pert PRO X-ray diffractometer[DB].The Netherlands:PANalytical,2003.
[11] Martin U,Boysen H,Frey F.Neutron powder investigation of tetragonal and cubic stabilized zirconia,TZP and CSZ,at temperatures up to 1400 K[J].Acta Crystallogr Sec B:Struct Sci,1993,49:403-413.
[12] Solis D,de la Rosa E,Meza O,et al.Role of Yb^{3+} and Er^{3+} concentration on the tunability of green-yellow-red upconversion emission of codoped ZrO_2:Yb^{3+}-Er^{3+} nanocrystals[J].J Appl Phys,2010,108:023103.
[13] Angeles-Chavez C,Salas P,Díaz-Torres L A,et al.Structural and chemical characterization of Yb_2O_3-ZrO_2 system by HAADF-STEM and HRTEM[J].Microsc Microanal,2009,15:46-53.
[14] Hyppänen I,Hölsä J,Kankare J,et al.Defect structure and up-conversion luminescence properties of ZrO_2:Yb^{3+},Er^{3+} nanomaterials[J].J Fluoresc,2008,18:1029-1034.
[15] Habazaki H,Yamasaki M,Kawashima A,et al.Methanation of carbon dioxide on Ni/(Zr±Sm)O_x catalysts[J].Appl Organometal Chem,2000,14:803-808.
[16] Moulder J F,Stickle W F,Sobol P E,et al.Handbook of X-ray photoelectron spectroscopy:a reference book of standard spectra for identification and interpretation of XPS data[M].Eden Prairie:Physical Electronics Inc,1995.

备注/Memo: 收稿日期:2013-05-24 基金项目:国家重点基础研究发展计划(973)项目(2011CBA00508); 优秀国家重点实验室基金项目(20923004); 教育部创新团队项目(IRT1036) *通信作者:hbzhang@xmu.edu.cn

更新日期/Last Update: 2013-08-15