学校编码：10384

学号：20520141151571

厦门大学

硕 士 学 位 论 文

有序介孔氧化铝负载钴催化剂的制备、表征及费托反应性能的研究

The Research on Preparation and Characterization of Ordered Mesoporous Alumina Supported Cobalt Catalysts and its Performance on Fischer-Tropsch Synthesis

范印瑞

指导教师：万惠霖　　黄传敬

专业名称：物理化学

答辩日期：2017年5月

厦门大学学位论文原创性声明

本人呈交的学位论文是本人在导师指导下,独立完成的研究成果。本人在论文写作中参考其他个人或集体已经发表的研究成果，均在文中以适当方式明确标明，并符合法律规范和《厦门大学研究生学术活动规范(试行)》。

另外，该学位论文为(　　　　　　　　　　　)课题(组)的研究成果，获得(　　　　　　　　　　　)课题(组)经费或实验室的资助，在(　　　　　　)实验室完成。(请在以上括号内填写课题或课题组负责人或实验室名称，未有此项声明内容的，可以不作特别声明。)

声明人(签名):

年　　月　　日

厦门大学学位论文著作权使用声明

本人同意厦门大学根据《中华人民共和国学位条例暂行实施办法》等规定保留和使用此学位论文，并向主管部门或其指定机构送交学位论文(包括纸质版和电子版)，允许学位论文进入厦门大学图书馆及其数据库被查阅、借阅。本人同意厦门大学将学位论文加入全国博士、硕士学位论文共建单位数据库进行检索，将学位论文的标题和摘要汇编出版，采用影印、缩印或者其它方式合理复制学位论文。

本学位论文属于：

(　　)1.经厦门大学保密委员会审查核定的保密学位论文，于　年　月　日解密，解密后适用上述授权。

(　　)2.不保密，适用上述授权。

(请在以上相应括号内打“√”或填上相应内容。保密学位论文应是已经厦门大学保密委员会审定过的学位论文，未经厦门大学保密委员会审定的学位论文均为公开学位论文。此声明栏不填写的，默认为公开学位论文，均适用上述授权。)

声明人(签名)：

年　　月　　日

摘　要

摘　　要

费托合成将从煤、生物质、天然气转化而来的合成气制备成清洁燃料和化学品，对于解决当前环境与能源问题有重要的意义和价值。本文以非离子嵌段共聚物P123为模板剂，采用乙醇挥发诱导自组装法(EISA)合成高热稳定性、大比表面积的有序介孔结构氧化铝（OMA)，以其为载体采用浸渍法制备负载钴催化剂并用于费托合成反应。结合XRD、BET、TEM、H2-TPR、XPS等表征技术，系统考察了制备方法以及添加稀土助剂对催化剂结构和性能的影响，探讨了该类催化剂结构和性能之间的关系。

（一）Co/OMA催化剂的研究

（1）分别采用水和非水溶剂（乙醇、甲醇、正丁醇）制备浸渍液，考察了浸渍液对Co/OMA催化剂费托反应性能影响。结果表明，非水溶剂制备的催化剂表现出更高的催化活性和C5+选择性。研究发现，水溶液浸渍制备的催化剂，其载体介孔结构遭到破坏，钴氧物种及还原后生成的金属钴分散度较差；而非水溶剂制备的催化剂具有较大的比表面积、规整的孔道结构和较高的金属分散度，这可能是导致两类催化剂性能差异的重要原因。

（2）考察了载体焙烧温度对Co/OMA催化剂结构和性能的影响，发现CO转化率和C5+选择性随着载体焙烧温度的提高而增加，当焙烧温度为700 oC时，费托反应性能最佳。在考察的焙烧温度（400 — 800 oC）范围内，催化剂均保持良好的有序介孔结构，且随着焙烧温度的升高，催化剂表面酸性位点减少，钴氧物种与载体之间的相互作用力减弱，催化剂可还原性提高。酸性减弱有助于抑制长链产物在催化剂表面发生氢解和异构化反应而提高C5+选择性，而催化剂可还原性能的改善则是其催化活性提高的重要原因。

（3）同时考察了负载量对Co/OMA催化剂费托反应性能的影响，发现当钴负载量由10 %增加到20 %时，CO转化率逐渐增加至最高值，继续提高负载量，CO转化率变化不大；而在考察范围内，催化剂负载量对其产物选择性影响不大。

（二）添加稀土助剂对Co/OMA催化剂结构与性能的影响

（1）在合成介孔氧化铝的过程中引入稀土助剂，制备添加不同稀土助剂的负载钴

催化剂（Co/R-OMA）。结果表明，引入Ce助剂，催化剂费托反应活性明显提高；引入La助剂，催化活性变化不大但C5+选择性提高；而引入Y、Nd、Eu、Gd助剂，催化剂的费托反应性能均明显降低。表征结果表明，添加Ce助剂使得催化剂的可还原性能以及金属钴分散度得以提高，由此导致其费托反应活性的提高；而引入La后，催化剂的可还原性能变化不大，推测其C5+选择性的提高可能与其La-Co之间的协同作用有关。

（2）在Co/Ce-OMA催化剂中，再通过浸渍法添加第2助剂La，发现其费托反应活性和C5+选择性均明显提高。研究表明，在上述催化剂中添加La并未破坏其有序介孔结构，但却进一步削弱了载体与钴物种之间的相互作用，抑制了$CoAl_2O_4$难还原物种的形成，并促进了钴物种的分散，这些可能是导致催化剂费托反应性能提高的重要原因。

关键词：费托合成；有序介孔氧化铝；负载钴催化剂；稀土助剂

关键词：费托合成；有序介孔氧化铝；负载钴催化剂；稀土助剂

Abstract

Abstract

Fischer-Tropsch synthesis (FTS) convers syngas(CO+H2) into clean hydrocarbon fuels or chemicals, which is of great significance and value to solve the current environment and energy problems. In this work, Ordered mesoporous alumina (OMA) with large surface area and high thermal stability was synthesized via ethanol evaporation induced self-assembly by using P123 as structure directing agent. The effects of preparation method and rare earth metals promoter on the structure of Co/OMA catalysts and their FTS catalytic performance were systematically studied. Cobalt based catalysts were prepared by incipient wetness impregnation the OMA. In order to reveal the relationship between structure and catalytic performance, the characteristic of the catalysts were identified by XRDH2-TPRBETTEM techniques etc.

Study on the Co/OMA catalysts

(1)Co/OMA catalysts were prepared by incipient-wetness impregnation with cobalt nitrate dissolved in water or anhydrous solvents(ethanol, methanol, n-butanol). The effects of impregnation solution on the structure of Co/OMA catalysts and their FTS catalytic performance were systematically studied. The results indicate that catalysts impregnated with anhydrous solutions showed higher F-T reaction activity and C5+ selectivity than Co/OMA prepared using water solution. Characterization results indicate that Co/OMA catalysts prepared with water solutions destroyed the original structure of OMA, while catalysts anhydrous solutions have large surface areasregular pore structure and higher metal dispersion degree, which may be the important reason for the difference of FTS performance between the two types of catalysts.

(2) Influence of support calcination temperature on the structure and catalytic performance of Co/OMA catalysts for FTS was studied. The results show that the

CO conversion and C5+ selectivity increased with the increase of calcination temperature. When the calcination temperature increased to 700 oC, Co/OMA show the best F-T performance. The characterization results show that the catalysts maintain the order mesoporous structure in the scope of 400-800 oC. In addition, the acid sites on the catalysts surface decrease with the increase of support calcination temperature, leading to the decrease of the interaction between cobalt oxygen species and carrier, and thus improved the reducibility of Co/OMA. Furthermore, low acidity can prevent the reaction of hydrogenolysis and isomerization, which appeared to be responsible for high C5+ hydrocarbon selectivity. The improvement of the reducibility of catalyst is the major reason for the improvement of catalytic activity.

(3) Influence of Co loadings on the catalytic performance of Co/OMA catalysts for FTS was also studied. The results show that when the loading amounts of cobalt increases from 10 wt% to 20 wt%, the conversion rate of CO gradually increased to the maximum value. The conversion rate of CO changed little when Co loadings continue to increase. The loadings of Co has little impact on C5+ selectivity in the investigation scale.

The study of cobalt catalysts supported on rare earth modified OMA

(1)Rare earth metal modified OMA was in-situ synthesized through a sol-gel route and then as support for the preparation of Co/R-OMA catalysts. The results show that Ce was favorable for CO conversion and La can improve C5+ selectivity significantly, while YNdEuand Ga have negative effect on the FTS performance of Co/OMA catalyst. The dispersion degree of cobalt species can be enhanced with the adding of Ce, and the reducibility of catalyst was also improved, which is helpful to the increase of FTS activity. While La has little effect on the reducibility of the catalyst. Perhaps the synergistic effect between La and cobalt is helpful to improve the selectivity of C5+.

(2) Ce-doped OMA was synthesized in a sol-gel system and then as support for

the preparation of Co/La/Ce-OMA catalysts, La promoter was introduced by incipient wetness impregnation method with ethanol solution of lanthanum nitrate. The results show that introduction of La further decreased the strong interaction between the carrier and the cobalt species and reduced the amount of CoAl2O4, thus improved the reducibility of catalysts. What's more, the introduction of La further improved the dispersion of cobalt species. These may be responsible for the improvement of the FTS catalytic performance of Co/OMA catalyst.
Key words: Fischer-Tropsch synthesis; Ordered Mesoporous Alumina; Supported cobalt catalyst; Rare earth promoter

Keywords: Fischer-Tropsch synthesis; Ordered Mesoporous Alumina; Supported cobalt catalyst; Rare earth promoter

参考资料

参 考 文 献

[1] K. Caldeira, M. I. Hoffert. Climate Sensitivity Uncertainty and the Need for Energy Without CO2 Emission [J]. Science, 2003, 299(5615):2052 – 2054.
[2] BP.p.l.c. BP Energy Outlook 2035, [R].United Kingdom, 2016.
[3] L. Petrus, M. A. Noordermeer. Biomass to biofuels, a chemical perspective [J].Green Chemistry, 2006, 38(3): 861 – 867.
[4] 国家统计局． 中国统计年鉴[M].北京：中国统计出版社,2016
[5] 严陆光,陈俊武,周凤起等.我国中远期石油补充和替代能源发展战略研究(续)[J].中国科学:电工电能新技术,2007, 26(01):1 – 12.
[6] M R. Raupach, G. Marland, P. Ciais, et al. Global and regional drivers of accelerating CO2 emissions [J]. Proceedings of the National Academy of Sciences of the United States of America, 2007, 104(24):10288 – 93.
[7] H. Jahangiri, J. Bennett, P. Mahjoubi, K. Wilson, S. Gu. A review of advanced catalyst development for Fischer – Tropsch synthesis of hydrocarbons from biomass derived syn – gas [J]. Catalysis Science & Technology, 2014, 8(4): 2210 – 2229.
[8] P. K. Swaina, L.M. Das, S.N. Naikb. Biomass to liquid: A prospective challenge to research and development in 21st century [J]. Renewable and Sustainable Energy Reviews, 2011, 15(9): 4917 – 4933.
[9] A. D. Klerk. Fischer – Tropsch fuels refinery design [J]. Energy & Environmental Science, 2011, 4(4): 1177 – 1205.
[10] M. E. Dry. Fischer – Tropsch reactions and the environment [J]. Applied Catalysis A: General, 1999, 189(2):185 – 190.
[11] 王野,成康,张庆红.一氧化碳加氢制碳氢化合物反应选择性的调控 [J].中国科学：化学, 2012, 42(4):363 – 373.
[12] H. Schulz. Major and Minor Reactions in Fischer – Tropsch Synthesis on Cobalt Catalysts [J]. Topics in Catalysis, 2003, 35(1):73 – 85.
[13] B. H. Davis. Fischer – Tropsch synthesis: current mechanism and futuristic needs [J]. Fuel Processing Technology, 2001, 71(1): 157 – 166.
[14] B. H. Davis. Fischer-Tropsch Synthesis: Reaction mechanisms for iron catalysts [J]. Catalysis Today, 2009, 141(1 – 2): 25 – 33.
[15] J. Gaube, H. F. Klein. Studies on the reaction mechanism of the Fischer – Tropsch synthesis on iron and cobalt [J] Journal of Molecular Catalysis A: Chemical 2008, 283(1 – 2): 60 – 68.
[16] B. W. Wojciechowski. The Kinetics of the Fischer-Tropsch Synthesis [J]. Catalysis Reviews, 1988, 30(4):629 – 702.
[17] G Henrici-Olive, S Olive. The Fischer – Tropsch synthesis: Molecular weight distribution of primary products and reaction mechanism [J]. Angewandte Chemie International Edition in English, 1976, 15(3):136 – 141.
[18] G. P. V. D. Laan, A. A. C. M. Beenackers. Kinetics and Selectivity of the Fischer – Tropsch Synthesis: A Literature Review [J]. Catalysis Reviews Science and Engineering, 1999, 41(3 – 4):255 – 318.
[19] R. A. V. Santen, I. M. Ciobica, E. V. Steen, M. M. Ghouri. Chapter 3. Mechanistic Issues in Fischer – Tropsch Catalysis [J]. Advances in Catalysis, 2011, 54(14):127 – 187.
[20] W.凯姆(主编), 黄仲涛(译).C1化学中的催化[M].北京:化学工业出版社,1989:1 – 292.
[21] R. J. Kokes, W. K. Hall, P. H. Emmett. Fischer-Tropsch Synthesis Mechanism Studies. The Addition of Radioactive Alcohols to the Synthesis Gas [J]. Journal of The American Chemical Society, 1957, 79(12):2989 – 2996.
[22] H. Pichler, H. Schulz. Neuere Erkenntnisse auf dem Gebiet der Synthese von Kohlenwasserstoffen aus CO und H2 [J]. Chemie Ingenieur Technik, 2010, 42(18):1162 – 1174.

[23] R. C. BradyIII, R. Pettit. Reactions of diazomethane on transition-metal surfaces and their relationship to the mechanism of the Fischer-Tropsch reaction [J]. Journal of the American Chemical Society, 1980, 102(91):6181 – 6182.
[24] A. A. Adesina. Hydrocarbon synthesis via Fischer-Tropsch reaction: travails and triumphs [J]. Applied Catalysis A: General, 1996, 138(2):345 – 367.
[25] R. Rauch, A. Kiennemann, A. Sauciuc. Chapter 12 Fischer – Tropsch Synthesis to Biofuels (BtL Process) [J]. The Role of Catalysis for the Sustainable Production of Bio-fuels and Bio-chemicals, 2013:397 – 443.
[26] J. V. D. Loosdrecht, F.G Botes, I. M Ciobica, A. Ferreira, P. Gibson, et al. 7.20 Fischer – Tropsch Synthesis: Catalysts and Chemistry [J]. Comprehensive Inorganic Chemistry II, 2013, 4(2):525 – 557.
[27] Q. H. Zhang, K. Cheng, J. C Kang, et al Fischer – Tropsch catalysts for the production of hydrocarbon fuels with high selectivity [J]. Chemsuschem, 2014, 7(5):1251 – 1264.
[28] V. Calemma, S. Correra, C. Perego, P. Pollesel, L. Pellegrini. Hydroconversion of Fischer – Tropsch waxes: Assessment of the operating conditions effect by factorial design experiments [J]. Catalysis Today, 2005, 106(1 – 4):282 – 287.
[29] Y. Liu, B. T. Teng, X. H. Guo, et al. Effect of reaction conditions on the catalytic performance of Fe – Mn catalyst for Fischer – Tropsch synthesis [J]. Journal of Molecular Catalysis A Chemical, 2007, 272(1 – 2):182 – 190.
[30] S. S. Ail, S. Dasappa. Biomass to liquid transportation fuel via Fischer Tropsch synthesis-Technology review and current scenario [J]. Renewable & Sustainable Energy Reviews, 2016, 58:267 – 286.
[31] M. Arsalanfar, A. A. Mirzaei, H. R. Bozorgzadeh, A. Samimi. A Review of Fischer-Tropsch Synthesis on the Cobalt Based Catalysts [J]. Physical. Chemistry. Research, 2014, 2(2):179 – 201.
[32] D. L. King. A Fischer – Tropsch study of supported ruthenium catalysts [J]. Journal of Catalysis, 1978, 51(3):386 – 397.
[33] M. Nurunnabi, K. Murata, K. Okabe, M. Inaba, I. Takahara. Performance and characterization of Ru/Al2O3 and Ru/SiO2 catalysts modified with Mn for Fischer – Tropsch synthesis [J]. Applied Catalysis A General, 2008, 340(2):203 – 211.
[34] L. Bruce, J. F. Mathews. The Fischer-Tropsch activity of nickel-zirconia [J]. Applied Catalysis, 1982, 4(4):353 – 369.
[35] S. Abell. Exploring Iron-based Multifunctional Catalysts for Fischer – Tropsch Synthesis: A Review [J]. Chemsuschem, 2011, 4(11):1538 – 1566.
[36] A. Y. Khodakov, W. Chu, F. Pascal. Advances in the Development of Novel Cobalt Fischer-Tropsch Catalysts for Synthesis of Long-Chain Hydrocarbons and Clean Fuel [J], 2007, 107:1692 – 1744.
[37] Q. H. Zhang, J. C. Kang, Y. Wang. Development of Novel Catalysts for Fischer – Tropsch Synthesis: Tuning the Product Selectivity [J]. Cheminform, 2010, 2(9):1030 – 1058.
[38] H. Karaca, O. V. Safonova, S. Chambrey , P. Fongarland, P. Roussel, et al. Structure and catalytic performance of Pt – promoted alumina-supported cobalt catalysts under realistic conditions of Fischer – Tropsch synthesis[J]. Journal of Catalysis, 2011, 277(1):14 – 26.
[39] S. E. De, B. M. Weckhuysen. The renaissance of iron – based Fischer – Tropsch synthesis: on the multifaceted catalyst deactivation behavior [J].Chemical Society Review, 2009, 37(12):2758 – 2781.
[40] M. D. Shroff, D. S. Kalakkad, K. E. Coulter, et al. Activation of Precipitated Iron Fischer – Tropsch Synthesis Catalysts [J]. Journal of Catalysis, 1995, 156(2):185 – 207.
[41] J. C. Kang, S. L. Zhang, Q. H. Zhang, Y. Wang, et al. Ruthenium nanoparticles supported on carbon nanotubes as efficient catalysts for selective conversion of synthesis gas to diesel fuel [J]. Angewandte Chemie International Edition, 2009, 48(14):2565 – 2568.
[42] A. N. Pour, M. R. Housaindokht. Studies on product distribution of nanostructured iron catalyst in Fischer – Tropsch synthesis: Effect of catalyst particle size [J]. Journal of Industrial and Engineering Chemistry, 2014, 20(2):591 – 596.
[43] Enrique Iglesia. Design, synthesis, and use of cobalt-based Fischer-Tropsch synthesis catalysts [J] Applied

Catalysis A: General, 1997, 161(1 – 2), 59 – 78
[44] J. P. den Breejen, P. B. Radstake, et al. On the Origin of the Cobalt Particle Size Effects in Fischer−Tropsch Catalysis [J]. Journal of the American Chemical Society, 2009, 131(7):7197 – 7203.
[45] J. Y. Park, Y. J. Lee, P. K. Khanna, K. W. Jun, et al. Alumina-supported iron oxide nanoparticles as Fischer – Tropsch catalysts: Effect of particle size of iron oxide [J]. Journal of Molecular Catalysis A: Chemical, 2010, 323(1 – 2):84 – 90.
[46] S. Bessell. Support effects in cobalt – based Fischer – Tropsch catalysis [J]. Cheminform, 1993, 96(96):253 – 268.
[47] S. Storsæter, B. Tøtdal, J. C. Walmsley, B. S. Tanem, A. Holmen. Characterization of alumina – , silica – , and titania – supported cobalt Fischer – Tropsch catalysts [J]. Journal of Catalysis, 2005, 236(1):139 – 152.
[48] I. E. Dan, M. Roy – Auberger, R. Revel. Differences in the characteristics and catalytic properties of cobalt-based Fischer – Tropsch catalysts supported on zirconia and alumina [J]. Applied Catalysis A General, 2004, 268(1 – 2):51 – 60.
[49] P. R. Karandikar, J. Y. Park, Y. J. Lee, et al. Fischer – Tropsch Synthesis Over Cobalt Supported On Silica-Incorporated Mesoporous Carbon [J]. Chemcatchem, 2013, 5(6):1461 – 1471.
[50] V. I. Isaeva, O. L. Eliseev, R. V. Kazantsev, et al. Fischer-Tropsch synthesis over MOF-supported cobalt catalysts (Co@MIL-53(Al)) [J]. Dalton Transactions, 2016, 45(30):12006 – 12014.
[51] W. Chao, K. M. Makar, L. E. Manzer, et al. Fischer-Tropsch processes and catalysts with promoters: US, US6489371 [P]. 2004.
[52] W. M. H. Sachtler, D. F. Shriver, W. B. Hollenberg, et al. Promoter action in Fischer-Tropsch catalysis [J]. Journal of Catalysis, 1985, 92(2):429 – 431.
[53] S. R. Craxford. The function of the promoters in the catalysts for the Fischer – Tropsch synthesis [J]. Transactions of the Faraday Society, 1946, 42(5):8515 – 8519.
[54] N. Tsubaki, S. Sun, K. Fujimoto. Different Functions of the Noble Metals Added to Cobalt Catalysts for Fischer – Tropsch Synthesis [J]. Journal of Catalysis, 2001, 199(2):236 – 246.
[55] A. Kogelbauer, R Oukaci. Ruthenium Promotion of Co/Al2O3 Fischer – Tropsch Catalysts [J]. Journal of Catalysis, 1996, 160(1):125 – 133.
[56] G. Jacobs, J. A. Chaney, P. M. Patterson, et al. Fischer – Tropsch synthesis: study of the promotion of Pt on the reduction property of Co/Al2O3 catalysts by in situ EXAFS of Co K and Pt LIII edges and XPS [J]. Journal of Synchrotron Radiation, 2004, 11(Pt 5):414 – 422.
[57] K. Shimura, T. Miyazawa, T. Hanaoka, et al. Fischer – Tropsch synthesis over alumina supported cobalt catalyst: Effect of promoter addition [J]. Applied Catalysis A: General, 2015, 494:1 – 11.
[58] C. Brabant, A. Khodakov, et al. Promotion of lanthanum – supported cobalt – based catalysts for the Fischer – Tropsch reaction [J]. Comptes Rendus Chimie, 2017, 20(1):40 – 46.
[59] J. S. Ledford, M. Houalla, L. Petrakis, et al. Influence of Lanthanum Oxide on the Surface Structure and Co Hydrogenation Activity of Supported Cobalt Catalysts [J]. Physica Status Solidi Applied Research, 1989, 45(18):6770 – 6777.
[60] Y. J. Zhang, K. Y. Li, J. L. Li, X. D. Zhan. Fischer – Tropsch Synthesis on Lanthanum Promoted Co/TiO2 Catalysts [J]. Catalysis Letters, 2010, 139(1):1 – 6.
[61] H. X. Zhao, H. L. Lü. Effect of La Promotion on Co/ZrO2 Catalysts in Fischer-Tropsch Synthesis[J]. Advanced Materials Research, 2013, 850 – 851:124 – 127.
[62] F. Pardo – Tarifa, S. Cabrera, M. Sanchez – Dominguez, et al. Ce – promoted Co/Al2O3 catalysts for Fischer – Tropsch synthesis [J]. International Journal of Hydrogenenergy, 2017, 42(15):9754 – 9765.
[63] X. H. Zhang, H. Q. Su, Y. L. Zhang, X. J. Gua. Effect of CeO2 promotion on the catalytic performance of Co/ZrO2 catalysts for Fischer-Tropsch synthesis [J]. Fuel, 2016, 184:162 – 168.
[64] F. Rohr, O. A. Lindvåg, A. Holmen, E. A. Blekkan. Fischer – Tropsch synthesis over cobalt catalysts supported on zirconia-modified alumina [J]. Catalysis Today, 2000, 58(4):247 – 254.

[65] W. Warayanona, S. Tungkamania, et al. Effect of Manganese Promoter on Cobalt Supported Magnesia Catalyst for Fischer – Tropsch Synthesis [J]. Energy Procedia, 2015, 79:163 – 168.
[66] L. Chen, G. X. Song, Y. C. Fu, J. Y. Shen. The effects of promoters of K and Zr on the mesoporous carbon supported cobalt catalysts for Fischer-Tropsch synthesis [J]. Journal of Colloid and Interface Science, 2012, 368(1):456 – 461.
[67] T. Wang, Y. J. Ding, J. M. Xiong, et al. Effect of Vanadium Promotion on Activated Carbon – Supported Cobalt Catalysts in Fischer – Tropsch Synthesis [J]. Catalysis Letters, 2006, 107(1):47 – 52.
[68] G. P. Huffman, N. Shah, J. M. Zhao, et al. In-Situ XAFS Investigation of K – Promoted Co Catalysts [J]. Journal of Catalysis, 1995, 151(1):17 – 25.
[69] S Tsunetake, O Makoto. Mesoporous Alumina: Synthesis, Characterization, and Catalysis [M] Advanced Nanomaterials. Wiley – VCH Verlag GmbH&Co. KGaA, 2010, 22(4):481 – 521.
[70] D. Gu, F. Schuth. Synthesis of non-siliceous mesoporous oxides [J]. Chemical Society Reviews, 2014, 43(1):313 – 44.
[71] Neeraj, M. Eswaramoorthy. Mesoporous alumina [J]. Journal of Chemical Sciences, 1998, 110(2):143 – 149.
[72] B. Y. Huang, C. H. Bartholomew, et al. Facile structure-controlled synthesis of mesoporous γ – alumina: Effects of alcohols in precursor formation and calcination [J]. Microporous and Mesoporous Materials, 2013, 177(5):37 – 46.
[73] Q. Liu, A. Q. Wang, X. D. Wang, T. Zhang. Ordered Crystalline Alumina Molecular Sieves Synthesized via a Nanocasting Route [J]. Chemistry of Materials, 2006, 18(22):5153 – 5155.
[74] Z. X. Li, et al. Highly Ordered Hierarchical Macroporous-Mesoporous Alumina with Crystalline Walls [J]. Catalysis Letters, 2016, 146(9):1712 – 1717.
[75] F. Vaudry, A. Shervin Khodabandeh, M. E. Davis. Synthesis of Pure Alumina Mesoporous Materials [J]. Chemistry of Materials, 1996, 8(7):1451 – 1464.
[76] H. C. Lee, H. J. Kim, et al. Synthesis of nanostructured γ -alumina with a cationic surfactant and controlled amounts of water [J]. Microporous & Mesoporous Materials, 2005, 79(1 – 3):61 – 68.
[77] Q. Yuan, L. L. Li, S. L. Lu, H. L. Duan, et al. Facile synthesis for ordered mesoporous gamma-aluminas with high thermal stability [J]. Journal of the American Chemical Society, 2010, 130(11):3465 – 3472.
[78] J. Čejka. Organized mesoporous alumina: synthesis, structure and potential in catalysis [J]. Applied Catalysis A: General, 2003, 254(2):327 – 338.
[79] C. Marquez-Alvarez, N. Zilkova, et al. ChemInform Abstract: Synthesis, Characterization and Catalytic Applications of Organized Mesoporous Aluminas [J]. Catalysis Reviews, 2008, 40(34):222 – 286.
[80] W Wu, Z. J. Wan, W. Chen, et al. A facile synthesis strategy for structural property control of mesoporous alumina and its effect on catalysis for biodiesel production [J]. Advanced Powder Technology, 2014, 25(4):1220 – 1226.
[81] S. Badoga, et al. Synthesis and characterization of mesoporous aluminas with different pore sizes: Application in NiMo supported catalyst for hydrotreating of heavy gas oil [J]. Applied Catalysis A: General, 2015, 489:86 – 97.
[82] H. Arbaga, S. Yasyerli, et al. Enhancement of catalytic performance of Ni based mesoporous alumina by Co incorporation in conversion of biogas to synthesis gas [J]. Applied Catalysis B Environmental, 2016, 198:254 – 265.
[83] S. Handjania, E. Marceau, et al. Influence of the support composition and acidity on the catalytic properties of mesoporous SBA-15, Al-SBA-15, and Al2O3-supported Pt catalysts for cinnamaldehyde hydrogenation [J]. Journal of Catalysis, 2011, 282(1):228 – 236.
[84] L. Kaluža, M. Zdražil, N. Žilkov á , et al. High activity of highly loaded MoS2, hydrodesulfurization catalysts supported on organised mesoporous alumina [J]. Catalysis Communications, 2002, 3(4):151 – 157.
[85] Y. H. Xiao, X. H. Zheng, X. H. Chen, L. H. Jiang, Y. Zheng. Synthesis of Mg – Doped Ordered

Mesoporous Pd-Al2O3 with Different Basicity for CO, NO, and HC Elimination [J].Ind. Eng. Chem. Res, 2017, 56, 1687−1695
[86] A. Lira, R. G. Tailleur. Dehydrogenation of C12 – C14 paraffins on PtCu/meso-structured Al2O3 catalyst for LAB production: Process simulation [J]. Fuel, 2012, 97:49−60.
[87] D. Glasser, D. Hildebrandt, X. Y. Liu, et al. Recent advances in understanding the Fischer – Tropsch synthesis (FTS) reaction [J].Current Opinion in Chemical Engineering, 2012, 1(3):296−302.
[88] X. W. Zhu, X. J. Lu, X. Y. Liu, et al. Study of Radial Heat Transfer in a Tubular Fischer−Tropsch Synthesis Reactor [J]. Industrial & Engineering Chemistry Research, 2010, 49(21):10682−10688.
[89] H. S. Song, D. Ramkrishna, et al. Operating strategies for Fischer – Tropsch reactors: A model−directed study [J]. Korean Journal of Chemical Engineering, 2004, 21(2):308−317.
[90] X. W. Zhu, X. J. Lu, X. Y. Liu, et al. Heat transfer study with and without Fischer – Tropsch reaction in a fixed bed reactor with TiO2 SiO2 and SiC supported cobalt catalysts [J]. Chemical Engineering Journal, 2014, 247(7):75 – 84.
[91] M. Shinoda, Y. Zhang, Y. Yoneyama, et al. New bimodal pore catalysts for Fischer – Tropsch synthesis [J]. Fuel Processing Technology, 2004, 86(1):73 – 85.
[92] N. Suzuki, Y. Yamauchi. One – step synthesis of hierarchical porous γ-alumina with high surface area [J]. Journal of Sol – Gel Science and Technology, 2010, 53(2):428 – 433.
[93] C. C Liu, J. L. Lia, Y. H. Zhang, et al. Fischer – Tropsch synthesis over cobalt catalysts supported on nanostructured alumina with various morphologies [J]. Journal of Molecular Catalysis A Chemical, 2012, 363 – 364:335 – 342.
[94] X. D. Hu, P. J. Loi, R. J. O'Brien. High surface area, small crystallite size catalyst for Fischer-Tropsch synthesis: WO, US 7585812 B2 [P]. 2009.
[95] A. M. Saib, M. Claeys, E. V. Steen. Silica supported cobalt Fischer-Tropsch catalysts: effect of pore diameter of support [J]. Catalysis Today, 2002, 71(3 – 4):395 – 402.
[96] Y. L. Wang, B. Hou, J. G. Chen, et al. Influence of pore regularity on Fischer – Tropsch synthesis with Co/SiO2 Catalysts [J]. Reaction Kinetics, Mechanisms and Catalysis, 2011, 102(1):155 – 164.
[97] K. Shimura, T. Miyazawa, T. Hanaoka, et al. Fischer-Tropsch synthesis over alumina supported cobalt catalyst: Effect of crystal phase and pore structure of alumina support [J]. Journal of Molecular Catalysis A Chemical, 2014, 394(10):22 – 32.
[98] L. Chen, X. C. Tian, et al. The effect of surface acidic and basic properties of highly loaded Co catalysts on the Fischer – Tropsch synthesis [J]. Catalysis Communications, 2012, 28(28):155 – 158.
[99] M. E. Dry, G. J. Oosthuizen. The correlation between catalyst surface basicity and hydrocarbon selectivity in the Fischer-Tropsch synthesis [J]. Journal of Catalysis, 1968, 11(1):18 – 24.
[100] W. Chu, P. A. Chernavskii, L. Gengembre, et al. Cobalt species in promoted cobalt alumina-supported Fischer – Tropsch catalysts [J]. Journal of Catalysis, 2007, 252(2):215 – 230.
[101] H. M. Koo, B. S. Lee, M. J. Park, et al. Fischer – Tropsch synthesis on cobalt/Al2O3-modified SiC catalysts: effect of cobalt – alumina interactions [J]. Catalysis Science & Technology, 2013, 4(2):343 – 351.

参 考 文 献

[1] 辛勤,罗孟飞. 现代催化研究方法[M]. 科学出版社, 2009.
[2] D. Schanke, S. Vada, E. A. Blekkan, et al. Study of Pt-promoted cobalt CO hydrogenation catalysts [J]. Journal of Catalysis, 1995, 156(1):85 – 95.
[3] J. Yang, V. Frøseth, D. Chen, A. Holmen, et al. Particle size effect for cobalt Fischer – Tropsch catalysts based on in situ CO chemisorption [J]. Surface Science, 2015, 648:67 – 73.

参 考 文 献

[1] Y. Liu, H. Q. Guo, L. T. Jia, et al. Fischer-Tropsch Synthesis over Alumina- Supported Cobalt-Based Catalysts: Effect of Support Variables [J]. Journal of Materials Science & Chemical Engineering, 2014, 02(12):19 – 27.
[2] Ø. Borg, S. Eri, E. Rytter, A. Holmen, et al. Fischer-Tropsch synthesis over different alumina

supported cobalt catalysts [J]. Am Chem Soc Div Fuel Chem, 2006, 51:699 – 701.
[3] J. L. Zhang, J. G. Chen, J. Ren, et al. Support effect of Co/Al2O3 catalysts for Fischer – Tropsch synthesis [J]. Fuel, 2003, 82(5):581 – 586.
[4] H. F. Xiong, Y. H. Zhang, S. G. Wang, et al. Fischer – Tropsch synthesis: the effect of Al2O3 porosity on the performance of Co/Al2O3 catalyst [J]. Catalysis Communications, 2005, 6(8):512 – 516.
[5] W. Ma, G. Jacobs, P. Gao, et al. Fischer-Tropsch synthesis: Pore size and Zr promotional effects on the activity and selectivity of 25 % Co/Al2O3 catalysts [J]. Applied Catalysis A: General, 2014, 475(5):314 – 324.
[6] T. O. Eschemann, W. S. Lamme, et al. Effect of support surface treatment on the synthesis, structure, and performance of Co/CNT Fischer – Tropsch catalysts [J]. Journal of Catalysis, 2015, 328:130 – 138.
[7] S. W. Ho, Y. S. Su. Effects of Ethanol Impregnation on the Catalytic Properties of Silica – Supported Cobalt Catalysts [J]. Journal – Chinese Chemical Society Taipei, 1997, 168(1):51 – 59.
[8] Y. Zhang, Y. Liu, G. H. Yang, et al. Effects of impregnation solvent on Co/SiO2, catalyst for Fischer – Tropsch synthesis: A highly active and stable catalyst with bimodal sized cobalt particles [J]. Applied Catalysis A:General, 2007, 321(1):79 – 85.
[9] Q. Yuan, A. X. Yin, C. Luo, et al. Facile synthesis for ordered mesoporous gamma-aluminas with high thermal stability [J] Journal of the American Chemical Society, 2010, 130(11):3465 – 3472.
[10] 袁荃. 稀土/锆基和稀土/铝基有序介孔结构的可控合成及性质研究[D]. 北京大学, 2009.
[11] G. Jacobs, Y. Ji, B. H. Davis, et al. Fischer – Tropsch synthesis: Temperature programmed EXAFS/XANES investigation of the influence of support type, cobalt loading, and noble metal promoter addition to the reduction behavior of cobalt oxide particles [J]. Applied Catalysis A:General, 2007, 333(2):177 – 191.
[12] A. Tavasoli1, A. N. Pour, et al. Kinetics and product distribution studies on ruthenium-promoted cobalt/alumina Fischer-Tropsch synthesis catalyst [J]. Journal of Natural Gas Chemistry, 2010, 19(6):653 – 659.
[13] T. K. Das, G. Jacobs, P. M. Patterson, et al. Fischer – Tropsch synthesis: characterization and catalytic properties of rhenium promoted cobalt alumina catalysts [J]. Fuel, 2003, 82(7):805 – 815.
[14] B. Todic, W. Ma, G. Jacobs, et al. Effect of process conditions on the product distribution of Fischer – Tropsch synthesis over a Re – promoted cobalt-alumina catalyst using a stirred tank slurry reactor [J]. Journal of Catalysis, 2014, 311(3):325 – 338.
[15] S. Farzad, A. Rashidi, et al. Study of effective parameters in the Fischer Tropsch synthesis using monolithic CNT supported cobalt catalysts [J]. Fuel, 2014, 132(4):27 – 35.
[16] J. S. Jung, G. Choi. The Characterization of Micro-Structure of Cobalt on Gamma-Al2O3 for FTS: Effects of Pretreatment on Ru-Co/Al2O3 [C]. 14 Aiche Meeting. 2014.
[17] 辛勤,罗孟飞. 现代催化研究方法[M]. 科学出版社, 2009.
[18] S. Bessell. Support effects in cobalt-based fischer-tropsch catalysis [J]. Cheminform, 1993, 96(96):253 – 268.
[19] D. Vanhove, Z. Zhang, L. Makambo, et al. ChemInform Abstract: Hydrocarbon Selectivity in Fischer – Tropsch synthesis in reaction to textural properties of supported cobalt catalysts [J]. Applied Catalysis, 1984, 9(3):327 – 342.
[20] R. B. Anderson, W. K. Hall, et al. Studies of the Fischer--Tropsch Synthesis. V. Activities and Surface Areas of Reduced and Carburized Cobalt Catalysts [J]. Journal of the American Chemical Society, 1949, 71(1):183 – 188.
[21] A. M. Saib, M. Claeys, E. V. Steen. Silica supported cobalt Fischer – Tropsch catalysts: effect of pore diameter of support.[J]. Catalysis Today, 2002, 71(3 – 4):395 – 402.
[22] Ø. Borg, E. A. Blekkan, S. Eri, et al. Effect of calcination atmosphere and temperature on γ – Al2O3 supported cobalt Fischer – Tropsch catalysts [J]. Topics in Catalysis, 2007, 45(1): 39 – 43.
[23] J. Y. Park, Y. J. Lee, et al. Fischer – Tropsch catalysts deposited with size – controlled Co3O4 nanocrystals: Effect of Co particle size on catalytic activity and stability [J]. Applied Catalysis A:General, 2012, 411 – 412:15 – 23.
[24] 张涛, 臧璟龄, 胡爱华, 等. 锂对于γ – Al2O3表面酸中心的调变作用及其积炭性能的影响 [J]. 催化学报, 1990, 11(5):341 – 347.

[25] J. L. Zhang, J. G. Chen, J. Ren, et al. Chemical treatment of γ – Al2O3 and its influence on the properties of Co – based catalysts for Fischer – Tropsch synthesis [J]. Applied Catalysis A General, 2003,243(1):121 – 133.
[26] H. X. Zhao, J. G. Chen, et al. Effect of Calcination Temperature of Support on Catalytic Performance of Co/ZrO2 for Fischer – Tropsch Synthesis [J]. Chinese Journal of Catalysis, 2003, 24(12):933 – 936.
[27] B. Jongsomjit, J. Panpranot, et al. Effect of zirconia-modified alumina on the properties of Co/ γ -Al2O3 catalysts [J]. Journal of Catalysis, 2003, 215(1):66 – 77.
[28] D. Schanke, S. Vada, E. A. Blekkan, et al. Study of Pt-promoted cobalt CO hydrogenation catalysts [J]. Journal of Catalysis, 1995, 156(1):85 – 95.
[29] A. Y. Khodakov, W. Chu, P. Fongarland. Advances in the Development of Novel Cobalt Fischer – Tropsch Catalysts for Synthesis of Long – Chain Hydrocarbons and Clean Fuel [J].Chemical Reviews, 2007, 107:1692 – 1744.
[30] A. U. R. Salman. Surface Modified γ – Alumina Supports For Cobalt Fischer – Tropsch Catalysts [J]. Norwegian University of Science and Technology, 2015.
参 考 文 献
[1] S. A. Hosseini, A. Taeb, F. Feyzi, et al. Fischer – Tropsch synthesis over Ru promoted Co/ γ -Al2O3 catalysts in a CSTR [J].Catalysis Communications, 2004, 5(3): 137 – 143.
[2] 武汉大学. 无机化学.下册-3版[M]. 高等教育出版社, 1994.
[3] S. H. Zeng, et al. Promotion effect of single or mixed rare earths on cobalt – based catalysts for Fischer – Tropsch synthesis [J]. Catalysis Communications, 2011, 13(1):6 – 9..
[4] G. J. Haddad, B. Chen, J. G. Goodwin. Effect of La 3+ Promotion of Co/SiO2 on CO Hydrogenation [J]. Journal of Catalysis, 1996, 161(1):274 – 281..
[5] 代小平,余长春,沈师孔. 助剂CeO2对Co/Al2O3催化剂上F-T合成反应性能的影响[J].催化学报,2001, 22(2):104 – 107.
[6] S. M. Morris, P. F. Fulvio, et al. Ordered mesoporous alumina – supported metal oxides [J]. Journal of the American Chemical Society, 2008, 130(45): 15210 – 15216.
[7] Q. P. Sun, Y. Zheng, Y. Zheng, et al. Synthesis of highly thermally stable lanthanum-doped ordered mesoporous alumina [J]. Scripta Materialia, 2011, 65(11):1026 – 1029.
[8] Q.Yuan, H. H. Duan, L. L. Li, et al. Homogeneously Dispersed Ceria Nanocatalyst Stabilized with Ordered Mesoporous Alumina [J]. Advanced Materials, 2010, 22(13):1475 – 1478.
[9] 袁荃. 稀土/锆基和稀土/铝基有序介孔结构的可控合成及性质研究[D]. 北京大学, 2009.
[10] B. Ernst, L. Hilaire, A. Kiennemann. Effects of highly dispersed ceria addition on reducibility, activity and hydrocarbon chain growth of a Co/SiO2, Fischer – Tropsch catalyst [J]. Catalysis Today, 1999, 50(2):413 – 427.
[11] 代小平,余长春,李然家等. Co/SiO2催化剂催化费托合成中CeO2助剂的作用[J]. 催化学报 ,2006,27(10): 904 – 910.
[12] X. H. Zhang, H. Q. Su, et al. Effect of CeO2 promotion on the catalytic performance of Co/ZrO2, catalysts for Fischer – Tropsch synthesis [J]. Fuel, 2016, 184:162 – 168.
[13] 孙燕, 孙启文, 刘继森,等. 稀土金属氧化物助剂对费托合成Co/ γ – Al2O3催化剂性能的影响[J]. 石油化工, 2014, 43(8):886 – 891.
[14] F. Pardo-Tarifa, S. Cabrera, M. Sanchez-Dominguez, et al. Ce – promoted Co/Al2O3 catalysts for Fischer – Tropsch synthesis [J]. International Journal of Hydrogen Energy, 2017, 42(15):9754 – 9765.
[15] J. Barrault, S. Probst, A. Alouche, et al. Characterization and Catalytic Properties of Nickel Oxioe Supported on Rare Earth Oxides. Description of the Metal – Support Interaction.[J]. Studies in Surface Science & Catalysis, 1991, 61:357 – 365.
[16] J. Barrault, A. Guilleminot, et al. Hydrogenation of carbon monoxide on carbon – supported cobalt rare earth catalysts [J]. Applied Catalysis, 1986, 21(2): 307 – 312.
[17] C. H. Bartholomew. Chapter 5 Recent Developments in Fischer – Tropsch Catalysis [J]. Studies in Surface Science & Catalysis, 1991, 64:158 – 224.
[18] M. R. Hemmati, M. Kazemeini, J. Zarkesh, et al. Effect of lanthanum doping on the lifetime of Co/ γ -

Al2O3 catalysts in Fischer-Tropsch synthesis [J]. Journal of the Taiwan Institute of Chemical Engineers, 2012, 43(5):704 – 710.
[19] G. J. Haddad, B. Chen, J. G. Goodwin. Characterization of La3+-Promoted Co/SiO2 Catalysts [J]. Journal of Catalysis, 1996, 160(1):43 – 51.
[20] 熊建民,丁云杰,王涛等. La2O3助剂对Co/AC催化剂上费-托合成反应性能的影响[J].催化学报, 2005, 26(10):874 – 878.
[21] S. Vada, B. Chen, J. G. Goodwin. Isotopic Transient Study of La Promotion of Co/Al2O3 or CO Hydrogenation [J]. Journal of Catalysis, 1995, 153(2):224 – 231.
[22] S. L. Sun, N. Tsubaki, K. Fujimoto. The reaction performances and characterization of Fischer – Tropsch synthesis Co/SiO2, catalysts prepared from mixed cobalt salts [J]. Applied Catalysis A:General, 2000, 202(1):121 – 131.
[23] D. Schanke, S. Vada, E. A. Blekkan, et al. Study of Pt – promoted cobalt CO hydrogenation catalysts [J]. Journal of Catalysis, 1995, 156(1):85 – 95.

参 考 文 献

[1] K. Shimura, T. Miyazawa, et al. Fischer – Tropsch synthesis over alumina supported cobalt catalyst: Effect of promoter addition [J]. Applied Catalysis A General, 2015, 494(25):1 – 11.
[2] S. H. Zeng, Y. Du, H. Q. Su, et al. Promotion effect of single or mixed rare earths on cobalt-based catalysts for Fischer – Tropsch synthesis [J]. Catalysis Communications, 2011, 13(13):6 – 9.
[3] L. L. He, B. T. Teng, Y. L. Zhang, et al. Development of Composited Rare-Earth Promoted Cobalt-Based Fischer – Tropsch Synthesis Catalysts with High Activity and Selectivity [J]. Applied Catalysis A:General, 2015, 505(25):276 – 283.
[4] Q. Yuan, H. H. Duan, L. L. Li, et al. Homogeneously Dispersed Ceria Nanocatalyst Stabilized with Ordered Mesoporous Alumina [J]. Advanced Materials, 2010, 22(13):1475 – 1478.
[5] Q. Yuan, A. X. Yin, C. Luo, et al. Facile synthesis for ordered mesoporous gamma-aluminas with high thermal stability [J]. Journal of the American Chemical Society, 2010, 130(11):3465 – 3472.
[6] 袁荃. 稀土/锆基和稀土/铝基有序介孔结构的可控合成及性质研究[D]. 北京大学, 2009.
[7] T. Wang, Y. J. Ding, et al. Influence of lanthanum on the performance of Zr – Co/activated carbon catalysts in Fischer – Tropsch synthesis [J]. Journal of Natural Gas Chemistry, 2008, 17(2):153 – 158.
[8] 辛勤,罗孟飞. 现代催化研究方法[M]. 科学出版社, 2009.
[9] N. E Tsakoumis, R. Dehghan, R. E. Johnsen, et al. A combined in situ, XAS – XRPD – Raman study of Fischer – Tropsch synthesis over a carbon supported Co catalyst [J]. Catalysis Today, 2013, 205(30):86 – 93.
[10] A. Kogelbauer, J. G. Goodwin, R. Oukaci. Ruthenium Promotion of Co/Al2O3 Fischer-Tropsch Catalysts [J]. Journal of Catalysis, 1996, 160(1):125 – 133.
[11] D. Schanke, S. Vada, E. A. Blekkan, et al. Study of Pt – promoted cobalt CO hydrogenation catalysts [J]. Journal of Catalysis, 1995, 156(1):85 – 95.
[12] G. Jacobs, J. A. Chaney, P. M. Patterson, et al. Fischer – Tropsch synthesis: study of the promotion of Pt on the reduction property of Co/Al2O3, catalysts by in situ, EXAFS of Co K, and Pt L III, edges and XPS [J]. Journal of Synchrotron Radiation, 2004, 11(Pt 5):414 – 422.
[13] A. M. Hilmen, D. Schanke, K. F. Hanssen, et al. Study of the effect of water on alumina supported cobalt Fischer – Tropsch catalysts [J]. Applied Catalysis A General, 1999, 186(1 – 2):169 – 188.
[14] B. A. Sexton, A. E. Hughes, T. W. Turney. An XPS and TPR study of the reduction of promoted cobalt – kieselguhr Fischer-Tropsch catalysts [J]. Journal of Catalysis, 1986, 97(2):390 – 406.