

利用硫酸氧钒制备钒炭催化剂用于烟气脱硫

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Using vanadyl sulfate to prepare carbon-supported vanadium catalyst for flue gas desulfurization

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摘要 利用硫酸氧钒制备钒炭催化剂用于烟气脱硫。研究发现,负载在活性炭上的硫酸氧钒极易被氧化为五价钒硫酸盐,这些五价钒硫酸盐具有很高的氧化SO₂的活性,极大地促进了SO₂在活性炭上的脱除。而且,通过煅烧可以将五价钒硫酸盐分解为五价钒氧化物,最佳煅烧温度为500℃,由于煅烧后用于储存硫酸的微孔孔容增加,SO₂的吸附容量得到了进一步提高,由此表明,利用硫酸氧钒可以制备传统的V₂O₅/AC催化剂。为了获得完全氧化的钒物种,对煅烧后的催化剂进行了空气中预氧化,但由于含氧官能团的形成、炭载体的烧蚀以及钒的还原,预氧化不利于脱硫。此外,研究中得到初步证据证明脱硫过程中V₂O₅/AC催化剂中五价钒氧化物转变成了五价钒硫酸盐,结合五价钒硫酸盐所表现出的氧化SO₂的能力,推测SO₂在V₂O₅/AC上的脱除遵循以下机理:五价钒氧化物先转变为五价钒硫酸盐,后者催化氧化SO₂为硫酸。

关键词: V₂O₅/AC 脱硫 硫酸钒 催化作用 低温

Abstract: Vanadyl sulfate (V^{IV}OSO₄) was used to prepare carbon-supported vanadium catalyst for flue gas desulfurization. The V^{IV}OSO₄ impregnated on activated carbon (AC) was easily oxidized into vanadium(V) sulfate phase (possibly V₂O₃(SO₄)₂) in air, which exhibited high catalytic activity toward SO₂ oxidation, thus significantly enhancing SO₂ retention on AC. Furthermore, the vanadium(V) sulfate can be decomposed upon calcination in nitrogen with optimum temperature of 500 °C to form vanadium(V) oxide, further improving SO₂ retention mainly due to increase in micropore volume suitable for sulfate storage and showing suitability of vanadyl sulfate to prepare traditional V₂O₅/AC catalyst. To obtain fully oxidized vanadium oxides, preoxidation was carried out on catalyst after calcination. However, due to ablation of carbon support, reduction of vanadium and/or formation of surface oxygen groups, the preoxidation was negative for SO₂ retention. Additionally, this paper provided preliminary evidence indicating transformation of vanadium(V) oxide in V₂O₅/AC into vanadium(V) sulfate during desulfurization. Combined with catalytic role of vanadium(V) sulfate for SO₂ oxidation, SO₂ removal on V₂O₅/AC likely followed a mechanism that the vanadium(V) oxide firstly transformed into vanadium(V) sulfate and the latter was then responsible for subsequent SO₂ oxidation into H₂SO₄.

Key words: V₂O₅/AC SO₂ removal vanadium(V) sulfate catalytic role low temperature

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- [1] LOÓPEZ D, BUITRAGO R, SEPUÚLVEDA-ESCRIBANO A, RODRÍGUEZ-REINOSO F, MONDRAGOÛN F. Low temperature catalytic adsorption of SO₂ on activated carbon[J]. *J Phys Chem C*, 2008, 112(39): 15335-15340.
- [2] ARCIBAR-OROZCO J A, RANGEL-MENDEZ J R, BANDOSZ T J. Reactive adsorption of SO₂ on activated carbons with deposited iron nanoparticles[J]. *J Hazard Mater*, 2013, 246-247: 300-309.
- [3] NAKTIYOK J, BAYRAKÖKEN H, ÖZER A K, G?LABOGLU M S. Flue gas desulfurization by calcined phosphate rock and reaction kinetics[J]. *Energy Fuels*, 2013, 21(3):1466-1472.
- [4] SAKAI M, SU C, SASAOKA E. Simultaneous removal of SO_x and NO_x using slaked lime at low temperature[J]. *Ind Eng Chem Res*, 2002, 41(20): 5029-5033.
- [5] KAMINSKI J. Technologies and costs of SO₂-emissions reduction for the energy sector[J]. *Appl Energy*, 2003, 75(3/4): 165-172.
- [6] DAVINI P. SO₂ and NO_x adsorption properties of activated carbons obtained from a pitch containing iron derivatives[J]. *Carbon*, 2001, 39(14): 2173-2179.
- [7] TSENG H H, WEY M Y. Study of SO₂ adsorption and thermal regeneration over activated carbon-supported copper oxide catalysts[J]. *Carbon*, 2004, 42(11): 2269-2278.
- [8] BOYANO A, GÁLVEZ M E, MOLINER R, LÁZARO M J. Carbon-based catalytic briquettes for the reduction of NO: Effect of H₂SO₄ and HNO₃ carbon support treatment[J]. *Fuel*, 2008, 87(10/11): 2058-2068.
- [9] XING X, LIU Z, YANG J. Mo and Co doped V₂O₅/AC catalyst-sorbents for flue gas SO₂ removal and elemental sulfur production[J]. *Fuel*, 2008, 87(8/9): 1705-1710.
- [10] MACÍAS-PÉREZ M C, BUENO-LÓPEZ A, LILLO-RÓDENAS M A, SALINAS-MARTÍNEZ DE LECEA C, LINARES-SOLANO A. SO₂ retention on CaO/activated carbon sorbents. Part III. Study of the retention and regeneration conditions[J]. *Fuel*, 2008, 87(15/16): 3170-3175.
- [11] MA J, LIU Z, LIU S, ZHU Z. A regenerable Fe/AC desulfurizer for SO₂ adsorption at low temperatures[J]. *Appl Catal B: Environ*, 2003, 45(4): 301-309.
- [12] PRZEPIÓRSKI J, CZYZEWSKI A, KAPICA J, MOSZY?SKI D, GRZMIL B, TRYBA B, MOZIA S, MORAWSKI A W. Low temperature removal of SO₂ traces from air by MgO-loaded porous carbons[J]. *Chem Eng J*, 2012, 191: 147-153.
- [13] MA J, LIU Z, LIU Q, GUO S, HUANG Z, XIAO Y. SO₂ and NO removal from flue gas over V₂O₅/AC at lower temperatures-Role of V₂O₅ on SO₂ removal[J]. *Fuel Process Technol*, 2008, 89(3): 242-248.
- [14] XIAO Y, LIU Q, LIU Z, HUANG Z, GUO Y, YANG J. Roles of lattice oxygen in V₂O₅ and activated coke in SO₂ removal over coke-supported V₂O₅ catalysts[J]. *Appl Catal B: Environ*, 2008, 82(1/2): 114-119.
- [15] 郭彦霞, 刘振宇, 李允梅, 刘清雅. 氨再生条件对V2O5/AC同时脱硫脱硝活性的影响[J]. *燃料化学学报*, 2007, 35(3): 344-348.
- [16] GUO Yan-xia, LIU Zhen-yu, LI Yun-mei, LIU Qing-ya. NH₃ regeneration of SO₂-captured V₂O₅/AC catalyst-sorbent for simultaneous SO₂ and NO removal[J]. *Journal of Fuel Chemistry and Technology*, 2007, 35(3): 344-348.
- [17] ZHU Z, NIU H, LIU Z, LIU, S. Decomposition and reactivity of NH₄HSO₄ on V₂O₅/AC catalysts used for NO reduction with ammonia[J]. *J Catal*, 2000, 195(2): 268-278.
- [18] COULSTON G W, THOMPSON E A, HERRON N. Characterization of VPO catalysts by X-ray photoelectron spectroscopy[J]. *J Catal*, 1996, 163(1): 122-129.
- [19] NEFEDOV V I, SALYN YA V, LEONHARDT G, SCHEIBE R. A comparison of different spectrometers and charge corrections used in X-ray photoelectron spectroscopy[J]. *J Electro Spectrosc Relat Phenom*, 1977, 10(2): 121-124.
- [20] KASPERKIEWICZ J, KOVACICH J A, LICHTMAN D. XPS studies of vanadium and vanadium oxides[J]. *J Electro Spectrosc Relat Phenom*, 1983, 32(2): 123-132.
- [21] GARCÍA-BORDEJÉ E, PINILLA J L, LÁZARO M J, MOLINER R, FIERRO J L G. Role of sulphates on the mechanism of NH₃-SCR of NO at low temperatures over presulphated vanadium supported on carbon-coated monoliths[J]. *J Catal*, 2005, 233(1): 166-175.
- [22] GIAKOUMELOU I, PARVULESCU V, BOGHOSIAN S. Oxidation of sulfur dioxide over supported solid V₂O₅/SiO₂ and supported molten salt V₂O₅-Cs₂SO₄/SiO₂ catalysts: Molecular structure and reactivity[J]. *J Catal*, 2004, 225(2): 337-349.
- [23] CHRISTODOULAKIS A, BOGHOSIAN S. Molecular structure of supported molten salt catalysts for SO₂ oxidation[J]. *J Catal*, 2003, 215(1): 139-150.
- [24] GIAKOUMELOU I, CARABA R M, PARVULESCU V I, BOGHOSIAN S. First in situ raman study of vanadium oxide based SO₂ oxidation supported molten salt catalysts[J]. *Catal Lett*, 2002, 78(1): 209-214.
- [25] LIZZIO A A, DEBARR J A. Effect of surface area and chemisorbed oxygen on the SO₂ adsorption capacity of activated char[J]. *Fuel*, 1996, 75(13): 1515-1522.
- [26] LIZZIO A A, DEBARR J A. Mechanism of SO₂ removal by carbon[J]. *Energy Fuels*, 1997, 11(2): 284-291.
- [27] RAYMUNDO-PIÑERO E, CAZORLA-AMORÓS D, LINARES-SOLANO A. Temperature programmed desorption study on the mechanism of SO₂ oxidation by activated carbon and activated carbon fibres[J]. *Carbon*, 2001, 39(2): 231-242.

- [28] RAYMUNDO-PIÑERO E, CAZORLA-AMORÓS D, SALINAS-MARTINEZ DE LECEA C, LINARES-SOLANO A. Factors controlling the SO₂ removal by porous carbons: Relevance of the SO₂ oxidation step[J]. Carbon, 2000, 38(3): 335-344.
- [29] ZHU Z, LIU Z, NIU H, LIU S, HU T, LIU T, XIE Y. Mechanism of SO₂ promotion for NO reduction with NH₃ over activated carbon-supported vanadium oxide catalyst[J]. J Catal, 2001, 197(1): 6-16.
- [30] ZHOU J H, SUI Z J, ZHU J, LI P, CHEN D, DAI Y C, YUAN W K. Characterization of surface oxygen complexes on carbon nanofibers by TPD, XPS and FT-IR[J]. Carbon, 2007, 45(4): 785-796.
- [31] LEE W H, LEE J G, REUCROFT P J. XPS study of carbon fiber surfaces treated by thermal oxidation in a gas mixture of O₂/(O₂+N₂) [J]. Appl Surf Sci, 2001, 171(1/2): 136-142.
- [32] MARTIN C, PERRARD A, JOLY J P, GAILLARD F, DELECROIX V. Dynamic adsorption on activated carbons of SO₂ traces in air: I. Adsorption capacities[J]. Carbon, 2002, 40(12): 2235-2246.
- [33] DAVINI P. Adsorption and desorption of SO₂ on active carbon: The effect of surface basic groups[J]. Carbon, 1990, 28(4): 565-571.
- [34] ZHU Z, LIU Z, LIU S, NIU H, HU T, LIU T, XIE Y. NO reduction with NH₃ over an activated carbon-supported copper oxide catalysts at low temperatures[J]. Appl Catal B: Environ, 2000, 26(1): 25-35.
- [35] TSENG H H, WEY M Y, LIANG Y S, CHEN K H. Catalytic removal of SO₂, NO and HCl from incineration flue gas over activated carbon-supported metal oxides[J]. Carbon, 2003, 41(5): 1079-1085.
- [36] XING X, LIU Z, WANG J. Elemental sulfur production through regeneration of a SO₂-adsorbed V₂O₅-CoO/AC in H₂[J]. Fuel Process Technol, 2007, 88(7): 717-722.
- [37] GARCÍA-BORDEJÉ E, PINILLA J L, LÁZARO M J, MOLINER R. NH₃-SCR of NO at low temperatures over sulphated vanadia on carbon-coated monoliths: Effect of H₂O and SO₂ traces in the gas feed[J]. Appl Catal B: Environ, 2006, 66(3/4): 281-287.
- [1] 韩奎华, 齐建荟, 李辉, 刘洪涛, 路春美. 木醋调质石灰石用于O₂/CO₂燃煤同时脱硫脱硝性能[J]. 燃料化学学报, 2013, 41(11): 1378-1383.
- [2] 陈振亚, 牛保伦, 汤灵芝, 张亮, 黄海东, 任韶然. 原油组分低温氧化机理和反应活性实验研究[J]. 燃料化学学报, 2013, 41(11): 1336-1342.
- [3] 龚娟, 米万良, 苏庆泉. 基于金属氧化物脱硫剂的天然气深度脱硫[J]. 燃料化学学报, 2013, 41(10): 1248-1255.
- [4] 张海永, 王永刚, 张培忠, 林雄超, 朱豫飞. NiW/Al₂O₃-Y催化剂的制备及其对煤焦油加氢处理的研究[J]. 燃料化学学报, 2013, 41(09): 1085-1091.
- [5] 张俊峰, 白云星, 张清德, 解红娟, 谭猗生, 韩怡卓. Zr改性Ni/Y-Al₂O₃催化剂用于浆态相合成气的低温甲烷化[J]. 燃料化学学报, 2013, 41(08): 966-971.
- [6] 殷长龙, 翟西平, 赵蕾艳, 刘晨光. 二苯并噻吩类硫化物在非负载型NiMoW催化剂上加氢脱硫反应机理[J]. 燃料化学学报, 2013, 41(08): 991-997.
- [7] 杨朋举, 王剑, 赵江红, 朱珍平. 罗丹明B敏化TiO₂可见光分解水产氢研究[J]. 燃料化学学报, 2013, 41(06): 735-740.
- [8] 孙林平, 李飞, 张龙. 稀土金属氧化物对Y分子筛吸附脱硝性能的影响[J]. 燃料化学学报, 2013, 41(04): 499-505.
- [9] 唐念, 盘思伟. 大型煤粉锅炉汞的排放特性和迁移规律研究[J]. 燃料化学学报, 2013, 41(04): 484-490.
- [10] 董世伟, 秦玉才, 阮艳军, 王源, 于文广, 张磊, 范跃超, 宋丽娟. 改性Y型分子筛对FCC汽油脱硫性能的研究[J]. 燃料化学学报, 2013, 41(03): 341-346.
- [11] 刘广波, 张清德, 韩怡卓, 椿范立, 谭猗生. MoO₃-SnO₂催化剂上二甲醚低温氧化高选择性制备甲酸甲酯[J]. 燃料化学学报, 2013, 41(02): 223-227.
- [12] 张晓鹏, 沈伯雄. Mn/Ce-ZrO₂催化剂低温NH₃-SCR脱硝性能研究[J]. 燃料化学学报, 2013, 41(01): 123-128.
- [13] 王永刚, 张海永, 张培忠, 许德平, 赵宽, 王芳杰. NiW/Y-Al₂O₃催化剂的低温煤焦油加氢性能研究[J]. 燃料化学学报, 2012, 40(12): 1492-1497.
- [14] 沈伯雄, 陈建宏, 姚燕, 胡国丽. 碱土金属对MnO_x-CeO₂/ZrO₂-PILC催化剂SCR活性影响研究[J]. 燃料化学学报, 2012, 40(12): 1487-1491.
- [15] 朱淼, 王晓红, 胡志宇. Al₂O₃负载Pt催化剂的合成及其甲醇低温催化燃烧性能研究[J]. 燃料化学学报, 2012, 40(11): 1403-1408.