

用于 NH₃ 选择性催化还原 NO 的非钒基催化剂研究进展

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摘要 NH₃ 选择性催化还原 NO (NH₃-SCR) 技术在燃煤电厂烟气脱硝过程中有着多年的工业应用经验, 也是最有望实际应用于柴油车尾气 NO_x 催化去除的技术之一。鉴于目前工业化应用的 V₂O₅-WO₃ (MoO₃)/TiO₂ 催化剂体系应用于柴油车尾气净化仍存在着诸多问题, 开发新型、高效、稳定且环境友好的非钒基 NH₃-SCR 催化剂体系成为 NO_x 催化净化领域的研究热点。以分子筛催化剂 (包括 Cu 基分子筛催化剂以及 Fe 基分子筛催化剂) 和氧化物催化剂 (包括 Fe 基氧化物催化剂、Mn 基氧化物催化剂以及其他非钒基氧化物催化剂) 为主线, 综述了近年来国内外有关非钒基 NH₃-SCR 催化剂的研究进展, 较为全面地总结了该系列催化剂的 NH₃-SCR 反应性能、活性中心结构、低温 SCR 活性改进、NH₃-SCR 反应机理、抗 H₂O 或抗 SO₂ 性能改善以及工业化应用的可行性, 并展望了该领域未来可能的发展方向和研究热点。

关键词: 选择性催化还原 烟气脱硝 柴油车尾气净化 非钒基催化剂 分子筛催化剂 氧化物催化剂 低温活性 反应机理

Abstract: Selective catalytic reduction of NO with NH₃ (NH₃-SCR) is a well-proven technique for the removal of NO_x from stationary sources such as coal-fired power plants, and is also one of the most promising techniques for the NO_x elimination from diesel exhaust under oxygen-rich conditions. Due to some inevitable disadvantages of the present V₂O₅-WO₃ (MoO₃)/TiO₂ catalyst for industrial use, many researchers focus on the development of novel, highly efficient, stable, environmental-friendly and vanadium-free NH₃-SCR catalysts. The research progress in the field of vanadium-free NH₃-SCR catalysts is reviewed, including zeolite catalysts (such as Fe-zeolite catalysts and Cu-zeolite catalysts) and oxide catalysts (such as Fe-based oxide catalysts, Mn-based oxide catalysts, and other vanadium-free oxide catalysts). Several aspects in this field, including the evaluation of catalytic performance, the structure analysis of active sites, the improvement of low temperature activity, the study of NH₃-SCR reaction mechanism, the enhancement of H₂O/SO₂ durability, and the feasibility analysis for industrial use, have been discussed in detail. The possible developing orientation and research interests in the field of vanadium-free NH₃-SCR catalysts are previewed.



Keywords: selective catalytic reduction, flue gas denitration, diesel exhaust purification, vanadium-free catalyst, zeolite catalyst, oxide catalyst, low temperature activity, reaction mechanism

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- [2] 火电厂大气污染物排放标准》编制组. 火电厂大气污染物排放标准 (编制说明征求意见稿). 北京: 中华人民共和国环境保护部科技标准司 (Drafting Group of "Emission Standard of Air Pollutants for Thermal Power Plants". Emission Standard of Air Pollutants for Thermal Power Plants (Draft for Soliciting Opinions). Beijing: De-partment of Science, Technology and Standards, Ministry of Environmental Protection of the People's Republic of China), 2009. 2 
- [3] usca G, Lietti L, Ramis G, Berti F. Appl Catal B, 1998, 18: 1 
- [4] 贺忠, 郝吉明, 陆永琪, 朱天乐. 中国环境科学 (Tian H Zh, Hao J M, Lu Y Q, Zhu T L. Chin Environ Sci), 2001, 21: 493
- [5] aker R, Block M. Diesel Construction Equipment Data-base and NO_x Control Technology Evaluation for Houston (Final Report for Texas Environmental Research Consortium-New Technology Research and Development Program). Austin (TX): ERC, 2007. 4

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- [6] dolf S S, Marcus P, Paul S, Yvonne D, Thomas K, Egbert L. US 6843971 B2. 2005
- [7] randenberger S, Kröcher O, Tissler A, Althoff R. Catal Rev, 2008, 50: 492 
- [8] elahay G, Kieger S, Tanchoux N, Trems P, Coq B. Appl Catal B, 2004, 52: 251 
- [9] ahiro H, Iwamoto M. Appl Catal A, 2001, 222: 163 
- [10] helef M. Chem Rev, 1995, 95: 209 
- [11] Iwamoto M, Yahiro H, Mizuno N, Zhang W X, Mine Y, Furukawa H, Kagawa S. J Phys Chem, 1992, 96: 9360 
- [12] Sullivan J A, Cunningham J, Morris M A, Keneavey K. Appl Catal B, 1995, 7: 137 
- [13] Sjövall H, Olsson L, Fridell E, Blint R J. Appl Catal B, 2006, 64: 180 
- [14] Baik J H, Yim S D, Nam I S, Mok Y S, Lee J H, Cho B K, Oh S H. Top Catal, 2004, 30-31: 37 
- [15] Park J H, Park H J, Baik J H, Nam I S, Shin C H, Lee J H, Cho B K, Oh S H. J Catal, 2006, 240: 47 
- [16] Sultana A, Nanba T, Haneda M, Hamada H. Catal Commun, 2009, 10: 1859 
- [17] Li Z, Li D, Huang W, Xie K. J Nat Gas Chem, 2005, 14: 115
- [18] Moden B, Donohue J M, Cormier W E, Li H X. Stud Surf Sci Catal, 2008, 174: 1219 
- [19] Kieger S, Delahay G, Coq B. Appl Catal B, 2000, 25: 1 
- [20] Komatsu T, Nunokawa M, Moon I S, Takahara T, Namba S, Yashima T. J Catal, 1994, 148: 427 
- [21] Pavulescu V I, Grange P, Delmon B. Catal Today, 1998, 46: 233 
- [22] Sjövall H, Blint R J, Olsson L. Appl Catal B, 2009, 92: 138 
- [23] Ma A Z, Grünert W. Chem Commun, 1999: 71
- [24] Long R Q, Yang R T. J Am Chem Soc, 1999, 121: 5595 
- [25] Long R Q, Yang R T. J Catal, 1999, 188: 332 
- [26] Long R Q, Yang R T. Catal Lett, 2001, 74: 201
- [27] Qi G, Yang R T. Appl Catal B, 2005, 60: 13 
- [28] Schwidder M, Kumar M S, Brückner A, Grünert W. Chem Commun, 2005: 805 
- [29] Devadas M, Kröcher O, Elsener M, Wokaun A, Mitrikas G, Söger N, Pfeifer M, Demel Y, Mussmann L. Catal Today, 2007, 119: 137 
- [30] Iwasaki M, Yamazaki K, Banno K, Shinjoh H. J Catal, 2008, 260: 205 
- [31] Brandenberger S, Kröcher O, Tissler A, Althoff R. Appl Catal B, 2010, 95: 348 
- [32] Long R Q, Yang R T. J Catal, 2002, 207: 224 
- [33] Long R Q, Yang R T. J Catal, 2001, 198: 20 
- [34] Huang H Y, Long R Q, Yang R T. Appl Catal A, 2002, 235: 241 
- [35] Devadas M, Kröcher O, Elsener M, Wokaun A, Söger N, Pfeifer M, Demel Y, Mussmann L. Appl Catal B, 2006, 67: 187 
- [36] Schwidder M, Heikens S, De Toni A, Geisler S, Berndt M, Brückner A, Grünert W. J Catal, 2008, 259: 96 
- [37] Grossale A, Nova I, Tronconi E, Chatterjee D, Weibel M. J Catal, 2008, 256: 312 
- [38] Savara A, Li M J, Sachtler W M H, Weitz E. Appl Catal B, 2008, 81: 251 
- [39] Forzatti P, Nova I, Tronconi E. Angew Chem, Int Ed, 2009, 48: 8366 
- [40] Qi G, Yang R T. Catal Lett, 2005, 100: 243 
- [41] Carja G, Delahay G, Signorile C, Coq B. Chem Commun, 2004: 1404
- [42] Li Z, Xie K, Huang W, Reschetilowski W. Chem Eng Technol, 2005, 28: 797 
- [43] Schwidder M, Kumar M S, Bentrup U, Pérez-Ramírez J, Brückner A, Grünert W. Microporous Mesoporous Mater, 2008, 111: 124 
- [44] Long R Q, Yang R T. Catal Lett, 1999, 59: 39 
- [45] Long R Q, Chang M T, Yang R T. Appl Catal B, 2001, 33: 97 
- [46] Long R Q, Yang R T. Appl Catal B, 2000, 27: 87 
- [47] Long R Q, Yang R T. J Catal, 1999, 186: 254 

- [48] Frey A M, Mert S, Due-Hansen J, Fehrmann R, Christensen C H. Catal Lett, 2009, 130: 1 [crossref](#)
- [49] Høj M, Beier M J, Grunwaldt J D, Dahl S. Appl Catal B, 2009, 93: 166 [crossref](#)
- [50] Balle P, Geiger B, Kureti S. Appl Catal B, 2009, 85: 109 [crossref](#)
- [51] Balle P, Geiger B, Klukowski D, Pignatelli M, Wohnrau S, Menzel M, Zirkwa I, Brunklaus G, Kureti S. Appl Catal B, 2009, 91: 587 [crossref](#)
- [52] Long R Q, Yang R T. J Catal, 2000, 190: 22 [crossref](#)
- [53] Klukowski D, Balle P, Geiger B, Wagloehner S, Kureti S, Kimmerle B, Baiker A, Grunwaldt J D. Appl Catal B, 2009, 93: 185 [crossref](#)
- [54] Kröcher O, Devadas M, Elsener M, Wokaun A, Söger N, Pfeifer M, Demel Y, Mussmann L. Appl Catal B, 2006, 66: 208 [crossref](#)
- [55] Li J, Zhu R, Cheng Y, Lambert C K, Yang R T. Environ Sci Technol, 2010, 44: 1799 [crossref](#)
- [56] Kern P, Klimczak M, Heinzelmann T, Lucas M, Claus P. Appl Catal B, 2010, 95: 48 [crossref](#)
- [57] van Kooten W E J, Liang B, Krijnsen H C, Oudshoorn O L, Calis H P A, van den Bleek C M. Appl Catal B, 1999, 21: 203 [crossref](#)
- [58] Carja G, Kameshima Y, Okada K, Madhusoodana C D. Appl Catal B, 2007, 73: 60 [crossref](#)
- [59] Qi G, Yang R T, Chang R. Catal Lett, 2003, 87: 67 [crossref](#)
- [60] Lin Q C, Hao J M, Li J H. Chin Chem Lett, 2006, 17: 991
- [61] Heck R M. Catal Today, 1999, 53: 519 [crossref](#)
- [62] Kato A, Matsuda S, Nakajima F, Imanari M, Watanabe Y. J Phys Chem, 1981, 85: 1710 [crossref](#)
- [63] Kato A, Matsuda S, Kamo T, Nakajima F, Kuroda H, Narita T. J Phys Chem, 1981, 85: 4099 [crossref](#)
- [64] Chen J P, Hausladen M C, Yang R T. J Catal, 1995, 151: 135 [crossref](#)
- [65] Yang R T, Chen J P, Kikkinides E S, Cheng L S, Cichanowicz J E. Ind Eng Chem Res, 1992, 31: 1440 [crossref](#)
- [66] Fabrizioli P, Bürgi T, Baiker A. J Catal, 2002, 206: 143 [crossref](#)
- [67] Ramis G, Yi L, Busca G, Turco M, Kotur E, Willey R J. J Catal, 1995, 157: 523 [crossref](#)
- [68] Larrubia M A, Ramis G, Busca G. Appl Catal B, 2001, 30: 101 [crossref](#)
- [69] Apostolescu N, Geiger B, Hizbullah K, Jan M T, Kureti S, Reichert D, Schott F, Weisweiler W. Appl Catal B, 2006, 62: 104 [crossref](#)
- [70] Liu F D, He H, Zhang C B. Chem Commun, 2008: 2043
- [71] Liu F D, He H, Zhang C B, Feng Z C, Zheng L R, Xie Y N, Hu T D. Appl Catal B, 2010, 96: 408 [crossref](#)
- [72] Liu F D, He H. J Phys Chem C, 2010, 114: 16929 [crossref](#)
- [73] Liu F D, Asakura K, He H, Liu Y, Shan W, Shi X, Zhang C B. Catal Today, 2011, 164: 488
- [74] Liu F D, He H, Zhang C B, Shan W, Shi X. Catal Today, 2011, doi:10.1016/j.cattod.2011.02.049
- [75] Teng H, Hsu L Y, Lai Y C. Environ Sci Technol, 2001, 35: 2369 [crossref](#)
- [76] Marbán G, Fuertes A B. Catal Lett, 2002, 84: 13 [crossref](#)
- [77] Kapteijn F, Singoredjo L, Andreini A, Moulijn J A. Appl Catal B, 1994, 3: 173 [crossref](#)
- [78] Park T S, Jeong S K, Hong S H, Hong S C. Ind Eng Chem Res, 2001, 40: 4491 [crossref](#)
- [79] Tang X, Hao J, Xu W, Li J. Catal Commun, 2007, 8: 329 [crossref](#)
- [80] Kang M, Park E D, Kim J M, Yie J E. Appl Catal A, 2007, 327: 261 [crossref](#)
- [81] Kang M, Yeon T H, Park E D, Yie J E, Kim J M. Catal Lett, 2006, 106: 77 [crossref](#)
- [82] Smirniotis P G, Sreekanth P M, Peña D A, Jenkins R G. Ind Eng Chem Res, 2006, 45: 6436 [crossref](#)
- [83] Smirniotis P G, Peña D A, Uphade B S. Angew Chem, Int Ed, 2001, 40: 2479 3.0.CO;2-7 target="_blank"> [crossref](#)
- [84] Peña D A, Uphade B S, Smirniotis P G. J Catal, 2004, 221: 421 [crossref](#)
- [85] Jiang B, Liu Y, Wu Z. J Hazard Mater, 2009, 162: 1249 [crossref](#)
- [86] Wu Z, Jiang B, Liu Y. Appl Catal B, 2008, 79: 347 [crossref](#)
- [87] Qi G, Yang R T. Appl Catal B, 2003, 44: 217 [crossref](#)
- [88] Wu Z, Jin R, Liu Y, Wang H. Catal Commun, 2008, 9: 2217 [crossref](#)
- [89] Wu Z, Jin R, Wang H, Liu Y. Catal Commun, 2009, 10: 935 [crossref](#)

- [90] Jin R, Liu Y, Wu Z, Wang H, Gu T. *Catal Today*, 2010, 153: 84 
- [91] Kijlstra W S, Biervliet M, Poels E K, Blik A. *Appl Catal B*, 1998, 16: 327 
- [92] Tang X, Hao J, Yi H, Li J. *Catal Today*, 2007, 126: 406 
- [93] Long R Q, Yang R T, Chang R. *Chem Commun*, 2002: 452
- [94] Qi G, Yang R T, Chang R. *Appl Catal B*, 2004, 51: 93 
- [95] Qi G, Yang R T. *J Catal*, 2003, 217: 434
- [96] Qi G, Yang R T. *Chem Commun*, 2003: 848
- [97] Eigenmann F, Maciejewski M, Baiker A. *Appl Catal B*, 2006, 62: 311 
- [98] Liu F D, He H, Ding Y, Zhang C B. *Appl Catal B*, 2009, 93: 194 
- [99] Liu F D, He H. *Catal Today*, 2010, 153: 70 
- [100] Casapu M, Kröcher O, Elsener M. *Appl Catal B*, 2009, 88: 413 
- [101] Kang M, Park J H, Choi J S, Park E D, Yie J E. *Korean J Chem Eng*, 2007, 24: 191 
- [102] Roy S, Viswanath B, Hegde M S, Madras G. *J Phys Chem C*, 2008, 112: 6002 
- [103] Zhu Z, Liu Z, Liu S, Niu H, Hu T, Liu T, Xie Y. *Appl Catal B*, 2000, 26: 25 
- [104] Xie G, Liu Z, Zhu Z, Liu Q, Ge J, Huang Z. *J Catal*, 2004, 224: 42 
- [105] Suárez S, Martín J A, Yates M, Avila P, Blanco J. *J Catal*, 2005, 229: 227
- [106] Si Z, Weng D, Wu X, Li J, Li G. *J Catal*, 2010, 271: 43 
- [107] Xu W, Yu Y, Zhang C, He H. *Catal Commun*, 2008, 9: 1453 
- [108] Xu W, He H, Yu Y. *J Phys Chem C*, 2009, 113: 4426 
- [109] Gao X, Jiang Y, Zhong Y, Luo Z, Cen K. *J Hazard Mater*, 2010, 174: 734 
- [110] Gao X, Jiang Y, Fu Y, Zhong Y, Luo Z, Cen K. *Catal Commun*, 2010, 11: 465 
- [111] Chen L, Li J, Ge M, Zhu R. *Catal Today*, 2010, 153: 77 
- Duffy B L, Curry-Hyde H E, Cant N W, Nelson P F. *Appl Catal B*, 1994, 5: 133 