

Editorial

Introduction of Heterogeneous Catalytic Materials for NO_x Treatment

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Stringent environmental regulations of the greenhouse gases, such as NO_x, emissions have driven extensive research in new and advanced functional materials. Recently, US Environmental Protection Agency (EPA) and Department of Transportation's National Highway Traffic Safety Administration (NHTSA) past new regulations on fuel economy and emission standards. The enforced standards are 20mg/mile for NO_x emission and 10mg/mile for non-methane organic gas (NMOG) [1]. European Union legislation also aims to decrease in the NO_x emissions down to 0.08 g/km for diesel and 0.06 g/km for gasoline engine [2]. NO_x is common term for mono-nitrogen oxides (NO and NO₂), which are exhausts from automobiles and stationary sources such as power plants during combustion of fossil fuels in the vehicles engines or coke in the electric power plants. Typically, NO_x emission from engine consists of a mixture of 95% NO and 5% NO₂ [3]. Although NO decomposition reaction is thermodynamically favorable ($\Delta G = -86$ kJ/mol), it is hindered by the high activation energy of 364 kJ/mol [3]. Thus, in order to decrease the activation energy barrier, advanced heterogeneous catalysts design and different NO decomposition reaction pathways (selective catalytic reduction (SCR) and lean NO_x trap (LNT)) have been developed.

The precious metals such as Pt, Pd, and Rh are generally used as three-way catalysts (TWCs) which are dispersed as individual atoms or small clusters of atoms over an oxide support [3]. Non-reducible oxide support like Al₂O₃ and SiO₂ plays a crucial role in catalytic activity and provides the high surface areas which enhance the dispersion of precious metal, while reducible rate-earth oxide like CeO₂ can release oxygen to create oxide ion vacancies [3]. Supported vanadium oxide catalysts have been used for stationary application of the SCR with urea (CO(NH₂)₂) or NH₃ [4]. In the case of V₂O₅-WO₃/TiO₂ catalyst, vanadium oxide provides an active acid site, while tungsten oxide prevents rutile TiO₂ phase formation from anatate one and increases the catalyst acidity [5]. An extensive characterization technique has been undertaken to understand the relationship between vanadium structure and activity by Raman, FTIR, XRD, NH₃-TPD, H₂-TPR, EXAFS and XPS [6-10]. It was proposed that the SCR rate is an increase with increasing the Brønsted acidic sites and the polymeric vanadate species are the active reaction site

[6,11]. Deactivation and sintering of the supported vanadium oxide catalyst can be occurred because of the V atoms valence change and it was observed that V⁺⁵ content was increased in the deactivated vanadium oxide catalyst [12]. Zeolite supported catalysts (e.g., Fe- or Cu-ZSM5, SSZ-13, BEA, Y) and mesoporous materials (SBA15) are currently being used and have been extensively investigated for mobile applications [13-16]. Kwak et al., observed that Cu/SSZ-13 catalyst provides a high catalytic activity and thermal stability compared to the Cu/ZSM5 and Cu/BEA catalysts. The active site of Cu/zeolites catalysts can be provided using an in situ or operando experimental method [17,18]. X-ray absorption near-edge structure (XANES) showed that a mixture of Cu(I) and Cu(II) are the active sites in Cu/zeolite catalysts [18]. Using H₂-TPR experiment, reduced oxidation state from Cu(II) to Cu(I) was found for Cu/SSZ-13, while Cu(0) was observed for Cu/ZSM5 and Cu/BEA [17]. Over Cu/(CHA or SAPO-34) catalysts, depend on the catalyst preparation methods, different Cu species can be exists within the zeolite pores, such as isolated mononuclear Cu²⁺ and CuAlO₂. It was also confirmed that isolate Cu²⁺ appears crucial role for catalytic activity, while CuAlO₂ species relate to a poor NO_x decomposition activity and an undesired byproduct, N₂O [19].

As mentioned above, various catalysts materials have been prepared for meeting emission standards in North America. However, current and conventional heterogeneous catalysts are not still meet pollutant emission regulations which was reported by the US Council for Automotive Research (USCAR); 90% conversion of emissions at temperatures around 150°C along with a 20% improvement in engine efficiency [20].

In summary, over the past few decades, extensive research has been conducted to develop new functional materials to remove and decrease nitrogen oxides (NO_x) emissions from stationary facilities and mobile engine exhaust. To avoid the growing concern in a public health and to satisfy the strict emission regulations, researchers in academia and industry should develop novel heterogeneous catalysts and alternative reaction pathways. In addition to a synthesis and an application of new materials, fundamental catalysis research using several spectroscopic techniques under in situ or operando conditions should be performed at the same time to provide intermediate species and reaction mechanisms.

References

1. Emission Standards Reference Guide. EPA.
2. EU Emission Standards for Passenger Cars. DieselNet.2007.
3. Roy S, Hegde MS, Madras G. Catalyst for NO_x abatement. Applied Energy. 2009; 86: 2283-2297.
4. Wu X, Yu W, Si Z, Weng D. Chemical deactivation of V₂O₅-WO₃/TiO₂ SCR catalyst by combined effect of potassium and chloride. Front. Environ. Sci. Eng. 2013; 7: 420-427.
5. Chen JP, Yang RT. Role of WO₃ in mixed V₂O₅-WO₃/TiO₂ catalysts for

- selective catalytic reduction of nitric oxide with ammonia. *Applied Catalysis A: General*. 1992; 80: 135–148.
6. Choo ST, Lee YG, Nam IS, Ham SW, Lee JB. Characteristics of V_2O_5 supported on sulfated TiO_2 for selective catalytic reduction of NO by NH_3 . *Applied Catalysis A: General*. 2000; 200: 177–188.
 7. Due-Hansen J, Boghosian S, Kustov A, Fristrup P, Tsilomelekis G, Ståhl K, et al. Vanadia-based SCR catalysts supported on tungstated and sulfated zirconia: Influence of doping with potassium. *J. Catal.* 2007; 251: 459-473.
 8. Amiridisa MD, Duevelb RV, Wachs IE. The effect of metal oxide additives on the activity of V_2O_5/TiO_2 catalysts for the selective catalytic reduction of nitric oxide by ammonia. *Applied Catalysis B: Environmental*. 1999; 20: 111-122.
 9. Kobayashi M, Kuma R, Masaki S, Sugishima N. TiO_2 - SiO_2 and V_2O_5/TiO_2 - SiO_2 catalyst: Physico-chemical characteristics and catalytic behavior in selective catalytic reduction of NO by NH_3 . *Applied Catalysis B: Environmental*. 2005; 60: 173–179.
 10. Marshneva VI, Slavinskaya EM, Kalinkina OV, Odegova GV, Moroz EM, Lavrova GV, et al. The influence of support on the activity of monolayer vanadia-itanian catalysts for selective catalytic reduction of NO with ammonia. *J. Catal.* 1995; 155: 171-183.
 11. Lietti L, Nova I, Ramis G, Dall'Acqua L, Busca G, Giamello E, et al. Characterization and Reactivity of V_2O_5 - MoO_3/TiO_2 De-NOx SCR Catalysts. *J. Catal.* 1999; 187: 419-435.
 12. Yu YK, He C, Chen JS, Meng XR. Deactivation mechanism of de-NOx catalyst (V_2O_5 - WO_3/TiO_2) used in coal fired power plant. *J. Fuel Chem Technol*. 2012; 40: 1359-1365.
 13. Kwak J, Tran D, Burton S, Szanyi J, Lee J, Peden C. Effects of hydrothermal aging on NH_3 -SCR reaction over Cu/Zeolites. *J Catal.* 2012; 287: 203-209.
 14. Kwak J, Tran D, Szanyi J, Peden C, Lee J. The effect of copper loading on the selective catalytic reduction of nitric oxide by ammonia over Cu-SSZ-13. *Catal Lett*. 2012; 142: 295-301.
 15. Zhu H, Kwak J, Peden C, Szanyi J. In situ DRIFTS-MS studies on the oxidation of adsorbed NH_3 by NOx over a Cu-SSZ-13 zeolite. *Catal. Today*. 2013; 205: 16-23.
 16. Liu X, Jiang Z, Chen M, Shi J, Shangguan W, Teraoka Y, et al. Characterization and performance of Pt/SBA-15 for low-temperature SCR of NO by C_3H_6 . *J Environ Sci (China)*. 2013; 25: 1023-1033.
 17. Szanyi J, Kwak JH, Zhu H, Peden CH. Characterization of Cu-SSZ-13 NH_3 SCR catalysts: an in situ FTIR study. *Phys Chem Chem Phys*. 2013; 15: 2368-2380.
 18. Kispersky VF, Kropf AJ, Ribeiro FH, Miller JT. Low absorption vitreous carbon reactors for operando XAS: a case study on Cu/Zeolites for selective catalytic reduction of NO(x) by NH_3 . *Phys Chem Chem Phys*. 2012; 14: 2229-2238.
 19. Deka U, Lezcano-Gonzalez I, Warrender SJ, Picone AL, Wright PA, Weckhuysen BM, et al. Changing active sites in Cu-CHA catalysts: deNOx selectivity as a function of the preparation method. *Microporous and Mesoporous Materials*. 2013; 166: 144–152.
 20. Future Automotive After treatment Solutions: The 150°C Challenge Workshop Report. USCAR HQ, Southfield, MI. 2012; 29-30.