

## Editorial

# Introduction of Heterogeneous Catalytic Materials for NO<sub>x</sub> Treatment

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Stringent environmental regulations of the greenhouse gases, such as NO<sub>x</sub>, 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<sub>x</sub> emission and 10mg/mile for non-methane organic gas (NMOG) [1]. European Union legislation also aims to decrease in the NO<sub>x</sub> emissions down to 0.08 g/km for diesel and 0.06 g/km for gasoline engine [2]. NO<sub>x</sub> is common term for mono-nitrogen oxides (NO and NO<sub>2</sub>), 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<sub>x</sub> emission from engine consists of a mixture of 95% NO and 5% NO<sub>2</sub> [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<sub>x</sub> 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 Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> 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 CeO<sub>2</sub> 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(NH<sub>2</sub>)<sub>2</sub>) or NH<sub>3</sub> [4]. In the case of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst, vanadium oxide provides an active acid site, while tungsten oxide prevents rutile TiO<sub>2</sub> 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, NH<sub>3</sub>-TPD, H<sub>2</sub>-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<sup>+5</sup> 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 H<sub>2</sub>-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 Cu<sup>2+</sup> and CuAlO<sub>2</sub>. It was also confirmed that isolate Cu<sup>2+</sup> appears crucial role for catalytic activity, while CuAlO<sub>2</sub> species relate to a poor NO<sub>x</sub> decomposition activity and an undesired byproduct, N<sub>2</sub>O [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<sub>x</sub>) 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.

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