

Low Temperature Selective Catalytic Reduction of NO_x over Vanadium-Based Catalysts

Vijay Narkhede, Dinesh Kumar, R M Cursetji, and Touquire A Sidique
Sud Chemie India Pvt Ltd.

ABSTRACT

Diesel engines are becoming popular because of more fuel efficient and durability. While the CO and HC impurities are significantly lower than in gasoline engines, the design strategies for reduction of Particulate Matter and Nitrogen Oxides remain a major challenge for environment. The work mainly focused on reduction of NO_x from diesel engines using SCR technology under Indian driving conditions and fuel availability. With BS III/IV fuel available in the country, the catalyst system of choice is the Vanadia Tungsten Titania (VWT) system because of its proven resistance to Sulfur poisoning. However, under urban driving conditions on Indian roads, the major obstacle is the low engine out temperatures which are below the normal operating temperature window (200 to 450 °C) of VWT - SCR.

The objective of the present investigation is to develop low temperature SCR catalyst system that outperforms the existing commercial catalytic system during the cold start and low load operating conditions. This work focused on modifying the preparation parameters so as to optimize the activity of Vanadium for NO_x reduction in the temperature range between 200 - 450 °C. With the help of sophisticated catalyst characterization tools, novel and highly active formulations of vanadium have been developed, which are more active at lower temperatures as well as do not catalyze the undesirable reactions such as those leading to N₂O formation. The metal oxide catalysts are designed and developed to obtain innovative and attractive solutions for the reduction of NO_x emissions during cold start and low load operating conditions. The influence of various operating parameters such as NO₂/NO_x ratio, NH₃/NO_x ratio, space velocity over the typical temperature range on performance of an optimized SCR formulation are investigated for proper design and sizing of the after treatment system.

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INTRODUCTION

Due to growing concerns over environment and human health, worldwide national governments are imposing stringent emission regulations for internal combustion engines. Particularly stringent NO_x and PM emission standards for diesel engines are on the anvil. It requires clean diesel technology and the application of highly efficient exhaust gas after treatment systems. To comply with BSIV/V regulations for heavy duty diesel engines, both the NO_x and PM must be reduced greatly to meet the regulatory limits. The BS IV emission standards cannot be achieved solely by engine management. Therefore aftertreatment systems together with advanced engine technology are essential to meet the norms.

Generally, the engine management system for a diesel engine is optimized to give very low PM, less than 0.02 g/kWh. However, the optimized combustion for reducing the PM leads to higher NO_x emissions [1,2]. Ammonia-SCR is mostly widely used to reduce the NO_x level up to 90 %. While improving fuel economy and reduction in CO₂ emission, advanced engine and related technologies have been

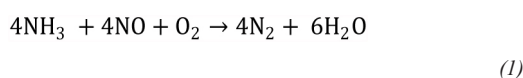
implemented to reduce NO_x from engine exhaust gas. It results in lowering the exhaust gas temperature that demands low temperature active catalyst for the reduction of NO_x. Moreover, low temperature exhaust gas is seen at low load operating conditions.

For an ammonia-SCR system, various catalysts, such as Pt/metal oxide, base metal/zeolite and Vanadium-Tungsten-Titanium (VWT) systems are available [3,4]. The temperature window for the Pt-based catalysts is very narrow (175 to 250 °C). At less than 200 °C exhaust temperature, undesirable ammonium nitrate is formed whereas above 225 °C the catalyst loses its selectivity for reduction and oxidation reactions of NH₃ to NO_x and N₂O are dominant. Base metal (Cu or Fe)/zeolite catalysts are commercially available. The main concerns of the base metal/zeolite catalysts for the SCR reaction are sulfur poisoning and thermal durability [4,5]. Moreover, the cost of the zeolite-based catalyst is higher than V-based catalysts. The impact of sulfur is more severe, particularly on Cu-based (working temperature window 150 to 450 °C) than on Fe-based zeolite catalysts (working temperature window 350 to 600 °C) for the NO_x activity.

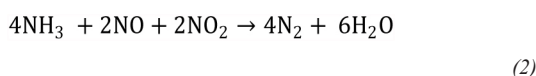
In recent research extensive efforts have been made to enhance low temperature activity. Manganese-based mixed oxides have received the most attention. While the selectivity and temperature needs to further improve compared to zeolite-based catalysts, the resistance of SO₂ on Mn-based oxide catalysts is a challenge for low temperature SCR. The doping cation in catalyst is reported to enhance NOx conversion and N₂ selectivity of manganese oxide-based catalysts in low-temperature SCR. Among many other catalysts for increasing the activity at low temperature regime, ceria-doped MnOx/TiO₂, Fe-Mn/TiO₂, Cu-Mn/TiO₂ and Cr-Mn/TiO₂ catalysts have been reported [6,7,8].

The main reactions involved in ammonia-SCR are as follows:

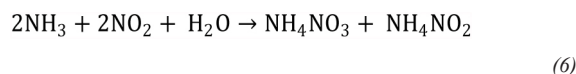
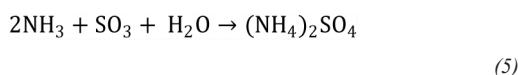
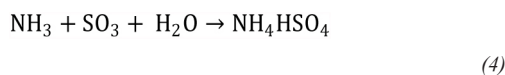
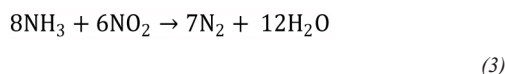
Standard reaction:



Fast reaction:



Slow reaction:



It is clear now that the VWT system emerges as the most robust catalytic system for an ammonia-SCR. It is highly active at medium temperature range (190 to 450 °C) and has superior resistance against sulfur poisoning. V₂O₅ in a highly dispersed form on TiO₂ is the catalytically active system whereas WO₃ improves the thermal stability of TiO₂, increases the acidity of the catalysts and also suppresses the undesirable oxidation of SO₂. Taking the advantage of its S-resistance and cost, the efforts were focused on enhancing the low temperature activity of the VWT-based catalyst.

EXPERIMENTAL SET UP

The catalyst SC-S was prepared from commercially available Tungsten-stabilized Titania. To improve the Redox and acid function, SC-D was prepared by in-house process, retaining the same composition.

In the catalyst optimization process for SC-D, several parameters such as pH, vanadium content and support preparation has been varied and the final process of the catalyst is optimized. The performance of these catalysts was measured and compared with reference VWT catalyst at two levels of V content.

Table 1. Details of catalyst studied

Sample code	Description	Support	Vanadium content, a.u.
SC-S-A	Reference catalyst	Commercially available WO ₃ -stabilized TiO ₂	100
SC-S-B	Reference catalyst with higher vanadia		140
SC-D-A	Developmental catalyst	In-house prepared WO ₃ -stabilized TiO ₂	100
SC-D-B	Developmental catalyst with higher vanadia		140

Compositionally all the samples were identical except for the variations in V content as given in table above

All the VWT catalysts including reference as well as developmental catalyst were washcoated on a ceramic honeycomb with wash coat loading in the range of 180 to 220 g/l.

The powders were characterized for Surface Area / XRD, Raman, TPR and TPD measurements. TPD measurements were conducted using 100 mg ground wash coat powder loaded in sample tube of Micromeritics Chemisorb 2720. After drying at 350 °C in helium at flow rate of 100 ml/min for 1 h, the catalyst was then cooled down to 120 °C, followed by saturating in 5% ammonia/He for 10 min. To remove excess/physisorbed of ammonia, helium gas was purged until the TCD signal was stabilized at the same temperature. After a stable baseline the sample temperature was ramped with 10 °C/min to 500 °C.

Temperature Programmed Reduction (TPR) measurements were performed on Quantachrome Chem BET Pulser instrument. In a typical measurement 50 mg of wash coat powder was dried at 350 °C in air with flow rate of 75 ml/min for 1 h, followed by cooling in pure nitrogen to room temperature. Then the gas flow was switched to 10% H₂/N₂ with heating rate of 10 °C/min to 900 °C. The hydrogen consumption was monitored by a TCD detector.

Raman spectra were recorded RAMNOR HG-2S spectrometer, JOBIN-YVON, FRANCE, with laser source of Ar-Laser and 4W power (all lines).

The experimental NOx reduction data were collected on typical test rig. The main reactor consists of quartz tube of 28 mm diameter and of 1200 mm length. The design temperature of the furnace could reach up to 600 °C. The gas analysis system consists of an FTIR spectrometer, paramagnetic O₂ analyzer and flame ionization detector for hydrocarbons. The feed gas composition is given in Table 2. The schematic of the test rig has been shown in Figure 1.