

Editorial

Automotive Emission Control Catalysts

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1. Background

Emission control catalysts constitute an essential part of today's vehicles powered by internal combustion engines, mitigating the harmful effects of pollutants in the exhaust such as carbon monoxide, hydrocarbons, nitrogen oxides, and particulate matter [1]. Impressive technical advances have been made since the introduction of the first catalytic converters in the 1970s for the abatement of carbon monoxide and hydrocarbon emissions from gasoline vehicles. In many countries today, exhaust gases from both gasoline and diesel engines are extensively cleaned up using a suite of advanced catalyst technologies, including: three-way catalyst (TWC), diesel particulate filter (DPF), diesel oxidation catalyst (DOC), selective catalytic reduction (SCR), and NO_x storage and reduction (NSR) catalysts.

Despite this success, significant research and development activities are under way in industry and academia to further enhance the performance of existing catalysts and to develop novel technologies (e.g., passive NO_x adsorbers, SCR on DPF and TWC on gasoline particulate filters). Much of the current efforts aim at helping address three major challenges facing the automotive industry [2,3]. First, the emission regulations around the world have become increasingly more stringent requiring continued catalyst activity, durability and selectivity improvements (e.g., reduced formation of byproducts such as N₂O, a potent greenhouse gas). Moreover, driven by the public concern regarding energy security and climate change, the efficiency of internal combustion engines is improving at a rapid pace. This efficiency gain entails a significant decrease in the exhaust temperature due to reduced waste heat generation. To successfully meet this so-called low-temperature challenge—to achieve over 90% conversion at 150 °C or lower without compromising emission control cost—innovative catalyst solutions and operating strategies need to be developed (e.g., new catalyst formulations and systems conducive to light-off temperatures below 150 °C) [4]. Finally, greater use of alternative fuels such as natural gas and biofuels presents the third major challenge in catalyst development, considering, for instance, specific reactivity of unburned methane from natural gas engines or biomass-derived fuel impurities impacting catalyst durability.

2. This Special Issue

Some of the leading experts contributed to this Special Issue of *Catalysts* reporting on recent advances made by their teams on various catalyst technologies relevant to future automotive emission control development including TWC, urea-SCR, NH₃-SCR, CH₄-SCR, NSRC, and DOC.

After giving a mini-review on modern three-way catalysts and systems in an Introduction, Zheng et al. describe fuel shutoff (an engine operating strategy practiced to enhance fuel economy) and resultant catalyst temperature increase leading to catalyst deactivation, specifically related to Rh which is a main TWC catalyst component responsible for NO reduction [5]. The authors' simulated bench reactor evaluation and catalyst characterization shows that Rh supported on Ce_xO_y-ZrO₂ is

less deactivated by fuel shutoff (i.e., oxidative thermal aging) and its regeneration via fuel-rich engine operation is faster than Rh on Al_2O_3 . Stronger metal-support interaction between Rh and Al_2O_3 leads to stable rhodium aluminate complex. Hydrogen generated in situ via steam reforming of fuel hydrocarbons over reduced Rh is believed to facilitate catalyst regeneration during the slightly fuel-rich operation.

In a companion paper [6], Zheng et al. investigate Pd (another major TWC component generally responsible for oxidation reactions) in the context of fuel shutoff influence and possibilities of rich regeneration. In contrast to Rh, Pd deactivation is mainly due to Pd metal sintering resulting in irreversible deactivation for both Pd/ Al_2O_3 and Pd/ $\text{Ce}_x\text{O}_y\text{-ZrO}_2$ catalysts. Fuel-rich operation and accompanying in situ H_2 generation via steam reforming is not effective in recovering catalyst activity. The authors point out that stabilizing PdO (active state of Pd) against decomposition into Pd would represent a breakthrough for TWC technology.

The paper co-authored by Xie et al. [7] aims to reveal the impact of phosphate-based lubricant additives on the aging and performance of commercial three-way catalyst (TWC) commonly used in passenger cars with stoichiometric gasoline engines. The CO, C_3H_6 and NO light-off temperatures after catalyst aging are compared for the engine operation without any lubricant additive, and with two different additives. The TWCs that converted exhaust gas from the engines operated with lubricant additives exhibit generally higher light-off temperature; however, the actual extent of catalyst deactivation depends on the nature of the additive. The variations are correlated with the build-up of different forms of phosphates within the catalyst support material when using different lubricant additives. The formation of aluminum phosphate is identified as less detrimental for TWC function than that of cerium phosphate.

While NH_3 -SCR catalysts are highly effective in lean NO_x control, due to safety reasons, NH_3 reductant needs to be generated from liquid urea-water solution stored on-board in a special tank and injected into exhaust pipe in front of the catalyst. This arrangement, however, results in additional complexities in designing catalytic systems to ensure efficient urea decomposition and hydrolysis into NH_3 molecules. Based on the results obtained from well-controlled micro-scale reactor experiments, Seneque et al. describe potential limitations of urea as an NH_3 carrier when urea residence time is not sufficient [8]. They further show that the observed lack of NH_3 availability can be attributed to the insufficient SCR catalyst activity for isocyanic acid (HNCO : urea decomposition product) hydrolysis, which can be complemented by adding an active hydrolysis catalyst (e.g., ZrO_2) upstream of the SCR catalyst.

Metal supported vanadia is an important NH_3 -SCR catalyst group available for diesel applications, and its performance is highly dependent on V loading. The paper by Marberger et al. [9] further clarifies the relationship between V loading and activity and selectivity, thus providing useful information for optimization of catalyst formulation and performance. An ideal V_2O_5 loading is found between 2.0 and 2.6 wt. %; the activity of $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$ is insufficient below 2.0 wt. %, while hydrothermal aging induced deactivation occurs above 2.6 wt. %. The loading and surface coverage of WO_x promoter is also an important parameter to control.

NO_x storage and reduction catalyst also known as lean NO_x trap (LNT) represents an exhaust gas aftertreatment technology used for abatement of nitrogen oxides from diesel and lean-burn gasoline engines. The catalyst is operated in periodical regime alternating between lean and rich phases. During the lean phase, NO_x adsorption takes place in excess of oxygen. Reduction of the accumulated NO_x is then achieved within the rich phase, characterized by increased concentration of CO, hydrogen and hydrocarbons formed by injecting extra fuel for a short duration. Kubiak et al. investigate reaction pathways during the reduction of the adsorbed NO_x [10]. They focus on the effect of precious metal in the catalyst formulation (Pt or Rh), taking into account the range of operating temperature and different forms of adsorbed NO_x species (nitrites or nitrates). The differences in NO_x conversions and selectivities to N_2 , N_2O and NH_3 are attributed to different oxidation activity, reducibility and dispersion of Pt and Rh in the examined catalysts.

Nowadays, the engines powered by natural gas gain increasing popularity in the automotive industry and their share on the market increases particularly in the segment of commercial vehicles where fuel economy is of high interest. The contribution from Mendes et al. systematically examines the role of Pd and Ce in Pd-MOR and PdCe-MOR zeolite catalysts for selective catalytic reduction of nitrogen oxides by methane under excess of oxygen [11]. The CH₄ and NO_x conversions and selectivities are measured for several different catalyst configurations, including the effects of Pd loading, impregnation method (incipient wetness or ion exchange at different temperatures), and the order of Pd and Ce component addition. This work underlines the importance of introducing Pd to zeolite via ion exchange and before Ce addition to achieve high CH₄-SCR activity.

NO oxidation to NO₂ in DOC affects the performance of other catalyst types found in diesel exhaust gas aftertreatment systems. NO₂ represents a more reactive form of nitrogen oxides and it can be utilized for soot oxidation in particulate filters, to accelerate NO_x adsorption in LNT or to achieve higher conversions in SCR. The team of Mihai, Creaser and Olsson presents a fundamental investigation of NO, oxygen and NO₂ adsorption, desorption and reaction steps over Pt/Al₂O₃ catalyst, using microcalorimetric study to evaluate the adsorption enthalpies [12]. While the heat of NO adsorption is practically constant, the oxygen adsorption enthalpy varies with oxygen coverage and it is further influenced by platinum oxide formation, which affects also the NO oxidation rate.

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