

Conversion of Short-Chain Alkanes by Vanadium-Based and Cu/Zeolite SCR Catalysts

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ABSTRACT

The oxidation of short-chain alkanes, such as methane, ethane, and propane, from the exhaust of lean-burn natural gas and lean-burn dual-fuel (natural gas and diesel) engines poses a unique challenge to the exhaust aftertreatment community. Emissions of these species are currently regulated by the US Environmental Protection Agency (EPA) as either methane (Greenhouse Gas Emissions Standards) or non-methane hydrocarbon (NMHC). However, the complete catalytic oxidation of short-chain alkanes is challenging due to their thermodynamic stability. The present study focuses on the oxidation of short-chain alkanes by vanadium-based and Cu/zeolite selective catalytic reduction (SCR) catalysts, generally utilized to control NO_x emissions from lean-burn engines. Results reveal that these catalysts are active for short-chain alkane oxidation, albeit, at conversions lower than those generally reported in the literature for Pd-based catalysts, typically used for short-chain alkane conversion. While the Cu/zeolite SCR catalyst had the highest conversion of CO, CH₄, and C₂H₆, the V-SCR catalyst had higher C₃H₈ conversion likely due to pore diffusion limitations of the small-pore Cu/zeolite SCR. None of the SCR catalysts stored short-chain alkanes or were impacted by water vapor, and only the Cu/zeolite catalyst was affected by sulfation. NO_x conversion was not impacted as a result of the presence of CO and short-chain alkanes. These results indicate that, in addition to NO_x conversion, SCR catalysts may be part of the short-chain alkane oxidation solution.

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INTRODUCTION

The complete catalytic oxidation of short-chain alkanes has been an open topic of research for at least the past 50 years [1]. These organic hydrocarbons, most notably methane, are thermodynamically stable, and, to date, research persists because available catalytic materials are not sufficiently active at temperatures typical of lean-burn natural gas exhaust and/or are deactivated under exhaust conditions [2, 3, 4, 5, 6, 7]. There is general agreement that Pd-based catalysts are the most practical solution for complete short-chain alkane oxidation from lean-burn exhaust emissions. But, the palladium loadings required for high catalytic activity make these catalysts costly, and their degradation by sulfur, water vapor, and carbon dioxide is well documented in the literature [2, 3, 4, 5, 6, 7]. Research will persist in this area, and with time these shortcomings may be addressed.

Selective catalytic reduction (SCR) catalysts, including vanadium-based (V-SCR) and Cu/zeolite (CuZ), are currently utilized worldwide for the reduction of nitrogen oxides (NO_x) from diesel exhaust emissions. Beginning in 2008 with Euro V heavy-duty truck standards and continuing in the US with EPA 2010 standards, these catalysts have enabled engine and aftertreatment manufacturers to successfully meet increasingly stringent worldwide NO_x emission standards.

While these catalysts are utilized for NO_x reduction in the diesel emissions industry, the same materials, especially vanadium, have been utilized in other industries to catalyze many other reactions.

Vanadium pentoxide's (V₂O₅) catalytic activity is exploited industrially to produce sulfuric acid, maleic anhydride, phthalic anhydride, etc. In addition, several studies have documented the ability of V-SCR catalysts to convert hydrocarbons present in diesel exhaust [8, 9, 10, 11, 12, 13]. Most recently Watling et al. and Ottinger et al. showed that these catalysts can achieve ~80% C₃H₆ conversion at 500°C, but that the reaction is not completely selective to CO₂. Copper oxide is active for the partial oxidation of acetone (a common classroom experiment) and the dehydrogenation of n-hexane and cycloalkanes, but the authors are unaware of a study devoted to diesel hydrocarbon conversion by CuZ SCR catalysts. Furthermore, the authors are unaware of a study that has evaluated the catalytic activity of typical vanadium- and copper-containing SCR materials for short-chain alkane oxidation.

The present study, as opposed to previous work that focuses on more traditional Pd-based oxidation catalysts, evaluates the activity of vanadium-based and Cu/zeolite SCR catalysts for short-chain alkane oxidation. Reactor-based experiments are conducted under realistic gas compositions selected to approximate those of lean-burn natural gas engines. Oxidation activity is reported for several short-chain alkanes at exhaust temperatures common of SCR catalysts, and typical degradation routes reported for short-chain alkane oxidation catalysts (i.e., sulfation and hydroxyl poisoning) are explored. Results are discussed in the context of previously published data from Pd-based oxidation catalysts.

EXPERIMENTAL

Experimental Conditions

Experiments in this study included the following: catalyst activity, short-chain alkane storage, sulfation, and desulfation, and impact on NO_x conversion. Catalyst activity was measured both with transient lightoff and at constant temperature conditions. Lightoff tests were conducted from 200 to either 550 or 600°C—the maximum catalyst temperature is equivalent to the degreening temperature discussed below—at a temperature ramp rate of 5°C/min. Steady-state activity was measured at 500°C. The washcoated V-SCR catalyst was only evaluated up to 550°C because of its lower thermal durability [14]. Gas concentrations for activity measurements were 10 volume percent (vol.%) O_2 , 11 vol.% H_2O , 1000 parts per million by volume (ppmv) CO , 500 ppmv CH_4 , 100 ppmv C_2H_6 , 40 ppmv C_3H_8 , and balance N_2 , referred to as the baseline gas mixture in this study.

Hydrocarbon (i.e., short-chain alkane) storage of these catalysts was evaluated at 200°C. The catalysts were exposed to the baseline gas mixture for 2 hrs at this temperature. CO and the short-chain alkanes were then shut off, and the temperature was ramped to either 550 or 600°C.

The impacts of sulfation and water vapor were investigated during both lightoff and steady-state experiments. An SO_2 concentration of 5 ppmv SO_2 was added to the baseline gases, defined above, for these tests. Lampert et al. estimated the exhaust sulfur concentration of a lean-burn natural gas vehicle under both cruise and idle conditions, and the authors reported an average value of ~ 1 ppmv sulfur [7]. A concentration of 5 ppmv SO_2 is used in this study to accelerate sulfation. The instantaneous impact of SO_2 was evaluated by co-feeding during lightoff experiments. In addition, SO_2 was pre-stored for 2 hours and co-fed during lightoff experiments in a follow-up test to determine the effect of low-temperature SO_2 storage. Steady-state, 500°C sulfation experiments were also conducted, and these experiments had a duration of 1 hr. After sulfation, the efficiency of reductive desulfation was investigated by exposing the catalysts to 11 vol.% H_2O , 500 ppmv NO , 500 ppmv CH_4 , 200 ppmv C_2H_6 , 60 ppmv C_3H_8 , and balance N_2 at 500°C. Reductive exposures had a duration of 10 minutes. Additional steady-state experiments were conducted at 500°C to determine if water vapor degrades catalyst activity as it has been shown to do on Pd-based catalysts [2, 6, 7].

Finally, since any SCR catalyst in a lean-burn natural gas or dual-fuel application would still need to convert NO_x as its primary function, the effect that short-chain alkanes have on NO_x conversion was evaluated. To do this, 200 ppmv NO and 200 ppmv NH_3 were added to the baseline gas mixture above, and experiments were conducted with and without CO and short-chain alkanes. Evaluations were from 170°C to either 550 or 600°C, depending on the SCR catalyst.

All experiments were performed at a gas hourly space velocity (GHSV) of 50,000 hr^{-1} , and CO_2 was omitted in order to better understand product formation from hydrocarbon oxidation.

SCR Catalysts

State-of-the-art vanadium-based SCR catalysts (commonly referred to in the literature as $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$) and a state-of-the-art small pore Cu/zeolite SCR catalyst (CuZ) were evaluated in this work. Catalyst samples had dimensions of 1" diameter by 3" long. Two different vanadium-based SCR catalysts were evaluated; one catalyst was of the washcoated type (V-SCR_WC), and was coated onto a cordierite substrate, while the other was an extruded catalyst (V-SCR_Extr). The formulations of these two catalysts were different, but specifics are not available for disclosure. The intent of this article is to evaluate the nascent potential of state-of-the-art materials and not to dissect the importance of catalyst preparation and active components, though certainly these are important considerations. The Cu/zeolite SCR was also coated onto a cordierite substrate. Catalyst samples were degreened for 2 hrs at either 550°C for the washcoated V-SCR or 600°C for the more refractory extruded V-SCR and Cu/zeolite SCR samples in 10 vol.% O_2 , 11 vol.% H_2O , and balance N_2 prior to any evaluations. The CuZ SCR and V-SCR_WC catalyst samples had cell densities of 300 cells per square inch (cps), while the V-SCR_Extr sample was 400 cps.

Catalyst Reactor

A catalyst core-reactor was used for all experimental work in this study. A schematic of the system is presented in Figure 1, and the reactor system has been explained in detail previously [7]. Briefly, the core-reactor consists of MKS™ mass flow controllers for gas metering, a Waters™ high performance liquid chromatography pump for water introduction, a Bronkhorst™ vapor delivery system for introduction of $\text{C}_{12}\text{H}_{26}$, a Lindberg™ 3-zone tube furnace for reactor temperature control, and a MKS 2030 HS Fourier transform infrared (FTIR) spectrometer for gas analysis. All lines are heated to approximately 190°C to eliminate condensation of water vapor and hydrocarbons. In addition, all FTIR calibrations were derived for gas-phase measurement at 191°C. The quartz reactor tubes used in this study were 39 inches (90 cm) long with inner and outer diameters of 1.1 inches (28 mm) and 1.26 inches (32 mm), respectively. The inlet 10 inches (25.4 cm) of the reactor were filled with 4 mm quartz beads to ensure that incoming gas is uniformly mixed and heated. All gases used in this study were provided by Airgas. Pure gases N_2 and O_2 were Ultra High Purity grade (99.999%), while two component mixtures (CO , CH_4 , C_2H_6 , and C_3H_8) in N_2 were National Institute of Standards and Technology (NIST) traceable Primary Standards.

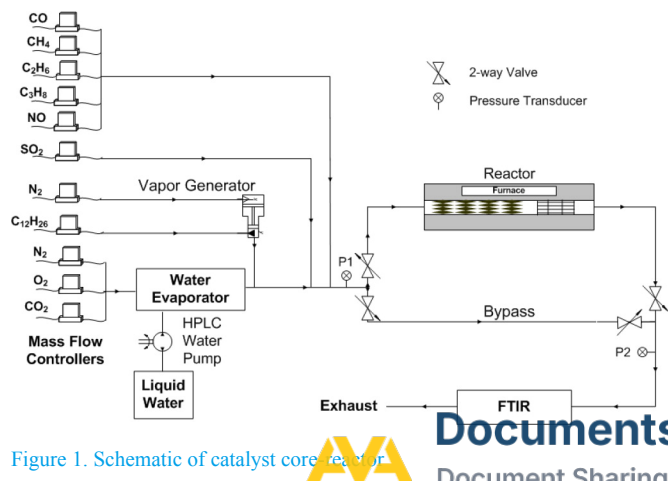


Figure 1. Schematic of catalyst core reactor