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Influence of hydrocarbon species on its adsorption on a VSCR catalyst under simulated diesel engine operating conditions

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ABSTRACT

Vanadia-SCR (VSCR) is a proven technology for reducing diesel engine NO_x emissions using urea hydrolysis derived NH_3 as a reductant. It is also known that VSCR is active for hydrocarbon (HC) oxidation. However, HC species from diesel engine exhaust may be adsorbed onto VSCR at low exhaust temperatures such as under low engine load or idle conditions. The adsorbed HC may be gradually transformed into more stable coke during engine operation. The accumulated HC or coke on VSCR can result in decreased NO_x conversion efficiency due to blockage of catalyst pores and active sites. In addition, rapid oxidation of accumulated HC or coke can lead to exotherms which can thermally damage the VSCR and may lead to vanadium and tungsten release. This work investigates the fundamental adsorption characteristics of HC species on a state-of-the-art VSCR catalyst in the low temperature region. Dodecane and toluene are used as model molecules for alkane and aromatic species from unburned diesel fuel, while squalane is used as a model molecule for unburned lube oil.

1. Introduction

NO_x (NO and NO_2), HC (hydrocarbon) and PM (particulate matter) are all emitted from diesel engines. The substantial reduction of these pollutants has been driven by more and more stringent regulations and enabled by new diesel engine, aftertreatment system, fuel and lube oil technologies [1,2]. Vanadia-based and metal promoted zeolite-based SCR catalysts are proven technologies for NO_x reduction. Because of VSCR's high NO_x conversion efficiency, low cost, excellent durability and chemical resistance to sulfur poisoning, VSCR catalysts are widely used for NO_x reduction in diesel exhaust aftertreatment systems, especially in Euro IV, Euro V and off-road applications. In these applications, VSCR catalysts are directly exposed to engine exhaust, and DEF (diesel exhaust fluid with 32.5 wt.% urea in aqueous solution) is injected upstream of the VSCR, producing the NH_3 required to reduce NO_x via the well documented SCR reactions. A significant amount of fundamental research has been conducted over the past several decades to understand the SCR reaction mechanism over VSCR catalysts in order to improve catalyst reactivity, stability and elucidate catalyst deactivation mechanisms from various poisons [3–7]. It was previously reported that VSCR catalysts can contribute to HC and PM reduction as well [8–11].

Diesel engine exhaust is a complex mixture. N_2, H_2O, CO_2 and O_2 are the main constituents resulting from lean combustion of diesel fuel. If complete combustion of fuel is assumed, the H_2O, CO_2 and O_2 concentration can be calculated as a function of air/fuel mass ratio as illustrated in Fig. 1. Increasing air/fuel mass ratio increases O_2 concentration, while the H_2O and CO_2 concentrations decrease. Diesel engines are typically operated with an air/fuel mass ratio from 20 to 30; therefore, 5–10% O_2 and 6–9% H_2O/CO_2 are typically observed in diesel engine exhaust. Under idle conditions, the air/fuel mass ratio may exceed 160 due to decreased fuel injection. Thus, significantly lower H_2O concentration (<2%) and much higher O_2 concentration (>18%) can be expected.

Engine out HCs resulting from diesel combustion can be attributed to unburned and/or partially-burned diesel fuel and lube oil. Total HC concentration, typically from tens to a few hundred ppm of C1 (methane equivalent), and composition highly depend on engine characteristics, fuel and lube oil properties, engine operating conditions, exhaust sampling and measurement techniques. Many studies have been carried out to speciate light and semi-volatile HCs from diesel combustion in order to optimize combustion processes and reduce emissions [12–18]. Light HCs (C12 and below), typically unsaturated, including alkenes and alkynes commonly sampled by Tedlar bag, are primarily from partially combusted products; while semi-volatile HCs, commonly sampled by resin trap, are generally considered from unburned diesel fuel [14,17,18]. For example, Hammerle et al. studied HC emissions from a diesel-fueled vehicle using a dilution tunnel, and

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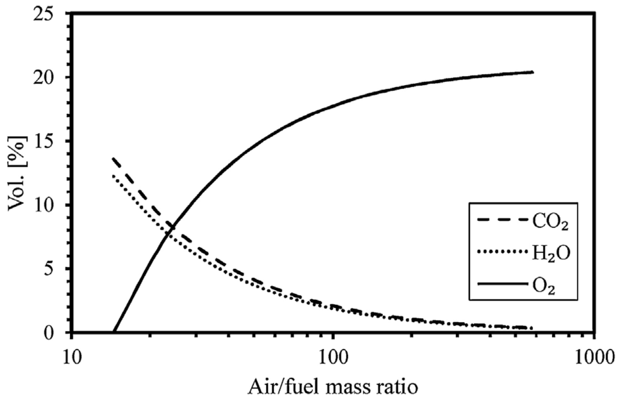

Fig. 1. Lean burn diesel engine emissions of CO_2, H_2O and O_2 volumetric concentration as a function of air/fuel mass ratio greater than the stoichiometric ratio of 14.5. Diesel fuel was assumed to be completely combusted to CO_2 and H_2O.

they reported total HC emissions of 91 mg/Km as measured by hot FID (flame ionization detector). Light HC (C12 and below) and semi-volatile HC accounted for 45% and 9% of the total HC, respectively [16]. In contrast, Han et al. conducted diesel engine exhaust HC speciation without dilution and they found that HC emissions from a conventional diesel engine are composed of 46% partially oxidized and 54% unburned diesel fuel [13]. In addition to light HCs and unburned diesel fuel, oxygenated organic species such as aldehydes, ketones and carboxylic acids etc. are also reported [2,14,19].

Lube oil is used in diesel engines to reduce the friction created by moving parts, such as pistons, valve stems, the turbo shaft etc., and increase the performance of the diesel engine. Lube oil consumption highly depends on engine operating conditions. As an approximation, the lube oil consumption rate is about 0.1% of diesel fuel consumption [20]. Because lube oil consists of relatively stable, high molecular weight HCs from approximately C14–C45 [21], and it is applied to the surfaces of moving parts, such as piston rings, where the temperature is significantly lower than combustion temperature, a significant portion of lube oil can survive combustion. Miller reported that 30–80%, with an average of 64%, of oil consumed can survive combustion and contribute to soluble organic fraction (SOF) formation on PM, and that the amount of oil derived SOF trends approximately linearly with oil consumption [20]. Lube oil derived HC can exist in the gas phase in the combustion chamber or in piping close to the engine where the exhaust temperature is high. As exhaust temperature decreases, due to the heat loss in the exhaust piping, aftertreatment system or exhaust sampling apparatus, the oil derived HC condenses onto soot particles, forming SOF. Thus, the SOF contributes to a significant portion of engine out PM [22]. Although both unburned diesel fuel, especially the high molecular weight fraction, and lube oil are both considered to contribute significantly to the SOF fraction of PM [2,22–24], many SOF chromatography analysis results indicate that the eluted SOF contents most closely resemble lube oil [15,24–26]. Sakurai et al. applied a thermal desorption particle beam mass spectrometer (TDPBMS) and tandem differential mobility analyzer (TDMA) to conduct online measurement of the chemical composition and volatility of diesel exhaust particles from a modern, heavy-duty diesel engine under various load conditions. The authors found that the organic components of diesel particles are almost entirely (95%) derived from unburned lube oil [15].

Gas phase HCs are known to inhibit NO_x conversion over VSCR catalysts [8,9]. The presence of gas phase HC, such as propylene, can also lead to lowered NO_x conversion in the mid and/or high temperature range due to excess NH_3 consumption via ammoxidation [27]. In addition, HC can adsorb and accumulate on vanadia-based catalysts and lead to catalyst deactivation. For example, Ottinger et al. observed carbonaceous materials accumulated on a field returned VSCR catalyst from a diesel aftertreatment system and found the NO_x conversion was significantly diminished on the as-received catalyst below 300 °C. Thermal treatment at 500 °C with the presence of O_2 can remove the carbonaceous deposit by oxidation and fully recover the catalyst performance [8]. In addition to the negative impact on NO_x conversion from accumulated carbonaceous materials, rapid oxidation of the accumulated HC or coke can lead to exotherms on the catalyst which can thermally damage the VSCR catalyst if the temperature exceeds 550 °C [28] and can lead to vanadium and tungsten release [29].

This work focuses on understanding the effect of different types of HC species on their adsorption on a state-of-the-art VSCR catalyst in the low temperature region under relevant diesel engine operating conditions. Dodecane and toluene are used as model molecules for alkane and aromatic species from unburned diesel fuel. Squalane, due to its physical and chemical similarities to lube oil, is chosen as a model molecule for unburned lube oil [30]. The effects of O_2 and H_2O are discussed in the context of engine operating conditions to elucidate the HC adsorption mechanisms and its chemical transformation behaviors.

2. Experimental

2.1. Catalyst sample

The micro-core catalyst samples were cut from the inlet face of a fresh, washcoated, state-of-the-art $V_2O_5/WO_3/TiO_2$ (VSCR) catalyst element with 300 CPSI (cells per square inch). The catalyst sample has ~6.4 mm (1/4 inch) diameter and 25.4 mm (1 inch) length containing 12 intact channels. The total mass of the micro-core sample is 0.48 g.

2.2. Flow reactor system

A flow through reactor was used to conduct the HC adsorption and temperature-programmed oxidation (TPO) experiments to characterize and quantify the adsorbed HC on the VSCR catalyst. The configuration of the reactor system has been reported in several previous publications [6,28,31]. Briefly, the reactor utilizes 14 MKS mass flow controllers (MFCs) for metering and monitoring reaction gas flow rate. The reaction gases, Ar, O_2, 400 ppm (parts per million by volume) toluene/Ar are supplied by AirGas in cylinders and are all UHP grade or higher. Water vapor in the reaction gas mixture is generated by feeding deionized water into a Bronkhorst liquid mass flow controller and evaporator system. Liquid HC, such as dodecane and squalane/dodecane mixture, was introduced to the reaction gas mixture with a second Bronkhorst liquid mass flow controller and evaporator system. The quartz reactor tube is 22 inches long with 7 and 9.5 mm for inner and outer diameters, respectively. The reactor tube is horizontally placed in a Lindberg Blue M miniMite tube furnace for temperature control. Type K thermocouples (0.02 inch diameter) are instrumented at both inlet and outlet of the catalyst bed for temperature control and measurement. The composition of the reaction gas mixture, either after passing through the catalyst bed or the reactor by-pass line, is analyzed by a MKS 2030 Fourier transform infrared (FTIR) spectrometer. All the gas lines are constructed using Swagelok stainless steel tubing and fittings, and they are heated to ~200 °C to avoid condensation and adsorption of H_2O and HC species.

2.3. HC adsorption experiments

To simulate the typical lean-burn diesel engine exhaust gas composition, 8 vol.% H_2O and 10 vol.% O_2 in balance Ar were used as baseline gas unless otherwise indicated. CO_2 was not included in