



Isocyanic acid and ammonia in vehicle emissions



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ABSTRACT

Vehicles are considered to be an important source of ammonia (NH₃) and isocyanic acid (HNCO). HNCO and NH₃ have been shown to be toxic compounds. Moreover, NH₃ is also a precursor in the formation of atmospheric secondary aerosols. For that reason, real-time vehicular emissions from a series of Euro 5 and Euro 6 light-duty vehicles, including spark ignition (gasoline and flex-fuel), compression ignition (diesel) and a plug-in electric hybrid, were investigated at 23 and -7°C over the new World harmonized Light-duty vehicle Test Cycle (WLTC) in the Vehicle Emission Laboratory at the European Commission Joint Research Centre Ispra, Italy. The median HNCO emissions obtained for the studied fleet over the WLTC were 1.4 mg km^{-1} at 23°C and 6 mg km^{-1} at -7°C . The fleet median NH₃ emission factors were 10 mg km^{-1} and 21 mg km^{-1} at 23 and -7°C , respectively. The obtained results show that even though three-way catalyst (TWC), selective catalytic reduction (SCR), and NOx storage catalyst (NSC) are effective systems to reduce NOx vehicular emissions, they also lead to considerable emissions of the byproducts NH₃ and/or HNCO. It is also shown that diesel light-duty vehicles equipped with SCR can present NH₃ emission factors as high as gasoline light-duty vehicles at both, 23 and -7°C over the WLTC. Therefore, with the introduction in the market of this DeNOx technology, vehicular NH₃ emissions will increase further.

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1. Introduction

Vehicular emissions significantly influence the atmospheric composition and have a strong impact on climate change (Uherek et al., 2010), environment and human health (Pope et al., 2002). Light-duty vehicles (LDVs) are considered to be an important source of ammonia (NH₃) and isocyanic acid (HNCO), being in some cases the main source in urban areas (Chitjian et al., 2000; Battye et al., 2003; Whitehead et al., 2007; Kean et al., 2009; Ianniello et al., 2010; Meng et al., 2011; Nowak et al., 2012; Reche et al., 2012; Wentzell et al., 2013; Yao et al., 2013; Woodward-Massey et al., 2014; Reche et al., 2015).

Abbreviations: TWC, three-way catalyst; SCR, selective catalytic reduction; DOC, diesel oxidation catalyst; NSC, NOx storage catalyst; LNT, lean-NOx trap; LDV, light-duty vehicles; LDGV, light-duty gasoline vehicles; LDDV, light-duty diesel vehicles; VELA, vehicle emission laboratory; FID, flame ionization detector; FTIR, fourier transform infrared; PTFE, polytetrafluoroethylene; EF, emission factor; SULEV, super ultra-low emission vehicles; ULEV, ultra-low emission vehicles; LEV, low emission vehicles; NEDC, new European driving cycle; NH₃, ammonia; HNCO, isocyanic acid; WLTC, world harmonized light-duty vehicle test cycle; THC, total hydrocarbons.

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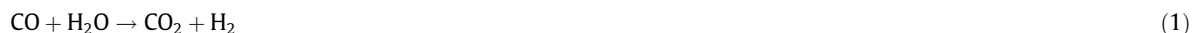
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Ammonia is classified under the European dangerous substances directive (67/548/EEC) as toxic, corrosive and dangerous for the environment. The U.S. Occupational Safety and Health Administration has set for ammonia an eight-hour exposure limit at 25 ppm and a short-term (15 min) exposure level at 35 ppm (Agency for Toxic Substances and Disease Registry, 2004). Ammonia is also a precursor in the formation of atmospheric secondary aerosols (Behera and Sharma, 2010). Its reaction with nitric and sulfuric acid leads to the formation of ammonium nitrate and ammonium sulfate. The particulate matter that is formed (ammonium nitrate and ammonium sulfate) is associated with adverse health effects (Pope et al., 2002). Furthermore, when transported to remote areas, their deposition leads to hypertrophication of waters and acidification of soils with negative effects on nitrogen-containing ecosystems (Sutton et al., 2000; Bouwman et al., 2002; Erisman et al., 2003). Recent studies have shown that LDVs are also one of the main sources of isocyanic acid (Wentzell et al., 2013; Brady et al., 2014; Woodward-Massey et al., 2014). Isocyanic acid has been shown to be a highly toxic gaseous acid and a potential health concern due to its dissociation at physiological pH (Roberts et al., 2011). Isocyanic acid and its aqueous anion (CNO⁻) isocyanate have been linked to several negative health effects such as atherosclerosis, cataracts, and rheumatoid arthritis through carbamylation reactions (Stark et al., 1960; Lee and Manning, 1973; Wang et al., 2007; Roberts et al., 2011). Carbamylation is a chemical process whereby amine, hydroxyl, and sulfhydryl groups in human proteins add across the N–C bond of the CNO group impairing protein function in the body (Stark et al., 1960; Lee and Manning, 1973; Wang et al., 2007). Roberts et al. (2011) estimated that inhalation of concentrations as low as 1 ppbv may be sufficient to commence carbamylation reactions in the human body. Recently, Wentzell et al. (2013) reported mean ambient HNCO mixing ratios of 85 pptv, with spikes as high as 990 pptv, in Toronto, Canada, suggesting that, there are circumstances where HNCO concentrations could be large enough to have a detrimental effect on human health. Despite its toxicity, HNCO-specific exposure or air quality standards do not exist. Consequently, ammonia and HNCO vehicular emissions should be thoroughly studied due to the close proximity between the sources, i.e., vehicles, and the population.

Vehicular emissions of total hydrocarbons (THC), CO and NO_x from LDV are legislated by the directive (EC) No 692/2008 (European Commission, 2008). In order to decrease their emissions, the automotive industry have introduced a series of different after-treatment systems over the last years, e.g., three-way catalyst (TWC), selective catalytic reduction (SCR), lean-NO_x trap (LNT) and NO_x storage catalyst (NSC). The introduction of the TWC was a major step towards the vehicular emissions control. Molecular nitrogen is the aimed reaction product during the reduction of NO_x over the TWC, but ammonia and HNCO have been found to be byproducts during this process (see reactions 1–4). In the TWC, ammonia is formed via steam reforming from hydrocarbons (Whittington et al., 1995) and/or via reaction of nitrogen monoxide (NO) with molecular hydrogen (H₂) (through reaction 2a or 2b) produced from a water-gas shift reaction between CO and water (reaction 1) (Bradow et al., 1977; Barbier and Duprez, 1994). High catalyst temperatures (<360 °C) are usually associated to NH₃ emissions (reactions 1 and 2). HNCO, on the other hand, is formed when NO, CO, and either H₂ or NH₃ react over precious metal catalysts (e.g., platinum, palladium, or rhodium), typically used in modern TWC, at relatively low temperatures (~250 °C; reaction 3) (Dümpelmann et al., 1995; Chambers et al., 2001; Cant et al., 2003, 2004, 2005). The HNCO is formed by reaction of NCO groups with adsorbed H₂ (Chambers et al., 2001). As the catalyst temperature increases H₂ is consumed and the majority of the surface bounded H₂ is formed following NH₃ dissociation. These studies suggested that despite the relatively high yields of HNCO from nitrogen on the catalyst surfaces present in a modern TWC, a rapid and complete hydrolysis of HNCO, leading to NH₃ formation, takes place on the oxide wash-coat of the TWC (reaction 4). In that case, light-duty gasoline vehicles (LDGVs) should emit negligible concentrations of HNCO. However, Brady et al. (2014), reported emission factors for HNCO from a fleet LDGVs and Wentzell et al. (2013), observed HNCO emissions factors from a single light-duty diesel engine operating under four different steady-state driving modes. These are, to our knowledge, the only studies that report HNCO vehicular emissions.



SCR, LNT and NSC after-treatment systems have recently been incorporated to LDVs as DeNO_x systems. The SCR is an after-treatment system whose goal is to reduce NO_x emissions by reacting the NO and NO₂ with NH₃ (formed by the reduction of the urea injected into the system) on a catalyst surface (see reactions 5–7). The over-doping of urea, and low temperatures in the system and/or the catalyst degradation may lead to ammonia emissions. Furthermore, previous studies have shown that HNCO is a byproduct in urea based SCR systems (Koebel et al., 2000; Heeb et al., 2011).



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