In-situ DRIFTS studies provide insight into competitive adsorption of VOCs and ozone on catalyst surfaces at low temperature

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Significance and Relevance

This study should lead to improve the understanding of the reaction pathways that take place during O_3 decomposition under realistic operating conditions, *i.e.* under the presence of other air pollutants such as volatile organic compounds (VOCs). Both O_3 and VOCs, that are highly harmful to human health, may be present simultaneously or sequentially in indoor environment such as aircraft cabins. Therefore, to ensure passenger safety and comfort, it is essential to understand the reaction mechanisms involved in the abatement of both indoor air pollutants at the molecular level. This will allow the optimization of a more advanced catalytic converter for aircraft.

Preferred and 2nd choice for the topic: Air cleaning and combustion and Fundamental advances in understanding catalysis
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Introduction and Motivations

The quality of the air inside an aircraft is a major concern for aviation safety. Indeed, the aircraft cabin environment presents unique challenges, as passengers and crew are exposed to a mixture of compressed jet engine air and recirculated cabin air, resulting in elevated levels of ozone (O_3). Furthermore, ozone is not the only pollutant of concern in aircraft cabins, as the air can also contain other pollutants such as VOCs[1]. These are hydrocarbons that come from kerosene vapors when the aircraft is on the ground, and from engine when the plane is flying even on the ground. The development of catalytic converters to improve cabin air quality and keep pollutants (O_3 and VOCs) levels within acceptable limits is crucial[2]. Furthermore, depending on the altitude, ozone and VOCs may be present simultaneously or sequentially, and although the interaction between them is well understood in the atmosphere, the way in which they compete for adsorption and reaction on the catalyst surface is much less studied. For example, the chemistry at the catalyst surface may depend on the sequence of introduction of different gaseous compounds that can adsorb and/or react with each other on the catalyst surface or the reaction temperature[3]. Therefore, relying on a rigorous *in-situ* Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFTS) approach, our study aims to identify the key intermediates and the reaction pathway involved in adsorption/decomposition of O_3 and/or VOCs.

Materials and Methods

Three materials, 1%Pt/1%Pd-2%Mn/γ-Al_2O_3, 2%Mn/Al_2O_3 and γ-Al_2O_3, were synthesized using a sol-gel method and characterized by different techniques to assess their physicochemical, textural, surface and acidic properties. Methods employed included N_2 sorption, X-ray diffraction, X-ray photoelectron spectroscopy, H_2 temperature-programmed reduction, pyridine infrared spectroscopy. As it was previously mentioned, the adsorption and catalytic decomposition of both toluene (as a model VOCs) and O_3 on the catalyst surface was evaluated by *in-situ* DRIFTS. The ozone generator was configured to produce 500 ppm ozone in a synthetic air stream at 50 ml/min. A saturator was used to set the concentration of VOCs (70 ppm of toluene) and a mass flow controller (Brooks) for synthetic air. The toluene-air and/or ozone-air mixtures were introduced into the DRIFTS chamber according to the pollutant sequences studied. Various pollutant injection sequences have been applied, for example, at 40°C: surface saturation with toluene (70 ppm-air) for 219 minutes followed by flow of O_3 (500 ppm-air) or a mixture of toluene/O_3 (70 ppm/500 ppm) for 30 minutes. The surface saturation with O_3 (500 ppm-air) for 219 min followed by a mixture of toluene/O_3 (70 ppm/500 ppm) for 30 minutes. The reaction temperature effect (40-120°C) was also investigated.

Results and Discussion

DRIFTS spectra (Figure 1 a) depict the adsorption/oxidation of toluene on the surface of 1%Pt/1%Pd-2%Mn/γ-Al_2O_3 catalyst at 40 °C prior to the ozone exposition for 30 min. These *in-situ* measurements evidenced the formation of peroxides (970-990 cm^{-1}) on the catalyst surface[4,5], which appear to contribute to the formation of partially oxidized surface by-products by accelerating the catalytic removal of toluene, comparing to the conventional catalytic oxidation (not shown). Indeed, the catalytic oxidation of toluene in air atmosphere was only clearly observed at 120 °C, while the ozonation of toluene was observed at 40 °C. The formation of benzyl alcohol, benzoates, benzaldehyde and maleic anhydride species was observed in both cases. Nevertheless, new species such as ketone (benzoquinone), phenyl C-H aromatic and peroxides were observed after O_3 exposition (Figure 1 a)[4-6], suggesting the formation of reactive oxygen radicals (O^{2-}, O_2^{2-}, O^-)[4,5] from the O_3 decomposition, which changes the reaction pathway. Due to the strong oxidation ability of these radicals, toluene can be further oxidized at room temperature. Surprisingly, the bands associated to previous-mentioned peroxides species and the consequently oxidized surface by-products were not observed when the surface catalyst was exposed to a mixture of toluene and ozone after the catalyst saturation with toluene for 219 minutes (Figure 1 b). These results suggest that the prior toluene adsorption potentially obstructs the active sites in this case[7]. This effect was not observed when O_3 was adsorbed prior to exposure to a mixture of toluene and ozone (not shown). However, the formation of peroxides species and new oxidized surface by-products was only clearly observed after 20 min of toluene/O_3 mixture exposition, which also suggests an inhibition effect. Indeed, the catalyst surface seems to be “poisoned” by O_3 at the beginning of the toluene ozonation reaction. Overall, these surface measurements indicate that the reaction pathway is highly dependent on the presence of ozone and on the simultaneous presence or absence of both ozone and toluene. However, further studies are needed to better understand the different observed reaction pathways.

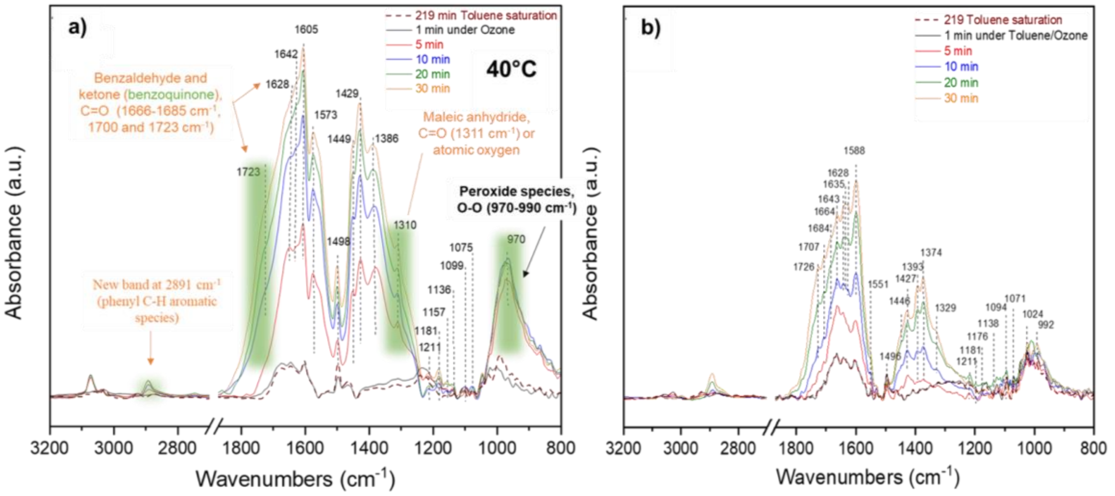

Figure 1. Spectra of **a)** toluene adsorption (dash line) followed by O_3 exposition (solid lines) and **b)** toluene adsorption (dash line) followed by the simultaneous exposition of a mixture of toluene and O_3 (solid lines), all at 40°C.

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