NOₓ conversion and selectivity in multi-layer and sequential DOC-LNT automotive exhaust catalysts: Influence of internal transport

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HIGHLIGHTS

- Multi-layer catalytic converters save space, cost and improve cold-start emissions.
- Dual-layer and sequential arrangements of LNT and DOC catalysts were compared.
- NOₓ storage and conversion in the dual-layer sample was limited by transport.
- At lower T top DOC layer in the dual-layer sample prevented slip of unreduced NOₓ.
- NOₓ conversion, 250 °C: dual-layer > sequential, 350 °C: dual-layer < sequential.

GRAPHICAL ABSTRACT
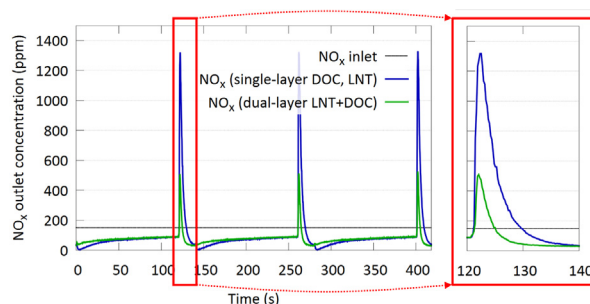
ARTICLE INFO

ABSTRACT

In order to pass strict emission standards, automobiles with internal combustion engines need to be equipped with complex exhaust gas aftertreatment systems. For example, Diesel engines are usually fitted with an oxidation catalyst (DOC), deNOₓ catalyst (either SCR or lean NOₓ trap – LNT) and a particulate filter. Integrating them into a single multi-functional device saves space, cost and weight while improving heat management during cold starts as well. This work investigates a compact DOC+LNT converter combining both catalyst types in a single device – porous layer of a DOC catalyst is added on top of a LNT washcoat. The performance of this dual-layer converter is compared with traditional single-layer DOC and LNT coated on two separate monoliths in series.

Laboratory reactor experiments showed that the performance of the dual-layer sample was affected by transport limitations – mainly internal diffusion through the catalytic layers. An increased NOₓ slip was observed during NOₓ adsorption in the dual-layer sample. The lower amount of stored NOₓ was however more than compensated during NOₓ reduction at lower temperatures near the light-off, where the compact dual-layer monolith exhibited higher efficiency of NOₓ reduction and lower selectivity to N₂O during rich regeneration periods. This was attributed to the fact that the NOₓ released from the bottom LNT layer has to pass through the top DOC layer where it can further react with the reducing agents from the rich feed. At higher temperatures, the two single-layer monoliths outperformed the compact dual-layer monolith.

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1. Introduction

Over the years, increasingly strict engine emission standards have prompted the development of advanced automotive exhaust gas aftertreatment systems. Several tasks have to be performed simultaneously: oxidation of CO, oxidation of unburnt and cracked hydrocarbons (HC), reduction of nitrogen oxides (NO_x), and the capture of particulate matter (soot, PM). For this reason, the exhaust aftertreatment units have grown in size and complexity, especially in lean-burn engines (all Diesel fuelled and an increasing number of gasoline powered vehicles), where a combination of multiple converters needs to be used – an oxidation catalyst (DOC) [1], particulate filter and a converter for NO_x reduction.

In current vehicles two deNO$_x$ technologies are mainly used – selective catalytic reduction catalyst (SCR) with a urea dosing unit (source of NH_3 as an active reducing agent), or a lean NO_x trap catalyst – LNT. In the case of LNT, the engine is periodically switched between two regimes by the engine control unit (ECU). NO_x adsorption occurs under lean ("normal") running conditions with excess of air. Short periodic phases with an excess of fuel are used to regenerate the system [2,3], where the incomplete combustion products can react with the NO_x to form nitrogen. The deNO$_x$ converter may be followed by an additional small "clean-up" catalyst for abatement of excess ammonia.

Such combined systems are very demanding both in terms of cost and space, and therefore a strong effort is placed on making the whole system more compact. A promising strategy is to apply multiple layers of different catalyst types upon each other in the channels of a monolithic substrate. Examples can be found in academic [4–10], technical [11,12] and patent literature [13,14], ranging from multi-layer combination of SCR with clean-up catalyst [4], LNT+SCR [9,10] and LNT+DOC [7,11,13,14], to LNT or SCR coated on a particulate filter [5,6,8,12,15]. Aside from space savings and related advantages, diffusion of the reactants may become the rate determining step instead of reaction kinetics, thus limiting the efficiency of multi-layer washcoat converters [7,9].

In our previous research, it was found that transport limitation is mainly dependent on top layer thickness and macroporosity (or mesoporosity when the macroporosity was low) [7,16,17]. Therefore, it is important to include terms describing gas diffusion in the global model of a catalytic converter, or at least lump the terms into an effective diffusivity parameter [16,17]. Our recent paper [7] compares a dual-layer LNT+DOC catalyst to either single LNT layer or LNT overlaid with an inert layer. The addition of a DOC layer increased NO_x conversion and selectivity to nitrogen, especially at low temperature. However, we were able to identify several issues hindering the LNT+DOC performance, such as limited uptake of NO_x in the beginning of the lean phase, changes in NO_x reduction selectivity, and time-shifted breakthrough of reactants in the rich phase. These effects prevailed at higher temperature at which a single LNT layer was active enough and performed better than the LNT+DOC [7].

In this work we focus on the comparison of (i) a single catalyst sample combining LNT and DOC catalyst layers in a dual-layer washcoat and (ii) two samples – DOC and LNT coated on separate monoliths in a sequential arrangement. Each of the monolith samples had the same volume, so that the dual-layer system was two times smaller than the serial configuration; a similar choice between the standard sequential arrangement and a more compact multi-layer system has to be made in a real automobile system. Catalyst loadings and gas flow rates were kept the same in both arrangements. It needs to be noted that the space velocity (SV, flow rate per total volume of the converters) doubles when using a single monolith instead of two, which may further limit the conversion in a compact dual-layer system. At low SV, the long residence time allows gases to be transported to the catalytic layer and fully converted. At high SV there is an increasing external transport limitation and if the flow rate is too high, part of the gas passes through without any contact with the catalytic material [7,18].

2. Experimental part

2.1. Sample characterisation

Model catalyst samples were supplied by Johnson Matthey. Cordierite monoliths were coated with a catalytically active layer – (i) LNT (Pt/Pd/Ba/Ce/Al$_2$O$_3$), (ii) DOC (Pt/Pd/Al$_2$O$_3$/zeolite) or (iii) both above-mentioned catalyst types coated in dual-layer arrangement, denoted LNT+DOC. In the latter case, the cordierite substrate was first coated with an LNT layer which was subsequently overlaid with a DOC layer. LNT washcoat loading was the same in the single-layer LNT and LNT+DOC samples and in the same way, loading of DOC was identical in the case of DOC and LNT+DOC.

For the lab reactor experiments, 3 cm long samples were cut from the central part of the monolith. Thickness and macroporosity of the layers was estimated from scanning electron microscopy (SEM) applied to small sections of the monolith located directly in front of and behind the samples used in lab reactor. The results revealed no significant variation of layer parameters along the monolith. The sections for SEM analysis were mounted in epoxy resin. The specimens were then cut in half, polished and sputtered with a several nanometers thin layer of gold. The samples were then scanned by a back-scattering electron detector of a Tescan VEGA 3 SBU microscope. Fig. 1 shows the cross-section of the LNT+DOC sample. Average macroporosity (ε_M) of individual layers (Table 1) was estimated by image analysis of several cross-sectional images. The thickness of the bottom layer was uneven due to the rectangular shape of the channel (cf. Fig. 1) – mean values both in the corner of the channel ($\delta_{corners}$) and straight part of the wall (δ_{wall}) were therefore calculated (Table 1).

2.2. Lab reactor

The catalytic activity testing was carried out in a laboratory minireactor developed at Department of Chemical Engineering, UCT Prague. The apparatus was fully described elsewhere [7,19], however, its arrangement will be described briefly: the inlet gas was mixed from gas vessels using mass flow controllers and brought to a nearly isothermal tube-flow reactor. Quick switching of two different reaction mixtures was made possible by a
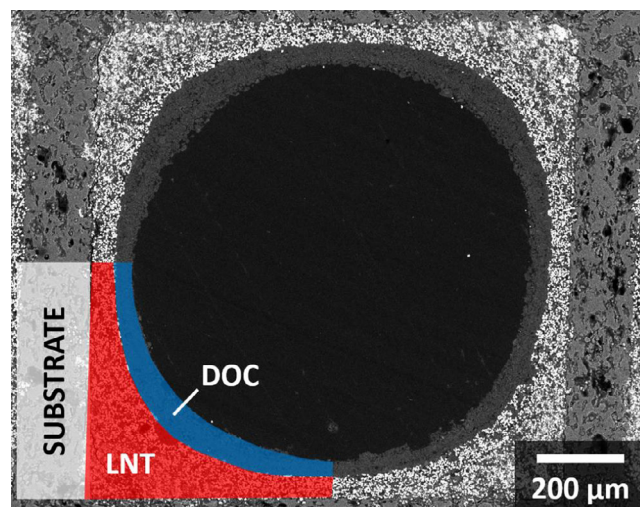

Fig. 1. Cross-sectional SEM micrograph of the LNT+DOC sample; magnification: 180×. Note the varying bottom layer (LNT) thickness (ca 30–200 μm).