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## *Catalyst-modulated discharge chemistry: Tailoring electron–surface interactions in the total oxidation of n-butane to $CO_2$ over a $MnO_2$/CaO-coated surface dielectric barrier discharge*

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Industrial exhaust streams often contain volatile organic compounds (VOCs) that pose risks to both the environment and human health. Conventional thermal oxidation achieves high conversion but requires substantial energy input at elevated temperatures. Non-thermal plasma (NTP) provides an alternative by generating reactive species for VOC decomposition at low gas temperatures. Surface dielectric barrier discharges (SDBDs) offer scalability, low flow resistance, and efficient operation in complex gas mixtures. However, NTP oxidation typically shows limited $CO_2$ selectivity and significant CO formation. Catalytic coatings improve selectivity towards $CO_2$, but pure $MnO_2$ coatings inhibit discharge, requiring scaffold materials such as $BaTiO_3$ or CaO.[1]
Here, we investigate a $MnO_2$/CuO/CaO (3:1) dual-component coating in a twin-SDBD reactor. Ultrasonic spray-coating applies uniform 3 mg/cm² loadings, characterized by laser scanning microscopy (15-25 µm coating thickness). The system operates in different $N_2$/$O_2$/*n*-butane mixtures at 2.5 and 10 standard liters per minute (slm) and 35-115 W dissipated power, examining plasma-catalyst interactions without external heating.
Results show distinct performance characteristics: at 2.5 slm/115 W, a $MnO_2$/CaO coated electrode configuration reaches 87.5% *n*-butane conversion and 95.0% $CO_2$ selectivity (compared to 82.0%/83.4% for a $MnO_2$/$BaTiO_3$ coated electrode configuration and 87.5%/56.5% for uncoated electrode configurations); at 10 slm/115 W, $CO_2$ selectivity is 76.1%. Carbon balances approach up to 100%, indicating complete carbon accounting. ICCD streamer imaging further reveals brighter streamers for $MnO_2$/CaO coatings compared to an uncoated electrode configuration.
These observations relate to CaO's material properties: low permittivity ($\varepsilon_r \approx 11.8$) could enhance microdischarges within pores through elevated electric fields, while the low work function (1.7 eV) promotes secondary electron emission.[2] This increases local electron density, ionization rates, and local plasma heating, facilitating $MnO_2$ activation for CO → $CO_2$ conversion via O radicals. Diluted $O_2$ conditions favor O-radical pathways over $O_3$/$NO_x$ formation, with residence time and energy density influencing reaction selectivity.
These findings demonstrate how scaffold material selection influences plasma-catalyst interplay in SDBD systems. This approach enables efficient VOC conversion through localized discharge heating, avoiding external thermal inputs, with potential for scalable exhaust treatment applications.
**Acknowledgement:** This work was supported by the German Research Foundation in the frame of the collaborative research center SFB 1316 (DFG327886311), project A7.

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