Oxygen migration and oxidation pathway for soot oxidation in presence of NO by two-step isotope experiment

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Significance and Relevance

NO plays a dual role in the NOx-assisted mechanism for soot oxidation. On one hand, NO facilitates oxidation by generating NO_2, a potent oxidant that reduces the overall oxidation temperature. On the other hand, NO competes with gas-phase oxygen for active sites on the catalyst, which can impede the oxidation rate. Thus, in the presence of NO, soot oxidation proceeds via two distinct pathways: a faster reaction involving direct interaction with lattice oxygen and a slower pathway where NO is first oxidized to NO_2 through a Langmuir-Hinshelwood mechanism before it participates in soot oxidation.

Preferred and 2nd choice for the topic: Automotive and stationary emission control and Fundamental advances in understanding catalysis
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Environmental pollution, especially the release of Particulate Matter (PM) such as soot and Nitrogen Oxides (NO_x), has gained significant attention recently. The primary issue has been obtaining NO_x-facilitated soot oxidation at moderate temperatures. The study of the oxidation mechanism of soot can lay a theoretical foundation for the development of high-performance catalysts.

Results and Discussion

To clarify NO_2's role in soot oxidation, we analyzed catalytic NO oxidation across all samples (**Fig.1A**), finding $CuCeO_x$ > CuO > CeO_2 in activity, with $CuCeO_x$ reaching 80% NO conversion at around 320 °C. In the primary soot oxidation range (250-500 °C), NO conversion remained high, with notable NO_2 presence. As temperature increased, NO converted to NO_2, reaching a peak level before decreasing in line with the thermodynamic equilibrium between NO and NO_2[1].

Temperature-Programmed Oxidation (TPO) tests on SO/PU oxidation showed that all catalysts reduced oxidation temperatures over a wide range (300-700 °C) (**Fig.1B**), ordered as $CuCeO_x$ > CuO > CeO_2. SO displayed a lower peak oxidation temperature than PU, attributed to more surface oxidizable functional groups. Each catalyst showed a narrow CO_2 peak, indicating complete oxidation. NO-TPO experiments further confirmed NO's role in lowering ignition temperatures and broadening CO_2 peaks, signifying its facilitative effect on oxidation. Soot from a diesel engine was also analyzed for oxidation characteristics. Compared to PU carbon, diesel soot had higher oxygen-functional groups (OFGs), enhancing its reactivity. TPO results showed CuCeOy to be most active (Tm = 352 °C in O_2/Ar, 342 °C in O_2+NO/Ar), likely due to Cu-[O] interactions boosting NO oxidation to NO_2.

While NO assists in soot oxidation, it also competes with oxygen for catalyst surface sites, slowing the overall rate. NO oxidation to NO_2 follows the slower Langmuir-Hinshelwood (LH) mechanism, which limits available reactive oxygen for soot oxidation. Though NO_2 lowers the temperature required, this slower pathway means an overall reduced reaction rate compared to direct oxidation by lattice oxygen.

IR experiments (**Fig.3C**) on CuCeOy revealed that NO lowered the temperature required to break down carbonates in the presence of oxygen, improving oxidation efficiency. Trends in nitrate and carbonate transformation suggested a pathway for intermediate species involved in soot oxidation. Bidentate nitrite concentrations peaked at 100 °C, with NO_2 production highlighting soot oxidation's complex chemistry.

Surface oxygen species were studied via Soot-TPR (**Fig.1D**) analysis in an oxygen-limited Ar atmosphere. Two main temperature regimes corresponded to oxygen species (O_2^- at 320-625 °C, and O_2^- at >625 °C), indicating that CuO had the highest adsorbed oxygen, followed by CuCeOy. Both catalysts displayed three soot reduction peaks, attributed to chemisorbed oxygen desorption, lattice oxygen, and active oxygen migration. CuCeOy's high activity, despite not having the largest reduction peak, was likely due to the synergy between copper and cerium, enhancing reactive oxygen species (ROS) [2,3].

In isotope-switching experiments (**Fig.1E**), lattice oxygen's direct reaction with soot was confirmed. $18O_2$ injections produced $C^{16}O^{16}O$, $C^{16}O^{18}O$, and $C^{18}O^{18}O$, showing that lattice oxygen participates actively in soot oxidation. CuCeOy had balanced CO_2 isotopes, indicating bulk-to-surface oxygen migration. A final experiment with NO revealed that competitive adsorption reduced $C^{16}O^{18}O$ and $C^{18}O_2$ production, slowing oxidation. The increase in $C^{16}O^{16}O$ suggested that nitrates from NO adsorption play a role in soot oxidation.

Based on these findings, we propose a mechanism for NO-assisted soot oxidation over CuCeOy (**Fig.1F**): (1) lattice oxygen directly oxidizes soot, with CeO_2 aiding oxygen migration, and (2) NO oxidizes on CuCeOy, producing NO_2 that facilitates soot oxidation. Oxygen migration in both pathways ensures continuous activity.

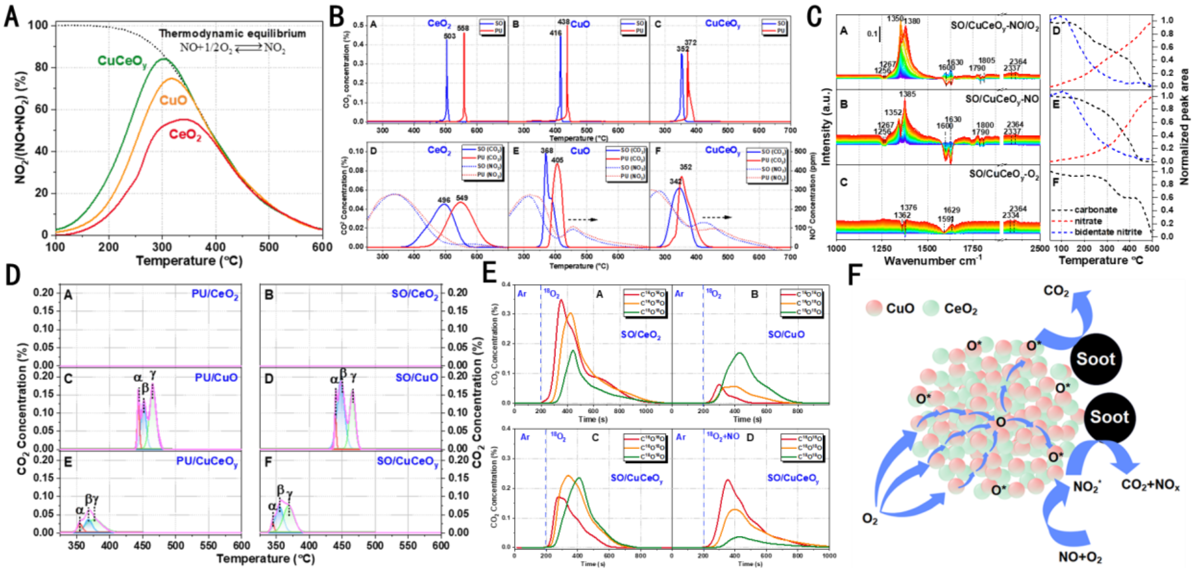

Figure 1 NO-TPO(A), Soot-TPO for SO/PU doped with CeO_2/CuO/$CuCeO_y$(B), IR spectra(C), Soot-TPR(D), instantaneous isotope switching experiment(E) and catalytic oxidation mechanism of soot particles by $CuCeO_y$ assisted with NOx(F).

References

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