PERSPECTIVE

Simultaneous Selective Catalytic Reduction of NO_x and CO Oxidation in Flue Gas: Emerging Catalyst Families for Combustion and Pyrolysis Applications

Guillermo Felix[1,2,*]

[1] Instituto Tecnológico de Los Mochis, Tecnológico Nacional de México, Los Mochis 81259, Mexico
[2] Department of Petroleum Engineering, Kazan Federal University, Kazan 420008, Russia

Abstract

Flue gas from the pyrolysis and combustion of biomass, plastic, and refuse-derived feedstocks typically contains both carbon monoxide (CO; 1–15 vol%) and nitrogen oxides (NO_x; 150–800 ppm), together with several volume percent of water vapor and tens to hundreds of ppm of SO_2. Because CO is an intrinsic reductant for NO_x, both pollutants can in principle be removed in a single catalytic reactor rather than in two energy-intensive non-catalytic units. This work synthesizes the catalyst families reported for the selective catalytic reduction (SCR) of NO_x and the catalytic oxidation of CO, namely vanadia-tungsta/titania, manganese oxides, Cu-exchanged small-pore zeolites, ceria-based mixed oxides, layered double hydroxide (LDH)-derived oxides, perovskites, and dual-site single-atom architectures. No single active phase satisfies the full pyrolysis flue-gas envelope; instead, the literature converges on a bifunctional design in which a redox-active transition metal supplies oxygen transfer while a second cation provides acid sites, mobile lattice oxygen, or dispersion stability. Atomically mixed LDH-derived oxides currently offer the best balance, with simultaneous NO_x and CO conversions of 87–100% and 96–100%, respectively, at 200–300 °C. Because this window matches the flue-gas temperature after heat recovery, a single reactor can be placed directly upstream of CO_2 capture. The near-term priority is therefore not the discovery of new active phases but the engineering of known bifunctional oxides into regenerable, sulfur- and tar-tolerant monoliths validated under realistic flue gas.

Keywords: selective catalytic reduction, CO oxidation, bifunctional catalysis, pyrolysis flue gas, Mars-van Krevelen mechanism.

1 Introduction

Pyrolysis of biomass and related feedstocks yields a CO-containing product gas that also carries tar [1], and combustion of fuel-bound nitrogen generates NO_x [2]. The resulting flue gas from pyrolysis and combustion of biomass, plastic, and refuse-derived feedstocks is

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***Corresponding author:**
✉ Guillermo Felix
jose.fl@mochis.tecnm.mx

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Table 1. Representative performance of catalyst families for NO_x and CO removal from CO-rich flue gas.

Catalyst family	Window (°C)	NO_x conv. (%)	CO conv. (%)	N_2 sel. (%)	Ref.
V_2O_5–WO_3/TiO_2	300–400	90–98	n.r.	>98	[8, 9]
MnO_x/TiO_2	150–250	80–98	85–98	90–99	[11, 12]
Cu-SSZ-13 (CHA)	175–350	78–100	n.r.	>98	[13, 14]
CuO/CeO_2 and CuCe oxides	100–300	n.r.	95–100	>90	[15, 16, 22]
Mn–Cu–Al LDO	200–300	87–100	96–100	95–99	[6, 17]
$LaCoO_3$-based perovskite	300–350	∼85	∼94	n.r.	[18]
Co-SA + CoO_x/CZO	250–400	>99	n.r.	100	[7]

CHA: chabazite framework; LDO: layered double oxide; Co-SA: Co single atoms; CZO: $Ce_{0.75}Zr_{0.25}O_2$; n.r.: not reported in the cited sources.

characteristically rich in both CO (1–15 vol%) and NO_x (150–800 ppm), while carrying several percent water vapor and, for sulfur- or chlorine-bearing feedstocks, tens to hundreds of ppm of SO_2 and HCl [3]. This composition is chemically convenient, because CO is itself a reductant for NO_x, and simultaneously demanding, as any catalyst added to the stream must tolerate high CO partial pressure, humidity, and acid-gas contaminants at once.

The conventional baseline, selective non-catalytic reduction (SNCR) with ammonia at 850–1100 °C [4] combined with a separate high-temperature CO oxidation stage (thermal or catalytic combustion) at 800–1000 °C [5], achieves only 30–70% NO_x removal, at an elevated energy cost. In contrast, catalytic integration of NO_x reduction and CO oxidation in the 200–400 °C heat-recovery window is reported to reach 87–100% NO_x and 96–100% CO conversion, with N_2 selectivity of 95–100% (Table 1) [6, 7]. This study does not catalogue every method documented for NO_x or CO removal; instead, it compares representative catalyst families and extracts, from the literature on catalysts, mechanisms, and operating conditions, the design principles and immediate priorities that will determine whether simultaneous NO_x/CO removal becomes common practice in pyrolysis-integrated biorefineries and waste-to-energy facilities.

2 The Catalyst Landscape: Convergence Toward Bifunctional Design

Seven catalyst families dominate the recent literature (Table 1). Vanadia-tungsta/titania remains the commercial NH_3-SCR reference, with recent operando spectroscopy revising the active-site model toward binuclear V-W pairs rather than isolated vanadyl species [8, 9]. Manganese oxides give the lowest light-off temperature of the earth-abundant NH_3-SCR phases but are sulfur-limited, although water-activated O_2 has been shown to regenerate sulfated MnO_x [10–12]. Copper-exchanged chabazite (Cu-SSZ-13, CHA framework) offers the best hydrothermal durability, and its low-temperature activity arises from a mobile, multinuclear Cu-site mechanism [13, 14]. Ceria composites are benchmark CO-oxidation catalysts via a Mars-van Krevelen (MvK) pathway that can bifurcate into Langmuir-Hinshelwood chemistry at a noble-metal-ceria interface [15, 16]. Layered double hydroxide (LDH)-derived oxides (layered double oxides, LDOs), in which an atomically mixed cation neighborhood shares oxygen between the NO_x- and CO-active sites, currently offer the best simultaneous-removal balance [6, 17]. Perovskites and dual-site single-atom architectures extend this same redox logic to higher temperatures and to maximal atom utilization, respectively [7, 18].

Across these families the design logic converges: the active phase is almost always a redox-active transition metal whose oxidation-state flexibility supplies oxygen transfer, while a second cation supplies acid sites for NH_3 storage, mobile lattice oxygen, or dispersion stability. Selecting a catalyst is therefore less a search for a single "best" oxide than a matter of aligning the mechanism and deactivation characteristics of a catalyst family with the temperature range, space velocity, and contaminant load of a specific stream.

3 Mechanistic Unification and the Operating Envelope

The mechanistic literature describes three recognized pathways: Mars-van Krevelen [19], Langmuir-Hinshelwood, and Eley-Rideal, the last two as resolved for NO reduction on Cu-SSZ-13 with NH_3 [20] and on $LaFeO_3$ with CO [21]. When CO serves as the reductant, these pathways combine into CO-assisted SCR (CO-SCR):

$$2\,NO + 2\,CO \rightarrow N_2 + 2\,CO_2, \tag{1}$$

with N_2O forming as a frequent intermediate that a second CO-mediated step can further reduce [22]:

$$2\,NO + CO \rightarrow N_2O + CO_2, \tag{2}$$

$$N_2O + CO \rightarrow N_2 + CO_2. \tag{3}$$

The decisive advantage of this coupling scheme is that the oxygen atom liberated from NO_x reduction is the same oxidant consumed by CO oxidation, so a truly bifunctional catalyst removes both pollutants through a shared oxygen-vacancy pool rather than through the two competing half-cycles of a physical mixture.

Temperature and space velocity remain the dominant operating variables. Water vapor (above roughly 5 vol%) can convert Lewis to Brønsted acid sites but generally inhibits low-temperature NO_x conversion on Mn-based catalysts through competitive adsorption [11]. SO_2 is the most damaging common contaminant, deactivating catalysts reversibly through ammonium bisulfate or irreversibly through stable metal sulfates such as $MnSO_4$ [11, 23].

4 Toward Integrated, Regenerable, Capture-Compatible Cleanup

Set against the non-catalytic baseline [4, 5], the case for catalytic integration is categorical, not marginal: it lowers the energy penalty while raising single-stage NO_x conversion from 30–70% to 87–100% and adding 96–100% CO conversion in the same reactor (Table 1) [6, 7]. Two priorities follow for future research. First, the near-term leading candidates (atomically mixed LDH-derived oxides and dual-site single-atom architectures) already achieve 87–100% NO_x conversion at 200–400 °C (and 96–100% CO conversion for the LDH-derived oxides) in laboratory streams; the outstanding task is translating that performance into monolith or sheet geometries that resist the tar, alkali, and SO_2 loads of real, waste-derived pyrolysis gas rather than idealized feeds [17]. Regenerability after sulfur exposure, as examined for Mn-Cu catalysts supported on activated coke [24], is a further design requirement.

Second, because the 200–300 °C operating-temperature window overlaps the temperature at which the flue gas is already available after heat recovery, a single reactor can be sited immediately upstream of CO_2 capture without an intermediate reheat step. Machine-learning-assisted screening of composition-activity relationships, demonstrated so far for NH_3-SCR catalysts, is beginning to accelerate catalyst optimization and should be directed specifically at the sulfur-water tolerance trade-off that currently separates laboratory performance from field durability [25].

5 Conclusion

SCR of NO_x and the catalytic oxidation of CO are well-established, mature technologies for emissions control. Combining these processes offers an energetically efficient route to the simultaneous removal of both pollutants from pyrolysis and combustion flue gases. However, no single catalyst family can currently operate effectively across the broad spectrum of temperature, humidity, and sulfur content. Despite this challenge, the literature converges on a common bifunctional design principle, a redox-active transition metal paired with a second cation, of which atomically mixed LDH-derived oxides (or LDOs) are presently the most effective realization. In the short to medium term, the primary focus should be on engineering durable, regenerable monolithic catalysts validated under the contaminant loads typical of real flue gases.

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Not applicable.

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Conflicts of Interest

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AI Use Statement

The author declares that no generative AI was used in the preparation of this manuscript.

Ethical Approval and Consent to Participate

Not applicable.

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Guillermo Felix received the Ph.D. degree in advanced technology from the National Polytechnic Institute (IPN), Mexico, in 2019, and has received various national recognitions in Mexico. He is the author and co-author of several scientific papers and book chapters, has participated in international conferences, and serves as a reviewer for international journals. He has participated in international studies on crude oil compatibility, the upgrading of heavy crude oil, and the development of novel kinetic and thermodynamic models. His current research focuses on the catalytic in situ upgrading of unconventional hydrocarbons (heavy crude oil, oil shale, and bitumen) by different technologies (steam injection, hydrocracking, and pyrolysis), as well as the evaluation of novel catalytic materials. (Email: jose.fl@mochis.tecnm.mx; KFeliks.Lugo@kpfu.ru)