Sustainable catalysts for gaseous pollutant removal: Catalytic decomposition of N_2O over natural zeolites

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Highlights

- Natural clinoptilolite is as a low-cost, sustainable support for N_2O decomposition catalysts
- Fe and Cu active phases deposited via Solution Combustion Synthesis (SCS) without hydrothermal steps
- Cu–Fe bimetallic systems show strong redox synergy, lowering the light-off temperature
- Natural zeolite route drastically reduces catalyst E-factor by eliminating alkaline wastewater and energy-intensive synthesis

1. Introduction

This work addresses the critical challenge of nitrous oxide (N_2O) abatement within the framework of Green Chemistry and sustainable catalysis. N_2O, primarily emitted from nitric acid and adipic acid production processes as well as post-combustion systems, presents a significant environmental threat despite its relatively low atmospheric concentration. With a Global Warming Potential (GWP) approximately 298 times higher than CO_2 and as the primary contributor to stratospheric ozone depletion, N_2O mitigation represents a crucial priority for climate change mitigation strategies.
The novelty of this research lies in replacing conventional synthetic zeolites (such as ZSM-5 or N2 physisorption at -196 °C) with natural clinoptilolite as a catalytic support. While synthetic zeolites offer excellent catalytic properties, their production requires energy-intensive hydrothermal synthesis protocols, prolonged crystallization times, and expensive, often toxic organic templates. Natural clinoptilolite—a hydrated aluminum silicate with an open-channel microporous structure—emerges as a sustainable alternative that, when appropriately functionalized, can serve as an active catalytic support without the environmental burden of synthetic production [1].

2. Materials and methods

The raw mineral was validated in its as-received form, without chemical pretreatments, to preserve both economic and environmental sustainability. Comprehensive physicochemical characterization employed complementary techniques: XRD analysis confirmed high crystallinity and absence of impurities, ensuring framework stability for subsequent metal loading. FT-IR spectroscopy mapped lattice vibrations and surface hydroxyl group density—key parameters for metal precursor interactions. N_2 physisorption at -196 °C analysis quantified surface area and porosity, demonstrating that while natural clinoptilolite exhibits lower porosity than synthetic variants, its channel architecture ensures efficient reactant diffusion. FESEM-EDX investigation confirmed the characteristic lamellar morphology and homogeneous distribution of native cations (Ca, Mg, K, Na).

Active phase deposition of Iron (Fe) and Copper (Cu) was accomplished via Solution Combustion Synthesis (SCS), an innovative methodology exploiting a highly exothermic, self-sustained redox reaction between metal nitrates (oxidizing agents) and organic fuel (urea). This approach generates nanostructured, highly dispersed metal oxides in remarkably short timeframes. SCS was selected for its ability to induce localized high temperatures that promote the formation of stable active phases firmly anchored to the natural support surface. Various metal loadings were investigated to optimize the balance between catalytic activity and thermal stability, with particular attention to synergistic effects between different metal oxidation states (Fe^{3+}/Fe^{2+} and Cu^{2+}/Cu^{+} redox couples), which are critical for promoting the N_2O decomposition catalytic cycle [2]. Experimental testing was conducted in a laboratory-scale fixed-bed U-shaped reactor fed with a model mixture (1000 ppm N_2O in He) at 50 mL/min.

3. Results and discussion

Comparative analysis revealed that copper integration creates a fundamental synergy with iron, significantly improving overall catalytic performance through enhanced low-temperature activity and a reduced light-off temperature. Although the natural support requires higher operating temperatures compared to synthetic counterparts, complete pollutant abatement is still achieved, fully meeting the "zero emissions" target — a temperature window shift that represents an engineering trade-off amply justified by the environmental and economic benefits derived from eliminating support synthesis processes.

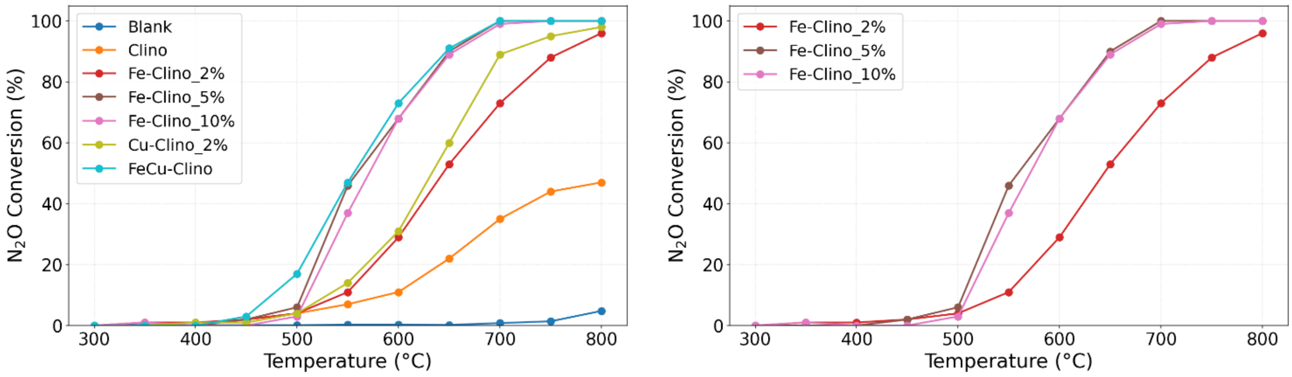

Figure 1 *- Catalytic activity profiles of the investigated samples: (left) full screening of all formulations; (right) optimization of Fe loading on Fe/clinoptilolite systems.*

Two sets of catalytic activity tests were performed to systematically assess catalyst performance. The first screening encompassed all synthesized formulations, demonstrating that the bimetallic Fe–Cu/clinoptilolite system, at the individually optimized metal loadings (Fe: 5 wt%; Cu: 2 wt%, as established from the literature [3]), performs better than all monometallic counterparts across the entire temperature range (left figure). The optimal Fe content was independently identified through a dedicated optimization study on Fe-only samples, in which 5 wt% Fe loading yielded the best catalytic performance" (right figure). These findings confirm that Cu incorporation at a well-defined loading amplifies the intrinsic activity of the Fe-based catalyst, lowering the light-off temperature and extending the operational window toward milder conditions.

4. Conclusions

The transition from synthetic to natural support proves not merely an ethical choice but a technically sound engineering strategy. Employing clinoptilolite "as-is" drastically reduces the Environmental Factor (E-factor) of catalyst production, eliminating alkaline wastewater and energy consumption associated with hydrothermal synthesis.

Balancing catalytic efficiency with environmental sustainability redefines standards for industrial gaseous effluent treatment. These results pave the way for future optimizations, including investigations of catalyst resistance in the presence of common poisons (SO_2 and water vapor), consolidating natural clinoptilolite's role as a cornerstone for next-generation atmospheric protection technologies.

References

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Keywords

N_2O decomposition, natural zeolites, clinoptilolite, solution combustion synthesis, green catalysis, sustainable catalysts