

Decomposition of N₂O on Redox Tuned Cobalt Spinel Catalysts – Molecular Orbital Resolution of Reaction Mechanism

Leszek NOWAKOWSKI, Camillo HUDY, Filip ZASADA, Zbigniew SOJKA*

Faculty of Chemistry Jagiellonian University, ul. Gronostajowa 2, 30-387 Krakow, Poland

* e-mail corresponding sojka@chemia.uj.edu.pl

Significance and Relevance

The key factors governing the redox activity of the cobalt spinel catalyst in N₂O decomposition were established. The crucial role of interactions between the virtual LUMO of N₂O and the SOMO of O_2^- with cobalt 3d orbitals, and the Fermi level position were found to play a crucial role in shuttling the electrons between the reactants and the cobalt active sites was shown for the first time. The proposed original conceptual molecular framework allows for a concise interpretation of the multifaceted redox features of the N₂O decomposition on p-type semiconductor catalysts.

Introduction and Motivations

Nitrous oxide belongs to the most important greenhouse gases, and the main sources of its anthropogenic emissions include nitric acid industry, transport, and agriculture. Despite the stoichiometric simplicity of the N₂O decomposition over oxide catalysts, the mechanism of this reaction can often exhibit a complex nature. In the present study, we address these points for catalytic N₂O decomposition, choosing well-defined cobalt spinel of the nanocubic shape and its Li and K-doped derivatives as dedicated model catalytic systems. The aim is to evaluate the redox behavior of cobalt spinel catalysts, and reveal the effects resulting from bulk and surface doping of Co_3O_4 with lithium and potassium, introduced alone or jointly. The resulting controlled electronic structure perturbations of the cobalt spinel matrix allow for straightforward clarification of the observed changes in the catalytic activity in terms of the interfacial orbital interactions, the Fermi level, and surface electrostatics variation, playing the key function.

Materials and Methods

Two series of singly and doubly (Li and K) doped Co_3O_4 catalysts of a well-cut nanocube shape were synthesized. For the catalyst obtained by one-pot hydrothermal synthesis (h-Li_xCo_{3-x}O₄ series), lithiation of the Co₃O₄ leads to the formation of {Li'_{8a}, Co'_{16d}} defects, decreasing steadily the work function and the catalytic activity. In contrast, for the catalysts prepared by post-synthesis impregnation (i-Li_xCo₃O₄), the formation of {Li'_{8a}, Co'_{16d}, Co⁻⁻_{16c}} defects leads to a volcano-type dependence of the catalytic activity, paralleled by the work function changes. Post-synthesis surface doping of the bare and lithiated spinel catalyst with potassium was achieved by dry impregnation with aqueous solution of KNO₃ (singly, i-K_y/Co₃O₄, and doubly doped i-K_y/Li_xCo₃O₄ series). All catalysts were thoroughly characterized by XAFS, XRD, XRF, XPS, RS, SEM, S/TEM/EDX, and Kelvin Probe techniques (work function measurements). Catalytic activity and the N₂O turnover frequencies were determined using TPSR and steady-state isothermal catalytic tests. Molecular orbital interpretation of the results was based on DFT modeling including Projected Crystal Orbital Hamilton Population (pCOHP) analysis of the catalyst |reactants electronic structure.

Results and Discussion

In the case of the i-Li_xCo₃O₄ series, a non-monotonous dependence of the N₂O conversion on the Li content was found. All the catalysts were more active than the parent Co₃O₄ and the h-Li_xCo_{3-x}O₄ catalysts, which were noticeably less sensitive to the doping level. For the h-Li_xCo_{3-x}O₄ catalysts, the



 ΔE_a values increase steadily with the Li doping level. Yet, in the case of the i-Li_xCo₃O₄ series the activation energy passes through a well-pronounced minimum, revealing a dramatically opposite catalytic behavior in response to the spinel redox tuning, which is governed by the route the lithium dopant was introduced and its concentration as well. Furthermore, the activation energies exhibit a striking sensitivity to the N₂O pressure, which for the most active i-Li_xCo₃O₄ is almost doubled upon passing from $pN_2O \rightarrow 0$ hPa ($\Delta E_a = 0.66 \text{ eV}$) to 50 hPa ($E_a = 1.16$). This behavior was associated with the buildup of negatively charged oxygen intermediates, since the resultant surface electrostatic field strongly influences the dynamics of the redox processes. The associated variation of the TOF values is directly correlated with the work function of the catalysts. For h-Li_xCo_{3-x}O₄ catalysts formation of the

 $\{Li'_{8a}, Co'_{16d}\}\$ defects decreases the work function due to the E_F energy lowering (TOF decreases), while for the i-Li_xCo₃O₄ catalyst, the formation of {Li'_{8a}, Co'_{16d}, Co''_{16c}} defects leads to an increase in the E_F level and the resultant lowering of the work function (TOF increases). The performance of the doubly promoted i-Ky/LixCo₃O₄ catalysts significantly outperforms those of the singly doped i-LixCo₃O₄, and i- $K_{y}/Co_{3}O_{4}$ counterparts, revealing a clear synergy of the lithium and potassium doping when both are introduced by the impregnation. The experimental results obtained, complemented by the DFT calculations, allowed us to construct a conceptual molecular orbital model of the redox interactions between the spinel catalysts and the N₂O and O₂ reactant molecules. In the proposed treatment, the conceivable redox steps of nitrous oxide decomposition, $2N_2O+2e \rightarrow [2O_{(ads)}^- \rightarrow O_2^{-} (ads)^- e \rightarrow O_2^{-} (ads)]$ $-e \rightarrow O_{2(g)} + N_{2(g)}$, are restricted to the two key molecular events of an initial dissociative reduction of N₂O (entrance into the catalytic cycle through an interfacial electron transfer, and a terminal evolution of O_2 (exit from the catalytic cycle upon back electron transfer). Redox interactions governing the catalyst activity depend critically on the surface DOS structure and the manifold of the FMO energy levels of the reactants and intermediates involved. The corresponding lineup of the (100) surface DOS features and the 3dz² orbital of Cobalt in particular with the frontier orbitals of the N₂O and O₂ reactant, and molecular orbital evolution during the principal reaction steps are shown in Figure below.



The established molecular orbital pattern, and the position of the Fermi level ($E_{\rm F}$ - blue line) control the trade-off between the interfacial electron transfer that triggers N₂O dissociation into the prime Co-O⁻_(ads) intermediates and N_{2(g)}, and the back electron transfer that drives the subsequent oxidative evolution of the secondary Co-O₂⁻ intermediates into final O_{2(g)}. The crucial role of overlap between the virtual LUMO 10a' and 3dz² orbitals in attaining the transference of electrons between the N₂O reactant (acceptor center) and the octahedral cobalt active sites (donor center) and the pivotal function of the $E_{\rm F}$ position in the N₂O decomposition process was conceptually ascertained thereby.

The constructed molecular framework allows for a concise account of the multifaceted redox features of the N₂O decomposition on cobalt spinel catalysts. It extends the classic picture of catalysis on semiconductors, pioneered by Wolkenstein and Hauffe, primarily by including a key hybridization of the molecular orbitals of the reacting species with the catalysts DOS features (3d), surface electrostatics (buildup of O^-/O_2^- intermediates), and reorganization energy of the reactants. The proposed model of redox behavior of singly and doubly doped cobalt spinel can be applied to any type of oxide catalysts, often used in fundamental studies and practical deN₂O applications, for straightforward molecular orbital rationalization of the structure-redox reactivity relationships.