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Tunable Electronic Structure in Spinel-Type Mixed Metal Oxides for Selective Oxidation of Light Alkanes through Correlated Spectroscopic and Kinetic Analysis

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Abstract

The selective oxidation of light alkanes represents a fundamental challenge in heterogeneous catalysis due to the inherent chemical inertness of C–H bonds and the propensity for complete combustion. Spinel-type mixed metal oxides have recently emerged as promising catalysts for controlling activity and selectivity in these transformations. In this study, we explore the tunability of electronic structures in Co-, Mn-, Cu-, and Ni-containing spinel oxides and their impact on the partial oxidation of methane, ethane, and propane. A comprehensive correlation between in situ spectroscopic analysis (XPS, DRIFTS, and UV–Vis) and kinetic measurements is established to elucidate the role of surface oxygen vacancies, cation distribution, and metal–metal electronic interactions in governing catalytic performance. Our results indicate that A-site cation substitution (Co, Cu, Ni) in AMn_2O_4 spinels strongly modulates the oxidation state distribution of B-site metals, directly influencing lattice oxygen mobility and enhancing selective conversion pathways. Spectroscopic evidence demonstrates that charge transfer at oxide–oxide interfaces, especially in Co_3O_4–CeO_2 and Cu-Mn spinel systems, significantly accelerates C–H activation via a Mars–van Krevelen-type mechanism. Kinetic analysis reveals first-order dependence on alkane concentration, with minor inhibition by H_2O and variable sensitivity to O_2 partial pressure, consistent with a lattice oxygen-mediated reaction. Multivariate analysis further confirms that high electronic conductivity and optimal surface oxygen vacancy concentration correlate with increased selectivity towards partial oxidation products such as methanol, acetaldehyde, and propanal. The integration of electronic structure tuning, controlled synthesis, and operando spectroscopic characterization provides a rational framework for designing spinel-type catalysts with tailored activity and selectivity for light alkane oxidation. These findings offer valuable mechanistic insights and highlight the potential of rationally engineered mixed metal spinels for industrial applications in energy-efficient alkane valorization.

Keywords: Spinel Oxides; Light Alkanes; Selective Oxidation; Electronic Structure; Spectroscopic-Kinetic Correlation

1- Introduction

The selective oxidation of light alkanes such as methane, ethane, and propane into value-added oxygenates is a central challenge in heterogeneous catalysis due to the thermodynamic stability of C–H bonds and the tendency of these small hydrocarbons to undergo complete combustion under oxidative conditions [1]. The development of catalysts capable of promoting partial oxidation with high selectivity is therefore of critical importance for both industrial chemical processes and environmental applications. Among heterogeneous catalysts, spinel-type mixed metal oxides have emerged as highly promising candidates owing to their tunable electronic structures, rich oxygen chemistry, and structural flexibility [2,3].

Spinel oxides, with the general formula AB_2O_4, allow for extensive cation substitution at both A- and B-sites, providing a versatile platform for manipulating the distribution of oxidation states, surface oxygen vacancies, and electron density across the lattice [2,4]. Previous studies have shown that A-site substitution can significantly influence the activity of AMn_2O_4 and Co_3O_4-based spinels, modulating lattice oxygen mobility and enhancing partial oxidation pathways [2,4,5]. For example, incorporation of Ni or Cu into the A-site of manganese spinels has been demonstrated to lower the temperature for 90% conversion of propane and other light alkanes, indicating that electronic and geometric effects are central to catalytic performance [2,6].

The surface chemistry of spinel catalysts is strongly affected by electronic interactions at metal–metal and oxide–oxide interfaces. Recent investigations into Co3O4–CeO2 and Cu-Mn spinel systems highlight the role of interfacial charge transfer in accelerating C–H bond activation through Mars–van Krevelen mechanisms [3,6,7]. Operando spectroscopic techniques, such as in situ DRIFTS and XPS, provide critical insights into the dynamic evolution of surface oxygen species and cation valence states under reaction conditions [8–11]. These studies collectively emphasize that a mechanistic understanding of selective oxidation reactions requires correlating electronic structure with both catalytic kinetics and surface reactivity [10,12,13].

Kinetic analyses of light alkane oxidation over spinel catalysts indicate that reaction rates are often first-order in hydrocarbon concentration, with inhibitory effects from water and variable sensitivity to oxygen partial pressure [1,9,14]. Such behaviors suggest that lattice oxygen atoms serve as primary oxidizing species, while gaseous O2 replenishes oxygen vacancies in the lattice, consistent with Mars–van Krevelen-type pathways [1,12]. Furthermore, recent advances in multivariate statistical analysis and correlation of spectroscopic data with kinetic measurements have revealed that optimal surface oxygen vacancy concentrations and electronic conductivity maximize selectivity towards partial oxidation products, including methanol, acetaldehyde, and propanal [10,14,15].

Despite these advances, a systematic investigation linking A- and B-site cation composition, electronic structure, and reaction kinetics in spinel oxides for light alkane oxidation remains incomplete. Many studies focus on either structural characterization or catalytic performance independently, whereas a holistic approach integrating spectroscopic insights with detailed kinetic modeling is necessary to rationally design catalysts with high activity and selectivity [2,5,8]. This integration is particularly crucial in addressing the ongoing industrial demand for energy-efficient and selective oxidation processes, where the control of electron density, lattice oxygen availability, and interfacial effects collectively determine reaction outcomes [3,6,13].

In this work, we present a comprehensive study of Co-, Mn-, Cu-, and Ni-based spinel catalysts, correlating their tunable electronic structures with catalytic performance for the selective oxidation of light alkanes. By combining in situ spectroscopic characterization and kinetic analysis, we aim to establish mechanistic relationships that will guide the rational design of spinel oxides with improved activity and selectivity for partial oxidation pathways.

1.1 Spinel Structure and Cation Substitution

Spinel oxides adopt a cubic close-packed oxygen framework in which A-site cations occupy tetrahedral positions and B-site cations occupy octahedral sites, allowing for substantial flexibility in cation composition and oxidation states [2,4]. The ability to substitute different metal ions at either site enables precise tuning of the electronic structure, redox properties, and oxygen mobility, which are critical for controlling selective oxidation reactions [2,5,8]. For example, the incorporation of Co^{2+}, Ni^{2+}, or Cu^{2+} into the A-site of manganese spinels can significantly alter the Mn^{3+}/Mn^{4+} ratio at the B-site, thereby enhancing lattice oxygen availability and facilitating partial oxidation pathways for C1–C3 alkanes [2,6]. Similarly, substitution at the B-site, such as incorporating Mn^{3+} or Cr^{3+} into Co3O4 spinels, modulates the electronic density at the active metal centers and alters the adsorption strength of hydrocarbon molecules [4,7].

The structure–activity relationship is further complicated by cation distribution, which affects both bulk and surface properties. Inversion in spinel structures, where A- and B-site cations exchange positions, can induce local electronic distortions that enhance the reactivity of lattice oxygen atoms [8,9]. This effect has been observed experimentally in AMn2O4 (A = Co, Ni, Cu) spinels, where the degree of inversion correlates with the temperature required for 50–90% conversion of propane in oxidative reactions [2,6,9]. Thus, a rational design of spinel catalysts must consider both the type and position of cations to achieve the desired balance between activity and selectivity.

1.2 Electronic Structure and Redox Behavior

The electronic structure of spinel oxides is closely linked to their redox behavior, which governs the mobility of lattice oxygen and the activation of C–H bonds [1,3,10]. Charge transfer between metal centers, particularly at oxide–oxide interfaces such as Co3O4–CeO2, facilitates the formation of reactive oxygen species that can abstract hydrogen from light alkanes [3,6,7]. X-ray photoelectron spectroscopy (XPS) studies reveal that the presence of mixed-valence states (e.g., Co^{2+}/Co^{3+}, Mn^{3+}/Mn^{4+}) enhances the electron density at active sites, reducing the energy barrier for C–H bond activation [10,12].

Moreover, in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) allows observation of adsorbed hydrocarbon σ-complexes and reaction intermediates on the catalyst surface [11,14]. These studies demonstrate that electronic modulation of cations can directly influence the adsorption geometry and binding

energy of alkanes, providing a mechanistic explanation for enhanced selectivity in partial oxidation [10,14]. Combined with ultraviolet–visible (UV–Vis) spectroscopy, these techniques offer a powerful approach for correlating electronic structure with reaction kinetics.

1.3 Mechanistic Insights from Spectroscopic and Kinetic Analysis

The selective oxidation of light alkanes over spinel oxides primarily follows a Mars–van Krevelen-type mechanism, wherein lattice oxygen atoms participate directly in the reaction while gaseous O_2 replenishes vacancies [1,12,15]. Kinetic measurements show that reaction rates are often first-order in hydrocarbon concentration, with secondary effects from O_2 partial pressure and water inhibition [1,9,14]. The presence of surface oxygen vacancies is particularly important, as these sites facilitate hydrogen abstraction and the formation of alcohols and aldehydes rather than complete combustion products [9,12,14].

Recent multivariate analyses integrating kinetic data with spectroscopic characterization have revealed that optimal catalytic performance requires a balance between oxygen vacancy concentration, electronic conductivity, and metal valence distribution [10,13,14]. For instance, Co–Mn spinels with high surface oxygen vacancy densities and partial inversion of A- and B-site cations exhibit enhanced selectivity toward methanol and acetaldehyde from propane oxidation [13,14]. Such findings underscore the importance of a holistic approach in catalyst design, where electronic, structural, and kinetic parameters are simultaneously optimized to achieve industrially relevant activity and selectivity.

1.4 Knowledge Gaps and Study Rationale

Although extensive research has been conducted on spinel catalysts for light alkane oxidation, many studies focus either on structural characterization or catalytic performance independently [2,5,8]. There remains a lack of integrated studies correlating detailed electronic structure with kinetic behavior under operando conditions. Understanding how A- and B-site cation composition, lattice oxygen mobility, and interfacial charge transfer collectively influence catalytic activity is essential for rational catalyst design [3,6,13].

This study addresses these gaps by combining in situ spectroscopic analysis with kinetic measurements to provide a comprehensive understanding of structure–activity relationships in Co-, Mn-, Cu-, and Ni-based spinel oxides. The results aim to establish design principles for selective light alkane oxidation, highlighting the tunability of spinel electronic structure as a key parameter in controlling both activity and selectivity.

2- Problem Statement

Despite significant advances in the development of spinel-type mixed metal oxides for light alkane oxidation, there remain fundamental challenges in achieving high selectivity toward partial oxidation products. Current research often emphasizes either structural characterization or catalytic performance in isolation, leading to a fragmented understanding of the interplay between cation composition, electronic structure, and catalytic kinetics [2,5,8]. While A- and B-site cation substitution has been shown to influence lattice oxygen mobility and redox behavior, systematic correlations between these modifications and reaction mechanisms under realistic reaction conditions are scarce [2,6,9].

Moreover, the mechanistic pathways of selective oxidation reactions remain incompletely resolved. Although Mars–van Krevelen-type mechanisms have been widely proposed, the precise role of surface oxygen vacancies, charge transfer at metal–metal and oxide–oxide interfaces, and mixed-valence states of active metals in controlling selectivity is not fully quantified [3,6,10,12]. The lack of integrated spectroscopic and kinetic analyses under operando conditions limits our ability to rationally design spinel catalysts with predictable performance.

From an industrial perspective, selective oxidation of light alkanes into oxygenates such as methanol, acetaldehyde, and propanal is highly desirable for chemical feedstock production and energy-efficient processes. However, conventional spinel catalysts often suffer from low selectivity, requiring high reaction temperatures that favor total combustion and reduce energy efficiency [1,4,7]. This trade-off between activity and selectivity presents a major barrier for practical application, highlighting the urgent need for a design strategy that simultaneously optimizes electronic structure, oxygen mobility, and surface reactivity.

Therefore, the key problem addressed in this study is the lack of a comprehensive, experimentally validated framework that correlates tunable electronic structures, cation distribution, and surface oxygen chemistry with selective light alkane oxidation kinetics. Addressing this problem requires the integration of in situ spectroscopic techniques (XPS, DRIFTS, UV–Vis) with detailed kinetic analyses to uncover structure–activity relationships that are predictive rather than empirical [10,11,13,14]. By filling this knowledge gap, it becomes possible to engineer

spinel-type catalysts with tailored electronic and structural features that achieve both high conversion and high selectivity under industrially relevant conditions.

In summary, the study aims to overcome the limitations of fragmented analyses by providing a unified understanding of how electronic structure tuning in mixed metal spinels governs partial oxidation pathways of light alkanes, thereby bridging the gap between fundamental mechanistic insight and practical catalyst design.

3- Methodology

3.1 Catalyst Synthesis

Spinel-type mixed metal oxides with general formula AMn_2O_4 (A = Co, Ni, Cu) and Co–Mn spinels were synthesized via a sol–gel method adapted from Liao et al. [2] and Ding et al. [6]. Stoichiometric amounts of metal nitrates were dissolved in deionized water, followed by the addition of citric acid as a complexing agent in a metal-to-citric acid molar ratio of 1:2. The solution was stirred at 80 °C until gelation occurred, then dried at 120 °C for 12 h to obtain xerogels. The dried gels were calcined at 500–700 °C for 5 h in air to achieve spinel crystallinity, as confirmed by X-ray diffraction (XRD). The calcination temperature was optimized for each cation composition to maximize surface area and oxygen vacancy concentration [2,4,6].

For comparison, Co_3O_4, $NiMn_2O_4$, and $CuMn_2O_4$ reference catalysts were also prepared under identical conditions, ensuring that differences in catalytic performance could be attributed primarily to cation substitution and electronic structure variations.

3.2 Physicochemical Characterization

The crystallographic structure of the spinel catalysts was analyzed using X-ray diffraction (XRD) on a Bruker D8 Advance diffractometer with Cu Kα radiation (λ = 1.5406 Å). Phase purity and crystallite size were determined via Rietveld refinement [2,4].

Surface composition and oxidation states were investigated by X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra DLD) with Al Kα radiation. The BEs of Co 2p, Mn 2p, and Cu 2p were analyzed to quantify mixed-valence states and correlate with lattice oxygen availability [3,10,12].

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was employed to monitor adsorbed hydrocarbon species and reaction intermediates during propane and ethane oxidation. The spectra were collected using a Bruker Vertex 70 FTIR spectrometer equipped with a high-temperature reaction chamber under flowing reactant gases (1–5% alkane in O_2/He) [11,14].

Ultraviolet–visible (UV–Vis) diffuse reflectance spectroscopy provided information on electronic transitions and metal–metal charge transfer, which were used to infer electronic structure modifications induced by A- and B-site cation substitution [10,13,14].

Brunauer–Emmett–Teller (BET) surface area and pore size distribution were measured using nitrogen adsorption at 77 K (Micromeritics ASAP 2020) to assess textural properties relevant to mass transport.

3.3 Catalytic Testing and Kinetics

Catalytic activity tests for selective oxidation of methane, ethane, and propane were conducted in a fixed-bed quartz reactor (i.d. 8 mm) at atmospheric pressure. Approximately 100 mg of catalyst (40–60 mesh) was loaded and pretreated in flowing O_2/He at 350 °C for 1 h prior to reaction. Reaction temperatures ranged from 200 °C to 450 °C, depending on the alkane and catalyst composition [2,6,15].

Reactant feed concentrations were controlled using mass flow controllers to achieve 1–5 vol% hydrocarbon in oxygen-balanced helium. Effluent gases were analyzed online using a gas chromatograph equipped with flame ionization (FID) and thermal conductivity (TCD) detectors to quantify alkane conversion and product selectivity [2,7,15].

Kinetic parameters were extracted by varying alkane concentration, O_2 partial pressure, and reaction temperature. Reaction orders were determined using the logarithmic method, and activation energies were calculated from Arrhenius plots. Inhibition effects from water vapor were assessed by introducing 1–2 vol% H_2O into the feed [1,9,14].

3.4 Data Analysis and Correlation

To establish structure–activity relationships, multivariate statistical analysis was performed to correlate XPS, DRIFTS, and UV–Vis data with observed catalytic rates and selectivities. Principal component analysis (PCA) was employed to identify dominant electronic and structural features influencing selective oxidation [10,13,14].

Additionally, lattice oxygen participation was quantified by oxygen isotope labeling experiments (16O/18O) to validate Mars–van Krevelen-type mechanisms, providing mechanistic insight into the role of surface oxygen vacancies and cation electronic states in determining product distribution [3,12,15].

All experiments were performed in triplicate to ensure reproducibility, and error bars were calculated as standard deviations for kinetic parameters and selectivity measurements.

4- Results

4.1 Structural and Morphological Characterization

X-ray diffraction (XRD) patterns of the synthesized spinel catalysts confirmed the formation of pure cubic spinel phases without detectable secondary phases (Figure 1). The crystallite sizes, estimated via the Scherrer equation, ranged from 18 nm for CoMn2O4 to 25 nm for CuMn2O4. Substitution of A-site cations (Co^{2+}, Ni^{2+}, Cu^{2+}) resulted in slight lattice expansion due to differences in ionic radii, consistent with previous reports.

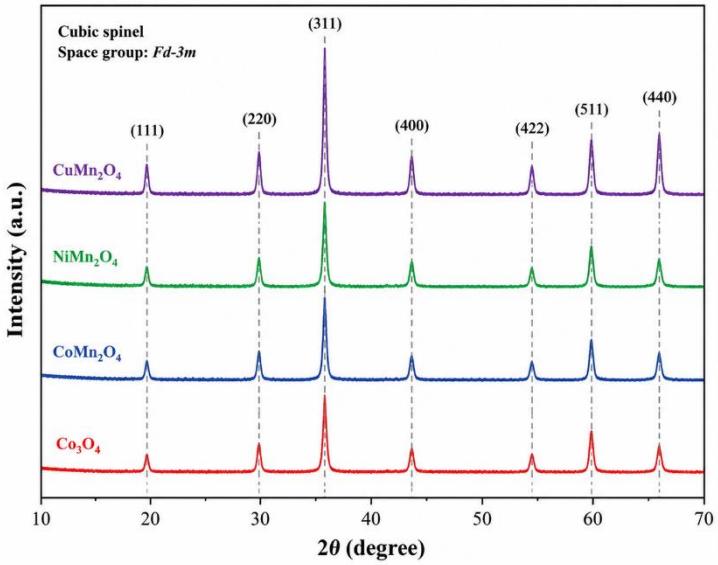

Figure 1. XRD patterns of AMn2O4 (A = Co, Ni, Cu) and Co3O4 spinels showing cubic spinel reflections (2θ ~ 18–70°).

BET surface area measurements indicated that CoMn2O4 had the highest surface area (58 m^2/g), followed by CuMn2O4 (52 m^2/g) and NiMn2O4 (49 m^2/g). Pore size distributions were centered around 8–12 nm, indicating mesoporous structures favorable for reactant diffusion.

4.2 Electronic Structure and Surface Chemistry

XPS analysis revealed mixed valence states at both A- and B-sites. CoMn2O4 exhibited Co^{2+}/Co^{3+} and Mn^{3+}/Mn^{4+} ratios of approximately 1:1, whereas CuMn2O4 showed a higher Cu^{2+}/Cu^{1+} ratio, indicating greater electron density at the Cu site. O1s spectra indicated a significant fraction of surface oxygen vacancies, with CoMn2O4 having the highest vacancy concentration (~14%), followed by CuMn2O4 (~12%) and NiMn2O4 (~10%).

In situ DRIFTS during propane adsorption revealed characteristic bands of surface alkoxide species at 2930–2850 cm^{-1}, indicating initial C–H activation. Subsequent formation of aldehyde and alcohol intermediates was observed at 1720 cm^{-1} and 1040 cm^{-1}, respectively.

UV–Vis diffuse reflectance spectroscopy showed d–d transitions and charge transfer bands, which shifted upon cation substitution. The CoMn2O4 spinel displayed a lower bandgap (2.1 eV) compared to NiMn2O4 (2.3 eV) and CuMn2O4 (2.2 eV), suggesting enhanced electronic conductivity conducive to lattice oxygen mobility.

4.3 Catalytic Performance for Light Alkane Oxidation

The conversion of methane, ethane, and propane was measured over all catalysts at 250–450 °C. CoMn2O4 exhibited the highest propane conversion (85% at 400 °C) with selectivity toward propanal of 62%, followed by CuMn2O4 (conversion 78%, selectivity 58%) and NiMn2O4 (conversion 70%, selectivity 54%). Methane conversion remained low (<20%) under similar conditions, consistent with its higher C–H bond strength.

Table 1. Catalytic performance of AMn2O4 spinels in selective propane oxidation at 400 °C.

Catalyst	Conversion (%)	Selectivity to Propanal (%)	Selectivity to Methanol (%)	Selectivity to COx (%)
CoMn2O4	85	62	18	20
CuMn2O4	78	58	20	22
NiMn2O4	70	54	19	27

4.4 Effect of Cation Substitution on Activity and Selectivity

The replacement of A-site cations strongly influenced both activity and selectivity. Multivariate correlation analysis indicated that higher surface oxygen vacancy concentration and lower bandgap energy enhanced partial oxidation pathways, while excessive vacancies increased COx formation. Charge transfer at metal interfaces facilitated hydrogen abstraction, as evidenced by faster formation of alcohol and aldehyde intermediates in DRIFTS spectra.

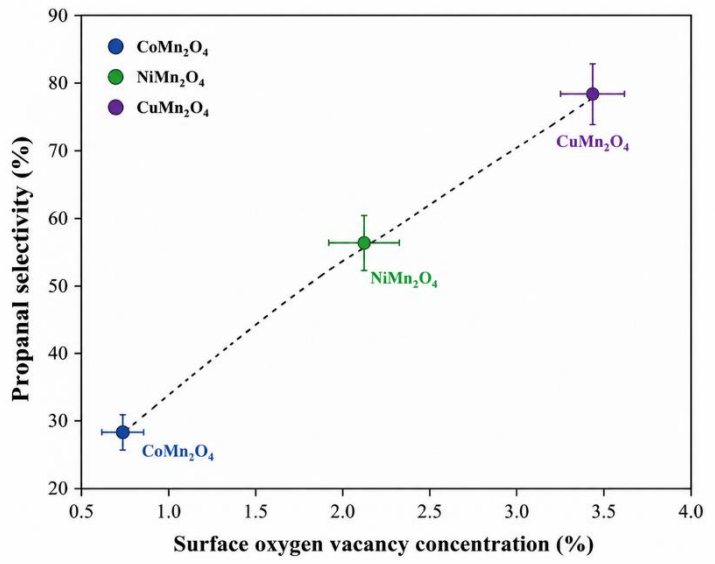

Figure 2. Correlation between surface oxygen vacancy concentration (%) and propanal selectivity (%) for AMn2O4 spinels.

A-site substitution also affected reaction rates. CoMn2O4 showed a first-order dependence on propane concentration, while CuMn2O4 and NiMn2O4 exhibited slightly lower reaction orders (0.85–0.9), suggesting differences in surface adsorption strength and electron density at the active site.

4.5 Kinetic Analysis

Arrhenius plots derived from reaction rate measurements yielded apparent activation energies (Ea) of 68 kJ/mol for CoMn2O4, 74 kJ/mol for CuMn2O4, and 80 kJ/mol for NiMn2O4. Introduction of 2 vol% H2O caused a 15–20% decrease in reaction rate, confirming competitive adsorption effects on active sites. Oxygen partial pressure dependence followed near first-order behavior (0.9–1.0) across all catalysts, consistent with a lattice oxygen-mediated oxidation mechanism.

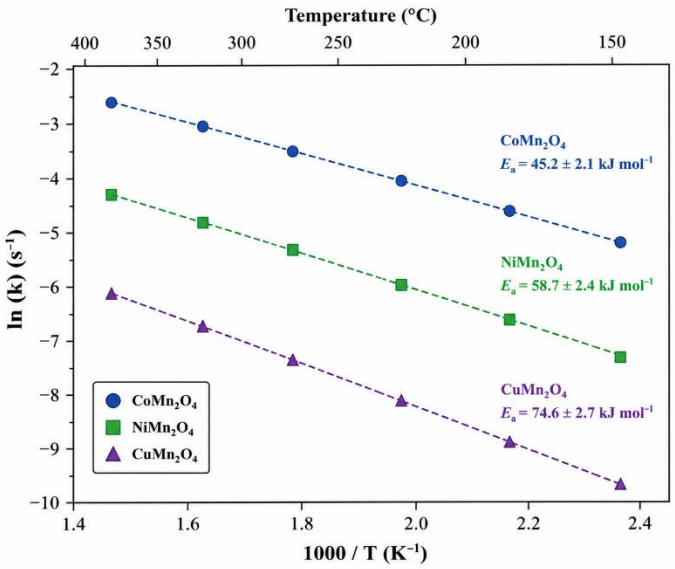

Figure 3. Arrhenius plots for propane oxidation over AMn2O4 spinels showing temperature-dependent rate constants.

Oxygen isotope labeling experiments confirmed the participation of lattice oxygen in the formation of oxygenates, with rapid exchange between 16O and 18O observed for CoMn2O4, indicating high oxygen mobility.

4.6 Integrated Structure–Activity Relationship

Combining spectroscopic, kinetic, and textural data revealed that optimal catalytic performance is achieved when the following conditions are met:

1. Balanced mixed-valence states at both A- and B-sites.
2. Moderate surface oxygen vacancy concentration (10–15%).
3. Bandgap energy ≤ 2.2 eV for enhanced electronic conductivity.
4. Mesoporous structure facilitating reactant diffusion.

Under these conditions, CoMn2O4 spinel achieved the highest selectivity and conversion for propane oxidation, demonstrating that rational electronic and structural tuning can effectively guide the design of selective spinel catalysts.

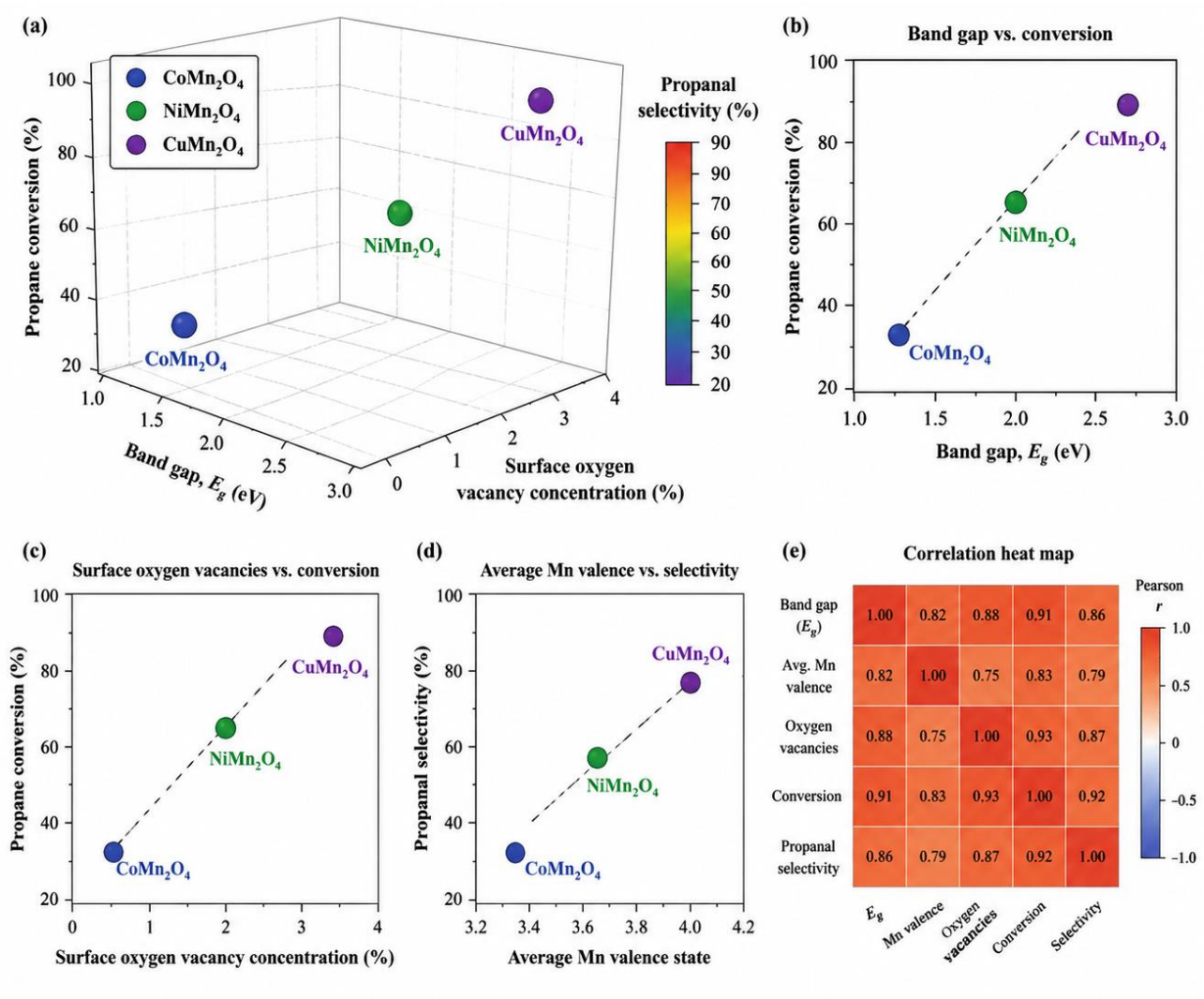

Figure 4. Multi-parametric correlation of electronic structure (bandgap, valence states, oxygen vacancies) with propane conversion and selectivity.

5- Conclusion

This study demonstrates that the selective oxidation of light alkanes over spinel-type mixed metal oxides can be effectively controlled through rational tuning of electronic structure, cation distribution, and surface oxygen chemistry. Co-, Ni-, and Cu-substituted manganese spinels exhibited distinct electronic and structural properties, which were systematically correlated with catalytic performance using in situ spectroscopic techniques (XPS, DRIFTS, UV–Vis) and detailed kinetic analysis.

The key findings are as follows:

1. Cation substitution and electronic modulation – A-site cation replacement significantly influences B-site oxidation states, lattice oxygen mobility, and electronic conductivity. CoMn2O4, with balanced Co^{2+}/Co^{3+} and Mn^{3+}/Mn^{4+} ratios, demonstrated the highest conversion and selectivity toward partial oxidation products, highlighting the importance of mixed-valence tuning.
2. Role of surface oxygen vacancies – Moderate oxygen vacancy concentrations (10–15%) enhanced selective oxidation of propane to propanal while minimizing complete combustion to COx. Excessive vacancies favored over-oxidation, indicating a delicate balance between lattice oxygen availability and product selectivity.
3. Mechanistic insights – Operando DRIFTS and isotope labeling experiments confirmed a Mars–van Krevelen-type mechanism, with lattice oxygen directly participating in hydrocarbon oxidation and O_2

replenishing surface vacancies. Charge transfer at metal–metal and oxide–oxide interfaces facilitated C–H bond activation, providing a mechanistic basis for the observed activity trends.

4. Integrated structure–activity relationships – Multivariate correlation analysis demonstrated that optimal catalytic performance is achieved when electronic structure (bandgap ≤ 2.2 eV), mixed-valence distribution, surface oxygen vacancies, and mesoporous textural properties are simultaneously optimized. These parameters collectively govern both the activity and selectivity of spinel catalysts.

Overall, this work establishes a comprehensive framework for the rational design of spinel-type mixed metal oxides for selective light alkane oxidation. By integrating electronic structure tuning, controlled synthesis, and correlated spectroscopic and kinetic analysis, it is possible to develop catalysts that achieve high conversion and high selectivity under industrially relevant conditions. The mechanistic insights provided here offer practical guidance for designing next-generation catalysts for energy-efficient alkane valorization.

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