

Phase-dependent Al leaching and crystal structure stability of CoAl₂O₄ in alkaline media

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

This manuscript reports a surface Al/Co ratio-dependent reconstruction behavior of sol-gel derived CoAl₂O₄ spinel particles in alkaline media. The findings reveal surface-composition-dependent phase evolution and dissolution behavior in multi-metal spinels, highlighting the relay-like formation and transformation of intermediate phases during mixed-metal oxide synthesis. Overall, this work provides insights into surface reconstruction mechanisms in spinel oxides, which may guide the design of stable multi-metal oxide materials. I would like to suggest a revision and hope the following comments help improve the manuscript.

1. In the "Calculation of CoAl₂O₄ stability with different Al occupation" section, the authors state that "taking one Al atom from inverse CoAl₂O₄ is easier than that from normal CoAl₂O₄, however note that it does not mean that taking one Al atom from the octahedral sites is easier than that from the tetrahedral sites." I suggest that the authors provide a more detailed explanation to clarify this statement.
2. The authors attribute the enhanced Al leaching mainly to the dissolution of Al-excess surface phases rather than to Al occupation in the lattice. However, the DFT calculations primarily focus on the stability of CoAl₂O₄ with different inversion degrees and the corresponding Al vacancy formation energies. It would be helpful if the authors clarify how these calculations quantitatively relate to the experimentally observed Al-excess surface.
3. The CoAl₂O₄ powders used in this work were synthesized at different annealing temperatures, which may lead to oxides with different surface areas. Could this also contribute to the observed differences in Al leaching behavior and why?
4. The alkaline leaching experiments were conducted in KOH solutions for up to 4 weeks. During this process, dissolved Al species and possible Co species may accumulate in the solution. The authors are suggested to clarify whether the solution composition was monitored (e.g., by ICP-OES) to quantify the amount of Al and Co dissolved.
5. The authors emphasize the importance of relay-like phase formation during mixed-metal oxide synthesis. However, the discussion remains somewhat brief. It is suggested that the authors expand on how this phenomenon might apply to other multi-metal oxide systems, and how synthesis protocols could be adjusted to control such intermediate phases.

Reviewer #2

(Remarks to the Author)

A strength of this paper is the consistent experiment study of Al leaching in CoAl₂O₄ synthesized under different conditions. Together, the identification of multiphase Al-rich surface domains in low T materials, and the demonstration that leaching is governed by surface comp and heterogeneity (not the bulk cation occupation), is strong. The observed termination of leaching after Al-rich spinel surface structures form provides a clear mechanistic insight.

A bit less obvious to me in the current form of the manuscript is the role of the DFT calculations. Reported values for bulk formation energies are straightforward. However, the authors use DFT energies of the reaction: $6\text{CoAl}_2\text{O}_4 + \text{O}_2 \rightarrow 2\text{Co}_3\text{O}_4 + 6\text{Al}_2\text{O}_3$ to "examine the spontaneity of Al leaching process." What that reaction represents is relative stability of bulk CoAl₂O₄ with respect to phase separation into Co₃O₄/Al₂O₃, in otherwords, a solid state decomposition. While meaningful measures of bulk stability, the reported values (about -0.5 to -4.5 eV) do not represent, as claimed, the thermodynamics of Al leaching in alkaline media, which is a surface-mediated process that relies on aqueous speciation, concentration, pH. Likewise the bulk vacancy formation energies (which range from about 6.3 to almost 9 eV) measure the cost of removing

lattice Al but do not correspond to dissolution into solution. These values are not directly comparable to the observed leaching process.

The current interpretation over extends the connection between the solid-state DFT results and the experimentally observed leaching behavior. The authors should avoid conflating bulk stability with aqueous dissolution thermodynamics. Unless the aqueous effects are incorporated, it should be made clear that only the solid state behavior is captured, and the link/interpretation to experiment should be appropriately cautious/conditional. That is, while I don't suggest removing the calculation results, their role should be more carefully framed. They provide evidence for the reduced bulk stability of inverse spinel, which may contribute to the formation of the Al-excess surface domains, for example. That would be in line with the experimental conclusion about surface composition and multiphase character in the observed leaching behavior.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The revised version is good. I think it can be accepted now.

Reviewer #2

(Remarks to the Author)

The authors have responded, appropriately and thoughtfully, to the main concern. They have clarified the scope and limitations of the DFT calculations. They no longer present the bulk calculations as direct measure of aqueous Al leaching thermodynamics and instead frame them as providing insight into relative bulk stability and a possible contribution to the formation of Al-rich surface domains. While the calculations might not establish a strong mechanistic connection to the experimental leaching process, the revised interpretation is appropriately cautious. I am satisfied with the revision.

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Point-by-point response to the reviewers' comments

Reviewer #1 (Remarks to the Author):

This manuscript reports a surface Al/Co ratio–dependent reconstruction behavior of sol–gel derived CoAl_2O_4 spinel particles in alkaline media. The findings reveal surface-composition–dependent phase evolution and dissolution behavior in multi-metal spinels, highlighting the relay-like formation and transformation of intermediate phases during mixed-metal oxide synthesis. Overall, this work provides insights into surface reconstruction mechanisms in spinel oxides, which may guide the design of stable multi-metal oxide materials. I would like to suggest a revision and hope the following comments help improve the manuscript.

Reply: We appreciate Reviewer's evaluation and we have revised the manuscript following Reviewer's suggestions. Overall, in the revised manuscript, we strengthened the motivation of solid-state DFT calculation and the correlation between calculation results and experimental observation. Simultaneously, we also emphasized the reaction process difference between the calculated bulk stability/Al vacancy formation energy and observed Al dissolution. We also gave our understanding of CoAl_2O_4 dissolution behaviours from the acid-base character in terms of electronegativity and chemical hardness/band gap, which were also obtained from calculations. We also added the analysis for soaking solution for different materials and conditions and discussed the dissolution difference in terms of surface area. We also expanded and discussed more cases that display the relay-like phase formation, and provided our understanding in controlling such intermediate phases. The Reviewer's comments were replied point-by-point as below. The changed parts are marked in blue in the revised manuscript.

1. In the “Calculation of CoAl₂O₄ stability with different Al occupation” section, the authors state that “taking one Al atom from inverse CoAl₂O₄ is easier than that from normal CoAl₂O₄, however note that it does not mean that taking one Al atom from the octahedral sites is easier than that from the tetrahedral sites.” I suggest that the authors provide a more detailed explanation to clarify this statement.

Reply: We appreciate Reviewer to point out this issue. We have provided a more detailed explanation in the revised manuscript, which is marked in blue. The changed parts in the revised manuscript are copied as follows:

“It means that taking one Al atom from inverse CoAl₂O₄ is easier than that from normal CoAl₂O₄. We further compared the Al vacancy formation energies at Oh and Td sites. Though we found the formation energies of one Al vacancy in Oh-1, Oh-2 and Oh-3 are lower than those in Td-1, Td-2 and Td-3 for the case of $\lambda = 0.375$, it does not mean that taking one Al atom from the octahedral sites is easier than that from the tetrahedral sites for any case of other inversion degree, for example in the case of $\lambda = 0.5$, where the formation energies of one Al vacancy in Oh-1 and Oh-2 (4.75 eV) are higher than that in Td (4.3 eV).”

2. The authors attribute the enhanced Al leaching mainly to the dissolution of Al-excess surface phases rather than to Al occupation in the lattice. However, the DFT calculations primarily focus on the stability of CoAl_2O_4 with different inversion degrees and the corresponding Al vacancy formation energies. It would be helpful if the authors clarify how these calculations quantitatively relate to the experimentally observed Al-excess surface.

Reply: We appreciate Reviewer to point out this issue. We are making efforts to establish a connection between the solid-state DFT results and the experimentally observed Al-excess surface and leaching behavior. For CoAl_2O_4 itself, $(\text{Co}_{1-\lambda}\text{Al}_\lambda)_{\text{Td}}[\text{Co}_\lambda\text{Al}_{2-\lambda}]_{\text{Oh}}\text{O}_4$ with tunable inverse degrees λ can be synthesized feasibly, and Al_2O_3 dissolution in alkaline is well-known knowledge, and thus we expected to find an occupation-leaching correlation for Al in CoAl_2O_4 in alkaline media. While Al leaching behavior in alkaline media is a surface-mediated process and the calculated results from bulk DFT are not directly comparable to the leaching process, it is indicated by Casey that the local forces and geometries of metal-oxygen local bonding are important factors in determining the oxide dissolution rate [*J. Colloid Interface Sci.* 1991, **146**, 586-589, doi: 10.1016/0021-9797(91)90225-W]. Recent works also correlated bulk calculation/thermodynamic results with electrochemical properties [*ACS Catal.* 2015, **5**, 869-873, doi: 10.1021/cs5016657; *Sci. Rep.* 2015, **5**, 12167, doi: 10.1038/srep12167]. These encourage us to look for the connection between bulk stability, Al vacancy formation energies and Al leaching behavior for CoAl_2O_4 with various inversion degrees. We copied the relevant content in the revised manuscript as below.

“Calculation of CoAl_2O_4 bulk stability with different Al occupation-Solid state behavior.

The Al leaching behavior in alkaline solution is a surface-mediated process and the calculated results from bulk DFT are generally not directly comparable to the leaching process. Casey indicated that the local forces and geometries of metal-oxygen bonding are important factors in determining the oxide dissolution rate, despite no simple theory linking reactivity and bonding¹⁰. Recent works also correlated bulk calculation/thermodynamic results with electrochemical properties^{11, 12}. These encourage us to investigate the connection between bulk stability, Al vacancy formation energies and Al leaching behavior for CoAl_2O_4 with various inversion degrees.”

The cited References 10-12:

10. Casey, W.H. On the relative dissolution rates of some oxide and orthosilicate minerals. *J. Colloid Interface Sci.* **146**, 586-589 (1991).

11. Calle-Vallejo, F., Díaz-Morales, O.A., Kolb, M.J., Koper, M.T.M. Why Is Bulk Thermochemistry a Good Descriptor for the Electrocatalytic Activity of Transition Metal Oxides? *ACS Catal.* **5**, 869–873 (2015).
12. Binninger, T. et al. Thermodynamic explanation of the universal correlation between oxygen evolution activity and corrosion of oxide catalysts. *Sci. Rep.* **5**, 12167 (2015).

Thus, we reply to this concern from four aspects based on the results we demonstrated: (1) CoAl₂O₄ formation with different inversion degrees and observed Al-excess surfaces, (2) solid-state decomposition process $6\text{CoAl}_2\text{O}_4 + \text{O}_2 \rightarrow 2\text{Co}_3\text{O}_4 + 6\text{Al}_2\text{O}_3$, (3) the Al vacancy formation energy and experimental leaching behavior, and (4) moreover, we added the discussion on dissolution behavior from the acid-base character of the materials in terms of electronegativity and band gap/chemical hardness.

(1) The stability of CoAl₂O₄ with different inversion degrees and observed Al-excess surfaces:

We compared the bulk stability of CoAl₂O₄ from the formation energy when the inversion degree varies. As the inversion degree increases, the formation energy increases as indicative of the reduced bulk stability of inverse spinel, which may contribute to the formation of the Al-excess surface domains in experiments.

(2) Solid-state decomposition process $6\text{CoAl}_2\text{O}_4 + \text{O}_2 \rightarrow 2\text{Co}_3\text{O}_4 + 6\text{Al}_2\text{O}_3$: The calculated stability from the decomposition process represents the relative stability of bulk CoAl₂O₄ with different λ , with respect to the phase separation into Co₃O₄/Al₂O₃. We found that the inverse spinel is more favorable for this decomposition process, which also corresponds to the reduced stability in inverse CoAl₂O₄. We understand that the bulk stability does not represent Al leaching thermodynamics in solution, which relies on aqueous speciation, concentration and pH, and involves the polarized and weakened critical metal-oxygen bonds by the reactants at the surface [*Geochim. Cosmochim. Acta* 1986, **50**, 1847-1860, doi: 10.1016/0016-7037(86)90243-7]. As we initially expected to attempt to establish a connection between bulk calculation and experimental observations, we demonstrated this calculation result as a possible indicator. We copied the relevant contents in the revised manuscript as below.

“We further attempted to establish a correlation between the solid-state decomposition process $6\text{CoAl}_2\text{O}_4 + \text{O}_2 \rightarrow 2\text{Co}_3\text{O}_4 + 6\text{Al}_2\text{O}_3$ and the spontaneity of Al leaching process for CoAl₂O₄ with different λ . CoAl₂O₄ with a higher inversion degree exhibits a more negative reaction Gibbs free energy at T = 300 K and P = 1 atm, indicating that this reaction is thermodynamically

more favorable (Fig. 1b). It should be emphasized that the calculated stability from the decomposition process represents the relative stability of bulk CoAl_2O_4 with different λ , with respect to the phase separation into $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$. This is different from leaching process in solution, which relies on aqueous speciation, concentration and pH, and involves the polarized and weakened critical metal-oxygen bonds by the reactants on the surface⁵. Thus, the bulk stability does not represent Al leaching thermodynamics.”

The cited Reference 5:

5. Furrer, G., Stumm, W. The coordination chemistry of weathering: I. Dissolution kinetics of $\delta\text{-Al}_2\text{O}_3$ and BeO. *Geochim. Cosmochim. Acta* **50**, 1847-1860 (1986).

(3) Al vacancy formation energy and experimental leaching behavior: It is emphasized that removing Al from the lattice does not correspond to dissolution into solution. However, dissolution process is controlled by rates of destruction of a metal-oxygen bond [*J. Colloid Interface Sci.* 1991, **146**, 586-589, doi: 10.1016/0021-9797(91)90225-W], which motivates us to calculate Al vacancy formation energy. The reason why we did not choose to calculate oxygen vacancy formation is as follows. In spinel structure, one oxygen atom is coordinated with one atom in the tetrahedral site and three atoms in octahedral sites [*Angew. Chem. Int. Ed. Engl.* 2019, **58**, 6042-6047, doi: 10.1002/anie.201902114]. Creating one oxygen vacancy in bulk means simultaneous destruction of Co-O and Al-O bonds not the single metal-oxygen bond. Thus, creating Al vacancy can directly reflect the destruction of Al-O bonds in different coordination environments.

We have added this motivation and limitations of calculating Al vacancy formation energy in the revised Results part as below.

“The situation also applies to the following calculation on removing lattice Al, which does not correspond to dissolution into solution. Instead, the dissolution process is controlled by the rates of metal-oxygen bond cleavage¹⁰, which motivates us to calculate Al vacancy formation energy. The reason why we did not choose to calculate oxygen vacancy formation is as follows. In spinel structure, one oxygen atom is coordinated with one atom in the tetrahedral site and three atoms in octahedral sites⁹. Creating one oxygen vacancy in bulk means simultaneous removal of Co-O and Al-O bonds instead of the single metal-oxygen bond. Thus, the Al vacancy formation energy can directly reflect the strength of Al-O bonds in different coordination environments.”

The cited References 9-10:

9. Sun, S. et al. Shifting Oxygen Charge Towards Octahedral Metal: A Way to Promote Water Oxidation on Cobalt Spinel Oxides. *Angew. Chem. Int. Ed. Engl.* **58**, 6042-6047 (2019).

10. Casey, W.H. On the relative dissolution rates of some oxide and orthosilicate minerals. *J. Colloid Interface Sci.* **146**, 586-589 (1991).

(4) Acid-base character of materials: we analyzed the acid-base character of the materials from our calculated results and discussed it from electronegativity and chemical hardness/band gap. We added the discussion in Discussion part as below.

“Regarding the dissolution behavior of Al-excess surface of CoAl_2O_4 in alkaline media, the dissolved surface should be at least amphoteric and even acidic. Thus, except for bulk stability analysis, we also attempted to interpret it from acid-base character by comparing the acidity of oxides based on the assumption that more acidic oxides could be readily dissolved in alkaline media. Oxide acidity can be evaluated from electronegativity and chemical hardness. Acidic oxides have a strong electronegativity with a strong chemical hardness³⁴. The electronegativity $\chi(\text{M}_x\text{O}_y)$ of the metal oxide M_xO_y can be calculated from the formula $\chi = [(\chi_{\text{M}})^x(\chi_{\text{O}})^y]^{1/(x+y)}$, where χ_{M} and χ_{O} stand for the electronegativity of metal and oxygen, respectively^{34, 35}. Based on the reported value of CoO (2.31) and Al_2O_3 (2.52)³⁴, the electronegativity of CoAl_2O_4 can be approximated as,

$$\chi(\text{CoAl}_2\text{O}_4) = (\chi(\text{CoO})\chi(\text{Al}_2\text{O}_3))^{1/2} = 2.41.$$

It indicates that CoAl_2O_4 is less acidic than Al_2O_3 due to its weaker electronegativity than Al_2O_3 . Besides, the electronegativity can be converted to the acid-base parameter Smith scale, $\alpha = 9.8 \chi(\text{oxide}) - 24.5$ ³⁶ or $\alpha = 11.13 \chi(\text{oxide}) - 29.3$ ³⁴. It suggests that increasing Al makes this system more acidic from CoAl_2O_4 to Al_2O_3 . Besides, we also evaluate the chemical hardness (η) by deriving from the band gap (E_g , $\eta = E_g / 2$) of the spinel-type oxides from Co_3O_4 to $\gamma\text{-Al}_2\text{O}_3$, thus providing qualitative comparison among spinel oxides. Although this relationship is more complex for transition metal oxide involving the contribution of d orbital electrons³⁴, the calculated band gap has a trend: Co_3O_4 (1.37 eV) < CoAl_2O_4 ($\lambda=0.5$) (1.72 eV) < CoAl_2O_4 ($\lambda=0.375$) (1.83 eV) < CoAl_2O_4 ($\lambda=0$) (2.47 eV) < $\gamma\text{-Al}_2\text{O}_3$ (4.92 eV), suggesting an increasing chemical hardness with increasing Al. It supports that $\gamma\text{-Al}_2\text{O}_3$ is more acidic than CoAl_2O_4 but fails to correlate the chemical hardness of CoAl_2O_4 with different inversion degrees with the dissolution behavior.”

The cited References 34-36:

34. Portier, J., Poizot, P., Tarascon, J.-M., Campet, G., Subramanian, M.A. Acid–base behavior of oxides and their electronic structure. *Solid State Sci.* **5**, 695–699 (2003),
35. Poole, R.T. et al. Electronegativity as a unifying concept in the determination of Fermi energies and photoelectric thresholds. *Chem. Phys. Lett.* **36**, 401-403 (1975).
36. Bratsch, S.G. Electronegativity and the acid-base character of binary oxides. *J. Chem. Educ.* **65**, 877-878 (1988).

3. The CoAl_2O_4 powders used in this work were synthesized at different annealing temperatures, which may lead to oxides with different surface areas. Could this also contribute to the observed differences in Al leaching behavior and why?

Reply: We thank Reviewer to point out this issue. The CoAl_2O_4 powders synthesized at different annealing temperatures have different areas, which contribute the observed differences in Al leaching behavior.

We added the adsorption-desorption isotherms of these three oxides CoAl_2O_4 -500, 700, and 900, which were annealed at 500, 700 and 900 degrees, respectively (Fig. R1). The Brunauer-Emmett-Teller (BET) surface areas of CoAl_2O_4 -500, 700 and 900 are 121.8115, 52.0479, and 14.4080 m^2/g , respectively. It indicates that the BET surface areas of CoAl_2O_4 synthesized by sol-gel and combustion method decreased with increasing annealing temperatures.

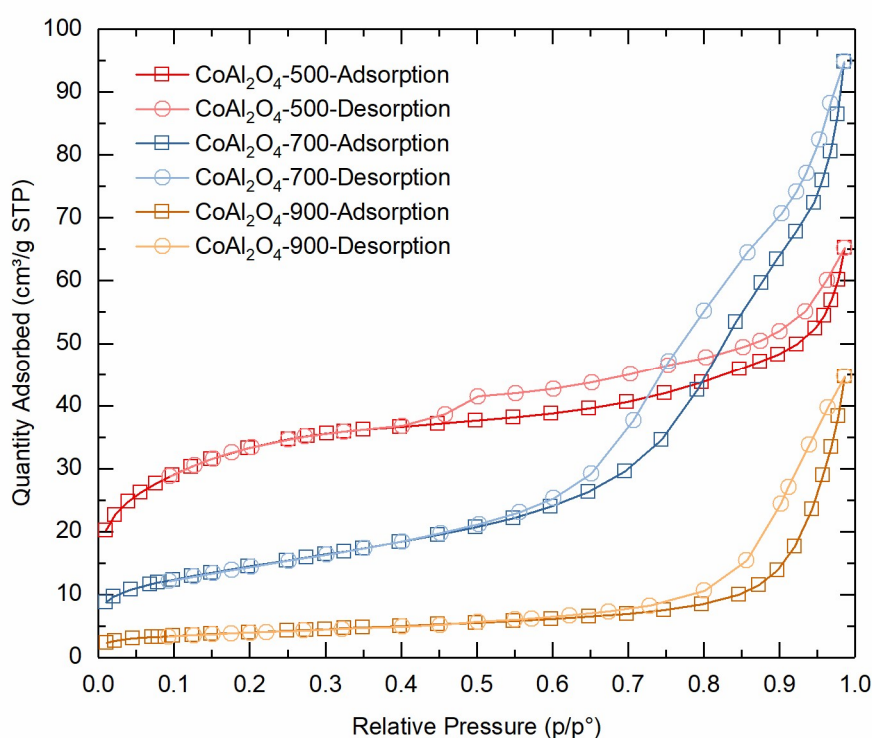


Fig. R1. The adsorption-desorption isotherms of CoAl_2O_4 -500, 700 and 900. Analysis adsorptive: N_2 . Analysis bath temperature: 77.350 K. The Brunauer-Emmett-Teller (BET) surface areas of CoAl_2O_4 -500, 700 and 900 are 121.8115, 52.0479, and 14.4080 m^2/g , respectively. This figure is shown in Supplementary Fig. 11.

We also analyzed the Co and Al concentrations in soaking solution, and the results is displayed in Table R1. The results in Table R1 are shown in Supplementary Table 1.

Table R1. The Co and Al concentrations in soaking solution electrolytes from ICP tests

	Al (mmol L ⁻¹)	Co (μmol L ⁻¹)
CoAl ₂ O ₄ -500_6M_4w	19.99	0.19
CoAl ₂ O ₄ -700_6M_4w	3.11	1.44
CoAl ₂ O ₄ -900_6M_4w	1.13	0.71

We added the relevant analysis in the revised manuscript as below.

“Analysis of the solution after soaking oxides. Inductively coupled plasma (ICP) results (Supplementary Table 1) indicate that Al concentration in solution is higher for soaking CoAl₂O₄ synthesized at a relatively low annealing temperature. For example, the Al concentrations for soaked CoAl₂O₄-500, 700 and 900 in 6 M KOH for 4 weeks are about 19.99, 3.11, and 1.13 mmol L⁻¹. It supports that Al leaching is more dramatic from CoAl₂O₄-500 than from CoAl₂O₄-700 and 900. In contrast, the Co concentrations in solution are 0.19, 1.44 and 0.72 μmol L⁻¹ for CoAl₂O₄-500, 700 and 900, respectively, which are much lower than Al concentrations. Taking the solution of soaking CoAl₂O₄-900 as an example, Al concentration (1.13 mmol L⁻¹) is about 1569 times larger than Co concentration (0.72 μmol L⁻¹), which means that the selected leaching of Al indeed occurs in CoAl₂O₄-900 but very little, even if we can consider the parts of Co and Al come from the trace amount of unfiltered CoAl₂O₄ particles in the analyzed solution. When estimating CoAl₂O₄ concentration in solution (100 mg / 176.89 g mol⁻¹) / 25 mL ~ 22.61 mmol L⁻¹, it means that 0.00084%, 0.0064% and 0.0032% Co exist in the soaked solution. It means that Co hardly leaches out in above cases. The difference in leached Al amounts can be explained from the aspects of material surface area and dissolution rate. Firstly, CoAl₂O₄ powders have decreasing specific surface areas with increasing annealing temperature (Supplementary Fig. 11), which means larger surface areas for CoAl₂O₄-500 are exposed in solution than those for CoAl₂O₄-900. Another factor is the dissolution rate, which is proportional to the rate constant, the mole fraction of dissolution active site, the probability to find a specific site in the coordinative arrangement of the precursor complex and the surface concentration of sites¹⁴. In our CoAl₂O₄-500 case, Al-excess surfaces mean a higher surface concentration of sites.”

The cited Reference 14:

14. Wieland, E., Wehrli, B., Stumm, W. The coordination chemistry of weathering: III. A generalization on the dissolution rates of minerals. *Geochim. Cosmochim. Acta* **52**, 1969-1981 (1988).

4. The alkaline leaching experiments were conducted in KOH solutions for up to 4 weeks. During this process, dissolved Al species and possible Co species may accumulate in the solution. The authors are suggested to clarify whether the solution composition was monitored (e.g., by ICP-OES) to quantify the amount of Al and Co dissolved.

Reply: We thank Reviewer for this suggestion. The monitored Al and Co concentrations up to 4 weeks are listed in Table R2, which is in Supplementary Table 1.

Table R2. The Co and Al concentrations in soaking solution from ICP tests

	Al (mmol L ⁻¹)	Co (μmol L ⁻¹)
CoAl ₂ O ₄ -500_2M_5.5h	20.09	9.19
CoAl ₂ O ₄ -500_2M_1d	19.50	7.9
CoAl ₂ O ₄ -500_2M_3d	18.80	1.50
CoAl ₂ O ₄ -500_2M_1w	19.79	1.03
CoAl ₂ O ₄ -500_2M_2w	20.67	0.046
CoAl ₂ O ₄ -500_2M_4w	20.43	0.035
CoAl ₂ O ₄ -500_6M_4w	19.99	0.19
CoAl ₂ O ₄ -700_2M_1w	2.78	1.24
CoAl ₂ O ₄ -700_2M_4w	3.27	0.28
CoAl ₂ O ₄ -700_6M_4w	3.11	1.44
CoAl ₂ O ₄ -900_2M_1w	0.67	1.12
CoAl ₂ O ₄ -900_2M_4w	1.27	0.17
CoAl ₂ O ₄ -900_6M_4w	1.13	0.71

The Al concentration of the solution soaking CoAl₂O₄-500 does not change obviously with soaking time, and Al concentration increase is observed for CoAl₂O₄-700 and 900. The Co concentrations in the solution soaking for CoAl₂O₄-500, 700 and 900 are very low, and do not show an increasing trend with soaking time. We added the relevant analysis on the amount of Al and Co dissolved as below.

“Moreover, the concentrations of dissolved Co and Al are monitored as a function of soaking time. For the solution soaking CoAl₂O₄-700 and 900 in 2 M KOH, Al concentrations increase from 2.78 to 3.27 mmol L⁻¹ and from 0.67 to 1.27 mmol L⁻¹, respectively, from 1 week to 4 weeks. In contrast, the dissolved Co concentrations do not show an increase with soaking time. This behavior can be attributed to the ppb level of Co in solution and the existence of trace amount of unfiltered CoAl₂O₄ particles in the analyzed solution. For the solution soaking CoAl₂O₄-500 in 2 M KOH, Al concentrations are around 20 mmol L⁻¹ and do not change obviously with the soaking time from ~5.5 h to 4 weeks, indicating a fast Al leaching process.

Co concentrations have an abnormal decrease from $9.19 \mu\text{mol L}^{-1}$ to $0.035 \mu\text{mol L}^{-1}$ with the soaking time from $\sim 5.5 \text{ h}$ to 4 weeks. It could be ascribed to a reducing dispersing ability of Co-based intermediate with the increase of soaking time, as we observed that the clear supernatant was more difficult to obtain during the centrifugation for the samples with short time soaking. Besides, increasing KOH concentration from 2 M to 6 M does not obviously influence the Al leaching amount, i.e. $20.43 \text{ mmol L}^{-1}$ and $19.99 \text{ mmol L}^{-1}$ in 2 and 6 M KOH for 4 weeks for $\text{CoAl}_2\text{O}_4\text{-500}$.”

5. The authors emphasize the importance of relay-like phase formation during mixed-metal oxide synthesis. However, the discussion remains somewhat brief. It is suggested that the authors expand on how this phenomenon might apply to other multi-metal oxide systems, and how synthesis protocols could be adjusted to control such intermediate phases.

Reply: We appreciate Reviewer 1 to point out this issue.

First, for the relay-like phase formation in our case, we further analyzed the reaction between the Al-excess surface and Co-rich bulk by a simplified chemical reaction, indicating the diffusion of Al in Al_2O_3 into Co_3O_4 and Co in Co_3O_4 into Al_2O_3 , and added the content above Discussion part, as below:

“For the relay-like phase formation in our cases, we further analyzed the reaction between Al-excess surfaces and Co-rich bulk by a simplified chemical reaction, describing the mutual cation substitution, in which Al from Al_2O_3 diffuses into the Co_3O_4 lattice and substitutes Co, while Co from Co_3O_4 diffuses into the Al_2O_3 lattice and substitutes Al:



The calculated reaction energy, ΔE , is 1.00 eV, when Co occupies the more stable octahedral site, Co(Oh), in Co-doped Al_2O_3 , rather than the tetrahedral site, Co(Td). The models and calculated energies are shown in Supplementary Fig. 34 and Supplementary Table 3. Obviously, this reaction is not spontaneous. Thus, increasing heating temperature is necessary for the interdiffusion of Co and Al atoms.”

The mentioned Supplementary Fig. 34 and Supplementary Table 3 can refer to Fig. R2 and Table R3 here.

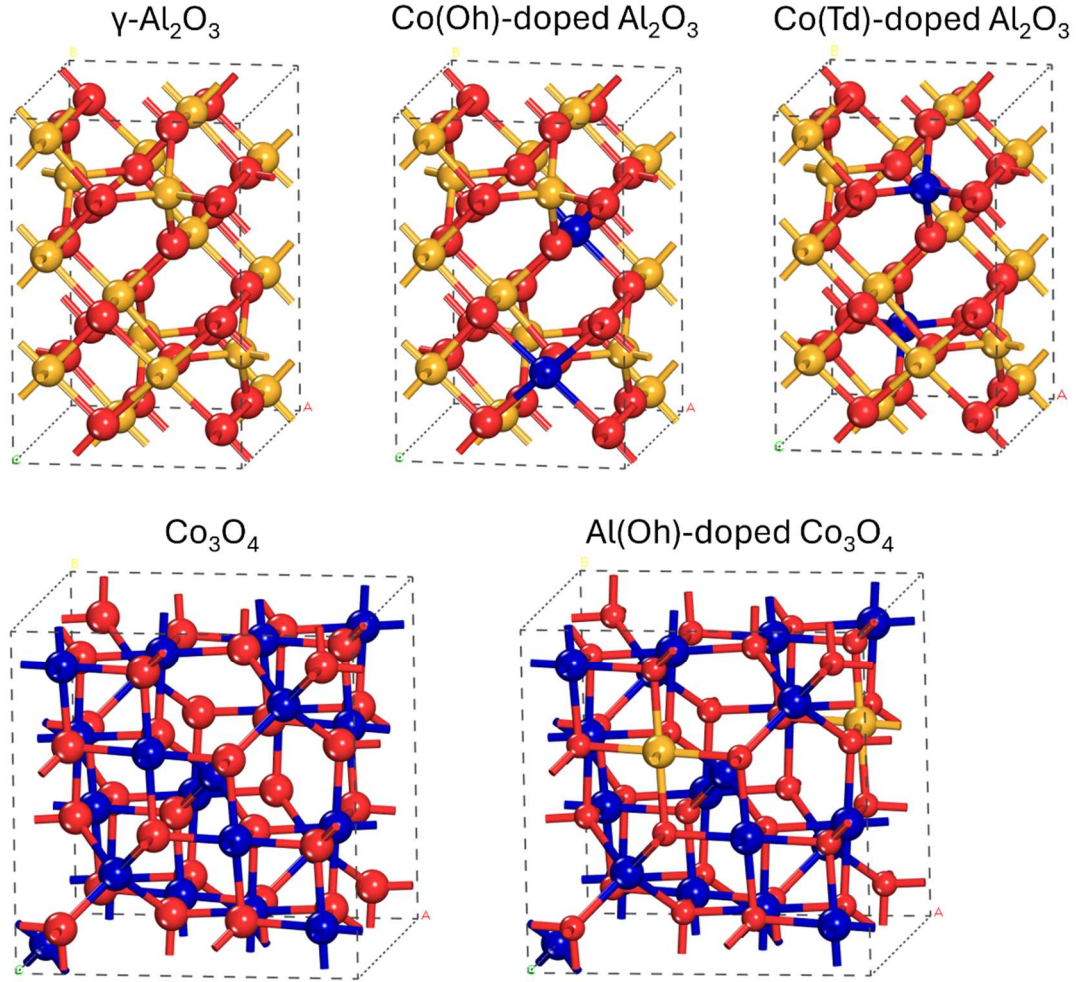


Fig. R2. The model used for the chemical reaction $\text{Al}_2\text{O}_3 + \text{Co}_3\text{O}_4 \rightarrow \text{Co-doped Al}_2\text{O}_3 + \text{Al-doped Co}_3\text{O}_4$. The red, orange and blue balls represent the O, Al and Co atoms, respectively. The number following Td/Oh indicates the specific position. We also compared energy of Co(OH)-doped Al_2O_3 (-290.87 eV) with that of Co(Td)-doped Al_2O_3 (-290.44 eV), where Co atoms dope into the octahedral (Co(Oh)) or tetrahedral (Co(Td)) sites, respectively. We found Co(Oh)-doped Al_2O_3 is more stable, and thus we selected the relatively stable Co(Oh)-doped Al_2O_3 for further calculation.

Table R3. The calculated energies used in $\text{Al}_2\text{O}_3 + \text{Co}_3\text{O}_4 \rightarrow \text{Co-doped Al}_2\text{O}_3 + \text{Al-doped Co}_3\text{O}_4$

	Number of each element in the bulk	E (eV)
$\gamma\text{-Al}_2\text{O}_3$	Al16+O24	-298.35
Co_3O_4	Co24+O32	-349.37
Co(Oh)-doped Al_2O_3	Co2+Al14+O24	-290.87
Co(Td)-doped Al_2O_3	Co2+Al14+O24	-290.44
Al(OH)-doped Co_3O_4	Al2+Co22+O32	-355.84

Secondly, following Reviewer's suggestion, we expanded the discussion on how this phenomenon applies to other multi-oxide systems and added the relevant discussion into Discussion part as below.

“Therefore, the phase purity and homogeneous distribution of cations within the synthesized particles are the prerequisites for correlating the performance, structure and composition.

In oxide synthesis, heat treatment plays a crucial role for the target phase formation. The relay-like phase formation in this work also applies to other metal oxide systems during increasing heat treatment temperatures. It should be emphasized that the required temperature strongly relies on the precursors and preparation methods. The combustion method used in this work involves an exothermic redox reaction between oxidant metal nitrates and reductant fuels, and thus a relatively low temperature is enough by combustion method compared with the solid-state reaction for some phase formation, for example obtaining a single-phase layer structure LiCoO_2 ²⁸. Coexistence of the spinel and the layer structure is observed at low temperatures (400 and 500°C) during LiCoO_2 synthesis by combustion method²⁸. Another example is the synthesis of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ by a coprecipitation method, in which the observed phases transform from only Co_3O_4 and NiO at 400°C, to Ni-rich $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ at 400 to 800°C, and finally to single phase of layer structure at 800°C²⁹. In the synthesis of P2 phase $\text{Na}_{0.67}\text{CoO}_2$ by solid-state reaction from CoO and Na_2O_2 , NaCoO_2 formed first followed by gradual decrease of Na until the formation of P2- $\text{Na}_{0.67}\text{CoO}_2$. This phenomenon has been attributed to fast non-equilibrium phase transformations due to the fast oxygen uptake and diffusion of Na cations into the CoO framework³⁰. The relay-like phase formation has also been observed in the process of synthesizing high-entropy/entropy-stabilized $\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{O}$ from the mixed monoxide with increasing heat treatment temperature, which exhibits prominent rocksalt and tenorite phases at 700°C. Reduction of tenorite phase fraction and full conversion to a single-phase rocksalt structure is achieved between 850 and 900°C³¹.”

The cited References 28-31:

28. Santiago, E.I., Andrade, A.V.C., Paiva-Santos, C.O., Bulhões, L.O.S. Structural and electrochemical properties of LiCoO_2 prepared by combustion synthesis. *Solid State Ion.* **158**, 91-102 (2003).

29. Caurant, D., Baffier, N., Garcia, B., Pereira-Ramos, J.P. Synthesis by a soft chemistry route and characterization of $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ ($0 \leq x \leq 1$) cathode materials. *Solid State Ion.* **91**, 45-54 (1996).
30. Bianchini, M. et al. The interplay between thermodynamics and kinetics in the solid-state synthesis of layered oxides. *Nat. Mater.* **19**, 1088–1095 (2020).
31. Rost, C.M. et al. Entropy-stabilized oxides. *Nat. Commun.* **6**, 8485 (2015).

Thirdly, following Reviewer's suggestion, we give our understanding on the synthesis protocols that could be adjusted to control such intermediate phases as below. We added it into Discussion part as below.

“Though the cases above indicates the significance of heat treatment for obtaining a single phase, it does not mean high-temperature treatment is beneficial to other oxides. The element evaporation and precipitation effects need to be carefully treated. For example, Antolini and Ferretti reported decomposition of LiCoO_2 and formation of cobalt oxide above 850°C caused by the evaporation of lithium oxide and oxygen³². Another example is decomposition of spinel ZnCo_2O_4 into ZnO and CoO , which is related to different cobalt redox processes under air atmosphere³³.”

“To achieve better control over the formation of intermediate phases or to obtain a desired single-phase microstructure, accurate phase identification is essential. Phase determination enables the distinction between single-phase and multiphase regions and facilitates the detection of any undesired impurity phases. Phase identification is relatively straightforward when diffraction patterns can be clearly indexed, as demonstrated by the tenorite and rock-salt phases formed during the synthesis of $\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{O}^{31}$. However, when the synthesized material consists of a crystalline phase together with an amorphous phase, the amorphous component is often difficult to identify using the conventional XRD analysis. Furthermore, in the present study, the oxides synthesized at low temperatures are nanoscale in size and possess similar crystal structures, while their elemental distributions vary continuously. Under such circumstances, distinguishing individual phases solely from XRD patterns becomes highly challenging. Therefore, direct characterization of crystal structures and elemental distributions is indispensable for elucidating phase formation mechanisms. In particular, high resolution analysis of particle interiors and interfaces is required to identify phase boundaries and local compositional variations. Although conventional solid-solution phase diagrams provide valuable guidance regarding composition, heat-treatment conditions,

and phase stability during materials synthesis, the emerging field of entropy-stabilized and high-entropy oxides offers additional opportunities for tailoring phase evolution and controlling the formation of intermediate phases or desired single-phase structures.”

The cited References 31-33:

31. Rost, C.M. et al. Entropy-stabilized oxides. *Nat. Commun.* **6**, 8485 (2015).
32. Antolini, E., Ferretti, M. Synthesis and Thermal Stability of LiCoO_2 . *J. Solid State Chem.* **117**, 1-7 (1995).
33. Peiteado, M., Caballero, A.C., Makovec, D. Thermal evolution of ZnCo_2O_4 spinel phase in air. *J. Ceram. Soc. Jpn* **118**, 337-340 (2010).

Point-by-point response to the reviewers' comments

Reviewer #2 (Remarks to the Author):

A strength of this paper is the consistent experiment study of Al leaching in CoAl₂O₄ synthesized under different conditions. Together, the identification of multiphase Al-rich surface domains in low T materials, and the demonstration that leaching is governed by surface comp and heterogeneity (not the bulk cation occupation), is strong. The observed termination of leaching after Al-rich spinel surface structures form provides a clear mechanistic insight.

A bit less obvious to me in the current form of the manuscript is the role of the DFT calculations. Reported values for bulk formation energies are straightforward. However, the authors use DFT energies of the reaction: $6\text{CoAl}_2\text{O}_4 + \text{O}_2 \rightarrow 2\text{Co}_3\text{O}_4 + 6\text{Al}_2\text{O}_3$ to “examine the spontaneity of Al leaching process.” What that reaction represents is relative stability of bulk CoAl₂O₄ with respect to phase separation into Co₃O₄/Al₂O₃, in otherwords, a solid state decomposition. While meaningful measures of bulk stability, the reported values (about -0.5 to -4.5 eV) do not represent, as claimed, the thermodynamics of Al leaching in alkaline media, which is a surface-mediated process that relies on aqueous speciation, concentration, pH. Likewise the bulk vacancy formation energies (which range from about 6.3 to almost 9 eV) measure the cost of removing lattice Al but do not correspond to dissolution into solution. These values are not directly comparable to the observed leaching process.

The current interpretation over extends the connection between the solid-state DFT results and the experimentally observed leaching behavior. The authors should avoid conflating bulk stability with aqueous dissolution thermodynamics. Unless the aqueous effects are incorporated, it should be made clear that only the solid state behavior is captured, and the link/interpretation to experiment should be appropriately cautious/conditional. That is, while I don't suggest removing the calculation results, their role should be more carefully framed. They provide evidence for the reduced bulk stability of inverse spinel, which may contribute to the formation of the Al-excess surface domains, for example. That would be in line with the experimental conclusion about surface composition and multiphase character in the observed leaching behavior.

Reply: We appreciate Reviewer's evaluation and point out the issue on the role of DFT calculations and the critical issue on linking the bulk stability and aqueous dissolution thermodynamics. It helps us to better correlate the bulk formation energy and Al-excess surface formation. The issue raised on the difference in removing Al from lattice and Al dissolution helps us to better clarify this phenomenon based on different reaction process. The changed contents are marked in blue in the revised manuscript.

For the role of the DFT calculations, we strengthened the motivation at the beginning of Results part in the revised manuscript, marked in blue. The relevant contents are copied as below.

“Calculation of CoAl₂O₄ bulk stability with different Al occupation-Solid state behavior.

The Al leaching behavior in alkaline solution is a surface-mediated process and the calculated results from bulk DFT are generally not directly comparable to the leaching process. Casey indicated that the local forces and geometries of metal-oxygen bonding are important factors in determining the oxide dissolution rate, despite no simple theory linking reactivity and bonding¹⁰. Recent works also correlated bulk calculation/thermodynamic results with electrochemical properties^{11, 12}. These encourage us to investigate the connection between bulk stability, Al vacancy formation energies and Al leaching behavior for CoAl₂O₄ with various inversion degrees. To evaluate the bulk stability of CoAl₂O₄ with different Al occupation, DFT calculations were performed to determine the formation energies of (Co_{1-λ}Al_λ)_{Td}[Co_λAl_{2-λ}]_{Oh}O₄ with inversion degree (λ) of 0.375 and 0.5, with a reference of normal CoAl₂O₄ (λ = 0) (Fig. 1a).”

The cited References 10-12:

10. Casey, W.H. On the relative dissolution rates of some oxide and orthosilicate minerals. *J. Colloid Interface Sci.* **146**, 586-589 (1991).
11. Calle-Vallejo, F., Díaz-Morales, O.A., Kolb, M.J., Koper, M.T.M. Why Is Bulk Thermochemistry a Good Descriptor for the Electrocatalytic Activity of Transition Metal Oxides? *ACS Catal.* **5**, 869–873 (2015).
12. Binninger, T. et al. Thermodynamic explanation of the universal correlation between oxygen evolution activity and corrosion of oxide catalysts. *Sci. Rep.* **5**, 12167 (2015).

For the concern on the correlation between the energies of the reaction: $6\text{CoAl}_2\text{O}_4 + \text{O}_2 \rightarrow 2\text{Co}_3\text{O}_4 + 6\text{Al}_2\text{O}_3$ and the energies of removing lattice Al with Al leaching behaviors, we emphasized the difference of the process in calculation and in Al leaching that this correlation should be conditional in the revised manuscript. The relevant contents are added in Results part and marked in blue. We copied them as below.

“We further attempted to establish a correlation between the solid-state decomposition process $6\text{CoAl}_2\text{O}_4 + \text{O}_2 \rightarrow 2\text{Co}_3\text{O}_4 + 6\text{Al}_2\text{O}_3$ and the spontaneity of Al leaching process for CoAl_2O_4 with different λ . CoAl_2O_4 with a higher inversion degree exhibits a more negative reaction Gibbs free energy at $T = 300\text{ K}$ and $P = 1\text{ atm}$, indicating that this reaction is thermodynamically more favorable (Fig. 1b). It should be emphasized that the calculated stability from the decomposition process represents the relative stability of bulk CoAl_2O_4 with different λ , with respect to the phase separation into $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$. This is different from leaching process in solution, which relies on aqueous speciation, concentration and pH, and involves the polarized and weakened critical metal-oxygen bonds by the reactants on the surface⁵. Thus, the bulk stability does not represent Al leaching thermodynamics. The situation also applies to the following calculation on removing lattice Al, which does not correspond to dissolution into solution. Instead, the dissolution process is controlled by the rates of metal-oxygen bond cleavage¹⁰, which motivates us to calculate Al vacancy formation energy. The reason why we did not choose to calculate oxygen vacancy formation is as follows. In spinel structure, one oxygen atom is coordinated with one atom in the tetrahedral site and three atoms in octahedral sites⁹. Creating one oxygen vacancy in bulk means simultaneous removal of Co-O and Al-O bonds instead of the single metal-oxygen bond. Thus, the Al vacancy formation energy can directly reflect the strength of Al-O bonds in different coordination environments.”

The cited References 5, 9 and 10:

5. Furrer, G., Stumm, W. The coordination chemistry of weathering: I. Dissolution kinetics of $\delta\text{-Al}_2\text{O}_3$ and BeO. *Geochim. Cosmochim. Acta* **50**, 1847-1860 (1986).
9. Sun, S. et al. Shifting Oxygen Charge Towards Octahedral Metal: A Way to Promote Water Oxidation on Cobalt Spinel Oxides. *Angew. Chem. Int. Ed. Engl.* **58**, 6042-6047 (2019).
10. Casey, W.H. On the relative dissolution rates of some oxide and orthosilicate minerals. *J. Colloid Interface Sci.* **146**, 586-589 (1991).

Also, we appreciated Reviewer to point out that the reduced bulk stability of inverse spinel may contribute to the formation of the Al-excess surface domains, and thus we added it in the revised manuscript marked in blue as below.

“More experimental evidence displaying the crystalline and Al-excess/rich surfaces of both pristine and soaked CoAl_2O_4 -500 particles are provided in Supplementary Figs. 12-15. It suggests that the formation of Al-excess surface domain could be evidenced by the reduced bulk stability of inverse CoAl_2O_4 spinel (Fig. 1a).”