

FROM α -Al₂O₃ PHASE PURITY TO SURFACE REACTIVITY: A CAUSAL DESIGN FRAMEWORK FOR SELECTIVE ETHYLENE EPOXIDATION OVER Ag/ α -Al₂O₃ CATALYSTSKhikmatullo Abdulazizovich Nasullaev¹, Saidxon G'anixonovich Shukurkhonov^{1,*}, Shuhratqodir Tashmatovich Gulomov¹, Ruslan Serverovich Khabipov¹, Nargiza Abduvaliyevna Igamkulova¹¹ Tashkent Institute of Chemical Technology, Tashkent, Uzbekistan

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ABSTRACT

Silver supported on α -alumina remains the industrially dominant catalytic platform for direct ethylene epoxidation, yet the support is often treated as a passive mechanical carrier even though recent studies show that phase purity, hydroxyl chemistry, exposed support area and Ag/support geometry can directly alter ethylene oxide (EO) selectivity and secondary EO loss. This critical review integrates evidence from phase-controlled α -Al₂O₃ synthesis, Ag particle and surface-ratio studies, EO degradation experiments, promoter studies, operando oxygen-species characterization and kinetic modeling. Four original synthesis contributions are proposed: (i) a **Phase-Surface Selectivity Envelope** that separates bulk phase purity from surface EO-loss propensity; (ii) a **Support-Exposure Penalty** concept that treats uncovered α -Al₂O₃ as an independent selectivity variable; (iii) a **Causal Control Matrix** for disentangling phase, surface modifier and Ag morphology effects; and (iv) a **Minimum Evidence Set** for claiming support-controlled selectivity. These contributions are not presented as experimentally validated laws; they are falsifiable design frameworks intended to guide the PhD program on phase-pure and surface-controlled Ag/ α -Al₂O₃ catalysts. The review concludes that the most defensible route to higher selectivity is not simply to maximize α -phase fraction, but to combine quantified phase purity with low secondary EO reactivity, controlled Ag coverage and promoter history under matched conversion conditions.

Keywords: ethylene oxide; silver catalyst; α -alumina; phase purity; surface hydroxyls; support reactivity; selectivity; catalyst design

АННОТАЦИЯ

Серебро, нанесённое на α -оксид алюминия (α -Al₂O₃), остаётся доминирующей в промышленности каталитической системой для прямого эпексидирования этилена, однако носитель часто рассматривается лишь как пассивный механический материал, несмотря на то, что недавние исследования показывают: фазовая чистота, гидроксильная химия поверхности, площадь открытой поверхности носителя и геометрия взаимного расположения Ag/носителя могут непосредственно влиять на селективность по оксиду этилена (ЭО) и вторичную потерю ЭО. В данном критическом обзоре обобщены и интегрированы данные исследований по синтезу α -Al₂O₃ с контролируемым фазовым составом, исследованиям частиц Ag и соотношения площадей поверхностей, экспериментам по деградации ЭО, изучению промоторов, характеристике кислородсодержащих форм в условиях operando, а также кинетическому моделированию. Предлагаются четыре оригинальных концептуальных положения для синтеза и анализа: (i) **пространство «фаза-поверхность-селективность» (Phase-Surface Selectivity Envelope)**, позволяющее разграничить объёмную фазовую чистоту и склонность поверхности к потере ЭО; (ii) **концепция «штрафа за экспонирование носителя» (Support-Exposure Penalty)**, рассматривающая непокрытую поверхность α -Al₂O₃ как независимую переменную, влияющую на селективность; (iii) **причинно-следственная матрица управления (Causal Control Matrix)** для разделения эффектов фазы, модификатора поверхности и морфологии Ag; и (iv) **минимальный набор доказательств (Minimum Evidence Set)**, необходимый для обоснованного утверждения о том, что селективность контролируется носителем. Эти положения не представлены как экспериментально подтверждённые законы; они являются проверяемыми и потенциально опровержимыми концептуальными рамками, предназначенными для разработки PhD-программы по созданию катализаторов Ag/ α -Al₂O₃ с контролируемой фазовой чистотой и поверхностными свойствами. В обзоре сделан вывод о том, что наиболее обоснованный путь к повышению селективности заключается не просто в максимизации доли α -фазы, а в сочетании количественно определяемой фазовой чистоты с низкой вторичной реакционной способностью по отношению к ЭО, контролируемым покрытием Ag и контролем истории введения промоторов при сопоставимых условиях конверсии.

Ключевые слова: оксид этилена; серебряный катализатор; α -оксид алюминия; фазовая чистота; поверхностные гидроксильные группы; реакционная способность носителя; селективность; дизайн катализатора.

ANNOTATSIYA

α -aluminium oksidiga (α -Al₂O₃) yotqizilgan kumush etilenni to'g'ridan-to'g'ri epoksidlash jarayoni uchun sanoatda ustun bo'lgan katalitik tizim bo'lib qolmoqda. Biroq tashuvchi ko'pincha faqat passiv mexanik tashuvchi sifatida qaraladi, holbuki so'nggi tadqiqotlar fazaviy tozalik, gidroksil kimyosi, tashuvchining ochiq yuzasi va Ag/tashuvchi geometriyasi etilen oksidi (EO) selektivligi hamda EO ning ikkilamchi yo'qotilishiga bevosita ta'sir qilishi mumkinligini ko'rsatmoqda. Ushbu tanqidiy sharh faza tarkibi nazorat qilingan α -Al₂O₃ sintezi, Ag zarrachalari va sirt maydonlari nisbatini o'rganish, EO degradatsiyasi bo'yicha tajribalar, promotorlar tadqiqotlari, operando sharoitida kislorod turlarini tavsiflash hamda kinetik modellashirish natijalarini birlashtiradi. To'rtta original sintez konsepsiyasi taklif etiladi: (i) «Faza-Sirt-Selektivlik» chegarasi (Phase-Surface Selectivity Envelope) — hajmiy fazaviy tozalikni sirtning EO yo'qotilishiga moyilligidan ajratish uchun; (ii) «Tashuvchining ochiq yuzasi jarimasi» konsepsiyasi (Support-Exposure Penalty) — qoplanmagan α -Al₂O₃ yuzasini selektivlikka ta'sir qiluvchi mustaqil o'zgaruvchi sifatida ko'rib chiqish uchun; (iii) faza, sirt modifikatori va Ag morfologiyasi ta'sirini bir-biridan ajratish uchun «Sababiy nazorat matritsasi» (Causal Control Matrix); hamda (iv) selektivlik tashuvchi tomonidan boshqarilishini da'vo qilish uchun zarur bo'lgan «Minimal dalillar to'plami» (Minimum Evidence Set). Ushbu konsepsiyalar eksperimental jihatdan tasdiqlangan qonunlar sifatida taqdim etilmaydi; ular α -Al₂O₃ ning fazaviy tozaligi va sirt xossalari nazorat qilinadigan Ag/ α -Al₂O₃ katalizatorlari bo'yicha PhD dasturini yo'naltirishga mo'ljallangan, eksperimental tekshirish va rad etish mumkin bo'lgan dizayn konsepsiyalaridir. Sharh natijasiga ko'ra, yuqori selektivlikka erishishning eng asosli yo'li faqat α -faza ulushini maksimal darajaga yetkazishdan iborat emas. Buning o'rniga miqdoriy jihatdan aniqlangan fazaviy tozalikni EO ga nisbatan past ikkilamchi reaktivlik, Ag qoplamasining nazorat qilinishi va promotor kiritilish tarixining nazorati bilan birlashtirish, bunda konversiya sharoitlari o'zaro taqqoslanadigan bo'lishi kerak.

Kalit so'zlar: etilen oksidi; kumush katalizatori; α -aluminium oksidi; fazaviy tozalik; sirt gidroksil guruhlari; tashuvchining reaktivligi; selektivlik; katalizator dizayni.

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1. Introduction

Direct oxidation of ethylene with molecular oxygen over supported silver is one of the defining examples of industrial selective oxidation. Modern commercial practice couples silver with solid and gas-phase promoters and operates in a narrow window where desired epoxidation competes with total oxidation and with secondary conversion of the desired EO product. Process development has progressively increased selectivity, but the economic and environmental leverage of even small selectivity gains remains large because carbon lost to CO₂ simultaneously consumes ethylene and oxygen, increases heat release, and raises downstream separation and recycle loads [1,20]. The catalyst support therefore cannot be judged only by its mechanical strength or surface area;

it must be evaluated by how it shapes Ag morphology, promoter state, transport and the chemical fate of EO after it is formed [2].

α -Al₂O₃ has historically been preferred because it is thermodynamically stable and comparatively weakly hydroxylated relative to transition aluminas. The practical assumption that α -Al₂O₃ is “inert”, however, is only conditionally valid. Miller et al. showed that α -Al₂O₃ can catalyze EO hydration, isomerization, dimerization and oxidation, while Ag surfaces additionally promote EO isomerization and combustion [9]. More recently, high-surface-area α -Al₂O₃ studies demonstrated that EO selectivity improves as the α -phase fraction increases, directly linking crystallographic purity to catalytic outcome [3]. These observations change the design problem: a support must not only be α -Al₂O₃ in a bulk diffrac-

tion sense; its exposed surface must also avoid sites that accelerate EO destruction.

A second conceptual difficulty is confounding. Thermal treatment used to increase α -Al₂O₃ phase purity simultaneously changes surface area, pore structure, hydroxyl population and the spatial distribution available for silver deposition. Likewise, washing or chemical modification intended to change trace alkali content can alter surface roughness and nucleation behavior. Ag particle size and Ag:Al₂O₃ surface ratio are themselves coupled to support surface area and Ag loading. Keijzer et al. showed that, under chloride-promoted conditions, the Ag:Al₂O₃ surface ratio can dominate the selectivity response more strongly than Ag particle size alone [4]. Thus, a correlation between “phase purity” and selectivity is not yet a causal explanation unless the exposed support and Ag geometry are independently constrained.

The present review is written to support a PhD program focused on “control of phase purity and surface reactivity of α -Al₂O₃ supports for selective ethylene oxide production over Ag/ α -Al₂O₃ catalysts.” It uses a critical, mechanism-oriented synthesis rather than a descriptive catalogue. The central question is: which support descriptors must be measured and controlled before a selectivity change can credibly be assigned to α -Al₂O₃ phase purity or surface reactivity? Four original review-level contributions are developed: the Phase–Surface Selectivity Envelope (PSSE), the Support–Exposure Penalty (SEP) concept, a Causal Control Matrix (CCM), and a Minimum Evidence Set (MES). Each is formulated as a testable framework rather than as a claim of new experimental discovery.

2. Materials and Methods

2.1. Review Question and Temporal Boundary

This review was finalized on 6 October 2026 as a structured, reproducible critical review rather than a formal systematic review. The primary question was: which independently measurable properties of α -Al₂O₃ phase state, surface chemistry and Ag/support geometry are required before an observed change in ethylene oxide (EO) selectivity can be attributed causally to the support? Historical studies were retained when they established structure-sensitivity or support chemistry, while the main evidentiary weight was assigned to 2017–2026 work directly addressing Ag/ α -Al₂O₃ preparation, phase purity, exposed support, EO degradation, surface hydroxyls, Ag particle distributions and metal/support interactions [1–4,9,19,20,22–45].

2.2. Search Sources and Query Architecture

Searches and cross-checks were performed across publisher platforms (ACS, Elsevier/ScienceDirect, Wiley and RSC), PubMed/PMC where applicable, institutional repositories, DOI-indexed scholarly discovery services and backward/forward citation chaining from the major synthesis and primary studies [1–4,19,20,22,23]. Four query blocks were used, with α -Al₂O₃/alpha-alumina spelling variants and Boolean equivalents. The exact logic is reported in Table M1. The query strings are database-portable and can be rerun in subscription indexes such as Scopus or Web of Science at submission-stage auditing.

2.3. Eligibility, Deduplication and Evidence Hierarchy

Eligible records were peer-reviewed primary studies or high-authority reviews that directly addressed gas-phase ethylene epoxidation over silver, α -Al₂O₃ support preparation/reactivity, Ag morphology or secondary EO conversion. Mechanistically relevant surface-science studies were retained when they resolved Ag–oxygen, Ag–chlorine or support-reactivity questions. Patent-only claims, unrelated oxidation systems, electrochemical epoxidation used only by analogy, duplicate DOI/title records and secondary commentary without traceable primary support were excluded from the evidentiary core. Duplicate records were reconciled at DOI/title level. No PRISMA-style database hit count is claimed because discovery combined publisher searching with citation chaining rather than a single exportable subscription-database search.

2.4. Data Extraction and Synthesis Limits

For each retained quantitative study, the extraction fields were: catalyst/support identity, α -Al₂O₃ phase descriptor, surface area and pore information, Ag loading, Ag particle-size descriptor, Ag/support surface-ratio information when available, promoter/feed composition, temperature, pressure, ethylene conversion, EO selectivity/reporting basis, time-on-stream and the study-specific limitation. Numerical values were combined in one table or plot only when their origin and reporting basis were explicit. Heterogeneous studies were used mechanistically rather than pooled into a meta-regression. Literature-derived numbers in Table 4 and Figure 5 are therefore presented as a benchmark dataset, not as new experiments or as a universal causal regression.

Search audit note. The review does not claim a PRISMA flow count because no single subscription-database export was used. Reproducibility is instead provided by dated search completion, explicit query blocks, eligibility rules, DOI/title-level deduplication, evidence-extraction fields and citation chaining. This prevents false precision while preserving a transparent route for an independent rerun.

3. Results

3.1. Why α -Al₂O₃ Must Be Treated as a Chemically Active Surface

The industrial rationale for α -Al₂O₃ is often summarized as low intrinsic reactivity, thermal stability and the ability to carry high silver loadings. This is directionally correct but insufficient for mechanistic interpretation. The relevant quantity is not the reactivity of an ideal α -Al₂O₃ crystal; it is the reactivity of the surface actually exposed to EO within a porous catalyst body after calcination, impregnation, drying, promoter addition and operation. Surface hydroxyls, residual transition alumina domains, trace inorganic species and defect-rich regions may all modify EO adsorption or isomerization probability. Therefore, bulk XRD phase purity and surface EO-loss propensity are related but non-identical variables.

The direct evidence from EO degradation experiments is especially important because it separates the fate of the product from its formation. Miller et al. found that α -Al₂O₃ surfaces can mediate hydration, isomerization, dimerization and oxidation, while Ag can catalyze EO isomerization and combustion [9]. Primary oxygenates generated over the support can then be consumed rapidly on Ag. This creates a bifunctional loss network in which an exposed support site need not produce CO₂ directly to lower overall EO selectivity; it can first convert EO into a more readily oxidized intermediate. Consequently, a support with lower primary epoxidation activity can still have a major effect on net selectivity.

This distinction also explains why Ag coverage of the support matters. If silver coverage increases while particle morphology remains catalytically acceptable, fewer reactive support sites remain directly accessible to EO. Van Hoof et al. argued that high silver loading and support coverage can suppress undesired consecutive reactions of EO on hydroxyl groups [19], and the later chloride-promoted study by Keijzer et al. explicitly identified Ag:Al₂O₃ surface ratio as a major selectivity factor [4]. The support therefore enters the selectivity balance both through its own chemistry and through the geometric fraction left uncovered by silver.

3.2. Phase Purity Is Necessary, but Not a Complete Descriptor

The 2023 ChemCatChem study provides the clearest recent demonstration that quantitative α -Al₂O₃ phase purity is catalytically meaningful [3]. By varying carbohydrate template size and heat treatment, high-surface-area supports spanning a substantial phase-purity range were produced, and EO selectivity increased as α -phase purity improved. This result is important because transition aluminas generally present higher hydroxyl densities and stronger surface reactivity than α -Al₂O₃. Yet the same thermal history that promotes the $\theta \rightarrow \alpha$ transformation also changes crystallite size, pore architecture and surface area. The scientifically stronger inference is therefore that phase purity is a necessary descriptor of support quality, not that phase fraction alone uniquely determines selectivity.

Table M1. Reproducible literature-search protocol used for the critical review

Block	Search string / logic	Evidence target
Q1 – support core	(“ethylene epoxidation” OR “ethylene oxide”) AND silver AND (“alpha alumina” OR “ α -Al ₂ O ₃ ”) AND (support OR carrier)	Direct support effects and industrial Ag/ α -Al ₂ O ₃ context
Q2 – phase/texture	Q1 AND (“phase purity” OR polymorph OR “surface area” OR pore OR macropore)	α -phase fraction, thermal transformation and pore architecture
Q3 – surface reactivity	Q1 AND (hydroxyl OR OH OR acidity OR basicity OR “support reactivity” OR “EO degradation”)	Secondary EO chemistry and surface-state descriptors
Q4 – Ag/support geometry	Q1 AND (“particle size” OR “particle size distribution” OR “Ag:Al ₂ O ₃ surface ratio” OR “support exposure”)	Ag morphology versus exposed-support effects

Table 1. Recent evidence most relevant to support-controlled EO selectivity

Study	System / method	Key finding	Implication for this PhD
Miller et al. 2020 [9]	Ag/ α -Al ₂ O ₃ , bare support, EO co-feed	Both Ag and α -Al ₂ O ₃ participate in secondary EO conversion	Support reactivity must be measured separately from primary epoxidation
Keijzer et al. 2022 [6]	Ag/ α -Al ₂ O ₃ aging and support comparison	Ag growth depends on atmosphere and spacing; higher-area support improves stability	Support architecture affects long-term Ag state, not only initial dispersion
Sun et al. 2022 [11]	In situ Ag precursor decomposition	Crystallization and decomposition are distinct; atmosphere alters Ag formation	Preparation history can confound support effects
Keijzer et al. 2023 [3]	High-area α -Al ₂ O ₃ with quantified phase purity	EO selectivity increased with α -Al ₂ O ₃ phase purity	Provides direct basis for a phase-purity variable
Keijzer et al. 2024 [4]	Chloride-promoted Ag/ α -Al ₂ O ₃	Ag:Al ₂ O ₃ surface ratio was a dominant selectivity descriptor	Exposed support area must be controlled
Keijzer et al. 2025 [5]	Alkali + chloride promotion	Promoters strongly alter EO degradation on Ag; support response is less affected	Promoter state must be matched when comparing supports
Jain & Stangland 2025 [2]	Support-focused industrial perspective	Support physicochemical properties influence catalyst efficiency and transport	Links laboratory descriptors to catalyst-body design

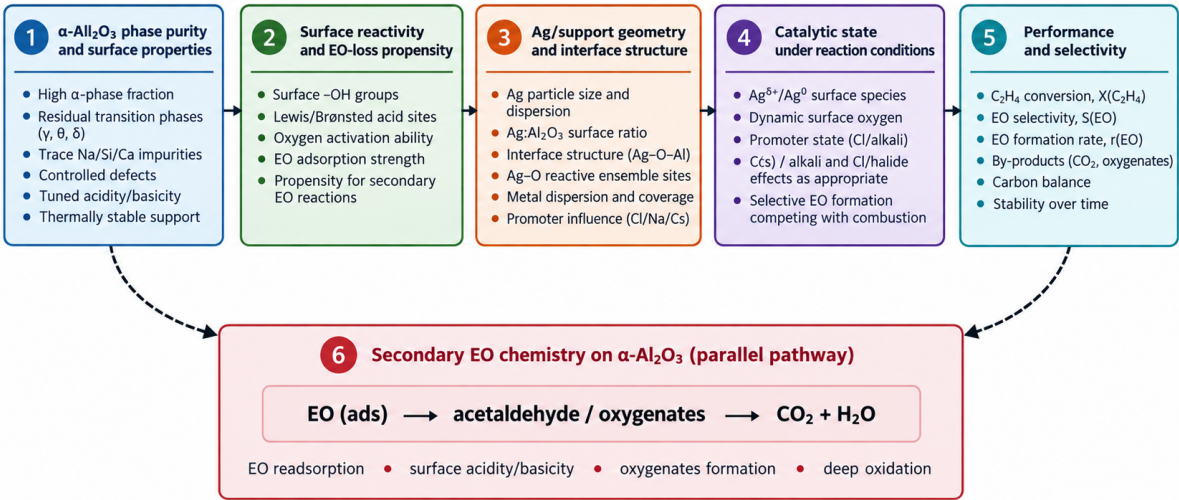


Figure 1. Causal chain connecting α -Al₂O₃ phase state, surface reactivity, Ag/support geometry and the observed EO performance (original synthesis framework based on evidence summarized in refs. [2–6,9])

For a PhD study, “phase purity” should be operationally defined by quantitative XRD with an internal standard and a stated detection limit. The expression “100% α -Al₂O₃” should be avoided unless the measurement uncertainty and amorphous fraction are explicitly constrained. A support can be XRD-pure yet retain chemically distinct surface hydroxyl states or trace impurities detectable by XPS, ICP or surface-probe spectroscopy. Conversely, a support containing a small bulk fraction of transition alumina may have little exposed transition-alumina area if those domains are internal or covered by Ag. This is the central reason to pair bulk phase analysis with surface-sensitive and catalytic probes.

The practical consequence is that phase purification should be judged against three possible penalties: loss of surface area, loss of pore accessibility and creation or removal of surface sites. Longer or hotter calcination may raise α -phase fraction while decreasing surface area and in-

creasing the average Ag interparticle distance after loading, which can in turn change sintering behavior. The optimal support is therefore not the material with the highest phase purity in isolation; it is the material that preserves adequate geometry for Ag while minimizing reactive exposed support.

3.3. Surface Reactivity: Hydroxyls, Acid–Base Sites and Secondary EO Loss

Surface reactivity is the hidden variable that links crystallography to EO chemistry. For the present PhD, it should be defined experimentally rather than inferred from phase identity. Useful descriptors include relative OH populations from controlled DRIFTS/FTIR, acid–base response measured with a suitable probe strategy, surface elemental ratios from XPS, bulk trace composition from ICP, and direct EO conversion over

the bare support under a safe and validated protocol. Each method captures a different part of the surface state. No single spectroscopic intensity should be converted into an absolute OH density without calibration and a defined surface-area basis.

Trace alkali illustrates why surface composition should not be treated simplistically. Alkali species can modify oxygen binding and the behavior of promoted Ag, while chloride also changes EO degradation on Ag [5,17]. Sodium remaining from support manufacture or washing could therefore act as a support impurity, a weak promoter, or an indirect modifier of Ag nucleation depending on its chemical form and location. The recommended approach is not to label Na as intrinsically harmful, but to deliberately construct a controlled low/intermediate/high surface-Na series while fixing Ag preparation and gas-phase promoter history. Washing controls and Na re-addition controls are required to determine whether the observed effect arises from Na itself or from collateral changes caused by washing.

A similar logic applies to Si, Ca and other manufacturing residues. Their importance depends on whether they alter surface acidity/basicity, hydroxylation, Ag anchoring or promoter binding. For a scientifically efficient PhD, only one surface modifier should be deliberately varied in the primary factorial study; other impurities should be monitored and held within a narrow range. This limits dimensionality while retaining mechanistic interpretability.

3.4. Ag/Support Geometry as an Independent Selectivity Variable

The apparent effect of the support can be strongly mediated by the amount of support that remains exposed. Ag loading, particle size, particle distribution and the support surface area jointly determine the geometric boundary experienced by EO. The chloride-promoted study of Keijzer et al. showed that Ag:Al₂O₃ surface ratio can be more predictive of selectivity than Ag particle size by itself [4]. This observation is especially important for high-surface-area α -Al₂O₃, where the same Ag weight fraction can leave much more uncovered support than on a low-area carrier.

Particle-size interpretation also requires care. Earlier structure-sensitivity work found that selectivity comparisons depend on how conversion is matched and how Ag surface area is estimated [10,19]. A nominally identical Ag loading does not guarantee identical Ag surface area, accessible support area or promoter density per exposed Ag surface. The PhD design should therefore report both mass-normalized and, where defensible, surface-normalized metrics, while avoiding turnover-frequency claims if active-site counts are not independently validated.

The support may also influence stability by changing interparticle distance and Ag mobility. Keijzer et al. found that higher-surface-area α -Al₂O₃ improved Ag stability under relevant conditions, with Ostwald ripening implicated as a dominant growth mechanism [6]. He et al. further showed that support surface treatment that changes roughness can suppress Ag aggregation and improve long-term performance [7]. These results make Ag geometry a dynamic variable: the support that minimizes exposed reactive area at the beginning of a test may not be the one that best preserves that condition during aging. Water response is likewise preparation-dependent [8].

3.5. Primary EO Formation versus Secondary EO Combustion/Isomerization

A key outcome of the literature synthesis is that net EO selectivity should be decomposed conceptually into two processes: the probability that reacting ethylene forms EO on Ag, and the probability that newly formed EO survives contact with Ag and exposed support until it exits the catalyst body. Most catalyst-development studies emphasize the first probability because it is associated with oxygen species, promoters and reaction mechanism. The second probability is equally important for support research and can obscure the interpretation of “selectivity” if it is not measured independently.

Supported-Ag operando studies show that multiple oxygen states can coexist and evolve under reaction conditions [12–14]. Pu et al. identified surface/near-surface oxygen species that differ in reactivity toward selective and non-selective pathways, while Guo et al. resolved distinct

oxygen populations on Ag surfaces [12–14]. These studies reinforce the idea that a support-induced change in Ag oxygen state could affect primary epoxidation even if the support itself is chemically inert toward EO. Thus, a proper support study needs two kinds of controls: bare-support EO conversion to diagnose direct secondary chemistry, and Ag-state characterization or matched Ag morphology to diagnose indirect electronic/geometric effects. Support-dependent electronic/pathway effects are also documented [16,21].

The most discriminating experiment is therefore not merely a steady-state selectivity test. It is a paired program that combines ethylene epoxidation with EO co-feed or EO-only control experiments under conditions chosen to isolate secondary chemistry. When coupled with carbon balance and oxygenate analysis, such tests can distinguish lower EO formation from higher EO destruction. A small selectivity difference that falls within carbon-balance uncertainty should not be used to claim a support effect.

3.6. Four Original Conceptual/Testable Contributions of the Review

Novel contribution 1 – Phase–Surface Selectivity Envelope (PSSE). The review separates “phase purity” from “surface EO-loss propensity” and treats them as orthogonal axes. A phase-pure support can still be catalytically unfavorable if its exposed surface is strongly hydroxylated or contaminated; a less phase-pure support can appear acceptable if reactive domains are buried or covered. The PSSE therefore defines the target region as high quantified α -phase purity combined with low directly measured secondary EO reactivity.

Novel contribution 2 – Support-Exposure Penalty (SEP). The review proposes that support effects be normalized not only to support chemistry but also to the fraction of support that remains exposed after Ag deposition. SEP is a conceptual penalty term proportional to exposed-support area multiplied by a directly measured EO-loss tendency. It is not yet a universal equation; its value is that it makes explicit why the same support can behave differently at different Ag loadings or Ag:Al₂O₃ surface ratios.

Novel contribution 3 – Causal Control Matrix (CCM). A 2 × 3 matrix is proposed in which two quantified phase states are crossed with three levels of one controlled surface modifier, while Ag preparation and promoter history are held constant. Independent re-preparation of the reference and lead catalyst, plus washing/re-addition and Ag-morphology controls, converts a simple correlation study into a falsifiable causal design.

Novel contribution 4 – Minimum Evidence Set (MES). A claim that “support phase/surface state controls EO selectivity” should require at minimum: quantitative phase analysis; surface/bulk composition; Ag morphology or Ag/support surface ratio; matched-conversion catalytic data; carbon balance; bare-support or EO-secondary-conversion control; and independent catalyst re-preparation. This evidence set is proposed as a quality gate for the dissertation and related publications.

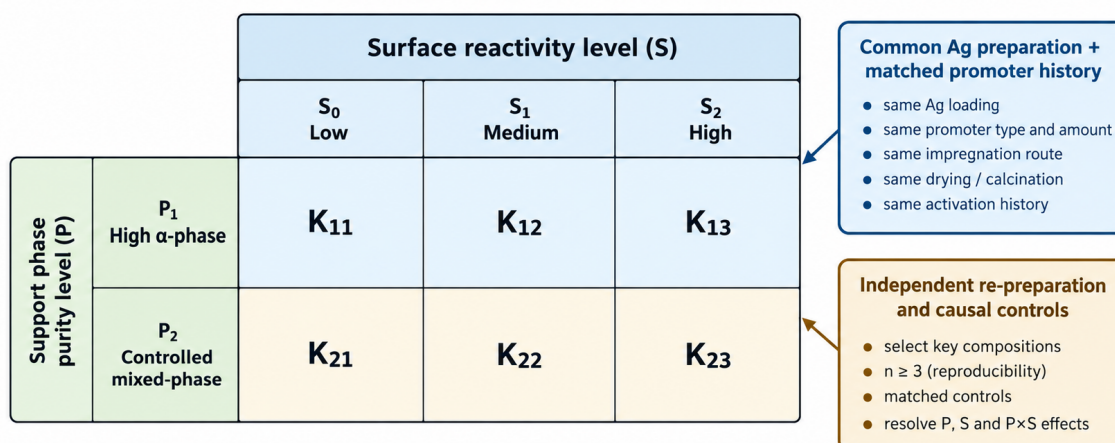
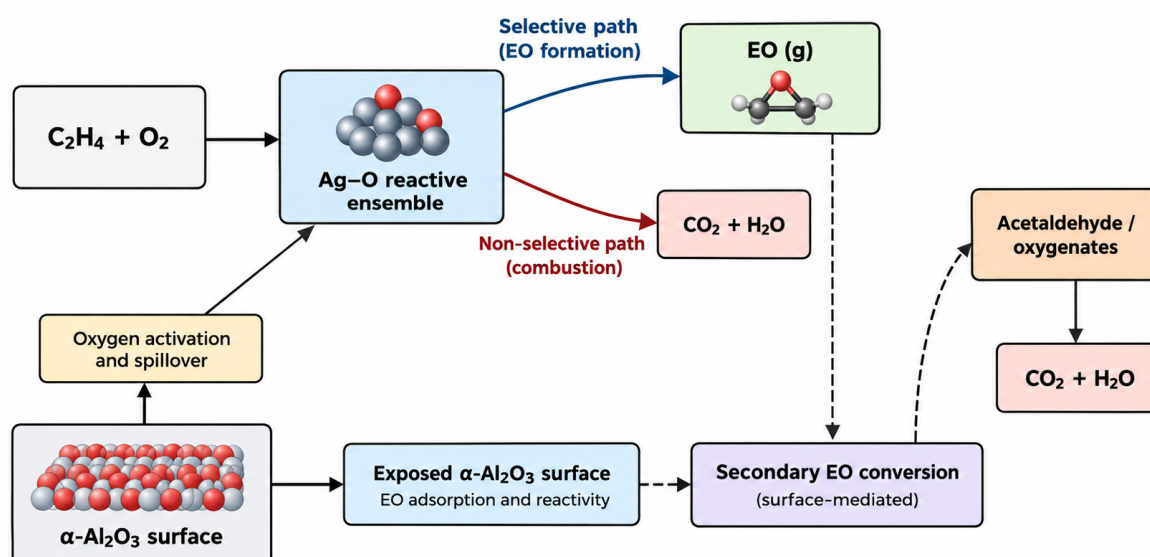
3.7. Quantitative Literature Benchmark: Phase Purity, Ag Geometry and EO Selectivity

A quantitative benchmark was extracted from the phase-controlled α -Al₂O₃ study of Keijzer et al. [3]. Table 4 deliberately preserves the authors’ reported catalyst identities and separates phase purity, support area, Ag loading and particle size instead of collapsing them into one descriptor. The data are suitable for mechanistic benchmarking because the four catalysts were studied within one experimental program, but they still do not constitute an isolated one-factor test: phase purity, Ag loading, Ag size and exposed support area vary together. The benchmark is therefore used to test the logic of the PSSE and SEP frameworks rather than to fit a universal phase-purity/selectivity equation.

Two observations are especially important. First, reducing phase purity from 100% to 98% did not produce a unique selectivity penalty: at 98% α -phase, EO selectivity was reported as 67% for 15Ag50/cellulose-6h but 78% for 30Ag70/cellulose-6h [3]. Second, the ~75% α -phase CG220-derived sample had much lower selectivity (56%), while the same study reported substantial acetaldehyde formation for this support family. These contrasts support a two-coordinate interpretation:

Table 2. Support descriptors, recommended measurements and interpretation limits

Descriptor	Primary method	What it establishes	What it does not establish alone
α -Al ₂ O ₃ phase fraction	Quantitative XRD/Rietveld + internal standard	Bulk crystalline phase composition	Surface chemistry or exposed phase fraction
Specific surface area / porosity	Gas adsorption; pore analysis appropriate to support	Textural availability and changes after heat treatment	EO reactivity or Ag active-site density
Surface OH state	DRIFTS/FTIR under controlled pretreatment	Relative hydroxyl populations and changes	Absolute OH/nm ² without calibration
Trace Na/Si/Ca	ICP for bulk; XPS for near-surface	Bulk vs surface enrichment	Catalytic role without controlled perturbation
Ag particle distribution	SEM/BSE; selected TEM/STEM	Size and spatial heterogeneity	Exact active-site population
Ag:Al ₂ O ₃ surface ratio	Combined geometry/coverage estimate [4]	Degree of support exposure	Intrinsic support reactivity
Bare-support EO conversion	Dedicated control experiment	Direct secondary EO reactivity	Primary ethylene epoxidation kinetics

Figure 2. Proposed 2 × 3 causal screening matrix: two quantified phase states (P₁, P₂) and three controlled surface-modifier states (S₀–S₂) with common Ag preparation and matched promoter historyFigure 3. Mechanistic separation of primary EO formation and secondary EO loss on Ag and exposed α-Al₂O₃ (critical synthesis of refs. [9,12–14,18,20])

phase state constrains the support, but exposed support chemistry and Ag/support geometry determine how strongly EO encounters secondary-conversion sites. Earlier carrier, crystallite-size and support-effect stud-

ies likewise show that pore structure, Ag particle distribution, support exposure and preparation route can alter the apparent selectivity response [22–36,41–45]. Recent work on modified alumina, shape-selective Ag

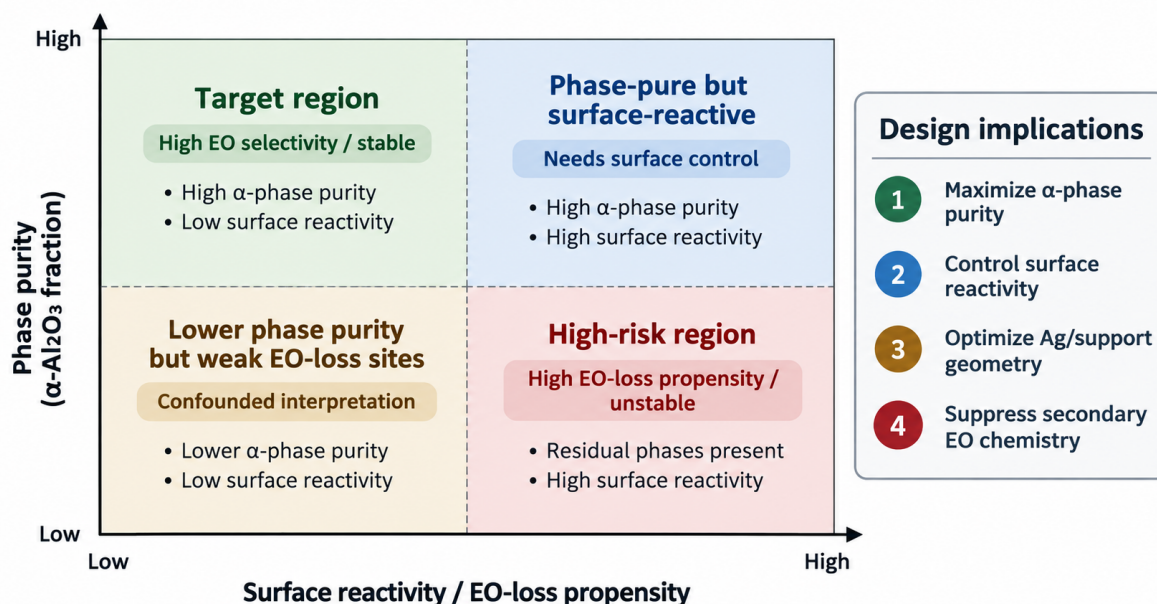


Figure 4. Phase–Surface Selectivity Envelope (PSSE), an original qualitative framework proposed in this review. Axes represent experimentally measured phase purity and surface EO-loss descriptors

Table 3. Major confounders in support studies and the controls needed to separate them

Apparent factor	Hidden co-variable	Risk	Required control
Higher α -phase fraction	Lower surface area / changed pore structure	Selectivity change may be geometric rather than phase-driven	Textural matching or explicit covariate analysis
Support washing	Roughness, ion removal, hydroxylation changes	Effect may not be due to targeted impurity	Equal wash control + impurity re-addition
Higher Ag loading	Higher particle size and support coverage	Ag morphology and support exposure change simultaneously	Ag:Al ₂ O ₃ surface ratio + microscopy
Promoter addition	Dynamic chloride/alkali state	Different equilibration can mimic support effect	Identical promoter history and equilibration criterion
Higher selectivity	Lower conversion	Selectivity–conversion coupling gives false advantage	Compare <i>S–X</i> behavior or matched conversion
Longer stability	Different initial Ag spacing	Initial geometry governs sintering rate	Fresh-state interparticle/size characterization

Table 4. Literature-extracted quantitative benchmark from Keijzer et al. [3] (reported data, not new experiments)

Catalyst	α -phase (%)	BET (m ² g ^{−1})	Ag (wt%)	Ag size (nm)	C ₂ H ₄ conv. (%)	EO select. (%)
15Ag50/C8	100	8	15.0	52 ± 26	3.5 ± 0.07	78 ± 1.7
15Ag50/cellulose-6h	98	21	16.1	47 ± 20	3.6 ± 0.22	67 ± 2.6
30Ag70/cellulose-6h	98	21	31.5	73 ± 30	2.8 ± 0.05	78 ± 3.7
30Ag50/CG220-6h	≈75	29	29.4	53 ± 22	2.8 ± 0.03	56 ± 4.6

and surface-OH engineering further reinforces the need to describe the support by chemically relevant surface descriptors rather than by BET area or phase label alone [37–40].

4. Discussion

The literature now supports a stronger formulation of the support problem than “use pure α -Al₂O₃.” A defensible support specification needs at least three layers: a bulk phase requirement, a surface-reactivity requirement, and an Ag/support-geometry requirement. These layers should be treated as independent until experiments demonstrate that they covary in a predictable way. This approach is more demanding than phase screening alone, but it prevents an important category error: assigning a selectivity response to crystallographic phase when the true cause is surface exposure or Ag morphology.

The proposed 2 × 3 matrix is deliberately modest. Two phase states are not sufficient to establish a universal threshold in α -phase content, but they are sufficient to test whether the direction and magnitude of a surface-modifier effect depend on phase state. If a significant interaction is observed, intermediate phase levels can be added near the relevant region. This sequential strategy minimizes sample count while preserv-

ing the ability to discover nonlinearity. It is better suited to a PhD than a large, poorly replicated factorial design.

The role of promoters must be kept conceptually separate from support chemistry. Chloride and alkali species modify oxygen binding, EO degradation and reaction-state equilibration [5,17]. A support comparison performed under unmatched promoter states is therefore ambiguous even if Ag size is identical. The preferred strategy is to establish the support/Ag relationship under one rigorously standardized promoter protocol and only then test whether the lead support remains advantageous when promoter conditions are varied. Promoter optimization should be a validation layer, not an initial screening dimension.

Mechanistic interpretation should also respect the limits of steady-state kinetics. Multiple kinetic mechanisms can reproduce similar steady-state trends, whereas non-steady-state data can better discriminate between surface-state models [15]. For the support-focused PhD, this does not require a full transient-kinetic campaign for every catalyst. A practical hierarchy is: matched steady-state *S–X* mapping for all six catalysts; EO-secondary-conversion tests for the reference and lead sam-

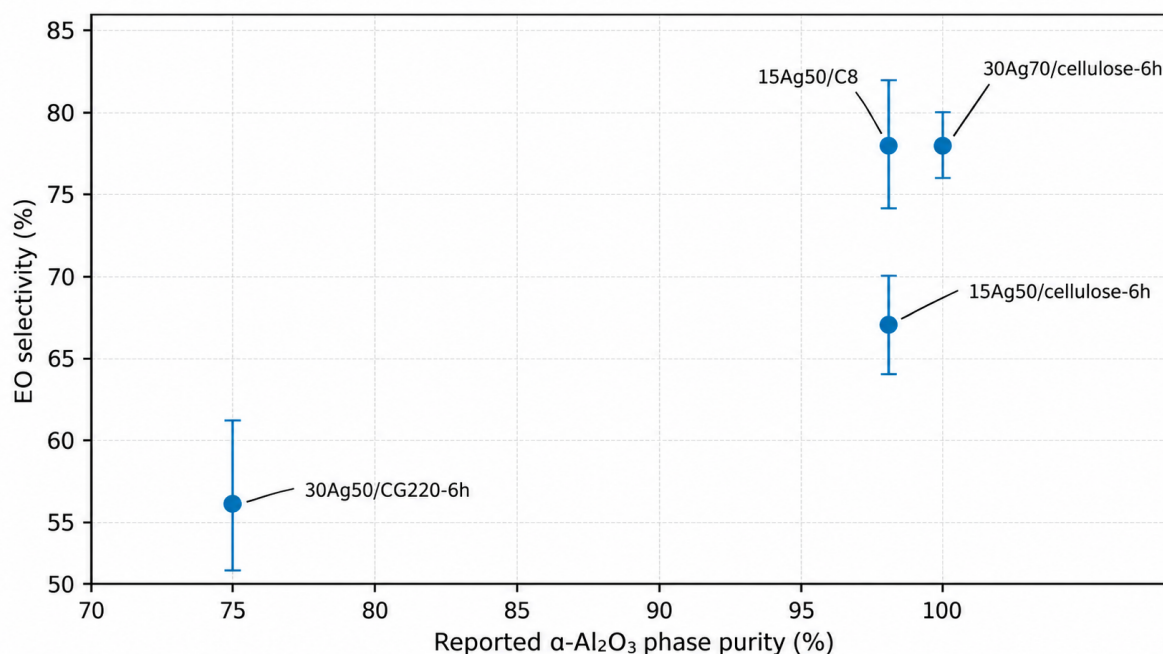


Figure 5. Literature-extracted α -Al₂O₃ phase purity versus EO selectivity for four catalysts reported by Keijzer et al. [3]. Points reproduce reported literature values with uncertainty bars

ples; and selected transient or perturbation tests only after the principal support effect has been reproduced independently.

The PSSE and SEP concepts are intended to generate falsifiable predictions. If two supports with similar α -phase fraction but different bare-support EO-loss rates show different selectivity at matched Ag/support geometry, the surface-reactivity axis is supported. If the selectivity difference disappears after increasing Ag coverage while preserving Ag catalytic state, the Support-Exposure Penalty interpretation gains support. Conversely, if selectivity tracks Ag oxygen-state changes while bare-support EO loss remains unchanged, the effect should be assigned primarily to support-mediated modification of Ag rather than direct EO degradation.

Scale-up adds transport constraints that are largely absent from powder-scale comparisons. Support pore architecture controls not only Ag placement but also local heat and mass transfer within shaped catalyst bodies [2]. A support modification that improves intrinsic selectivity but creates diffusion limitations or larger intrapellet temperature gradients may not remain beneficial at process scale. The dissertation should therefore end with a transport-aware technology assessment rather than a direct claim that laboratory powder performance will reproduce industrial reactor performance.

The principal limitation of the present review is the heterogeneity of published catalysts and operating conditions. Different studies use different Ag loadings, support areas, promoter packages, pressures and equilibration protocols, so numerical selectivity values should not be compared across papers as if they belonged to one dataset. The value of the literature is instead mechanistic: it identifies which variables can materially alter the catalyst state and which controls are required before cause is assigned. The PhD can add value by studying those variables in one internally consistent catalyst family.

Bibliographic separation was also imposed between the two companion reviews. The present article concentrates its expanded evidence base on support preparation, alumina phase/texture, support-mediated EO chemistry, Ag particle distributions and exposed-support effects [22–45]. Water/promoter aging literature is cited only where it is needed to control a support-reactivity interpretation. This division reduces duplication and makes the causal scope of the article explicit.

5. Conclusions

Recent literature establishes that α -Al₂O₃ is more than a passive Ag carrier. Quantified phase purity influences EO selectivity [3]; Ag/support surface ratio changes the extent to which reactive support remains exposed [4]; the support participates in secondary EO chemistry [9]; and support structure affects Ag stability during operation [6,7]. These effects are coupled, so a single descriptor cannot explain performance.

The four original contributions of this review—the PSSE, SEP, CCM and MES—convert the literature into a specific experimental logic for the PhD. Their common principle is causal separation: bulk phase, surface reactivity, Ag morphology, promoter state and conversion must be distinguished before a selectivity benefit is attributed to the support.

For the dissertation, the strongest initial strategy is therefore to construct two quantified α -phase states, cross them with three controlled surface states, hold Ag preparation and promoter history constant, and independently re-prepare the reference and lead catalysts. Bare-support EO-loss tests, matched-conversion catalytic data and post-test Ag characterization should accompany the primary epoxidation measurements. Such a design can generate defensible scientific novelty without relying on invented thresholds or unsupported claims of universal optimal composition.

Source integrity statement. Quantitative literature values in this review are explicitly attributed to their original studies and are not presented as experimental results generated in the present work. DOI metadata were cross-checked during finalization; conceptual frameworks introduced in this review remain hypotheses/frameworks until experimentally validated.

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Table 5. Proposed validation matrix for the four review-level innovations

Innovation	Primary observable	Critical falsification test	PhD deliverable
PSSE	Quantified α -phase state + direct support EO-loss metric	A phase-pure surface can still show high EO-loss propensity	2D phase-surface map with uncertainty
SEP	Exposed support estimate + EO-loss rate	Selectivity difference should shrink when exposed support is reduced without changing Ag state	Coverage-normalized selectivity interpretation
CCM	2×3 phase $\times$ surface-modifier matrix	No interaction or effect after independent re-preparation	Factorial evidence with controls and replication
MES	Completeness of phase/surface/Ag/catalytic evidence	Claim fails if alternative explanation remains uncontrolled	Publication/dissertation quality checklist

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