

SEPARATING THE EFFECT OF HUMIDITY FROM TIME-ON-STREAM AGING IN AG/ α - Al_2O_3 CATALYSTS: A DRY-WET-DRY HYSTERESIS PROTOCOL

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Abstract: *Water vapor can alter oxygen states on Ag, promoter balance, and hydroxylation of the support in Ag/ α - Al_2O_3 catalysts. A simple before/after-humidity comparison does not distinguish the effect of humidity from natural time-on-stream aging; non-steady-state experiments may provide stronger mechanistic evidence than a single steady-state endpoint [5]. Two scientific contributions are proposed. The first is a Dry-Wet-Dry protocol that combines wet exposure, return to dry conditions, and a time-matched parallel dry control. The second is classification of changes into reversible surface-state effects and persistent structural changes by combining a recovery coefficient with structural diagnostics. The framework treats water tolerance as a time-dependent catalyst state rather than a single selectivity value.*

Keywords: *Ag/ α - Al_2O_3 ; water vapor; ethylene epoxidation; stability; hysteresis; deactivation.*

Introduction

The industrial value of a catalyst is determined not only by its initial EO selectivity but also by its ability to maintain that performance over time. Ag particle growth, changes in promoter state, and interaction with water can modify selectivity and activity as a function of time [1-4]. A 2025 study showed that the effect of water vapor on Ag catalysts depends on competitive oxygen-water adsorption and on preparation history [3].

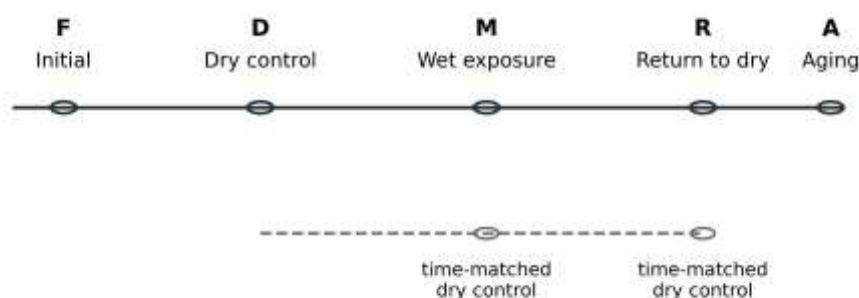
However, an observation that “humidity was introduced and activity decreased” does not prove permanent deactivation. The response may be rapid and reversible because of surface coverage, or it may reflect slower changes in Ag morphology or promoter distribution. In addition, the catalyst may age with time even in the absence of added humidity. A time-matched dry control is therefore essential.

Materials and Methods

Reference and promising catalysts are first stabilized under the same dry reference condition (state F). One branch is then transferred to

controlled wet exposure (M), after which the exact initial dry condition is restored and a new stabilized state (R) is obtained. A parallel branch remains under dry conditions for the same elapsed time (D). Results are compared at matched elapsed-time points. A longer aging stage may subsequently be introduced.

For a selected performance indicator P, recovery is expressed as $H = (P_R - P_M) / (P_F - P_M)$. Here, $H \approx 1$ indicates that most of the decline under humid conditions is recovered after returning to dry operation, whereas $H \approx 0$ indicates little recovery. H is not a universal kinetic constant; it is used only for internal comparison of catalysts tested under identical conditions. Interpretation is combined with the time-matched D branch and fresh/spent physicochemical characterization.



The humidity effect is not confounded with the effect of time.

Figure 1. Dry-Wet-Dry sequence with a parallel time-matched dry control for separating humidity effects from time-on-stream aging.

Table 1. States and diagnostics within the Dry-Wet-Dry protocol.

		What is the reference active state?	X, S(EO), rEO, carbon balance; fresh morphology
	Dry only, matched elapsed time	How much natural time-on-stream aging occurs?	Comparison under the same conditions as F
		What is the rapid response to humidity?	
			H coefficient + comparison with D

		Does a persistent change remain?	Ag particle distribution, surface composition, OH state

Proposed Framework and Discussion

The first proposed scientific contribution is addition of a time-matched counterfactual dry branch to the humidity experiment. If the catalyst fully recovers along the M→R route but the D branch also declines slowly during the same interval, humidity cannot be identified as the sole cause of permanent deactivation. Conversely, if the R state remains substantially below the D state, the evidence for a water-specific persistent change becomes stronger.

The second proposed scientific contribution is to link recovery behavior with post-test structural analysis. If rEO and selectivity recover after return to dry conditions and the Ag particle-size distribution remains unchanged, the hypothesis of a reversible surface-state change is strengthened. If recovery is incomplete and Ag particles have grown, structural aging becomes more likely [2]. If morphology is unchanged but surface composition or OH/promoter indicators have shifted, chemical surface state becomes the focus of subsequent verification.

The scientific value of the protocol lies in replacing the generic phrase “water-resistant catalyst” with explicitly measurable states. Catalysts can then be compared not only by a single maximum selectivity under humid conditions, but by their humidity response, recovery, and time-matched aging behavior.

Conclusion

The Dry-Wet-Dry protocol separates the humidity response of Ag/ α - Al_2O_3 catalysts from natural time-on-stream aging. Its two proposed scientific contributions are causal comparison using a parallel dry control and differentiation of reversible versus persistent changes by combining a recovery coefficient with structural diagnostics. This protocol materially strengthens the stability component of the PhD project.

REFERENCES:

1. Keijzer CJ, van de Ven NMT, Dalebout R, Lohr TL, Lockemeyer JR, van den Brink P, de Jongh PE. Influence of alkali and chloride promoters on

silver catalysts in ethylene epoxidation. *Journal of Catalysis*. 2025;450:116206. <https://doi.org/10.1016/j.jcat.2025.116206>.

2. Keijzer PH, van den Reijen JE, Keijzer CJ, de Jong KP, de Jongh PE. Influence of atmosphere, interparticle distance and support on the stability of silver on α -alumina for ethylene epoxidation. *Journal of Catalysis*. 2022;405:534-544. <https://doi.org/10.1016/j.jcat.2021.11.016>.

3. Chu Y, Liang H, Lin Q, Huang H, Che P, Han Y. Effect of water vapor on the structure and performance of silver catalysts for ethylene oxidation. *Chemical Engineering Journal*. 2025;518:164442. <https://doi.org/10.1016/j.cej.2025.164442>.

4. He C, Lu X, Liu Y, Yan Z, et al. Stability enhancement for silver catalyst in ethylene epoxidation by support treatment. *Catalysis Communications*. 2023;178:106669. <https://doi.org/10.1016/j.catcom.2023.106669>.

5. Brandão L, Reece C. Non-steady state validation of kinetic models for ethylene epoxidation over silver catalysts. *Catalysis Science & Technology*. 2024;14(13):3596-3608. <https://doi.org/10.1039/D4CY00052H>.