

The 29th North American Catalysis Society Meeting (NAM29)

June 8-13, 2025 | Hyatt Regency Atlanta, GA

MORE

ABOUT	+
SPONSOR & EXHIBIT	+
PROGRAM	+
GENERAL INFORMATION	+

The 29th North American Catalysis Society Meeting (NAM29)

June 8, 2025 to June 13, 2025

Hyatt Regency Atlanta, GA



[NACS Homepage](#)

[STAY INFORMED ABOUT NAM29](#)

[ADD TO CALENDAR](#)

Technical Program Now Available!

See the Technical Program at the link here: [TECHNICAL PROGRAM](#)

Join other NAM29 attendees at social activities throughout the week of NAM29.

See scheduled activities here: [SOCIAL ACTIVITIES](#)

Ethane dehydrogenation with CO₂ using LDH-Derived mixed oxides of V, Mn, and Ga

Gabriel L. Catuzo¹, Rosembergue G. L. Gonçalves¹ and Elisabete M. Assaf^{1*}

¹University of São Paulo, São Carlos Institute of Chemistry, São Carlos, SP 13566-590, Brazil
*eassaf@iqsc.usp.br

Introduction

Ethane dehydrogenation with simultaneous CO₂ reduction (CO₂-ODHE) offers a pathway to transform underutilized feedstocks into high-value chemicals, ethylene and CO. Ethylene is a precursor for polymers, oxides, and other compounds like ethylene glycol and acetone. CO is used in Fischer-Tropsch synthesis. In CO₂-ODHE, CO₂ acts as a mild oxidant, enhancing catalyst stability and shifting the equilibrium toward ethylene formation by consuming H₂ through the reverse water gas shift (r-WGS) reaction. However, side reactions like ethane cracking to CH₄ and dry reforming compromise ethylene selectivity, emphasizing the need for the development of active and selective catalysts. In this context, layered double hydroxides (LDHs) can be employed as precursors for generating a variety of mixed oxide catalysts through controlled thermal decomposition, yielding materials with high thermal stability, large specific surface area, low cost, and high flexibility in composition, structure, and morphology, alongside abundant Lewis acid sites [1]. This work explores the application of LDH-derived mixed oxides of V, Mn, and Ga in ethane dehydrogenation with CO₂.

Materials and Methods

The precursors, MgZnM₃₊ (M³⁺= Ga, V, and Mn)-LDH materials, were synthesized via coprecipitation at a pH of 10 using Na₂CO₃ and latter NaOH as base solutions, followed by hydrothermal treatment for 24 h at 65 °C. The precursor salts were weighed to achieve molar ratios of M²⁺/M³⁺=3 and Mg²⁺/Zn²⁺=3. After synthesis, the suspended solids were washed with deionized water, dried at 70 °C, and calcined at 700 °C. Catalysts were characterized through XRD, N₂ physisorption, SEM, and TPO techniques. The reaction at 650 °C was conducted in a continuous flow fixed-bed reactor using 100 mg of catalyst and C₂H₆:CO₂:N₂ flows = 10:10:20 mL/min. The products were analyzed using a Varian CP-3800 gas chromatograph with Porapak N and molecular sieve columns, both using thermal conductivity detectors (TCD).

Results and Discussion

XRD of HDL precursors (Fig. 1a) confirmed the presence of typical hydrotalcite peaks [2] (and MnCO₃ phase, for MgZnMn-LDH sample). Notably, the MgZnGa-LDH sample is much more well-crystallized among the three materials, probably due to the higher stability of Ga in the 3+ state oxidation. XRD of the calcined materials (Fig. 1b) indicates the formation of mixed oxides of ZnO and MgO, doped with Ga and Mn atoms, for the MgZnGa and MgZnMn samples, respectively. For the MgZnV sample, a Mg₃V₂O₈ phase was formed. SEM images of HDL precursors (Fig. 1c) reveals uniform hexagonal platelet arrangements spatially interconnected and distributed homogeneously, with a three-dimensional porous network structure. The catalytic performance of the calcined materials was investigated at 650 °C, with results detailed in Table 1. The initial ethane conversion followed the order: MgZnGa > MgZnV > MgZnMn. The ethylene CO-free selectivity is also in Table 1. While ethylene was the primary product, methane was also identified as a byproduct, indicating that both cracking reactions and dehydrogenation occurred. Nonetheless, an increase in ethylene selectivity was observed across all catalysts throughout the reaction. It indicates an enhanced capability for

selectively cleaving C-H bonds over C-C bonds, implicating that the deactivation process more significantly impacted ethane cracking than ethane dehydrogenation.

To investigate the carbon content in the samples, TPO analyses were conducted, and the results are detailed in Table 1. Notably, the amount of carbonaceous deposits on each catalyst correlated positively with their respective BET surface areas (also in Table 1), suggesting that larger surfaces enhance the formation and retention of carbon compounds. Nevertheless, the MgZnGa spent catalyst maintained the highest BET surface area. Furthermore, the pore volume of this sample remained consistent, indicating that a significant proportion of the active sites was preserved during the reaction, contributing to its superior catalytic activity over 5 h.

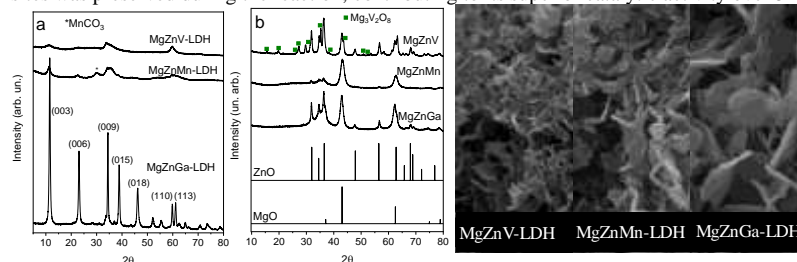


Figure 1. A) XRD patterns of LDH precursors, (B) XRD patterns of calcinated catalysts, c) SEM images of LDH precursors.

Table 1. BET surface area and pore volume for calcinated and spent catalysts; Ethane and CO₂ conversion, and ethylene selectivity; carbon content for spent catalysts.

Sample	BET area (m ² /g) ¹	Pore volume (cm ³ /g) ¹	Ethane conversion ¹	CO ₂ conversion ¹	Ethylene selectivity ¹	Carbon content (wt%)
MgZnV	44 (32)	0.28 (0.09)	19 (6)	30 (1)	44 (95)	2.7
MgZnMn	31 (17)	0.10 (0.09)	7 (6)	8 (2)	88 (94)	1.9
MgZnGa	92 (69)	0.29 (0.29)	23 (12)	18 (5)	67 (89)	7.3

1. The results inside the brackets were obtained at 5 h of reaction.

Significance

The LDH-derived catalysts doped with V, Mn, and Ga exhibited significant activity in ethane dehydrogenation. Particularly, the MgZnGa sample achieved an ethylene yield of 479 μmol min⁻¹.g⁻¹ even after 5 h of reaction. Notably, this catalyst maintained a high BET surface area even after coke accumulation, thereby enhancing accessibility for reactants and intermediates.

Acknowledgment

The authors acknowledge FAPESP for the financial support (grants 2024/12434-0, 2023/10582-9, 22/10615-1, and 20/15230-5).

References

- Xie, Q., Miao, C., Hua, Y., Gao, Z., *Ind. Eng. Chem. Res.* 60, 11707 (2021).
- Xu, S., Dong, S., Chen, T., Liu, H., Zou, X., Ji, M., Han, Z., Shu, D., Wang, C., Chen, D. *Fuel* 347, 128401 (2023).