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From Methanol to C_2 Products: Active Surface Oxygen–Mediated Pathways in Methane Conversion over Ce–LaO_x Catalysts

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Methane (CH_4) is abundant but also a potent greenhouse gas, with a global warming potential ~85 times higher than CO_2. Selective conversion of CH_4 into value-added products such as CH_3OH or C_2 hydrocarbons could mitigate its environmental impact while offering economic value. However, the high inertness of the C–H bond and the propensity for over-oxidation make selective oxidation highly challenging.[1] Ce–LaO_x mixed oxides have emerged as promising catalysts due to their excellent oxygen mobility and tunable surface properties, yet the mechanisms governing product selectivity remain poorly understood.

Our recent studies show that Ce–LaO_x exhibits strong dependence of product selectivity on temperature and gas atmosphere: Methanol prevails at 250–400 °C, whereas C_2 products dominate above 450 °C. The presence of water vapor further alters the product distribution, suggesting distinct pathways at low vs. high temperature regimes.

To elucidate the origin of this selectivity, we combine operando DRIFTS and time-resolved AP-XPS to track the evolution of surface intermediates and oxidation states under reaction conditions. TPD–MS is used to probe the adsorption, activation, and desorption behavior of reactants (CH_4, H_2O, O_2) and products (CH_3OH). Systematic comparison of atmospheres with and without O_2 and water vapor directly links surface chemistry to product selectivity, providing mechanistic insights into methane activation and C–C coupling on Ce–LaO_x catalysts.

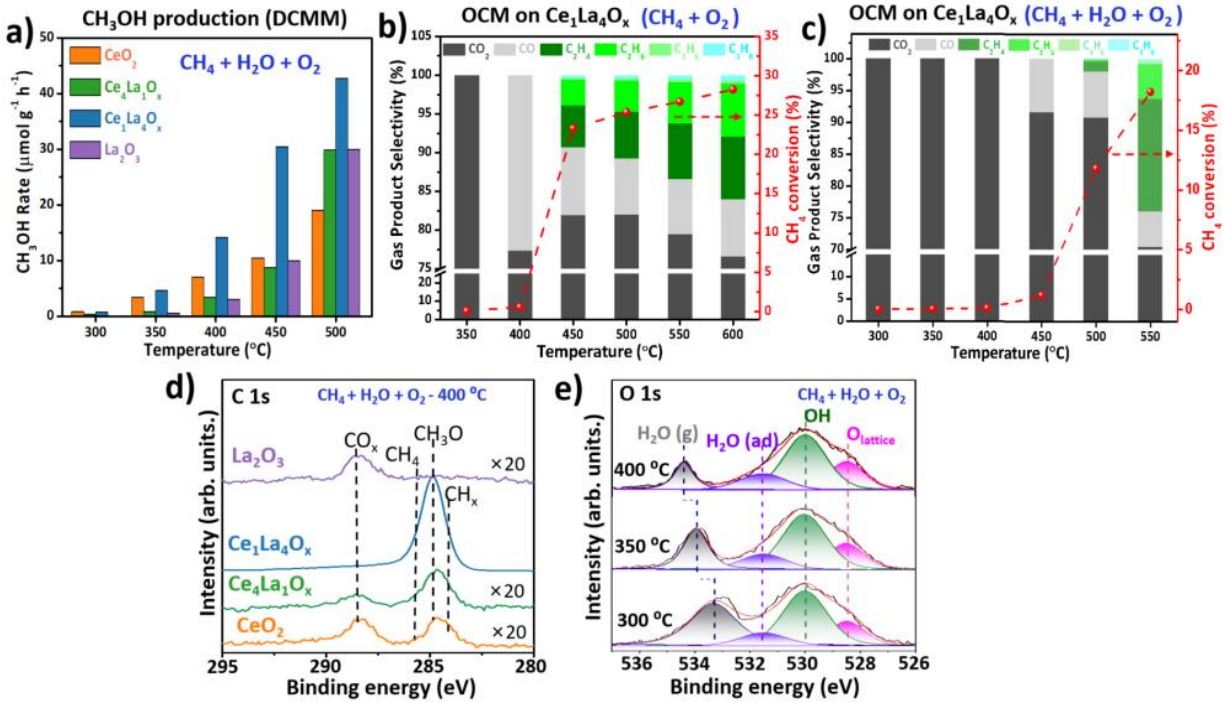

Fig. 1. (a) CH_3OH yields over Ce-LaO_x; OCM selectivity and CH_4 conversion of $Ce_1La_4O_x$ under (b) $CH_4 + O_2$ and (c) $CH_4 + H_2O + O_2$; (d) AP-XPS C 1s spectra of Ce–LaO_x under $CH_4 + O_2 + H_2O$ at 400 °C; (e) Temperature-dependent AP-XPS O 1s spectra of $Ce_1La_4O_x$ under $CH_4 + H_2O + O_2$ at 300–400 °C.

References:

1. Li, W.; Shi, J.; Tangpakonsab, P. L.; Zhang, B.; Haunold, T.; Genest, A.; Yigit, N.; Atzl, L.; Kokkonen, E.; Qin, Y.; Rupprechter, G. *ACS Catalysis* **2025,** 15, (24), 20496-20511.