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Elastic, mechanical and vibrational properties of antiperovskite nitrides ANCa3:A=As,Sb &Bi: A first-principles study

Biomass-derived molecules represent a promising resource for the development of a sustainable chemical industry. However, their relatively large size and structural complexity pose significant challenges in elucidating their catalytic conversion mechanisms. In this context, computational chemistry offers powerful tools to complement experimental investigations. This work focuses on the industrially attractive thermocatalytic conversion of methyl-levulinate (ML) to γ-valerolactone (GVL), a versatile platform molecule, (Figure 1a) over tetragonal zirconia (t-ZrO2), an inexpensive yet industrially attractive catalyst. Despite its potential, strategies to enhance catalytic performance and mitigate deactivation remain limited due to insufficient mechanistic understanding.1,2 We employed a computational approach combining periodic density functional theory (DFT), enhanced sampling molecular dynamics, and machine-learned interatomic potentials3 to investigate the adsorption, activation, and conversion of ML on t-ZrO2 surfaces. Our simulations reveal the conversion of ML into strongly bound surface carboxylates involving t-ZrO2 surface oxygen atoms, as supported by the comparison of calculated vibrational spectra with in situ and operando DRIFTS experiments (Figure 1b). These stable intermediates hinder further transformation into angelica lactones (ALs), which have been proposed as key reaction intermediates, thus providing an explanation for the observed surface poisoning. Furthermore, our findings indicate that surface hydroxyl groups might play a crucial role in destabilizing these carboxylates, thereby promoting ML conversion in line with experimental data. These insights enable the identification of deactivation pathways and active species, and might guide the rational design of better performing catalysts.

[1] Tabanelli T., et al., ACS Sustainable Chem. Eng. 2019, 7 (11), 9937−9947 [2] Cavani F. et al., ACS Sustainable Chem. Eng. 2019, 7, 9, 8317−8330 [3] Tosello Gardini, A., Raucci, U. & Parrinello, M, Nat Commun 16, 2475 (2025).

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