

“Kinetics, Reaction Mechanism and Stability of Sol-Gel Synthesized LaNiO₃ and LaCoO₃ Perovskite Catalysts for Syngas formation from Steam Reforming of Palm Oil Mill Effluent (POME)”

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The flourishing development of local oil palm industry inflicts concomitant generation of enormous, highly polluted palm oil mill effluent (POME). The prevalent open ponding treatment was land-intensive, sluggish, and incompetent to degrade POME to below discharge threshold yet being accused for greenhouse gases (CO₂ and CH₄) emission. This study investigated the potentiality of novel catalytic POME steam reforming over LaNiO₃ and LaCoO₃ to valorise pollutant-laden POME into valuable H₂-rich syngas. The POME feedstock was a brownish ($A = \sim 1.93$), acidic (pH of 5), and highly polluted (COD = ~ 70000 mg/L, BOD₅ = ~ 11000 mg/L, and TSS = ~ 7700 mg/L) wastewater. POME was composed of 99.73 mol% water and 0.27 mol% organics (mainly carboxylic acids, phenol, and alcohols). Through minimisation of total Gibbs free energy, thermodynamic simulation from 573 – 1173 K confirmed syngas production from POME steam reforming and predicted the likelihood of side reactions. Subsequently, LaNiO₃ and LaCoO₃ were synthesised using modified citrate sol-gel route. Combination of CO₂-TPD and NH₃-TPD asserted the net-acidity of LaNiO₃ and the net-basicity of LaCoO₃. Before POME steam reforming, the catalysts were reduced by H₂ to form well dispersed active metal (Ni or Co) on La₂O₃ support. Specifically, the active metal catalysed the reaction while the La₂O₃ support suppressed the coking deactivation. For both catalytic POME steam reforming, the optimum syngas yield and degradation efficiencies were determined by tuning temperature (T), POME flow rate (\dot{V}_{POME}), catalyst weight (W_{cat}), and particle size (d_{cat}). The syngas yield and degradation efficiencies increased with greater T up to 873 K, higher \dot{V}_{POME} up to 0.09 mL/min, greater W_{cat} up to 0.3 g, and smaller d_{cat} down to 74 μm . When $T \geq 973$ K, the catalysts experienced significant coking and sintering deactivation. If $\dot{V}_{POME} > 0.09$ mL/min, coking deactivation of catalysts was conspicuous. For $W_{cat} > 0.3$ g, the catalysts certainly agglomerated into a plate-like structure with reduced catalytic surface. When $d_{cat} < 74$ μm , pore occlusion of catalysts responsible for appreciably declined catalytic activity. Thus, the optimum conditions of both catalytic POME steam reforming were $T = 873$ K, $\dot{V}_{POME} = 0.09$ mL/min, $W_{cat} = 0.3$ g, and $d_{cat} = 74 - 105$ μm . However, the net-acidic LaNiO₃ granted higher amount of H₂-rich syngas ($F_{Syngas} = 132.47$ $\mu\text{mol}/\text{min}$, $y_{Syngas} = 72.60\%$, and HHV = 220.31 kJ/mol) than the net-basic LaCoO₃ ($F_{Syngas} = 86.60$ $\mu\text{mol}/\text{min}$, $y_{Syngas} = 70.71\%$, and HHV = 231.14 kJ/mol). In addition, the optimal catalytic treatment over LaNiO₃ generated a less polluted liquid condensate (COD = 326 mg/L and BOD₅ = 27 mg/L) than LaCoO₃ (COD = 435 mg/L and BOD₅ = 62 mg/L). The net-acidity favoured the cracking of POME's organics before steam reforming while net-basicity promoted the carbon-consuming reverse Boudouard reaction by facilitating CO₂ adsorption. Conclusively, the novel catalytic POME steam reforming over LaNiO₃ or LaCoO₃ is alluring as it harnesses syngas while degrading the POME wastewater.

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