MODELING OF SORPTION AND SURFACE REACTION MICROKINETICS FOR VAPOR-PHASE HYDRO(DEOXY)GENATION OF LEVULINIC ACID OVER NI/ZSM-5

Grilc, Miha[1,2], Lavrič, Žan[1,2], Vu, Hue-Tong[1], Kostyniuk, Andrii[1], Zabukovec Logar, Nataša[1,2], Djinović, Petar[1,2], Novak Tušar, Nataša[1,2], Likozar, Blaž[1]

[1] National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia
[2] University of Nova Gorica, Vipavska 13, 5000 Nova Gorica, Slovenia
E-mail: miha.grilc@ki.si

ABSTRACT

Various Ni/ZSM-5 catalysts were tested for levulinic acid (LA) hydrogenation. Higher Ni content increased γ-valerolacton (GVL) yield, showing the importance of Ni sites. Increasing Al content decreased LA conversion but increased propyl levulinate (PL) yield, indicating reaction competition. A low Al content catalyst accelerated PL to GVL conversion. The combination of experimental and modeling methodology proves to be useful for insightful exploration of sorption characteristics and catalytic activities of Ni/ZSM-5 and other mono/bi-functional catalysts.

Key words: property-activity relationship; Ni/ZSM-5; levulinic acid; vapor-phase hydrogenation; microkinetic modeling;

INTRODUCTION

The environmental crisis stems largely from massive CO2 emissions due to heavy fossil fuel reliance. Biomass conversion offers a solution, utilizing abundant lignocellulosic resources for chemical production [1,2]. Levulinic acid (LA) is a key product, with commercial importance and diverse industrial applications [3-4]. LA can further be converted into γ-valerolactone (GVL) and pentanoic/valeric acid (PA), precursors to sustainable biofuels [5, 6]. Continuous flow setups are pivotal for sustainable production, as seen in various studies [7].

This study investigates the property-activity relationship of Ni/ZSM-5 catalysts for vapor-phase hydrogenation of levulinic acid (LA) with isopropanol (IPA). We introduce a new approach combining experimental and kinetic investigation in a fixed-bed reactor at moderate temperatures and ambient pressure. By using IPA as a solvent, long operation times with less frequent maintenance are achieved. ZSM-5 supports with various Si to Al ratios were prepared using a green method, allowing systematic investigation of acidic properties and catalytic activity correlation [8]. The study builds on previous work examining nickel and framework Al in ZSM-5 and demonstrates a new methodology for determining relevant kinetic parameters. Results elucidate the relationship between catalytic sites and performance, aiding in catalyst optimization for high conversion with controlled selectivity.

EXPERIMENTAL

Catalysts were placed in a tubular reactor (9 mm inner diameter, 305 mm length) with glass beads. After heating to 400 °C under N_2 flow for 1 hour, the reactor was switched to H_2 for 2 hours. Levulinic acid (1 wt.%) in isopropanol was fed into the reactor at 0.03 g min^{-1}. Gas and liquid streams merged, passing through a 6-port valve into the reactor hosted in a hot box at 170 °C. Gas products were analyzed by micro GC Fusion, while liquid products were collected hourly and analyzed by GC-MS using calibration curves.

Molar balances were used to create partial differential equations (PDE) for gas phase and catalyst surface components. These equations were solved using MATLAB 2021b software, with PDEs modified into ordinary differential equations (ODE) for faster regression and

reduced computational time. The concentration and surface coverage of each species at each position were solved over time using ODE 15s solver. Activation energies and reaction rate constants at the reference temperature were determined through regression analysis. The Nelder-Mead algorithm minimized the objective function, while the Levenberg-Marquardt algorithm was employed to establish 95 % confidence intervals.

RESULTS AND DISCUSSION

Regardless of the catalyst, angelica lactone (AL) is consistently detected in product mixtures, indicating GVL likely forms via dehydration followed by hydrogenation. Microkinetic study suggests esterification and consecutive hydrogenation as the dominant pathway to GVL. Experiments with AL and PL as reactants confirm this, showing faster conversion to GVL than back to LA. Similar yields of GVL and PA at higher temperature and longer catalyst bed lengths suggest the same pathway with LA as reactant. This trend holds for different catalysts.
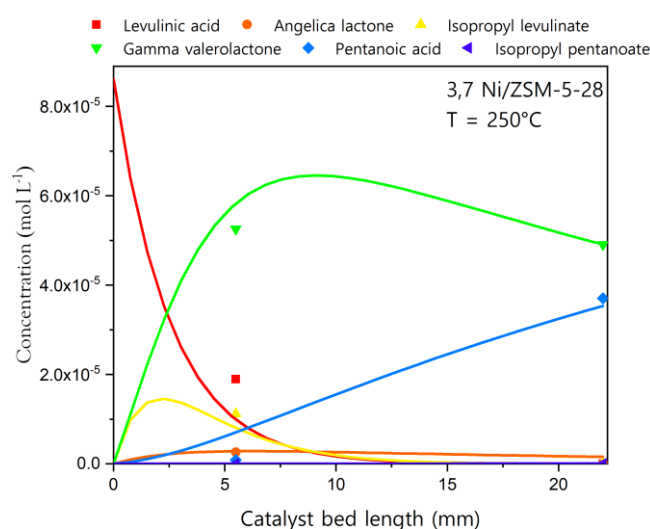

Figure 1 *Model prediction and experimental data for 3.7 Ni/ZSM-5-28 catalyst at 250 °C.*

CONCLUSION

This study examined Ni/ZSM-5 catalysts for LA hydrogenation. Microkinetic modeling revealed a dominant pathway to GVL. The 3.7Ni/ZSM-5-28 catalyst was optimal for GVL production at 210°C. Catalysts rich in Al favored esterification, while those high in Si to Al ratio enhanced PA formation. This research shows catalyst versatility and introduces a novel modeling approach for process optimization.

REFERENCES

[1]   A. Lambin, J.M. Corpart, UN sustainable development goals and green chemistry, key points for sustainably innovating at Roquette, a global leader in plant-based ingredients, Curr. Opin. Green Sustain. Chem. 13 (2018) 137–139. https://doi.org/10.1016/j.cogsc.2018.04.007.

[2]   E. Emmanouilidou, S. Mitkidou, A. Agapiou, N.C. Kokkinos, Solid waste biomass as a potential feedstock for producing sustainable aviation fuel: A systematic review, Renew. Energy 206 (2023) 897–907. https://doi.org/10.1016/J.RENENE.2023.02.113.

[3]   360 Market Updates, Global levulinic acid market research report 2020, 2020. https://www.360marketupdates.com/global-levulinic-acid-market-14828624.

[4]   D. Di Menno Di Bucchianico, Y. Wang, J.C. Buvat, Y. Pan, V. Casson Moreno, S. Leveneur, Production of levulinic acid and alkyl levulinates: a process insight, Green Chem. 24 (2022) 614–646. https://doi.org/10.1039/D1GC02457D.

[5]   W. Leitner, J. Klankermayer, S. Pischinger, H. Pitsch, K. Kohse-Höinghaus, Advanced Biofuels and Beyond: Chemistry Solutions for Propulsion and Production, Angew. Chemie Int. Ed. 56 (2017) 5412–5452. https://doi.org/10.1002/ANIE.201607257.

[6]   W.P. Xu, X.F. Chen, H.J. Guo, H.L. Li, H.R. Zhang, L. Xiong, X. De Chen, Conversion of levulinic acid to valuable chemicals: a review, J. Chem. Technol. Biotechnol. 96 (2021) 3009–3024. https://doi.org/10.1002/JCTB.6810.

[7]   R. Gérardy, D.P. Debecker, J. Estager, P. Luis, J.C.M. Monbaliu, Continuous Flow Upgrading of Selected C2-C6Platform Chemicals Derived from Biomass, Chem. Rev. 120 (2020) 7219–7347. https://doi.org/10.1021/ACS.CHEMREV.9B00846/ASSET/IMAGES/MEDIUM/CR9B00846_0154.GIF.

[8]   H.T. Vu, I. Arčon, D.O. De Souza, S. Pollastri, G. Dražić, J. Volavšek, G. Mali, N. Zabukovec Logar, N. Novak Tušar, Insight into the interdependence of Ni and Al in bifunctional Ni/ZSM-5 catalysts at the nanoscale, Nanoscale Adv. 4 (2022) 2321–2331. https://doi.org/10.1039/D2NA00102K.