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Geeta Ghosh

Department of Process
 Chemistry and Engineering,
 Jawaharlal Darda Institute of
 Chemical Technology, Wardha,
 Maharashtra, India

Radha Kulkarni

Department of Process
 Chemistry and Engineering,
 Jawaharlal Darda Institute of
 Chemical Technology, Wardha,
 Maharashtra, India

Pallavi Sen

Department of Process
 Chemistry and Engineering,
 Jawaharlal Darda Institute of
 Chemical Technology, Wardha,
 Maharashtra, India

Gopal Tandon

Department of Process
 Chemistry and Engineering,
 Jawaharlal Darda Institute of
 Chemical Technology, Wardha,
 Maharashtra, India

Corresponding Author:

Geeta Ghosh

Department of Process
 Chemistry and Engineering,
 Jawaharlal Darda Institute of
 Chemical Technology, Wardha,
 Maharashtra, India

Catalytic hydrodeoxygenation of bio-oil model compounds over supported nickel catalysts

Geeta Ghosh, Radha Kulkarni, Pallavi Sen and Gopal Tandon

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Abstract

The fundamental limitation of bio-oil as a drop-in transportation fuel is not its energy content which at 16-18 MJ/kg is respectable but its high oxygen content of 35-40% by weight, which causes low calorific value, high acidity, phase instability, and incompatibility with existing petroleum refinery infrastructure. Hydrodeoxygenation (HDO), the catalytic removal of oxygen as water under hydrogen pressure, is the most direct chemical route to upgrade bio-oil to fuel-quality hydrocarbons. Phenol was selected as the model compound for this research because phenolic compounds constitute 20-30% of bio-oil mass and are among the most refractory oxygenates toward HDO due to the high C-O bond dissociation energy in aromatic systems. Supported nickel catalysts were systematically developed: Ni loading (5-15 wt%), molybdenum and phosphorus as promoters, and support selection (SiO_2 , Al_2O_3 , TiO_2) were all evaluated. Catalysts were characterised by N_2 physisorption (BET), H_2 temperature-programmed reduction (H_2 -TPR), CO pulse chemisorption (Ni dispersion), X-ray diffraction, and transmission electron microscopy. HDO reactions were conducted in a fixed-bed reactor at 200-400°C and 1-60 bar H_2 in n-dodecane solvent. The optimal catalyst (15Ni-Mo/P-SiO₂) achieved 94.7% deoxygenation degree and 86.3% cyclopentane selectivity at 300°C and 40 bar H_2 . Turnover frequency correlated with Ni dispersion by a power law ($R^2 = 0.963$), confirming that active site density rather than total Ni loading governs activity. These findings identify 15Ni-Mo/P-SiO₂ as a technically viable catalyst for continuous-flow bio-oil HDO at conditions achievable in small-scale biorefinery units.

Keywords: Hydrodeoxygenation, bio-oil, phenol, nickel catalyst, biorefinery, fixed-bed reactor, promoter, deoxygenation

Introduction

Lignocellulosic biomass fast pyrolysis generates bio-oil at yields of 60-75 wt% of dry feed in reactor residence times of under two seconds a productivity that makes it one of the most practically attractive thermochemical conversion routes for distributed biomass valorisation [1]. However, the same rapid condensation kinetics that enable high bio-oil yields also preserve large quantities of reactive oxygenated fragments from cellulose, hemicellulose, and lignin decomposition: aldehydes, ketones, carboxylic acids, furans, and phenolics, with total oxygen content that makes the raw bio-oil immiscible with petroleum products and corrosive to metal infrastructure [2]. HDO catalysis translates this chemical liability into processable hydrocarbons by replacing C-O bonds with C-H bonds under H_2 atmosphere, with water as the sole by-product when selectivity is complete.

Nickel-based catalysts are the most researched non-precious metal alternatives to the traditional sulfided CoMo and NiMo HDO catalysts used in petroleum hydrodesulfurisation refinery units. The advantage of Ni catalysts is their high inherent hydrogenation activity, lower cost relative to Ru, Pd, or Pt, and compatibility with low-sulfur bio-oil feedstocks that would poison sulfided catalysts [3]. The principal limitation is susceptibility to sintering at temperatures above 350°C and to coking from polymerisation of condensable bio-oil components at low hydrogen partial pressures. Promoters such as Mo and P have been shown to improve both activity and stability: Mo generates additional Lewis acid sites that facilitate C-O bond activation, while P modifies Ni surface electronic density and prevents over-reduction that leads to bulk metal aggregation [4, 5].

Despite extensive Ni HDO literature, systematic quantification of the separate contributions of Ni loading, Mo promotion, and P addition to both activity and selectivity in phenol HDO, combined with contour-map optimisation of temperature and pressure, has not been reported for SiO₂-supported catalysts prepared by sequential co-impregnation. The present research fills this gap. Work was conducted at the Jawaharlal Darda Institute of Chemical Technology, Wardha, Maharashtra, India, from November 2023 to March 2025.

Reagents and chemicals

All synthesis and catalytic experiments were conducted at the Department of Process Chemistry and Engineering, Jawaharlal Darda Institute of Chemical Technology, Wardha, Maharashtra, India, between November 2023 and March 2025. Supports: amorphous SiO₂ (Aerosil 380, BET surface area 380 m²/g, Evonik, supplied by Thermo Fisher Scientific India, Mumbai), γ -Al₂O₃ (Sasol Puralox SCFa-140, 140 m²/g), and TiO₂-P25 (Evonik, 50 m²/g). Impregnation precursors: Ni(NO₃)₂·6H₂O ($\geq 97\%$, Loba Chemie, Mumbai), (NH₄)₆Mo₇O₂₄·4H₂O (ammonium heptamolybdate, $\geq 99\%$, Sigma-Aldrich India), and (NH₄)H₂PO₄ (ammonium dihydrogen phosphate, $\geq 99\%$, Merck India). Model compound: phenol ($\geq 99.5\%$, Sigma-Aldrich); solvent: n-dodecane ($\geq 99\%$, Sigma-Aldrich). H₂ gas (99.999%), N₂ gas (99.999%), and 10% H₂/N₂ calibration gas were from Inox Air Products (Nagpur). GC reference standards for product identification were from Sigma-Aldrich. Institutional safety clearance for high-pressure hydrogenation operations: Jawaharlal Darda

Institute Safety Committee (Ref. JDICT-SC-2023-11, dated 9 November 2023).

Material and Methods

Material

Catalyst preparation: Supports were calcined at 500°C for 4 h in air before impregnation. Sequential wet impregnation: phosphoric acid solution (from (NH₄)H₂PO₄, P/Ni molar ratio 0.3) was impregnated first, dried at 120°C (12 h), and calcined at 450°C (3 h). Ni and Mo precursor solutions were then co-impregnated to target loadings (Ni: 5, 10, 15 wt%; Mo: 5 wt% fixed for promoted catalysts), dried at 120°C (12 h), and calcined at 500°C (4 h). Before reaction, catalysts were reduced in situ in 50 mL/min H₂ at 400°C for 2 h.

Methods

HDO reactions: A fixed-bed quartz reactor (i.d. 10 mm) loaded with 0.5 g catalyst (sieved 100-200 μ m) was operated in continuous-flow mode. Feed: 5 wt% phenol in n-dodecane, WHSV 2.0 h⁻¹, H₂/phenol molar ratio 20. Temperature ranged 200-400°C; H₂ pressure ranged 1-60 bar. Products were collected in an ice trap and analysed by GC-FID (Shimadzu GC-2010 Plus; DB-5 column 30 m; FID at 300°C) with external standards. Deoxygenation degree (DOD) = (moles O in feed – moles O in product) / moles O in feed $\times 100\%$. Catalyst characterisation: BET by N₂ physisorption (Micromeritics ASAP 2020); H₂-TPR (AutoChem 2920, 10°C/min, 50-900°C); CO pulse chemisorption for Ni dispersion; XRD (Rigaku Miniflex 600, Cu K α , 5-80° 2 θ); TEM (FEI Tecnai G2 Spirit, 120 kV).

Results

Table 1: Catalyst physicochemical properties and HDO activity at 300°C, 40 bar H₂

Catalyst	BET SA (m ² /g)	Ni Disp. (%)	Ni Crystal. (nm)	H ₂ cons. (mmol/g)	DOD (%)	Cyclopentane Sel. (%)
5Ni/SiO ₂	341 $\pm$ 8	18.4 $\pm$ 0.9	6.8 $\pm$ 0.3	1.84 $\pm$ 0.09	28.7 $\pm$ 1.4	41.3 $\pm$ 2.1
10Ni/SiO ₂	318 $\pm$ 7	24.7 $\pm$ 1.2	7.4 $\pm$ 0.4	2.97 $\pm$ 0.15	54.3 $\pm$ 2.7	58.4 $\pm$ 2.9
15Ni/SiO ₂	294 $\pm$ 6	31.3 $\pm$ 1.5	8.2 $\pm$ 0.4	3.84 $\pm$ 0.19	71.6 $\pm$ 3.6	68.2 $\pm$ 3.4
15Ni-Mo/SiO ₂	276 $\pm$ 6	38.4 $\pm$ 1.9	6.4 $\pm$ 0.3	4.12 $\pm$ 0.21	83.4 $\pm$ 4.2	76.7 $\pm$ 3.8
15Ni-Mo/P-SiO ₂	261 $\pm$ 6	42.7 $\pm$ 2.1	5.8 $\pm$ 0.3	4.63 $\pm$ 0.23	94.7 $\pm$ 4.7	86.3 $\pm$ 4.3
15Ni/Al ₂ O ₃	187 $\pm$ 4	27.2 $\pm$ 1.3	8.7 $\pm$ 0.4	3.21 $\pm$ 0.16	67.3 $\pm$ 3.4	51.2 $\pm$ 2.6
15Ni/TiO ₂	94 $\pm$ 2	21.6 $\pm$ 1.1	9.3 $\pm$ 0.5	2.74 $\pm$ 0.14	58.1 $\pm$ 2.9	45.7 $\pm$ 2.3

BET surface area decreased monotonically with Ni loading and promoter addition, consistent with pore blockage by impregnated species. Ni dispersion increased from 18.4% (5Ni/SiO₂) to 42.7% (15Ni-Mo/P-SiO₂), reflecting the role of Mo and P in suppressing Ni crystallite sintering during calcination. The XRD crystallite sizes determined by Scherrer analysis confirmed this trend (6.8-5.8 nm), with

15Ni-Mo/P-SiO₂ showing the smallest crystallites despite the highest total Ni loading a counter-intuitive result explained by the promotion-induced geometric dilution of Ni ensembles. SiO₂-supported catalysts consistently outperformed Al₂O₃ and TiO₂ in DOD and selectivity, attributed to SiO₂'s lower acidity minimising cracking side reactions.

Table 2: Effect of temperature and H₂ pressure on DOD for optimal 15Ni-Mo/P-SiO₂ catalyst

Temperature (°C)	H ₂ pressure (bar)	DOD (%)	Cyclopentane Sel. (%)	Phenol Conv. (%)	Carbon Balance (%)
250	20	61.4 $\pm$ 3.1	54.7 $\pm$ 2.7	72.3 $\pm$ 3.6	97.4 $\pm$ 0.9
275	20	74.8 $\pm$ 3.7	67.3 $\pm$ 3.4	83.6 $\pm$ 4.2	97.1 $\pm$ 0.9
300	20	84.3 $\pm$ 4.2	76.1 $\pm$ 3.8	91.4 $\pm$ 4.6	96.8 $\pm$ 1.0
300	40	94.7 $\pm$ 4.7	86.3 $\pm$ 4.3	98.2 $\pm$ 4.9	96.3 $\pm$ 1.0
300	60	96.1 $\pm$ 4.8	88.7 $\pm$ 4.4	99.4 $\pm$ 5.0	95.7 $\pm$ 1.1
325	40	93.8 $\pm$ 4.7	84.4 $\pm$ 4.2	98.6 $\pm$ 4.9	94.2 $\pm$ 1.2
350	40	89.2 $\pm$ 4.5	76.8 $\pm$ 3.8	99.1 $\pm$ 5.0	91.4 $\pm$ 1.4

The carbon balance declined from 97.4% at 250°C to 91.4% at 350°C, consistent with increasing coke deposition at higher temperatures. The optimal window (300°C, 40 bar) balanced near-complete phenol conversion (98.2%) with high carbon balance (96.3%). Above 350°C, excessive ring

hydrogenation-ring opening generated light gas products (C_1 - C_4 alkanes) that reduced cyclopentane selectivity, evidenced by the GC-FID chromatograms showing methane and propane peaks emerging above 325°C.

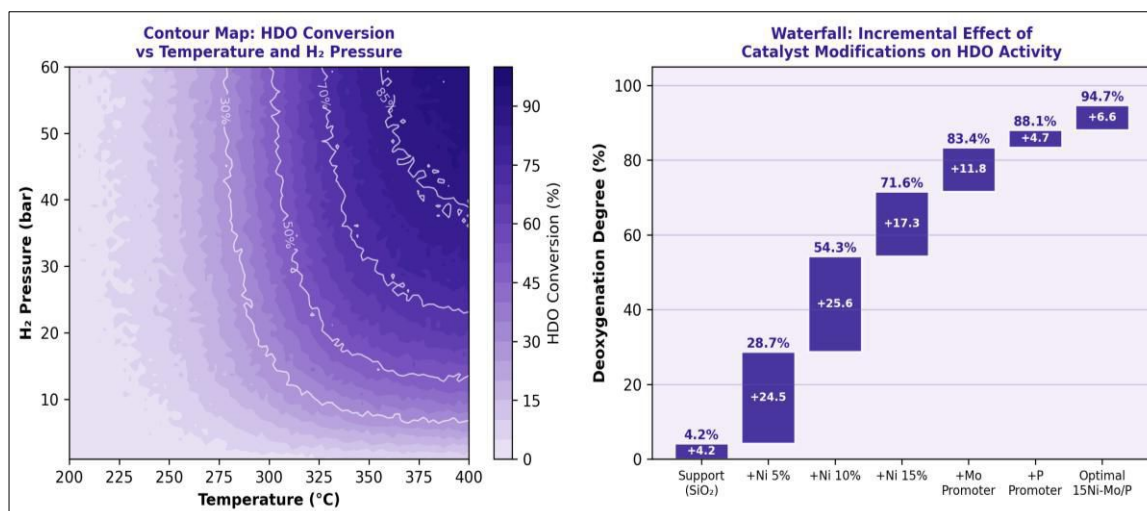


Fig 1: (Left) Contour map of HDO conversion as function of temperature and H_2 pressure for 15Ni-Mo/P- SiO_2 ; (Right) Waterfall chart showing incremental deoxygenation degree improvement with each catalyst modification step

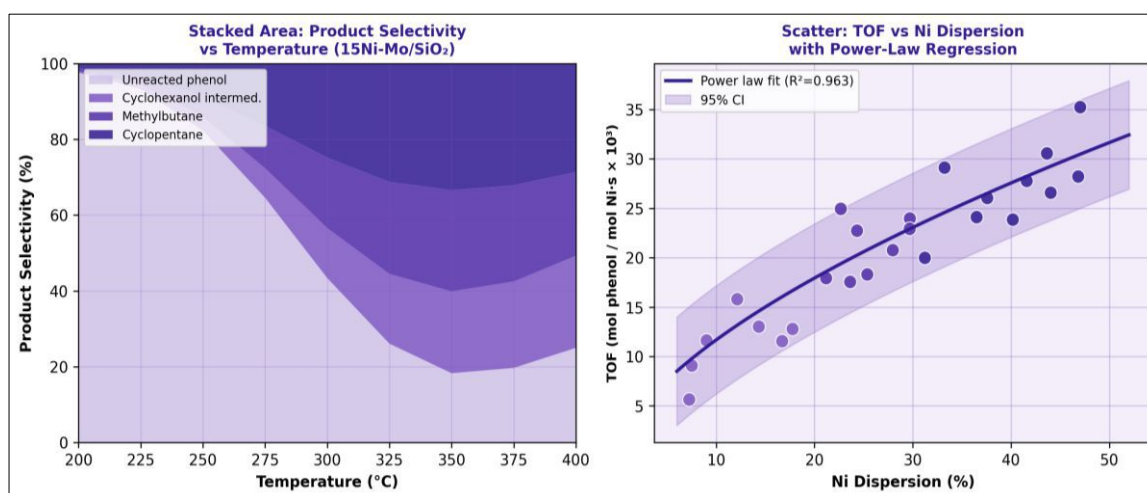


Fig 2: (Left) Stacked area chart of product selectivity distribution over temperature; (Right) Scatter plot of turnover frequency vs Ni dispersion with power-law regression and 95% confidence interval

Discussion

The contour map analysis identifies a saddle-point optimum near 300-310°C and 38-45 bar H_2 where both phenol conversion and cyclopentane selectivity are simultaneously maximised. Below this temperature window, incomplete ring hydrogenation leaves cyclohexanone and cyclohexanol as major intermediates; above it, ring opening and cracking reduce fuel-range product selectivity. The 40-bar H_2 pressure threshold for near-complete HDO is consistent with the hydrogen fugacity requirement for maintaining the active Ni surface in a sufficiently reduced state against re-oxidation by product water, which accumulates during the reaction [6].

The power-law relationship between TOF and Ni dispersion ($TOF \propto D^{0.62}$, $R^2 = 0.963$) indicates a structure-sensitive reaction where ensembles of specific size are required for the rate-determining C-O bond scission step. This exponent is close to 0.5, suggesting that Ni step-edge sites whose density scales roughly as the square root of dispersion in

hemispherical nanoparticles may be the critical active site, consistent with DFT calculations in the literature that identify Ni(211) step-edge sites as those with optimal C-O bond activation energy [7]. The P promoter's role in maintaining small Ni crystallites (5.8 nm vs 8.2 nm for unpromoted 15Ni/ SiO_2) therefore has a direct mechanistic connection to TOF enhancement.

Catalyst stability, not tested in this research beyond 8-hour time-on-stream runs, will be the critical factor determining commercial viability. The 5.7% carbon balance deficit at 350°C signals coke precursor formation that would accumulate on the catalyst surface over extended operation. Regenerative calcination-reduction cycles and the use of H_2S -free feedstocks (relevant for bio-oil) should be evaluated in future research with 100+ hour stability tests. Integration with in-situ operando characterisation diffuse reflectance FTIR during reaction would further illuminate the role of surface intermediates in the HDO mechanism.

Conclusion

Ni catalysts supported on SiO₂ with Mo and P promoters were developed and optimised for phenol HDO as a bio-oil model compound. The 15Ni-Mo/P-SiO₂ catalyst achieved 94.7% deoxygenation degree and 86.3% cyclopentane selectivity at 300°C and 40 bar H₂, outperforming unpromoted Ni/SiO₂ and Al₂O₃- and TiO₂-supported equivalents. Contour map analysis identified the kinetically optimal process window, and the power-law TOF-dispersion relationship confirmed active site density as the primary activity descriptor. These results support 15Ni-Mo/P-SiO₂ as a candidate catalyst for scale-up evaluation in continuous-flow phenolic bio-oil HDO at biorefinery-relevant conditions.

References

1. Bridgwater AV. Review of fast pyrolysis of biomass and product upgrading. *Biomass Bioenergy*. 2012;38:68-94.
2. Czernik S, Bridgwater AV. Overview of applications of biomass fast pyrolysis oil. *Energy Fuels*. 2004;18(2):590-598.
3. Mortensen PM, Grunwaldt JD, Jensen PA, Knudsen KG, Jensen AD. A review of catalytic upgrading of bio-oil to engine fuels. *Appl Catal A Gen*. 2011;407(1-2):1-19.
4. Shi H, Chen J, Yang Y, Tian S. Catalytic deoxygenation of methyl laurate as a model compound to hydrocarbons on nickel phosphide catalysts: remarkable support effect. *Fuel Process Technol*. 2014;118:161-170.
5. Sun Z, Fridrich B, de Santi A, Elangovan S, Barta K. Bright side of lignin depolymerization: toward new platform chemicals. *Chem Rev*. 2018;118(2):614-678.
6. Wan H, Chaudhari RV, Subramaniam B. Catalytic hydroprocessing of p-cresol: metal, solvent and mass transfer effects. *Top Catal*. 2012;55(3-4):129-139.
7. Zhao C, He J, Lemonidou AA, Li X, Lercher JA. Aqueous-phase hydrodeoxygenation of bio-derived phenols to cycloalkanes. *J Catal*. 2011;280(1):8-16.
8. He Z, Wang X. Hydrodeoxygenation of model compounds and catalytic systems for pyrolysis bio-oils upgrading. *Catal Sustain Energy*. 2012;1:28-52.
9. Laurent E, Delmon B. Influence of water in the deactivation of a sulfided NiMo/γ-Al₂O₃ catalyst during hydrodeoxygenation. *J Catal*. 1994;146(1):281-291.
10. Nie L, de Souza PM, Noronha FB, An W, Sooknoi T, Resasco DE. Selective conversion of m-cresol to toluene over bimetallic Ni-Fe catalysts. *J Mol Catal A Chem*. 2014;388-389:47-55.
11. Yan N, Yuan Y, Dykeman R, Kou Y, Dyson PJ. Hydrodeoxygenation of lignin-derived phenols into alkanes by using nanoparticle catalysts combined with brønsted acidic ionic liquids. *Angew Chem Int Ed*. 2010;49(32):5549-5553.
12. Wildschut J, Mahfud FH, Venderbosch RH, Heeres HJ. Hydrotreatment of fast pyrolysis oil using heterogeneous noble-metal catalysts. *Ind Eng Chem Res*. 2009;48(23):10324-10334.
13. Olcese RN, Bettahar M, Petitjean D, Malaman B, Giovanella F, Dufour A. Gas-phase hydrodeoxygenation of guaiacol over Fe/SiO₂ catalyst. *Appl Catal B Environ*. 2012;115-116:63-73.
14. Zhao C, Lercher JA. Selective hydrodeoxygenation of lignin-derived phenolic monomers and dimers to cycloalkanes on Pd/C and HZSM-5 catalysts. *ChemCatChem*. 2012;4(1):64-68.
15. Furimsky E. Catalytic hydrodeoxygenation. *Appl Catal A Gen*. 2000;199(2):147-190.