
Title

Alkali-driven selectivity of products on carbon-supported Ni-based catalysts during the HDO of guaiacol

Abstract

The catalytic hydrodeoxygenation (HDO) of guaiacol as a representative bio-oil molecule was studied using a series of carbon-supported Ni-based catalysts. The promoter effect of alkali metals (Ca and Mg) on the catalytic activity and selectivity was verified. Catalysts were prepared by wetness incipient method and N₂ gas adsorption/desorption isotherms, X-ray diffraction, reduction/desorption temperature-programed, and CO chemisorption analysis were performed to characterize the catalysts. In terms of the initial reaction-rate catalysts with 1 wt% alkali-promoters showed an increase in the activity up to ca. 1.4 and 1.2 times higher on Ni-Ca(1 %)/AC and Ni-Mg(1 %)/AC, respectively, compared to Ni/AC catalyst. The increase to 5 wt% in alkali promoters slightly reduced the initial activity of Ni. However, the turn-over frequencies estimated showed higher values when alkali content is increased from 1 wt% to 5 wt%. These apparent contradictory results suggest the formation of new active sites along reaction, probably constituted by a mixture of oxides NiO-CaO and NiO-MgO. The selectivity of products showed remarkable changes due to the presence of alkali-promoters and a mechanism or reaction is proposed based on the kinetics of formation and evolution of products. Mg-promoted led to the formation of cyclohexane. On the contrary, Ca-promoted catalysts led the mechanism to representative benzene yields. This is remarkable result regarding the efficiency of a HDO biorefinery. In general, it can be concluded that Ni-based catalysts promoted with alkali metals are an economical alternative for the catalytic conversion of representative target molecules from a bio-oil feed. © 2024 Elsevier Ltd

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Alkali-promotors; Biorefinery; Guaiacol conversion; Ni-based catalysts; Selectivity

Index Keywords

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References

Toumey C., Reading Feynman into nanotechnology: a text for a new science, Techné: Res Phil Technol, 13, pp. 133-168, (2008); (2023); Jin W., Pastor-Perez L.,

Villora-Pico J.J., Sepulveda-Escribano A., Gu S., Reina T.R., Investigating new routes for biomass upgrading: “H₂-Free” hydrodeoxygenation using Ni-based catalysts, *ACS Sustain Chem Eng*, 7, pp. 16041-16049, (2019); Dabros T.M.H., Kramer H., Hoj M., Sprenger P., Grunwaldt J.-D., Gabrielsen J., Et al., The influence of active phase loading on the hydrodeoxygenation (HDO) of ethylene glycol over promoted MoS₂/MgAl₂O₄ catalysts, *Top Catal*, 62, pp. 752-763, (2019); Cordero-Lanzac T., Palos R., Arandes J.M., Castano P., Rodriguez-Mirasol J., Cordero T., Et al., Stability of an acid activated carbon based bifunctional catalyst for the raw bio-oil hydrodeoxygenation, *Appl Catal B: Environ*, 203, pp. 389-399, (2017); Cordero-Lanzac T., Hita I., Garcia-Mateos F.J., Castano P., Rodriguez-Mirasol J., Cordero T., Et al., Adaptable kinetic model for the transient and pseudo-steady states in the hydrodeoxygenation of raw bio-oil, *Chem Engin J*, 400, (2020); Fan X.-D., Wu Y.-J., Tu R., Sun Y., Jiang E.-C., Xu X.-W., Hydrodeoxygenation of guaiacol via rice husk char supported Ni based catalysts: the influence of char supports, *Renew Energy*, 157, pp. 1035-1045, (2020); Wu X., Ge Q., Zhu X., Vapor phase hydrodeoxygenation of phenolic compounds on group 10 metal-based catalysts: reaction mechanism and product selectivity control, *Catal Today*, 365, pp. 143-161, (2021); Blanco E., Dongil A.B., Garcia-Fierro J.L., Escalona N., Insights in supported rhenium carbide catalysts for hydroconversion of lignin-derived compounds, *Appl Catal A: Gen*, 599, (2020); Blanco E., Diaz de Leon J.N., Garcia-Fierro J.L., Escalona N., Study of supported bimetallic MoRe carbides catalysts for guaiacol conversión, *Catal Today*, 367, pp. 290-296, (2021); Rong Z., Lu J., Yu G., Li J., Wang M., Zhang S., Promoting selective hydrodeoxygenation of guaiacol over amorphous nanoporous NiMnO₂, *Catal Comm*, 140, (2020); Matos J., Diaz K., Garcia V., Cordero T.C., Brito J.L., Methane transformation in presence of carbon dioxide on activated carbon supported nickel-calcium catalysts, *Catal Lett*, 109, pp. 163-169, (2006); Matos J., Rosales M., Promoter effect upon activated carbon-supported Ni-based catalysts in dry methane reforming,

Eurasian Chem Technol J, 14, pp. 5-7, (2012); Benedetti V., Ail S.S., Patuzzi F., Baratieri M., Valorization of char from biomass gasification as catalysts support in dry methane reforming, Front Chemistry, 7, (2019); Li X., Wang Y., Zhang G., Sun W., Bai Y., Zheng L., Et al., Influence of Mg-promoted Ni-based catalyst supported on coconut shell carbon for CO₂ methanation, Chem Select, 4, pp. 838-845, (2019); Zhang J., Sudduth B., Sun J., Kovarik L., Engelhard M.H., Wang Y., Elucidating the active site and the role of alkali metals in selective hydrodeoxygenation of phenols over iron-carbide-based catalyst, ChemSusChem, 14, pp. 4546-4555, (2021); Wu C., Shen C., Gong Y., Wang J., Domino reactions for biofuel production from zymotic biomass wastes over bifunctional Mg-containing catalysts, ACS Sustain Chem Eng, 7, pp. 18943-18954, (2019); Matos J., Brito J., Laine J., Activated carbon supported Ni-Mo: effects of pretreatments and composition on catalyst reducibility and on ethylene conversion, Appl Catal A: General, 152, pp. 27-42, (1997); Matos J., Laine J., Ethylene conversion on activated carbon supported NiMo catalysts: effect of the Support, Appl Catal A: General, 241, pp. 25-38, (2003); Laine J., Severino F., Labady M., Gallardo J., The synergistic participation of the support in sulfided Ni-Mo/C hydrodesulfurization catalysts, J Catal, 138, pp. 145-149, (1992); Laine J., Severino F., Labady M., Optimum Ni composition in sulfided Ni-Mo hydrodesulfurization catalysts: effect of the support, J Catal, 147, pp. 355-357, (1994); Blanco E., Cabeza P., Naharro Ovejero V., Contreras C., Dongil A.B., Tyrone Ghampson I., Et al., Effect of carbon support and functionalization on the synthesis of rhenium carbide and its use on HDO of guaiacol, Catal Today, 420, (2023); Diaz K., Garcia V., Matos J., Activated carbon supported Ni-Ca: influence of reaction parameters on activity and stability of catalyst on methane reformation, Fuel, 86, pp. 1337-1344, (2007); Goscianska J., Pietzrak R., Matos J., Catalytic performance of ordered mesoporous carbons modified with lanthanides in dry methane reforming, Catal Today, 301, pp. 204-216, (2018); Velasco L.F., Carmona R.J., Matos J., Ania C.O., Performance of activated

carbons in consecutive phenol photooxidation cycles, *Carbon*, 73, pp. 206-215, (2014); Andrade M.A., Carmona R.J., Mestre A.S., Matos J., Carvalho A.P., Ania C.O., Visible light driven photooxidation of phenol on TiO₂/Cu-loaded carbon catalysts, *Carbon*, 76, pp. 183-192, (2014); Matos J., Fierro V., Montana R., Rivero E., Martinez de Yuso A., Zhao W., Et al., High surface area microporous carbons as photoreactors for the catalytic photodegradation of methylene blue under UV-vis irradiation, *Appl Catal A: General*, 517, pp. 1-11, (2016); Walker P.L., Rusinko F., Austin L.G., Gas Reactions of Carbon, *Adv Catal*, 11, pp. 133-221, (1959); Walker P.L., Janov J., Hydrophilic oxygen complexes on activated graphon, *J Coll Inter Science*, 28, pp. 449-458, (1968); Radovic L.R., Walker P.L., Jenkins R.G., Importance of carbon active sites in the gasification of coal chars, *Fuel*, 62, pp. 849-856, (1983); Bandosz T.J., Policicchio A., Florent M., Li W., Poon P.S., Matos J., Solar light-driven photocatalytic degradation of phenol on S-doped nanoporous carbons: the role of functional groups in governing activity and selectivity, *Carbon*, 156, pp. 10-23, (2020); Ania C.O., Armstrong P.A., Bandosz T.J., Beguin F., Carvalho A.P., Celzard A., Et al., Engaging nanoporous carbons in “Beyond Adsorption” applications: characterization, challenges and performance, *Carbon*, 164, pp. 69-84, (2020); Thommes M., Kaneko K., Neimark A.V., Olivier J.P., Rodriguez-Reinoso F., Rouquerol J., Et al., Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), *Pure Appl Chem*, 87, pp. 1051-1069, (2015); Dubinin M.M., Description of adsorption equilibria of vapors on zeolites over wide ranges of temperature and pressure, *Adv Chem Ser*, 102, pp. 69-85, (1971); Helmich M., Luckas M., Pasel C., Bathen D., Characterization of microporous activated carbons using molecular probe method, *Carbon*, 74, pp. 22-31, (2014); Matos J., Garcia-Lopez E., Palmisano L., Garcia A., Marci G., Influence of activated carbon in TiO₂ and ZnO mediated photo-assisted degradation of 2-propanol in gas-solid regime, *Appl Catal B*, 99, pp. 170-180, (2010); Yung T.Y., Huang L.Y., Chan T.Y., Wang K.S., Liu T.Y., Chen P.T., Et al.,

Synthesis and characterizations of Ni-NiO nanoparticles on PDDA-modified graphene for oxygen reduction reaction, *Nanoscale Res Lett*, 9, (2014); Calles J.A., Carrero A., Vizcaino A.J., Garcia-Moreno L., Hydrogen production by glycerol steam reforming over SBA-15-supported nickel catalysts: effect of alkaline earth promoters on activity and stability, *Catal Today*, 227, pp. 198-206, (2014); Kaewdaeng S., Sintuya P., Nirunsin R., Biodiesel production using calcium oxide from river snail shell ash as catalyst, *Energy Proc*, 138, pp. 937-942, (2017); Ghods B., Meshkani F., Rezaei M., Effects of alkaline earth promoters on the catalytic performance of the nickel catalysts supported on high surface area mesoporous magnesium silicate in dry reforming reaction, *Int J Hydrogen Energy*, 41, pp. 22913-22921, (2016); Dongil A.B., Bachiller-Baeza B., Rodriguez-Ramos I., Garcia-Fierro J.L., Escalona N., The effect of Cu loading on Ni/carbon nanotubes catalysts for hydrodeoxygenation of guaiacol, *RSC Adv*, 6, pp. 26658-26667, (2016); Awadallah A.E., Abdel-Mottaleb M.S., Aboul-Enein A.A., Yonis M.M., Aboul-Gheit A.K., Catalytic decomposition of natural gas to CO/CO₂-free hydrogen production and carbon nanomaterials using MgO-supported monometallic iron family catalysts, *Chem Eng Comm*, 202, pp. 163-174, (2015); Noh J.S., Schwarz J.A., Relationship between metal ion adsorption and catalytic properties of carbon-supported nickel catalysts, *J Catal*, 127, pp. 22-33, (1991); Meyer V.J., Niggemann M., Highly chemoselective calcium-catalyzed propargylic deoxygenation, *Chem A Eur J*, 18, pp. 4687-4691, (2012); Zhang J., Li C., Chen X., Guan W., Lian C., Insights into the reaction pathway of hydrodeoxygenation of dibenzofuran over MgO supported noble-metals catalysts, *Catal Today*, 319, pp. 155-163, (2019); Romero A., Yustos P., Santos A., Dehydrogenation of cyclohexanol to cyclohexanone: influence of methylcyclopentanols on the impurities obtained in ϵ -caprolactam, *Ind Eng Chem Res*, 42, pp. 3654-3661, (2003)

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