Hydroconversion of lignocellulose-derived molecules over oxide-supported catalysts

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Location of Hungary



Hungary Area: 93,030 km² Population: 9,678,000 Capital: Budapest Official language: Hungarian Currency: Forint (HUF)

Hungary



Budapest





Budapest











Research Centre for Natural Sciences



• the new building was inaugurated in 2013





Instruments













Instruments











Trip to Tezpur (By walk ③)



Trip to Tezpur (By plane and car ~ 25 hr)



INDO-HUNGARIAN INTER-GOVERNMENTAL SCIENCE & TECHNOLOGY COOPERATION PROGRAMME

From February 1, 2021 to January 31, 2024

Applied research and development for industrial realization of lignin recycling and conversion to value-added international market products
Theme and tasks of this project



- From July 1, 2016 to June 30, 2019
- ✓ Biochemicals and biofuels from lignocellulosic biomass by green catalytic processes

Lignocellulose as source of carbon and energy

Current carbon and energy resources





<u>Utilization of waste biomass</u> (agriculture, forestry, food- and paper industry)

Organic compounds \implies CO₂ + H₂O + energy \uparrow photosynthesis

- \succ less CO₂ emission
- keep biological carbon in bound form as long as possible (fuel, chemical)
- > Our goal is to establish the scientific background for biotechnological processes

Structure of lignocellulose





Gy. Onyestyák, Gy. Novodárszki et al., Catal. Sci. Technol. 6 (2016) 4516 Chem. Soc. Rev. 41 (2012) 8075 2016,6,



Conversion of lignocellulosic biomass to useful materials



Levulinic acid-based chemicals



Gy. Novodárszki et al., RSC Adv. 4 (2014) 2081; J. Tukacs, Gy. Novodárszki et al., Green Chem. 14 (2012) 2057

Catalysis





- Catalyst lowers the activation energy for both forward and reverse reactions
- Catalysts increase reaction rate without themselves being changed
- The design of catalysts implies a compromise involving mechanical, physico-chemical, and catalytic properties

Catalysis: homogeneous, heterogeneous



- > The catalyst usually is a solid material, whereas the reactants are gaseous or liquid substances
- Easy separation of the product and recycling of the catalyst allows for efficient processes on large scales

Consecutive reactions of Levulinic Acid



Metal and acid site concentrations of the catalysts and their relative amount determine the dominating reaction path of LA conversion to GVL and in GVL hydrogenolysis.

Gy. Novodárszki et al., Catal. Sci. Technol. 9 (2019) 2291; Gy. Novodárszki et al., Reaction Kinetics, Mechanisms and Catalysis 126 (2019) 795

Catalyst preparation for Levulinic Acid hydroconversion

Catalyst	Precursor	Support	
4,6Co/SiO ₂ (I)			
8,1Co/SiO ₂ (I)		SiO ₂ (Cabosil M5; 200 m ² /g)	
13,3Co/SiO ₂ (I)			
8,0Co/SiO ₂ (II)	Co(NO₃)₂*6H₂O	SiO ₂ (Cabosil EH5; 385 m ² /g)	
7,7Co/Al ₂ O ₃		γ-Al ₂ O ₃ (Ketjen CK300; 170 m ² /g)	
7,2Co/HBETA		H-Beta (Valfor Cp; Si/Al = 12,5; 582 m ² /g)	
6,6Ni/SiO ₂ (II)	Ni(CH ₃ COO) ₂ *4H ₂ O	SiO ₂ (Cabosil EH5; 385 m ² /g)	

Impregnation: metal salt solution

> Calcination: 500 °C, 2 h
$$\longrightarrow \frac{\text{Co}_3\text{O}_4}{\text{NiO}}$$

> In situ reduction: 450 °C, 2 h, H₂ $\longrightarrow \frac{\text{Co}^0}{\text{Ni}^0}$

> Catalytic experiments were carried out in a continuous flow-through fixed-bed microreactor

Determination of crystallite size: X-ray diffraction (XRD)



- \succ With thermal decomposition of precursors 20-40 nm Co₃O₄ and NiO crystallites were formed
- > On the reduced catalysts: Ni⁰: 6-10 nm (higher hydrogenation activity)

Co⁰ : 20-40 nm

- > The size of the metal particles does not change on the used catalysts
- \blacktriangleright The specific surface area of the SiO₂ support does not affect the size of the Co oxide and metallic Co crystallites

Gy. Novodárszki et al., Microporous and Mesoporous Materials 360 (2023) 112732; Gy. Novodárszki et al., Catalysis Today 336 (2019) 50

Reducibility (H₂-TPR) and acidity (FT-IR spectra of adsorbed pyridine)

- \succ The degree of reduction at 450 °C:
 - SiO₂ supported $\sim 90 \%$
 - Al_2O_3 supported ~55 %
 - H-Beta supported ~65 %

- > 1446/1597 cm⁻¹ : pyridine coordinating to the silanol group by H-bonding
- > $1450/1608 \text{ cm}^{-1}$: pyridine coordinated at Lewis acid (L) sites
- > $1545/1637 \text{ cm}^{-1}$: the pyridinium ion formed at the Brönsted acid (B) sites
- The interaction of the unreduced Co and Ni oxide species with the silica support create weak Lewis acid sites.

Gy. Novodárszki et al., Microporous and Mesoporous Materials 360 (2023) 112732; Gy. Novodárszki et al., Catalysis Today 336 (2019) 50; Gy. Novodárszki et al., Reac. Kin., Mech.and Cat. 126 (2019) 795

Stabilization of the catalyst as a function of the Co content

> On the 4.6Co/SiO₂(I) catalyst AL intermediate was detected in the product mixture from the 13^{th} hour of the reaction

- > Angelica lactone is the intermediate in the production of GVL
- \blacktriangleright GVL is formed on Co/SiO₂ and Co/Al₂O₃ catalysts after the steady state

Gy. Novodárszki et al., Catal. Sci. Technol. 9 (2019) 2291

Effect of metal and support in the hydroconversion of LA

> The hydroconversion of LA on the Ni catalyst does not stop at the formation of GVL

> On H-Beta zeolite due to the Brønsted acid centers of the support, the GVL ring opens in the direction of pentanoic acid formation

Gy. Novodárszki et al., Catal. Sci. Technol. 9 (2019) 2291; Gy. Novodárszki et al., Reaction Kinetics, Mechanisms and Catalysis 126 (2019) 795

Effect of temperature in the hydroconversion of LA

- ➢ At higher reaction temperature LA can be converted into 2-MTHF
- \blacktriangleright On Co/Al₂O₃ catalyst GVL is selectively formed in the hydroconversion of LA in a wide temperature range

Gy. Novodárszki et al., Catal. Sci. Technol. 9 (2019) 2291

Selective 2-MTHF production on 8,1Co/SiO₂(I)

- Surface carboxylate anions were detected
- > The enol form of levulinate, 4-hydroxy-3-pentenoate, is the activated form leading to the formation of GVL
- > At higher reaction temperature LA can be converted into 2-MTHF

Gy. Novodárszki et al., Catal. Sci. Technol. 9 (2019) 2291

Hydrodeoxygenation of γ-valerolactone

Conversion of GVL on catalysts with different acidity resulted in different product mixtures

Over Co/H-Beta catalyst containing strong Brønsted and Lewis acid sites PA was formed from GVL trough pentenoic acid intermediate
 On Co/Al₂O₃ and Co/SiO₂ catalysts containing only Lewis acid sites 2-MTHF was formed

Gy. Novodárszki et al., Microporous and Mesoporous Materials 360 (2023) 112732; Gy. Novodárszki et al., Catalysis Today 336 (2019) 50; Gy. Novodárszki et al., Catalysts 13 (2023) 7

Mechanism of GVL ring opening

> Over Co/H-Beta catalyst pentanoic acid was formed through pentenoic acid intermediate

> On Co/Al₂O₃ and Co/SiO₂ catalysts the intermediate of GVL hydroconversion to 2-MTHF is 2-hydroxy-5-methyltetrahydrofuran

Gy. Novodárszki et al., Microporous and Mesoporous Materials 360 (2023) 112732; Gy. Novodárszki et al., Catalysis Today 336 (2019) 50; Gy. Novodárszki et al., Catalysts 13 (2023) 7

Conclusions of LA and GVL hydroconversion

- The interaction of the unreduced Co and Ni oxide species with the silica support create weak Lewis acid sites.
- Using Co/SiO₂ and Ni/SiO₂ catalysts consecutive steps of LA hydroconversion can be selectively directed to more valuable products, such as GVL, 2-MTHF or PA by applying appropriate reaction conditions.
- The most abundant surface species are Co-carboxylates formed from LA. The hydrogenation activity is affected also by the carboxylate coverage of the catalyst surface.
- Increasing the reaction temperature, the reaction of LA HDO over the Co/SiO₂ catalyst shifts from GVL formation to 2-MTHF formation. (the carboxylate coverage of the active cobalt centers is reduced)
- The C-O bond in the GVL ring breaks giving either 2-MTHF or PA primary products. Selectivity is controlled by the acidity of the supported Co catalyst.
- > Co/SiO₂ and Co/ γ -Al₂O₃ catalysts have high activity and selectivity in GVL hydroconversion to 2-MTHF.
- > Over Co/H-beta with Broensted acid sites the formation of pentanoic acid is preferred.

Guaiacol-based chemicals

Products from GUA could replace the materials of fossil origin

Gy. Novodárszki et al., Molecules (2023), under review

Reaction pathways of guiacol hydrodeoxygenation

optimization of HDO catalysts

 \succ

Catalysts Precursors		Supports	
SiO ₂			
5Co/SiO ₂			
10Co/SiO_2	$Co(NO_3)_2 \cdot 6H_2O$	SiO (Cabosil: EH5)	
15Co/SiO_2		510 ₂ (Cabosii, E115)	
$10Cu/SiO_2$	$Cu(CH_3Coo)_2 * H_2O$		
5Ni/SiO ₂	$Ni(NO_3)_2 \cdot 6H_2O$		
Al_2O_3			
$10Co/Al_2O_3$	$Co(NO_3)_2 \cdot 6H_2O$		
$5Ni/Al_2O_3$	$Ni(NO_2)$ · 6H ₂ O	γ -Al ₂ O ₃ (Alfa Aesar)	
20Ni/Al ₂ O ₃			
$0,5Pd/Al_2O_3$	$Pd(NH_3)_4(NO_3)_2$		
$Al_2O_3(P)$			
$5Ni/Al_2O_3(P)$	$Ni(NO_2)_2 \cdot 6H_2O$	γ -Al ₂ O ₃ (Alfa Aesar)	
$20 \text{Ni}/\text{Al}_2\text{O}_3(\text{P})$		impregnated with H_3PO_4 solution	
$0,5Pd/AI_2O_3(P)$	$Pd(NH_3)_4(NO_3)_2$		
H-BETA(12,5)			
10Co/HBETA(12,5)	$Co(NO_3)_2 \cdot 6H_2O$	Beta zeolit (Si/Al=12,5; CP814E)	
5N1/HBETA(12,5)	$N_1(NO_3)_2 \cdot 6H_2O$		
20N1/HBEIA(12,5)			
$\mathbf{\Pi} - \mathbf{D} \mathbf{E} \mathbf{I} \mathbf{A} (1 9)$		Data realit $(C_{1}^{2}/\Lambda_{1}, 10, CD_{2}^{2})$	
$\frac{JINI}{HDEIA} (19)$	$Ni(NO_3)_2 \cdot 6H_2O$	Beta Zeolii (SI/AI=19; CP814C)	
$\frac{20101}{100} = \frac{100}{100} $			
$A_1 O_3 (\Pi - D \Pi N)$			

Catalysts	Precursors	Supports	
SiO ₂			
5Co/SiO ₂			
10 Co/SiO $_2$	$Co(NO_3)_2 \cdot 6H_2O$	SiO (Cabosil: EH5)	
15Co/SiO_2		SIO_2 (Cabosii, EII5)	
10Cu/SiO ₂	$Cu(CH_3Coo)_2*H_2O$		
5Ni/SiO ₂	$Ni(NO_3)_2 \cdot 6H_2O$		
Al_2O_3			
10Co/Al ₂ O ₃	$Co(NO_3)_2 \cdot 6H_2O$		
$5Ni/Al_2O_3$	Ni(NO ₂) ₂ ·6H ₂ O	γ -Al ₂ O ₃ (Alfa Aesar)	
20Ni/Al ₂ O ₃			
$0,5Pd/Al_2O_3$	$Pd(NH_3)_4(NO_3)_2$		
$Al_2O_3(P)$			
$5Ni/Al_2O_3(P)$	$Ni(NO_2)_2 \cdot 6H_2O$	γ -Al ₂ O ₃ (Alfa Aesar)	
$\frac{20Ni}{Al_2O_3(P)}$		impregnated with H_3PO_4 solution	
$0,5Pd/Al_2O_3(P)$	$Pd(NH_3)_4(NO_3)_2$		
H-BETA(12,5)			
10Co/HBETA (12,5)) $\operatorname{Co}(\mathrm{NO}_3)_2 \cdot 6\mathrm{H}_2\mathrm{O}$	Beta zeolit (Si/Al=12,5; CP814E)	
5N1/HBETA(12,5)	$N_1(NO_3)_2 \cdot 6H_2O$		
20N1/HBETA (12,5)			
H-BETA(19)			
SN1/HBETA(19)	$Ni(NO_3)_2 \cdot 6H_2O$	Beta zeolit (Si/AI=19; CP814C)	
20N1/HBETA(19)	N 3' L L		
AI_2O_3 (HI-BIM)		γ -Al ₂ O ₃ (Bimodal; Alfa Aesar)	
$SN1/AI_2O_3$ (HI-BIM)) $N_1(NO_3)_2 \cdot 6H_2O$		

Catalyst preparation for Guaiacol hydroconversion

Catalyst	Precursor	Support
5Ni/SiO ₂		SiO ₂ (Cabosil EH5; 385 m ² /g)
5Ni/Al ₂ O ₃		γ-Al ₂ O ₃ (Alfa Aesar)
20Ni/Al ₂ O ₃	Ni(NO ₃) ₂ ·6H ₂ O	
5Ni/Al₂O₃(P)		γ-Al ₂ O ₃ (Alfa Aesar)
20Ni/Al₂O₃(P)		impregnated with H ₃ PO ₄ solution
5Ni/HBETA		H-Beta (Valfor Cp; Si/Al = 12,5; 582 m ² /g)

Catalytic experiments were carried out in a continuous flow-through fixed-bed microreactor

Catalysts structure and reducibilty

- γ-Al₂O₃ is the only detectable phase of catalysts with low metal loading (NiO crystallites are well dispersed on the Al₂O₃ surface)
- The XRD pattern of 20Ni/Al₂O₃ and 20Ni/Al₂O₃(P) catalysts show the reflections of NiO

Gy. Novodárszki et al., Molecules (2023), under review; Gy. Novodárszki et al., Reaction Kinetics, Mechanisms and Catalysis 126 (2019) 795; A. Vikár, Gy. Novodárszki et al., Journal of Catalysis 404 (2021) 67

FT-IR spectra of adsorbed pyridine

- ▶ 1446/1597 cm⁻¹ : pyridine coordinating to the silanol group by H-bonding
- > 1450/1608 cm⁻¹ : pyridine coordinated at Lewis acid (L) sites
- > 1545/1637 cm⁻¹ : the pyridinium ion formed at the Brönsted acid (B) sites

Gy. Novodárszki et al., Molecules (2023), under review; A. Vikár, Gy. Novodárszki et al., Journal of Catalysis 404 (2021) 67

Catalyst characterisation: Summary

Catalysts	Metal content ^a wt%	SSA ^b m²/g	Reduction degree ^c	Average Ni ⁰ diameter ^d	Acidity ^e
SiO ₂	-	385	-	-	-
5Ni/SiO ₂	5.6	252	91	11	$\mathbf{L}_{\mathbf{w}}$
Al ₂ O ₃	-	196	-	-	L _s
5Ni/Al₂O₃	5.2	192	4.5	<5	$\mathbf{L}_{\mathbf{s}}$
20Ni/Al ₂ O ₃	19.9	190	68	11	$\mathbf{L}_{\mathbf{s}}$
$Al_2O_3(P)$	-	167	-	-	$\mathbf{L}_{\mathbf{s}}$
$5Ni/Al_2O_3(P)$	5.1	165	0.5	<5	$\mathbf{L}_{\mathbf{s}}$
$20\mathrm{Ni}/\mathrm{Al}_{2}\mathrm{O}_{3}(\mathrm{P})$	20.1	160	65	14	L _s
HBETA	-	582	-	-	L _s /B _s
Ni/HBETA	5.1	579	70	10	L_s/B_s

^aDetermined by the ICP-MS method.

^bSpecific Surface Area (SSA), determined by the Brunauer-Emmett-Teller (BET) method.

^cCalculated from temperature-programmed H₂-reduction (H₂-TPR) curves.

^dCalculated from the XRPD pattern of the catalysts reduced at 450 °C for 1 h in H₂ flow.

^eDetermined by the FT-IR band of adsorbed pyridine (Py) (L_w - weak Lewis acid sites; L_s - strong Lewis acid sites; L_s/B_s - strong Lewis and Brønsted acid sites).

Activity of supports

- \succ SiO₂ support is inactive in the conversion of GUA
- \triangleright On Al₂O₃, Al₂O₃(P) and HBETA support demethylation (DME) and transalkylation (AL) are the main reactions
 - CAT derivatives are the main products
 - Demethoxylation (DMO) and dehydroxylation (DHO) also takes place
 - PHE derivatives were also formed

Activity and stability

300 °C, 10 bar, 1 g_{cat}/g_{GUA} *h, $H_2/GUA = 20$

- \succ The activity of 5Ni/SiO₂ and 5Ni/Al₂O₃ catalysts did not change with TOS
 - O-free compounds were mainly formed at 300 °C
- > The activity of 5Ni/HBETA catalyst decrease in function of TOS

Effect of temperature

- weak Lewis acid sites
- strong Lewis acid sites
- strong Lewis and Brønsted acid sites

10 bar, 1 g_{cat}/g_{GUA} *h, H₂/GUA=20

- \blacktriangleright At 225 °C cyclohexanols were the main products on 5Ni/SiO₂ and 5Ni/Al₂O₃ catalysts
 - With temperature the yield of benzenes increased
- > The amount of PHE derivatives increased with temperature on 5Ni/HBETA

Activity and stability of Al₂O₃ and Al₂O₃(P) supported catalysts

Activity and stability of Al₂O₃ and Al₂O₃(P) supported catalysts

FT-IR spectra of phenol adsorbed on Al₂O₃ and Al₂O₃ support

Gy. Novodárszki et al., Molecules (2023), under review

Conclusions of GUA hydroconversion

- > The sequential steps of GUA hydroconversion can be controlled by modifying the alumina support.
- > Demethylation of GUA on Al_2O_3 , $Al_2O_3(P)$ and HBETA supports leads to catechol formation.
- ➢ Ni/SiO₂ and Ni/Al₂O₃ catalyzed hydroconversion of GUA to O-free compounds like cyclohexane.
- > At lower temperature and space time cyclohexanols were formed in large amounts.
- > With temperature the yield of benzenes increased.
- Ni/Al₂O₃(P) catalysts are selective to aromatics. These catalysts remain active in demethylation and demethoxylation, but lose their ability to hydrogenate the aromatic ring. Weak interaction of phenol intermediate was observed on the Al₂O₃(P) support.
- > The HBETA zeolite supported Ni catalyst activity decrease due to strong Lewis and Brønsted acidity.

Nemzeti Kutatási, Fejlesztési És Innovációs Hivatal

Thank you for your kind attention!

The Earth has enough resources to meet the needs of all but not enough to satisfy the greed of even one person.

- Mahatma Gandhi-

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