Gamma-valerolakton hidrokonverziója alumínium-oxid és Beta zeolit hordozós Co katalizátorokon: a katalizátor savasságának szerepe a reakcióút szabályozásában

Hydroconversion of γ-valerolactone over Co/γ-Al₂O₃ and Co/H-Beta zeolite catalysts: Acidity and selectivity

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Lignocellulose as carbon- and energy source



Products from levulinic acid platform compound



Reaction pathways



- Selectivity is controlled by the relative rates of the **metal-catalyzed hydrogenation** and the **acid catalyzed ring opening**.

- The corresponding rate constants are in turn dependent on the **balance of the metallic and acidic functions**, as well as the **applied reaction condition**.

Catalysts

γ-Al₂O₃ (Ketjen CK300), **H-Beta** (Valfor Cp; Si/Al = 12,5)

> Impregnation: $Co(NO_3)_2 * 6H_2O$ solution (7.2% Co/γ -Al₂O₃; 7.8%Co/H-Beta)

> Calcination: 500 °C, 2h \longrightarrow Co₃O₄ (on γ -Al₂O₃ and H-Beta)

> In situ reduction: 450 °C, 2h, $H_2 \longrightarrow CoO (on \gamma - Al_2O_3)$ Co²⁺ (on H-Beta, ion-exchange)

Acidic properties (pyridine adsorption, FT-IR)



Pyridine adsorption at 200 °C for 30 min, then evacuated at this temperature for 30 min. L and B denotes characteristic bands of pyridine bound to Lewis or Brønsted acid centers, respectively.

H-Beta:

- Brønsted acid sites (bridging OH-groups)
- Lewis acid sites (extra framework Al sites [AlO⁺], defective framework Al-sites)

Co/H-Beta:

- Lower Brønsted acid site concentration (1/3) due to Co^{2+} ion-exchange
- New Lewis acid sites (Co^{2+} ions) at the expense of defective Al-sites

γ-Al₂O₃:

- Two types of Lewis acid sites (tetrahedral or octahedral Al with one coordinative unsaturation)
- No Brønsted acid sites

Co/γ - Al_2O_3 :

- Same type of Lewis acid sites in somewhat lower concentration
- No Brønsted acid sites

Catalyst characterization

Support or Catalyst	Co content wt%	SSA m² g ⁻¹	Pore diameter nm	Co reduction degree %	Average Co ^o diameter nm	Brønsted sites mmol g ⁻¹	Lewis sites mmol g ⁻¹
H-Beta	_	582	-	-	-	0.366	0.427
Co/H-Beta	7.2	508	-	65 (66)*	32	0.122	0.457
Al ₂ O ₃	-	189	9.1	-	-	-	0.167
Co/Al ₂ O ₃	7.7	159	8.7	56 (98)*	11	-	0.150

* Reduction degree up to 450 °C (up to 800 °C) from H_2 -TPR

After reduction at 450 °C:

XRD measurements: only Co⁰ in Co/H-Beta, both Co⁰ and CoO in Co/ γ -Al₂O₃

Co/H-Beta: Co^{0} (2/3) and Co^{2+} (1/3) in ion-exchange positions

 $Co/\gamma-Al_2O_3$: **Co**⁰ (1/3) and **CoO** (2/3, strongly interacting with the support)

Adsorption of CO



Catalytic results

GVL conversion on γ -Al₂O₃ and H-Beta supports

	т, °С	Conv., %	Yield, mol %			
Catalyst			PE	PA	C4⁼	Others
γ-Al ₂ O ₃	225	5.3	5.0	0.3	-	-
	250	8.0	7.7	0.3	-	-
	275	13.7	13.2	0.5	-	-
	225	16.9	14.6	0.9	1.1	0.3
H-Beta	250	24.7	18.2	1.7	4.3	0.6
	275	33.9	25.0	1.6	6.6	0.7



Main product: pentenoic acid

Main product: pentenoic acid or 2-MTHF

In situ DRIFT spectroscopic investigations

GVL (430 ppm)/He flow, continuous heating from 30 to 275 °C at a rate of 2 °C/min (transient mode)



Monodentate: on Lewis acid sites

Brønsted acid sites are not affected

Bidentate: in reaction with surface OH-groups (water formation)

Same processes on Co/γ -Al₂O₃ and Co/H-Beta in He carrier gas

GVL ring opening on Brønsted and Lewis acid sites



- is in equilibrium with carbenium ion intermediates
- desorption regenerates Brønsted acid sites
- formation of -CH=CH- groups

On Lewis acid sites:

- in reaction with Lewis acid (Al⁺) Lewis base (O⁻) pair sites
- formation of carboxyl group via proton transfer followed by product desorption and site regeneration
- formation of strongly bound carboxylate species via transformation of the activated complex or re-adsortion of pentenoic acid
- formation of CH₂=CH- groups

 Co/γ -Al₂O₃ catalyst





- The formation of saturated surface carboxylate in the presence of H₂ cleavage of the [CH₃CH-O] bond proceeds
- Carboxylate species are strongly bound to the alumina surface
- Increasing of the temperature speeds up all the reactions
- Increase of pentanoic acid desorption rate from Co/γ -Al₂O₃ is not so steep than that of hydrogenation
- The carboxylic acid product appeared in the gas phase over Co/γ-Al₂O₃ only at high temperatures (>250 °C), whereas formation of 2-MTHF prevails at lower temperatures

Co/H-Beta catalyst

GVL (430 ppm)/H₂ flow, continuous heating from 30 to 275 °C at a rate of 2 °C/min (transient mode) 982 Β õ GVI 0.1 8 2878 õ T, °C . °С 30 a.u. 50 50 .70 70 90 90 100



- The ring opening reaction and pentanoic acid formation on the Co/H-Beta catalyst is catalyzed mainly by Brønsted acid sites, which are not blocked by carboxylate
- In the lack of strong carboxylate bonding the Brønsted acid catalyzed ring opening reaction was strongly accelerated by the elevation of the reaction temperatures
- Pentanoic acid formation prevails over the Co/H-Beta catalyst even at temperature as low as 200 °C

Conclusions

- Acid sites of γ -Al₂O₃ and zeolite H-Beta induces the ring opening of GVL at the [CH₃CH-O] bond giving **pentenoate carboxylate**, bound to Lewis acid sites, and **pentenoic acid**.
- Introduction of Co hardly influenced the Lewis acidity of γ -Al₂O₃, whereas the Lewis acid sites in H-Beta were partly converted to new type of Lewis acid sites represented by Co lattice cations.
- Over these latter sites no carboxylate species were formed, thus the concentration of surface carboxylates was significantly lower on Co/H-Beta than on the H-Beta support. **The Brønsted acid sites did not take part in carboxylate formation.**
- In the presence of hydrogenation function (Co⁰) and H₂, the unsaturated carboxylate species were hydrogenated to saturated surface carboxylates, while the hydrogenation of the carbonyl group leading to intermediate of 2-MTHF formation was also initiated.
- The strong bonding of monodentate carboxylates to the Lewis sites of γ-Al₂O₃ prevented the acid catalyzed ring opening reaction at temperatures below about 250 °C, thus the 2-MTHF formation prevailed due to the dominating hydrogenation activity.
- In contrast, carboxylate formation did not block the Brønsted acid sites of H-Beta thus the ring opening reaction leading to PA formation prevailed over the hydrogenation reaction above about 175 °C.

Köszönöm a megtisztelő figyelmet!

