

# One-pot Conversion of Furfural to $\gamma$ -Valerolactone over Heteropolyacid Supported on Zr-Beta Zeolites

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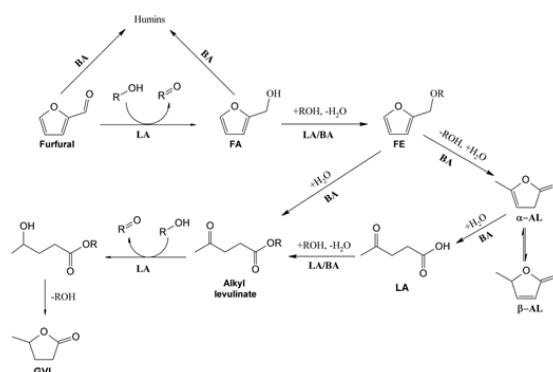
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$\gamma$ -Valerolactone (GVL), which can be obtained from C5-C6 carbohydrates, has recently been considered as a sustainable platform molecule for the production of various fuels and chemicals, such as polymer precursors, diesel and jet fuels [1]. However, the production of GVL from biomass typically involves a multi-step process, the acid-catalyzed dehydration of sugars to furfural, the hydrogenation and hydrolysis of furfural to levulinic acid (LA) and the hydrogenation of LA to GVL, which increases the process cost. Therefore, several researchers have studied the integrated process for the direct synthesis of GVL from furfural through the sequential Meerwein-Ponndorf-Verley (MPV) and hydrolysis reactions using zeolites with Lewis and Brønsted acid sites (e.g., Zr-Al-Beta), as shown in Fig. 1 [2, 3]. Although a Beta zeolite containing Sn or Zr (Lewis acids) and Al (Brønsted acids) was able to catalyze the sequential MPV and hydrolysis of furfural, the final GVL yield was low and the conversion required harsh conditions (e.g., 190 °C). In this work, we have investigated the effect of heteropolyacid (HPA) addition as the source of Brønsted acidity to Zr-Beta zeolites on the selective conversion of furfural to GVL.

Zr-Beta was prepared via a post-synthesis procedure, which consisted of the dealumination of Al-Beta followed by a solid-state ion exchange with zirconocene dichloride. Two HPAs (HPW and HSiW) were impregnated onto Zr-Beta by the incipient-wetness method. The catalytic tests were conducted in a 80 ml autoclave reactor with 0.11 M of furfural in 20 mL of 2-propanol with 80 mg of catalysts at 140–160 °C.

Characterization of HPA/Zr-Beta with XRD, N<sub>2</sub>-physisorption, Raman, and pyridine-FT-IR confirmed the formation of Brønsted acid sites without any significant pore blockage, while UV-Vis and XPS measurements indicated that Zr was predominantly coordinated within the zeolite framework, inducing isolated Lewis acid sites. The catalytic tests with HPA/Zr-Beta showed that the addition of HPA to the Zr-Beta markedly enhanced the GVL production with HPW being the more active HPA component (Table 1). The GVL yield over HPW/Zr-Beta reached ~63% after 24 h and was 3 times higher than that over Zr-Al-Beta. The hydrolysis rate of FA over HPW/Si-Beta was also considerably faster than that over Al-Beta, suggesting that the higher GVL yield over HPA/Zr-Beta is mainly due to its enhanced Brønsted acidity.



**Fig. 1.** Reaction networks for GVL production from furfural.

**Table 1** Catalytic test results over various catalysts.

Catalyst	Temp (°C)	Time (h)	Conv (%)	GVL yield (%)
Zr-Beta-5 (5% Zr)	140	6	100	12.3
5% HSiW/Zr-Beta-5	140	6	100	14.6
5% HPW/Zr-Beta-5	140	6	100	23.0
5% HPW/Zr-Beta-5*	160	24	100	62.5
Zr-Al-Beta [2]	170	24	100	22.6

## REFERENCES

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