

Supporting information

Alkali cations enhance Zr Beta zeolite selectivity in citronellal Meerwein-Ponndorf-Verley reduction

Jan Přech*, Jun Xie, Mariya Shamzhy, Jiří Čejka*

Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Albertov 6, 128 43 Prague 2, Czech Republic

*Corresponding authors: jan.prech@natur.cuni.cz, phone: +420 221 95 1322 (J.P.),
jiri.cejka@natur.cuni.cz, phone: +420 221 95 1032 (J.C.)

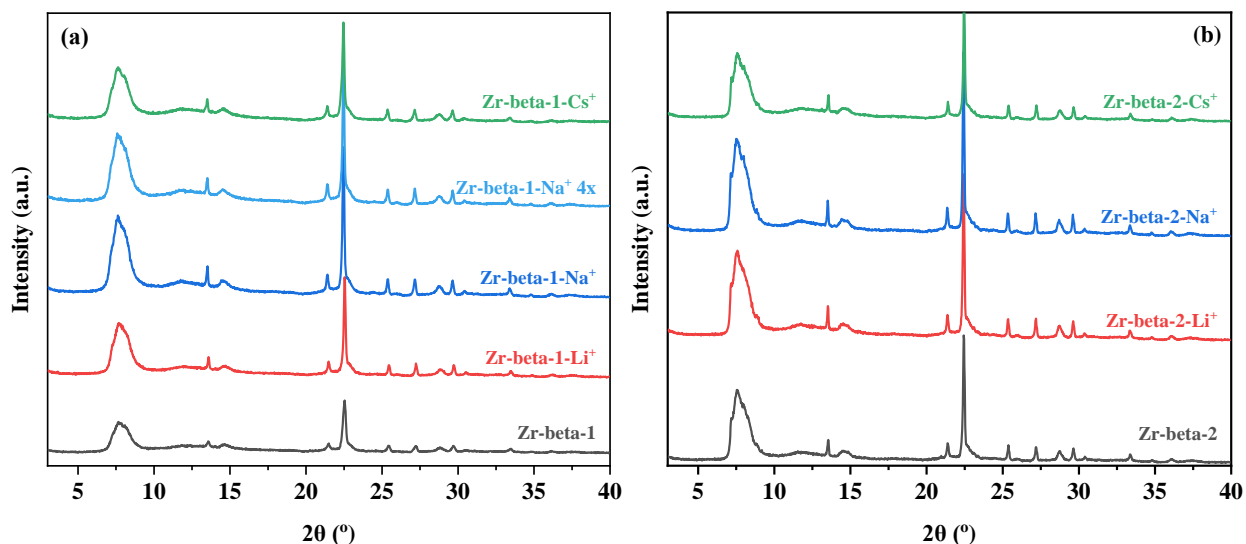


Figure S1: X-ray Diffraction (XRD) patterns of (a) Zr-beta-1 (Zr-beta-1-M⁺; M = Na⁺, Li⁺, Cs⁺) and (b) Zr-beta-2 (Zr-beta-2-M⁺; M = Na⁺, Li⁺, Cs⁺) before and after ion exchange

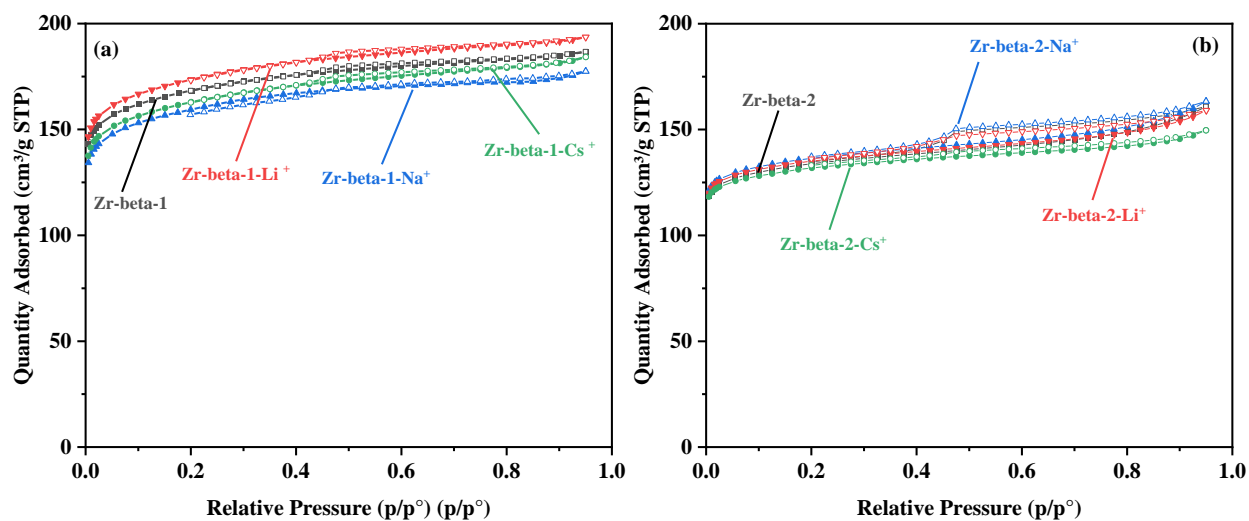


Figure S2: N₂ physisorption isotherms of the catalysts Zr-beta-1-M⁺ and Zr-beta-2-M⁺, M = Na⁺, Li⁺, Cs⁺, with solid and empty symbols denoting adsorption and desorption, respectively

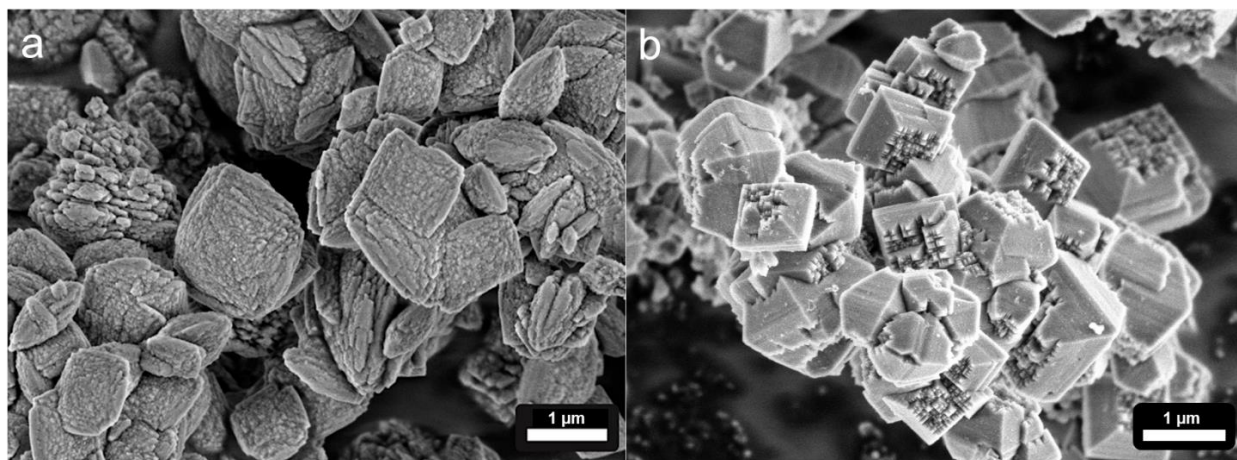


Figure S3: Scanning electron microscopy (SEM) images of (a) Zr-beta-1 and (b) Zr-beta-2

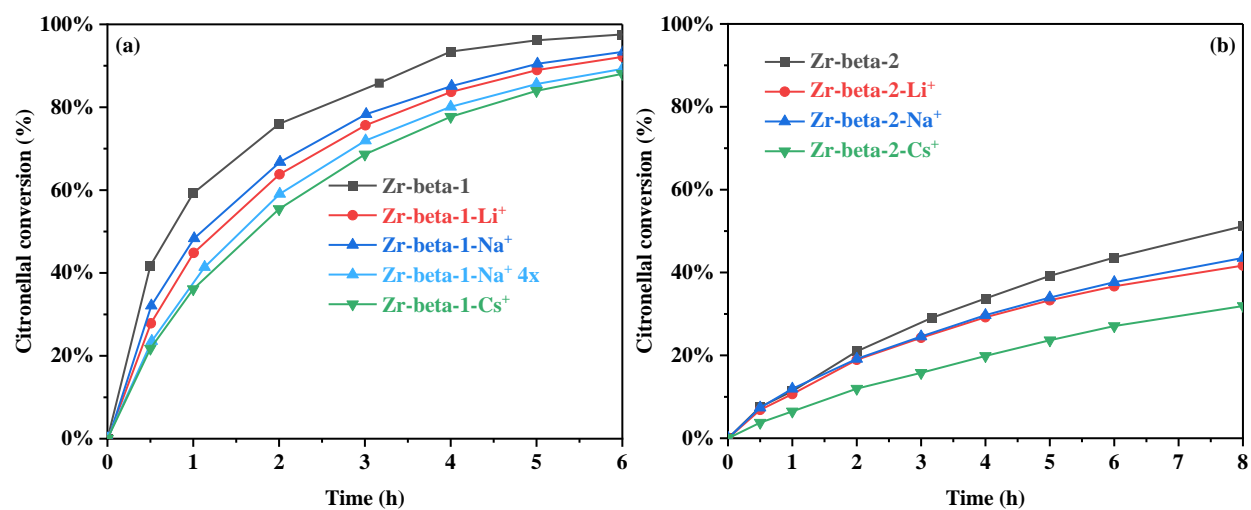


Figure S4: Citronellal conversion curves over sets of (a) Zr-beta-1 and (b) Zr-beta-2 catalysts

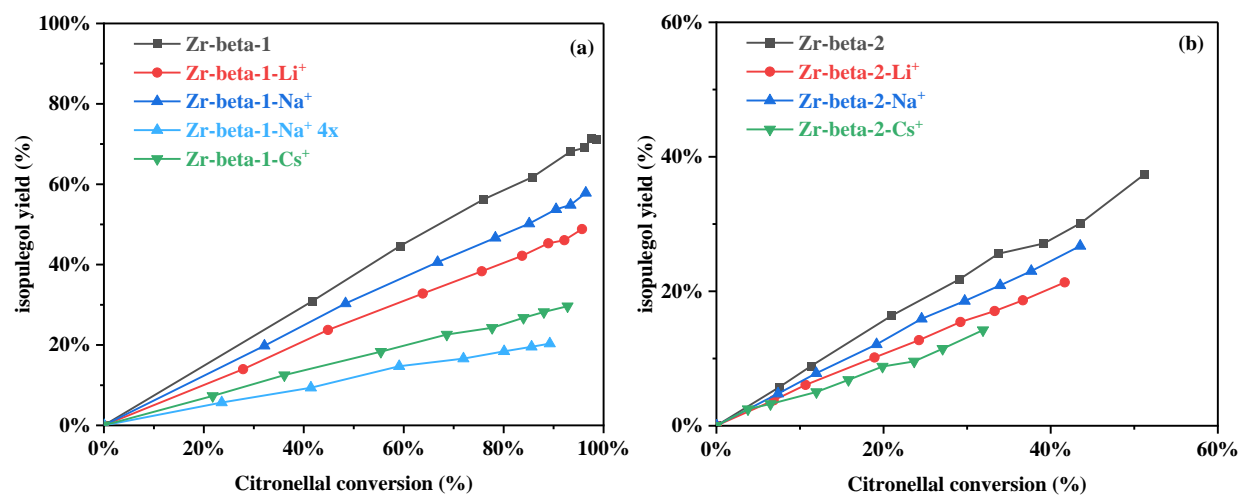


Figure S5: Variation of isopulegol yield as a function of citronellal conversion over sets of (a) Zr-beta-1 and (b) Zr-beta-2 catalysts

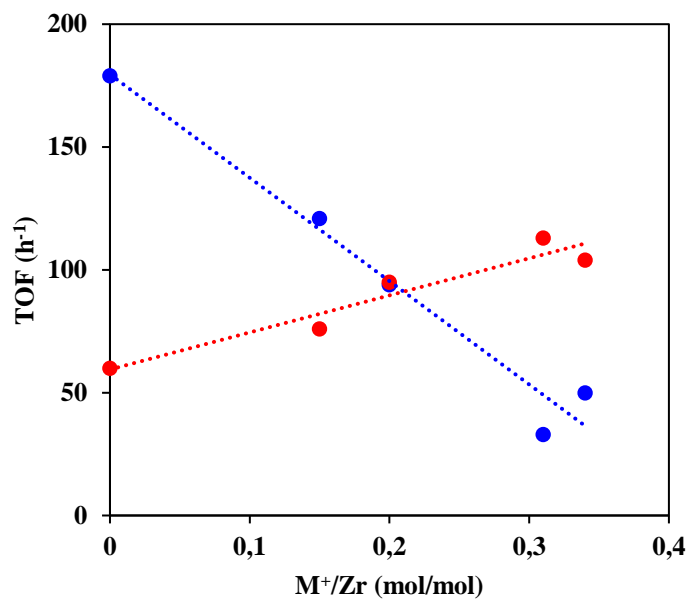
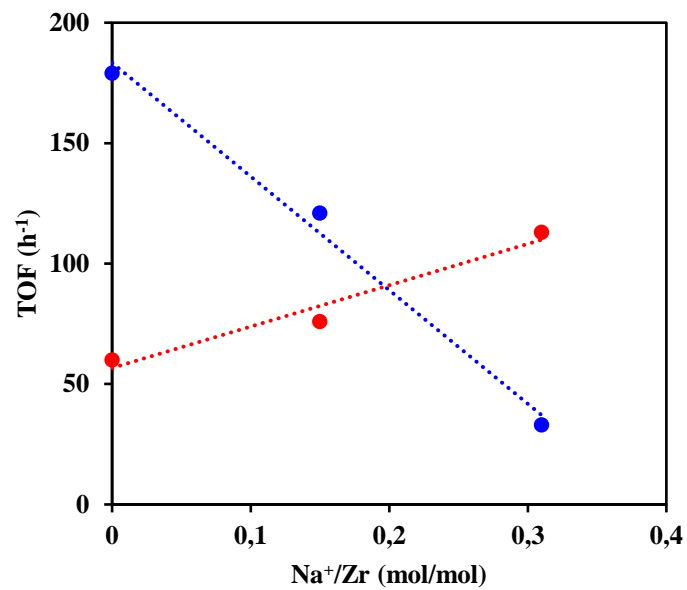


Figure S6: Turnover frequency (TOF) of MPV reduction (red) and carbonyl-ene cyclization (blue) as a function of Na⁺/Zr ratio (top) and extended TOF as a function of M⁺/Zr ratio (M⁺ = Li⁺, Na⁺, Cs⁺; bottom) in Zr-beta-1-based catalysts

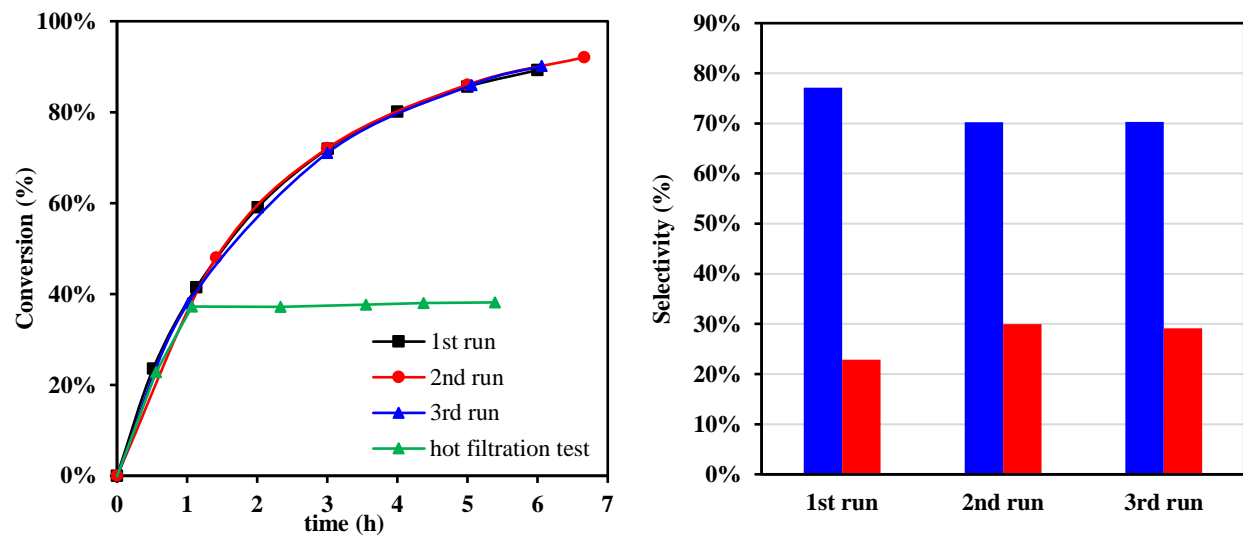


Figure S7: Citronellal conversion curves (left) and citronellol (right, blue columns) and isopulegol (right, red columns) selectivity values in the recycling test with the Zr-beta-1- $\text{Na}^+ 4x$ catalyst. Selectivity is assessed as the slope of the curve of product yield vs. citronellal conversion. The hot filtration test (left, green curve) was performed using a fresh catalyst, which was removed immediately after collecting the sample at 1 h of reaction.

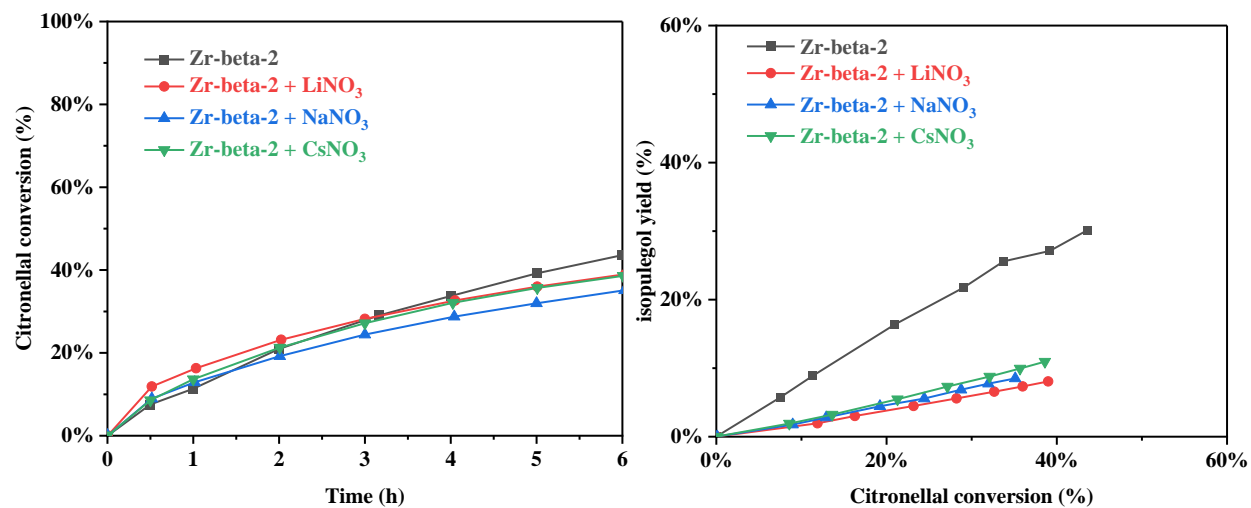


Figure S8: Variation of citronellal conversion as a function of time (left) and isopulegol yield as a function of citronellal conversion (right) over Zr-beta-2 with nitrate salts added directly to the reaction mixture.

Table S1. Semi-quantitative analysis of acetone (AC) and acetonitrile (CD₃CN) adsorption on Zr-beta zeolites expressed as band area

Sample	weaker Lewis sites	stronger Lewis sites	“open” sites
	AC 1710 cm ⁻¹	AC 1698 cm ⁻¹	CD ₃ CN 2306 cm ⁻¹
Zr-beta-1	1.5	19.8	6.3
Zr-beta-1-Li ⁺	4.3	15.4	4.8
Zr-beta-1-Na ⁺	2.1	12.0	5.0
Zr-beta-1-Na ⁺ 4x	5.4	14.3	3.5
Zr-beta-1-Cs ⁺	4.5	13.6	3.8
Zr-beta-2	1.3	4.6	1.5
Zr-beta-2-Li ⁺	1.8	5.3	1.7
Zr-beta-2-Na ⁺	1.7	6.6	2.2
Zr-beta-2-Cs ⁺	1.6	3.9	2.4