

Supporting Information

Tuning supported Ni catalysts by varying zeolite Beta heteroatom composition: effects on ethylene adsorption and dimerization catalysis

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Supporting Information.

N₂ Physisorption. Samples, loaded into a capped tube in the glovebox to exclude exposure to moisture and air, were transferred to a Micromeritics 3Flex instrument and degassed at 350°C for 4 h before measurements under dynamic vacuum. Samples were weighed in a glovebox before and after analysis to ensure a dry weight was obtained. N₂ adsorption isotherms were taken at -196°C. BET surface area was determined in the relative pressure range 0.001-0.05. Micropore volume was calculated using the t-plot method using Harkins-Jura thickness equation relating relative pressure to thickness of adsorbed layer.

Acid Site Titration. Acid site titration with isopropylamine was performed in a Netzsch Jupiter F209 TGA-MS. The sample was exposed to isopropylamine in-situ at 30°C. The sample was then heated to 527°C at 5°C/min in N₂, 80mL/min total flow, with a 1 hour hold at 180°C to remove physisorbed isopropylamine. The mass to charge ratios 17 (ammonia), 41 (propene), 44 (isopropylamine), and 58 (isopropylamine) were monitored during the experiment.

Table S1. Rate of deactivation of catalysts of the last 3 h of catalysis.

Catalyst	Deactivation over 3 h		
	No H ₂	H ₂	H ₂ – No H ₂
Ni-[Al]-Beta	25%	17%	-8%
Ni-[Ga]-Beta	30%	25%	-5%
Ni-[Fe]-Beta	20%	18%	-2%
Ni-[DeAl]-Beta	91%	-	-

Table S2. Acid site density, Si/X, and Ni/X of [X]-Beta zeolites. ^aDetermined via isopropylamine titration, ^bdetermined via ICP-MS.

Heteroatom	Acid Site Density ^a [$\mu\text{mol/g}$]	Si/X ^a	Si/X ^b	Ni/H ⁺	Ni/X ^b
Al	735	22	19	0.24	0.21
Ga	616	25	24	0.27	0.27
Fe	712	22	19	0.24	0.22

Table S3. Surface areas and micropore volumes of catalysts derived from nitrogen physisorption

Extra-Framework Cation	Heteroatom	BET SA [m^2/g]	Micropore Vol [cm^3/g]	External SA [m^2/g]
Na ⁺	B	699	0.239	68.5
H ⁺	Ga	665	0.199	159
Ni, H ⁺	Ga	643	0.188	169
H ⁺	Al	694	0.204	174
Ni, H ⁺	Al	690	0.201	184
-	DeAl	599	0.17	156
Ni	DeAl	632	0.19	145
H ⁺	Fe	705	0.204	186
Ni, H ⁺	Fe	695	0.220	128

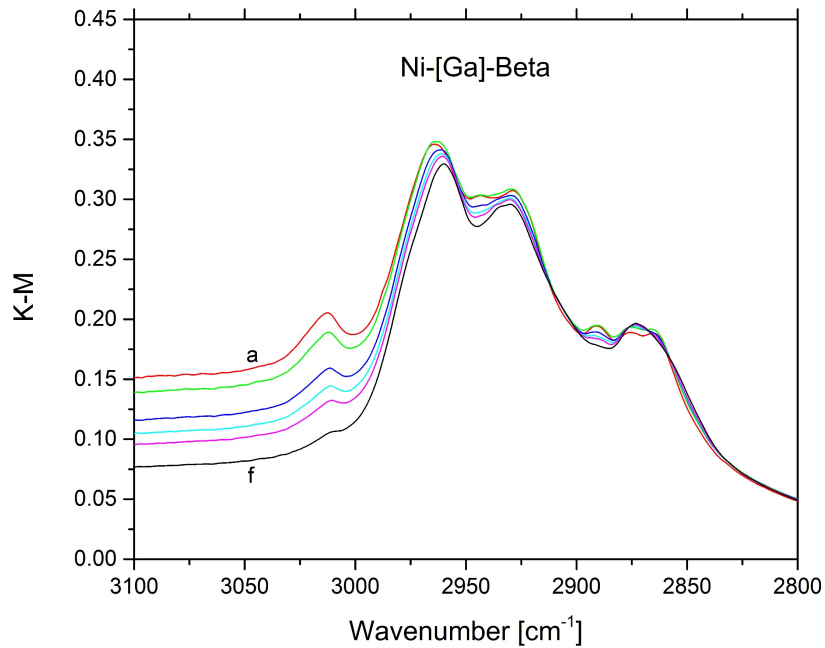


Figure S1. C_2H_4 adsorption onto oxidized Ni-[Ga]-Beta catalyst. C_2H_4 was pulsed into drifts cell and purged from a to f. Spectra show butene bands desorb over time.

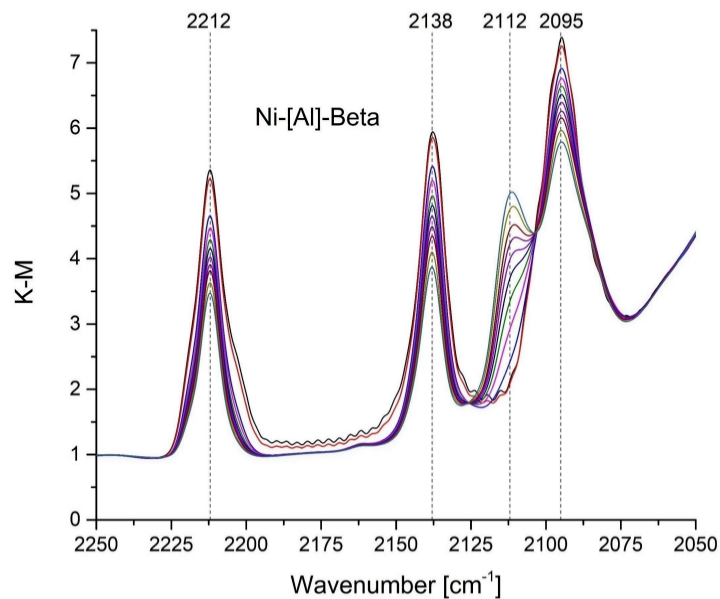


Figure S2. CO adsorption at 30°C after reduction with CO at 300 ° C onto Ni-[Al]-Beta, spectra after CO pulse a-f.

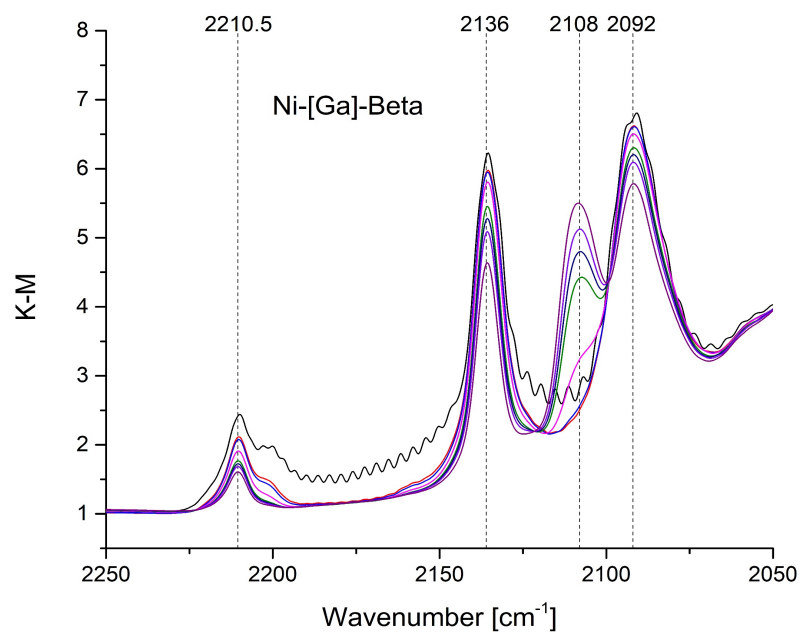


Figure S3. CO adsorption at 30°C after reduction with CO at 300°C

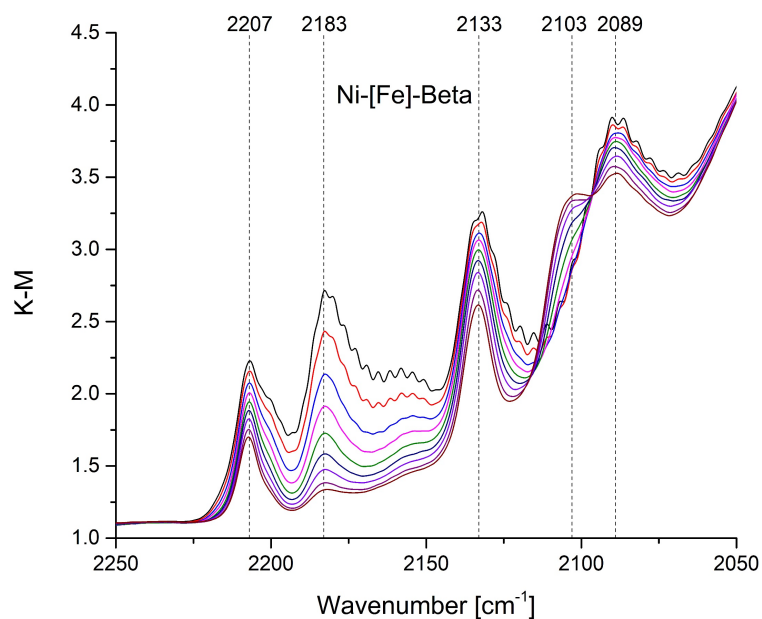


Figure S4. CO adsorption at 30°C after reduction with CO at 300°C onto Ni-[Fe]-Beta, spectra after CO pulse a-f. Bands at 2207, 2133, 2103, 2089 cm⁻¹ correspond to Ni carbonyls while the band at 2183 cm⁻¹ corresponds to extraframework Fe²⁺ carbonyl.

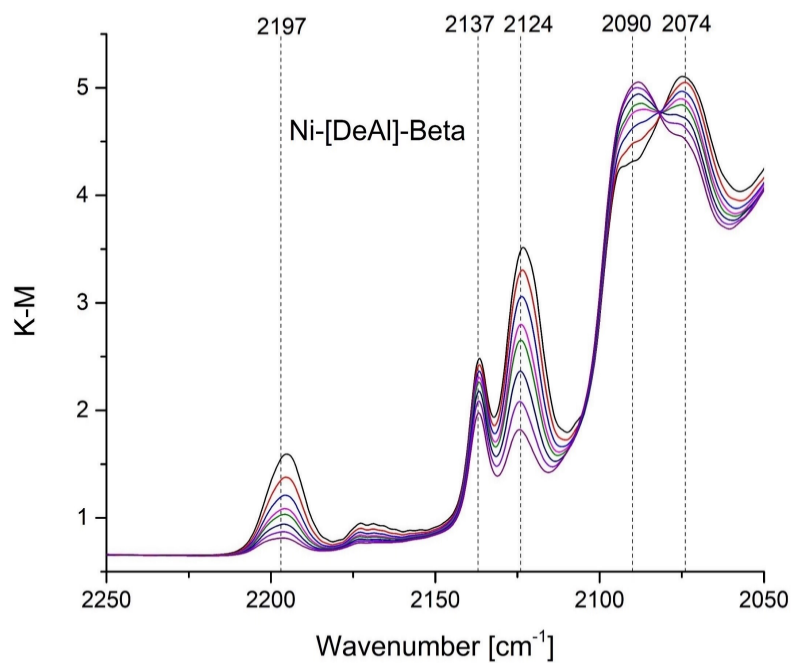


Figure S5. CO adsorption at 30°C after reduction with CO at 300 ° C onto Ni-[DeAl]-Beta, spectra after CO pulse a-f.

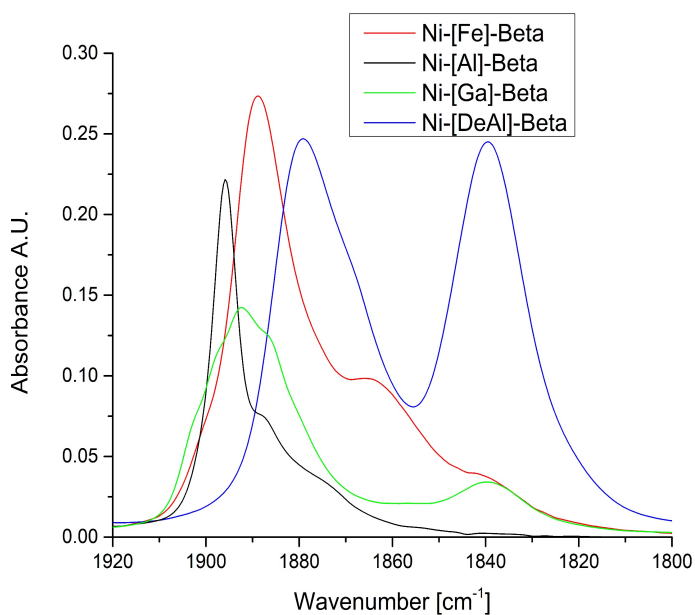


Figure S6. NO adsorption at room temperature onto oxidized Ni-[X]-Beta, where X= Al, Ga, Fe, or DeAl.

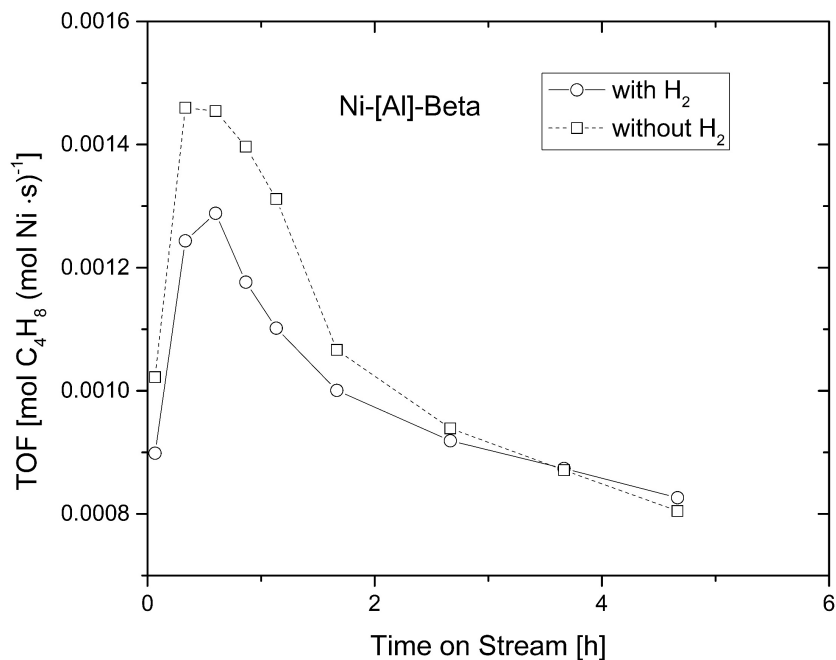


Figure S7. TOF of Ni-[Al]-Beta with and without H₂. The addition of H₂ reduces of the TOF but decrease the rate of deactivation.

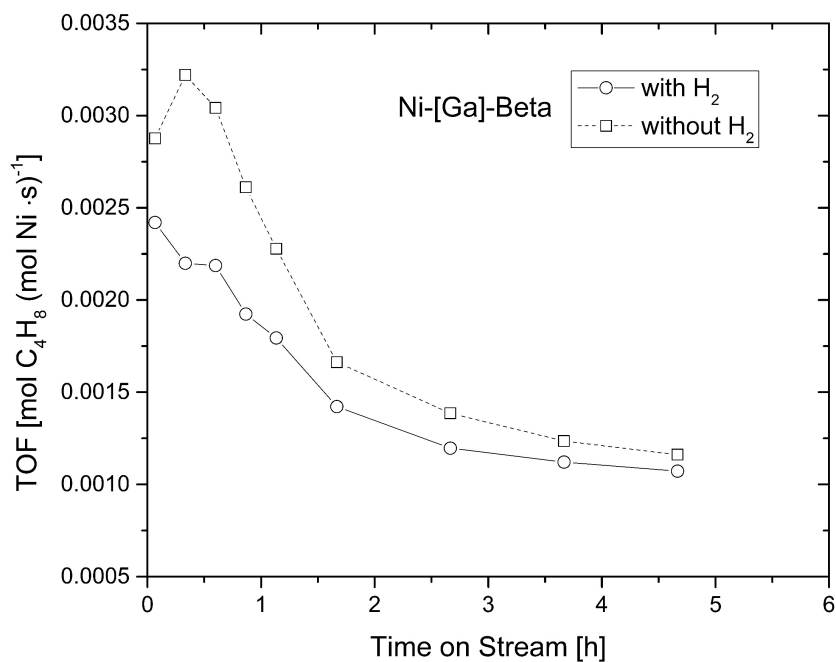


Figure S8. TOF of Ni-[Ga]-Beta with and without H₂. The induction period is not observed in the presence of H₂. The TOF decreases in the presence of H₂.

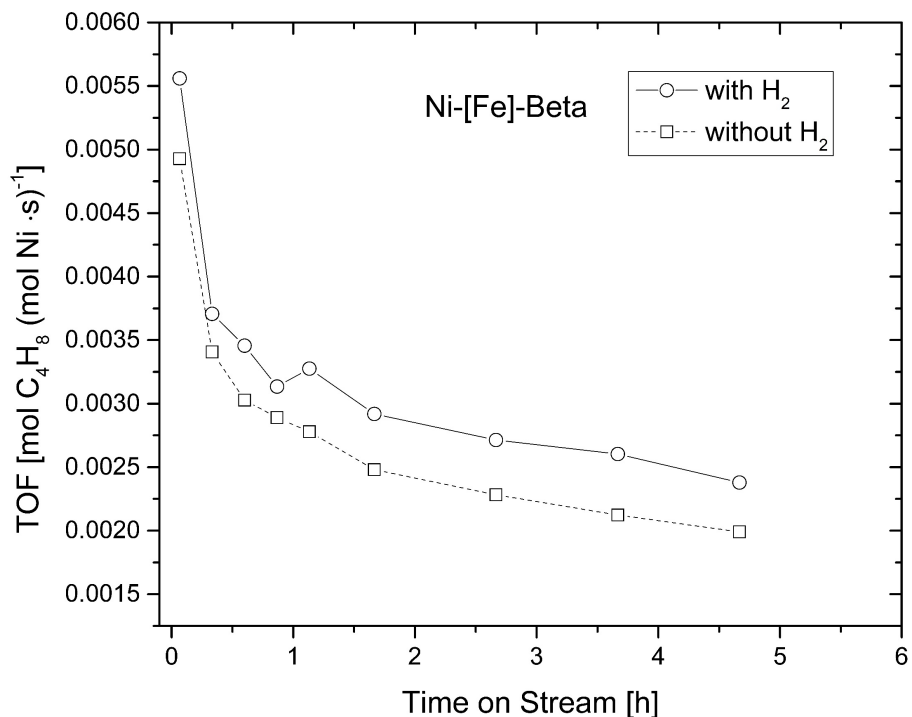


Figure S9. TOF of Ni-[Fe]-Beta with and without H₂. The activity is increased in the presence of H₂, the rate of deactivation is not significantly altered.

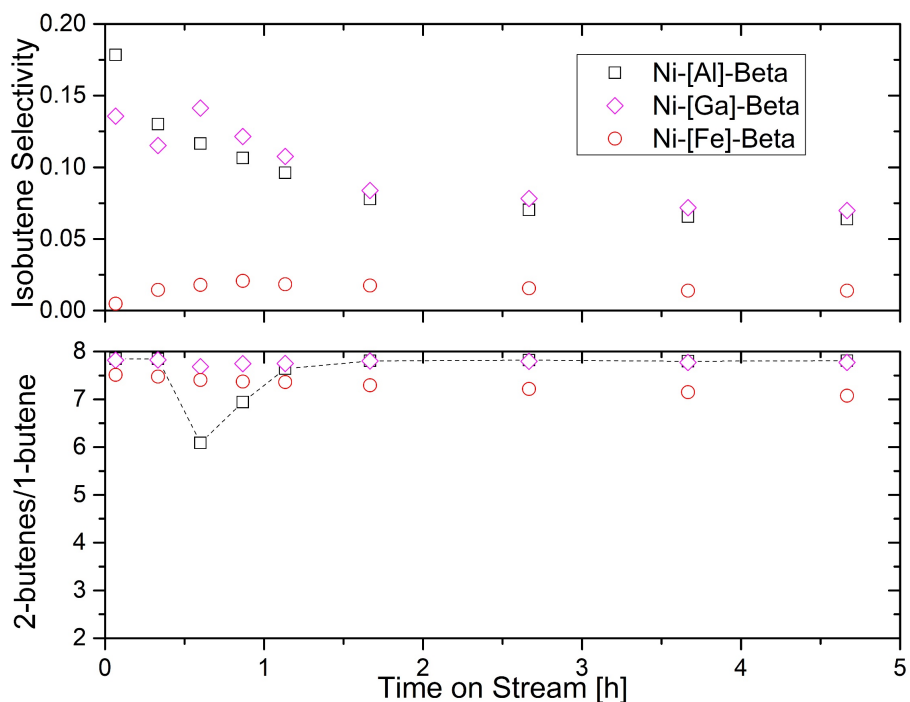


Figure S10. Top: Selectivity of isobutene relative to total butene formation. Bottom: ratio of total 2-butene formation to 1-butene. Results for dimerization carried out in the presence of H₂.

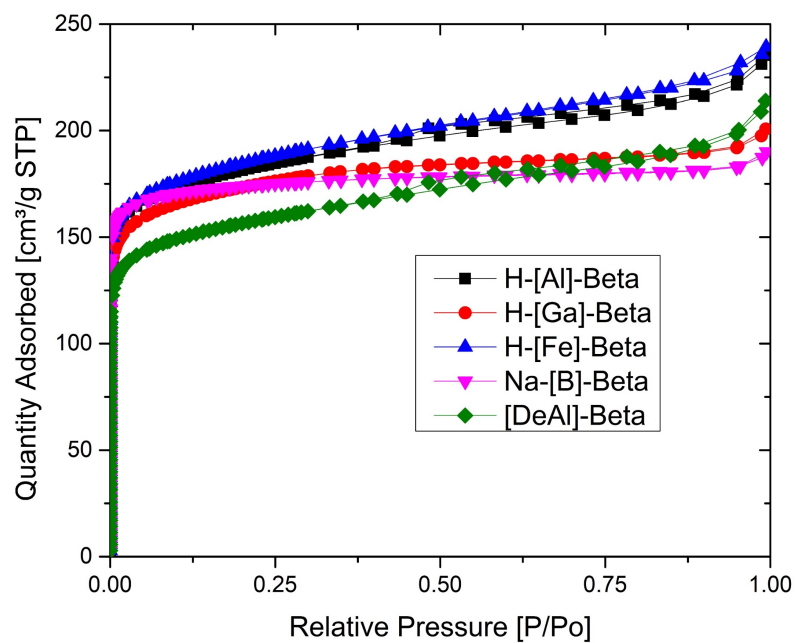


Figure S11. N₂ physisorption isotherms for supports without dispersed Ni.

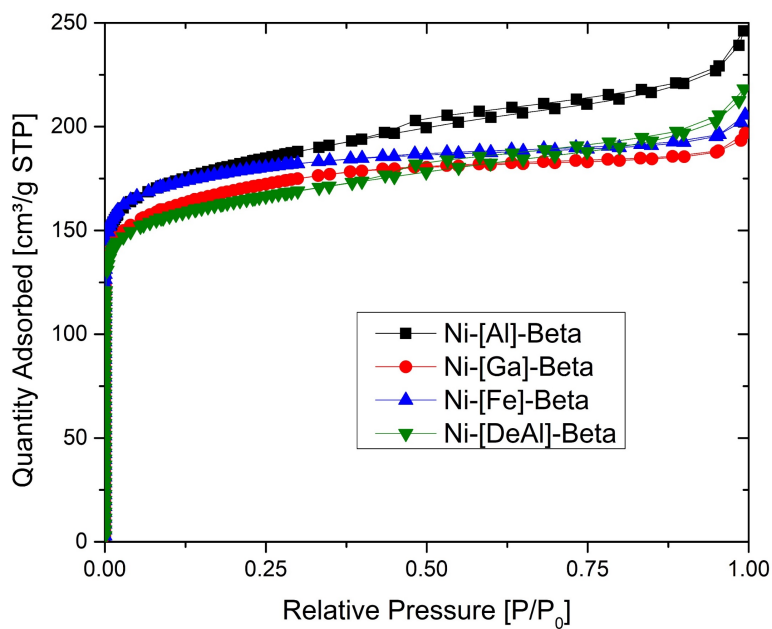


Figure S12. N₂ physisorption isotherms for catalysts with dispersed Ni

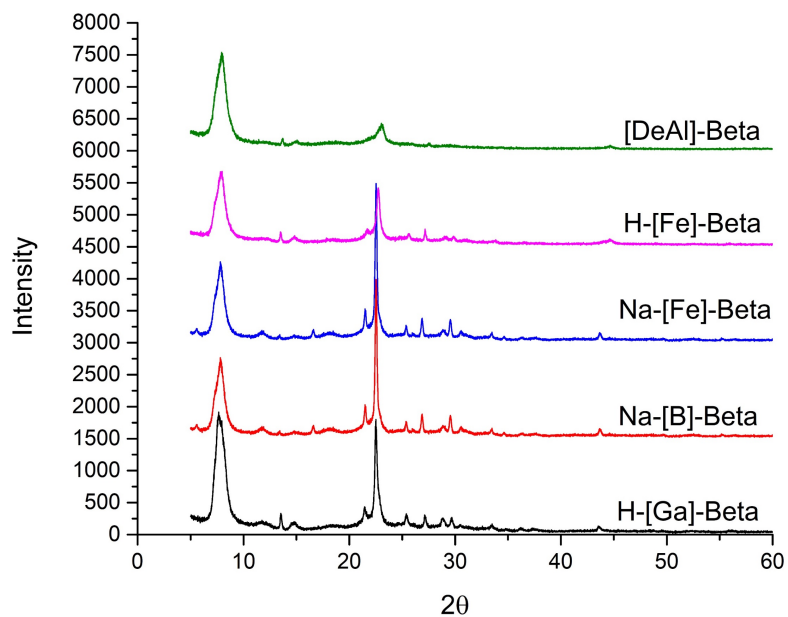


Figure S13. Powder XRD spectra for Beta supports without dispersed Ni

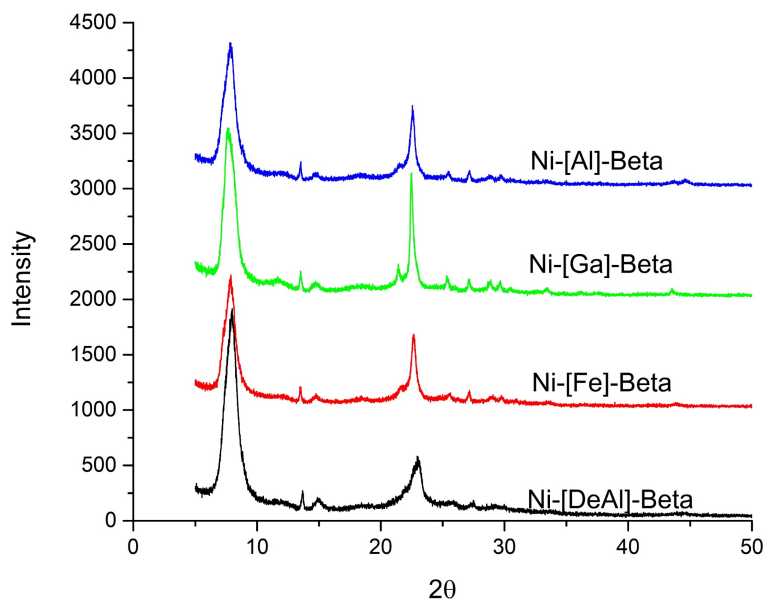


Figure S14. Powder XRD spectra for Beta catalysts with dispersed Ni

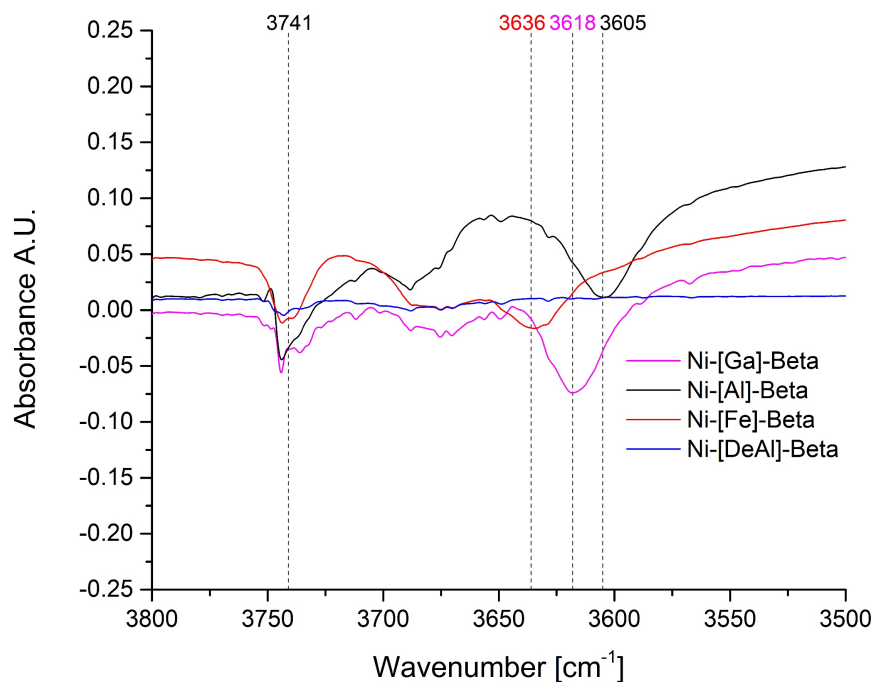


Figure S15. FTIR spectra of the OH region of catalysts after C_2H_4 adsorption (CH region shown in Figure 1). Spectra show a decrease in the isolated silanol band (3741 cm^{-1}) as well as acidic silanol bands (3605 , 3618 , and 3636 cm^{-1} respectively) for Ni-[Al]-, -[Ga]-, and -[Fe]-Beta catalysts

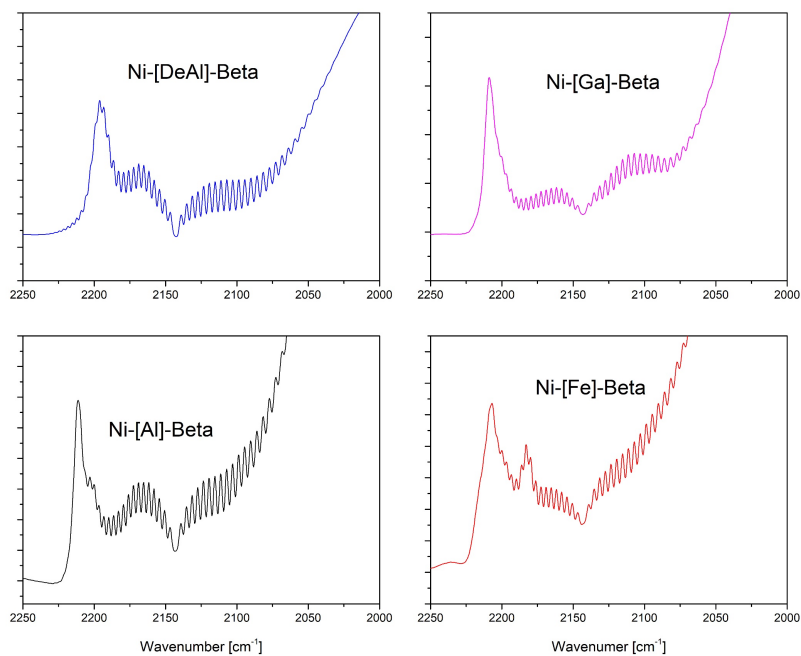


Figure S16. FTIR spectra of CO adsorption of catalysts after oxidative treatment to remove $Ni(acac)_2$ ligands. Spectra show Ni^{2+} (2197 , 2209 , 2212 , and 2206 cm^{-1}) in all catalysts as well as Fe^{2+} (2183 cm^{-1}) in the Ni-[Fe]-Beta catalyst (band assignments seen in Table 2).