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Chemical Synthesis

Supplementary Materials

Highly selective production of renewable methyl acrylate via aldol condensation over Cu modified nitrogen-containing Beta zeolites

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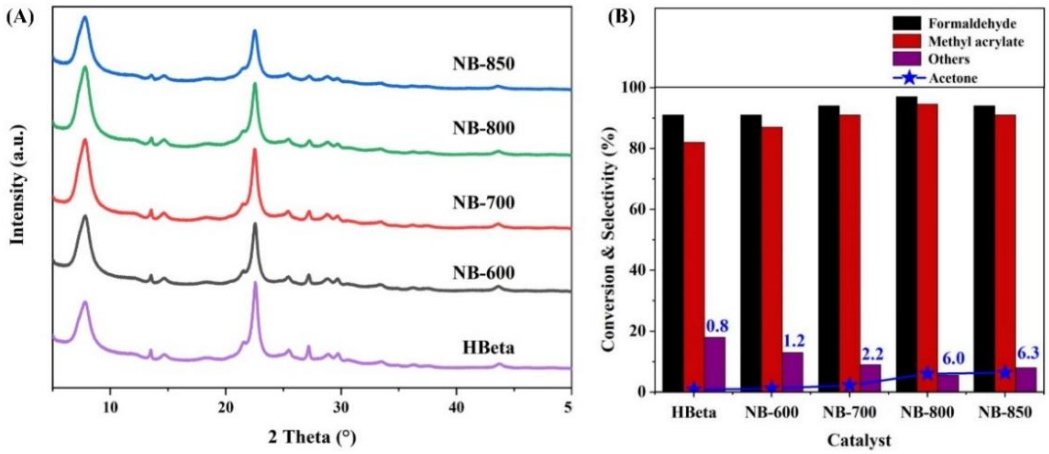
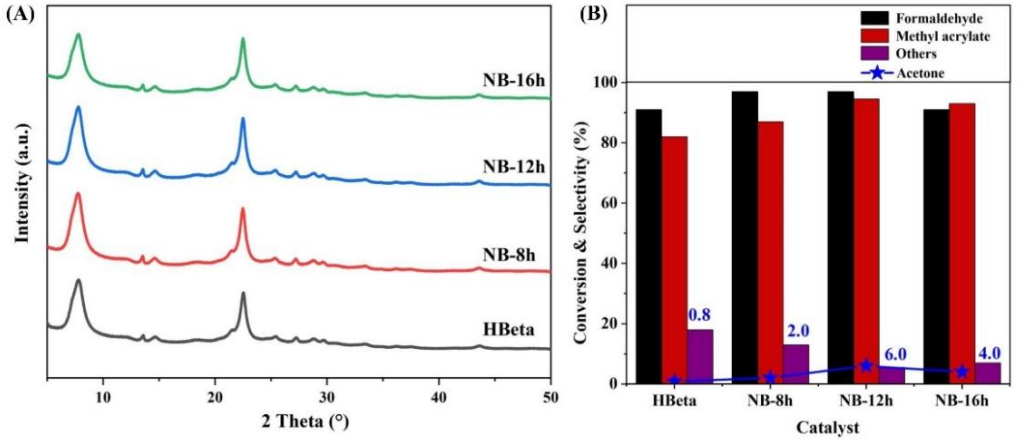
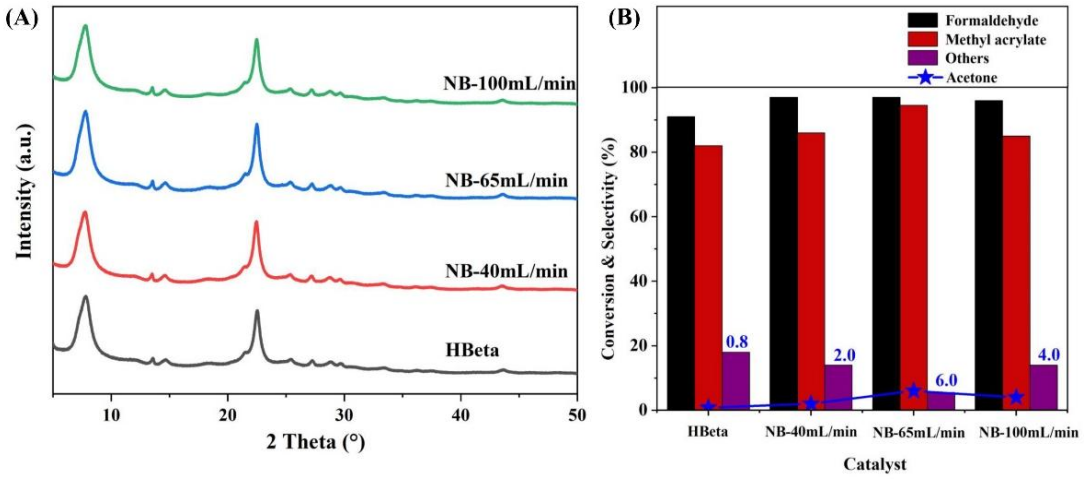


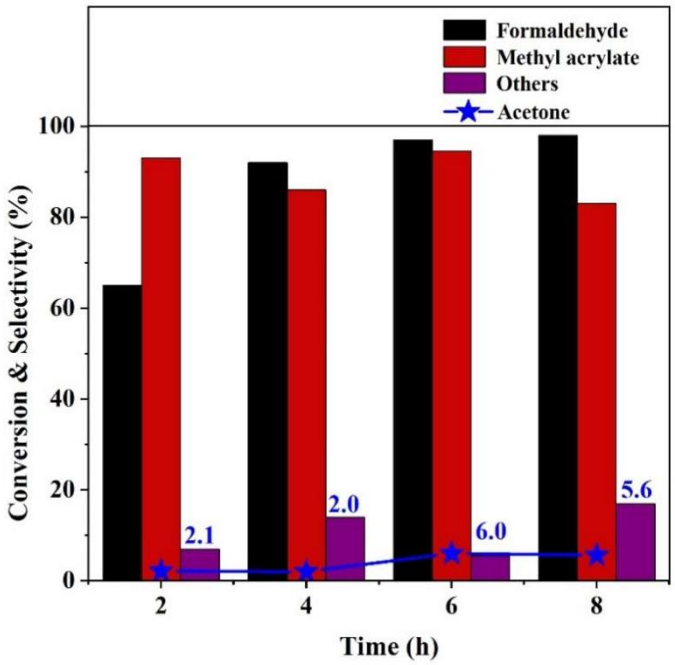
Supplementary Figure 1. (A) XRD patterns and (B) effect of nitridation temperature on catalytic performance. Reaction conditions: 320 ℃, 6 h, methyl acetate/formaldehyde molar ratio = 4.



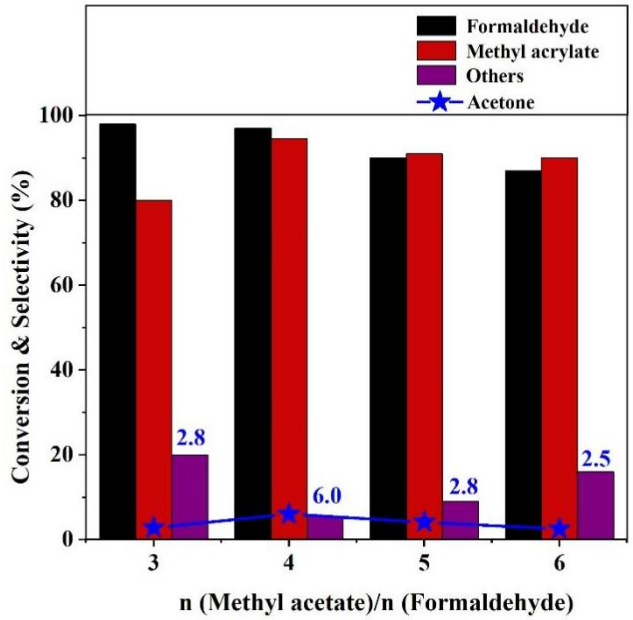
Supplementary Figure 2. (A) XRD patterns and (B) effect of nitridation time on catalytic performance. Reaction conditions: 320 ℃, 6 h, methyl acetate/formaldehyde molar ratio = 4.



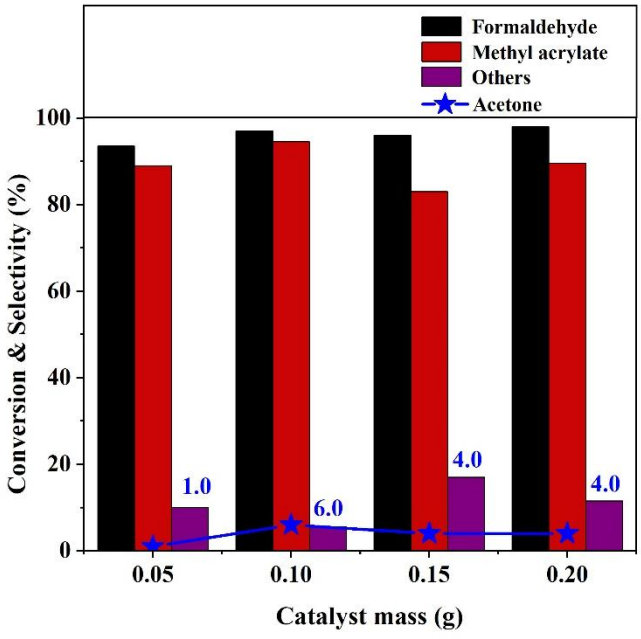
Supplementary Figure 3. (A) XRD patterns and (B) effect of ammonia flow rate on catalytic performance. Reaction conditions: 320 ℃, 6 h, methyl acetate/formaldehyde molar ratio = 4.



Supplementary Figure 4. Effect of reaction time on catalytic performance. Reaction conditions: 0.1 g NB-800, 320 ℃, methyl acetate/formaldehyde molar ratio = 4.

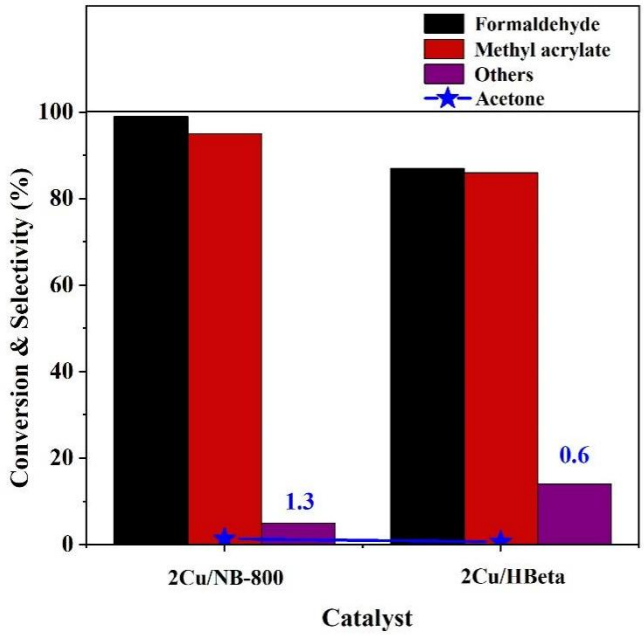


Supplementary Figure 5. Effect of methyl acetate and formaldehyde molar ratio on catalytic performance. Reaction conditions: 0.1g NB-800, 320 ℃, 6 h.

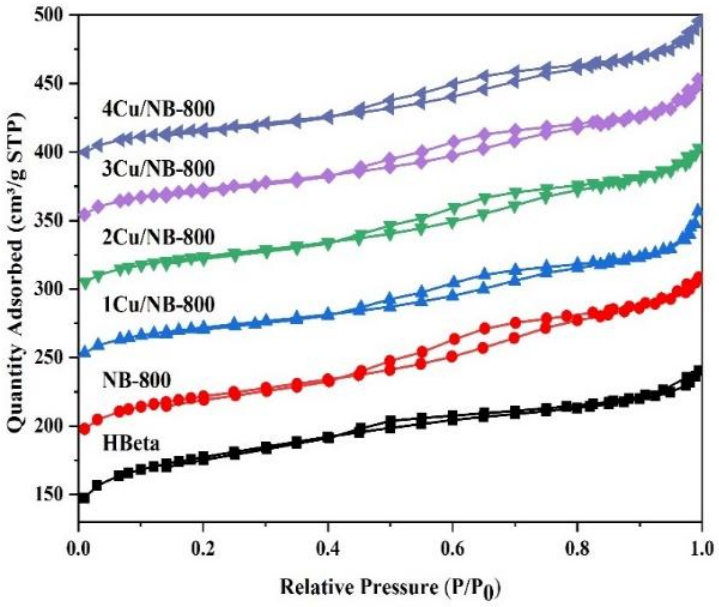


Supplementary Figure 6. Effect of catalyst mass on catalytic performance.

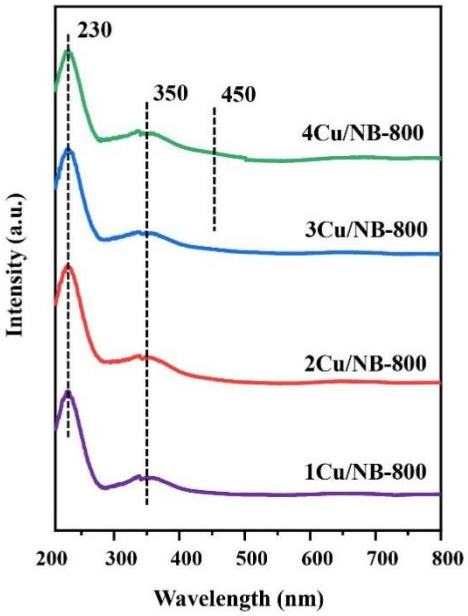
Reaction conditions: NB-800, 320 ℃, 6 h, methyl acetate/formaldehyde molar ratio = 4.



Supplementary Figure 7. Reaction performance of HBeta, 2Cu/NBeta and 2Cu/HBeta catalysts. Reaction conditions: 320 ℃, 6 h, methyl acetate/formaldehyde molar ratio = 4.

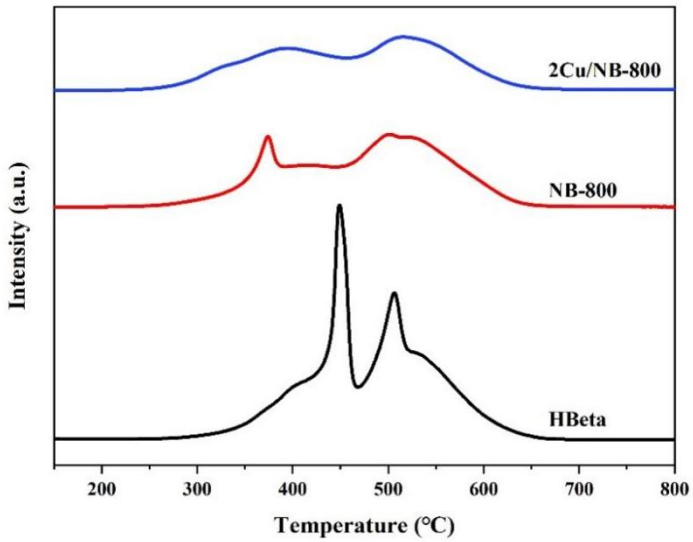


Supplementary Figure 8. N_2 adsorption-desorption isotherms of HBeta and NBeta zeolites with different Cu loadings. The isotherm of each sample was offset vertically by 50 cm^3/g for better separation.

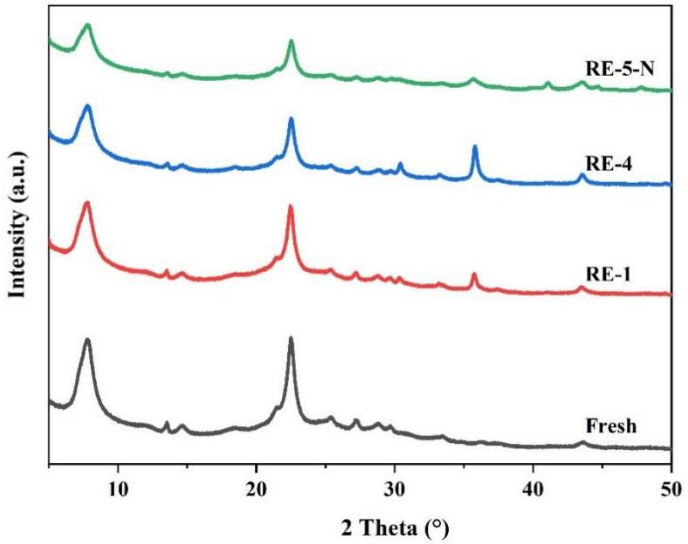


Supplementary Figure 9. UV-vis spectra of NBeta zeolites with different Cu loadings.

To investigate the existing state of Cu species in the catalyst, UV-vis characterization was performed on NBeta catalysts with different Cu loadings, and the results are shown in Supplementary Figure 9. The absorption peaks at around 230 and 350 nm are attributed to the charge migration of $O^{2-} \rightarrow Cu^{2+}$ and Cu^{2+}-O-Cu^{2+}, respectively, representing the presence of isolated Cu^{2+} and clustered CuO[1]. It can be seen that most of the Cu species exist in the form of isolated Cu^{2+}. With the increase of Cu loading, the number of clustered CuO increases, especially when the Cu loading is 4 wt%, a new peak appears at ~450 nm, which can be attributed to more complex clustered CuO species[2,3].



Supplementary Figure 10. TPO profiles of coked samples after aldol reaction.



Supplementary Figure 11. XRD patterns of 2Cu/NBeta catalysts before and after regeneration cycles.

Supplementary Table 1. Acidic and basic properties of 2Cu/NBeta catalysts before and after regeneration cycles.

Samples	Acidic site (μmol/g)			Total acid amount (μmol/g)	Basic site (μmol/g)			Total base amount (μmol/g)
	Weak	Middle	Strong		Weak	Middle	Strong	
Fresh	3	10	3	16	2.3	5.0	—	7.3
RE-1	2.8	9.1	4.1	16	2.4	3.8	—	6.2
RE-4	6	12	3.4	21.4	1.0	1.1	—	2.1
RE-5-N	2.3	8.2	4.5	15	2.6	6.2	—	8.8

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