Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Boric Acid Treated HZSM-5 for Improved Catalyst Activity in Non-oxidative Methane Dehydroaromatization

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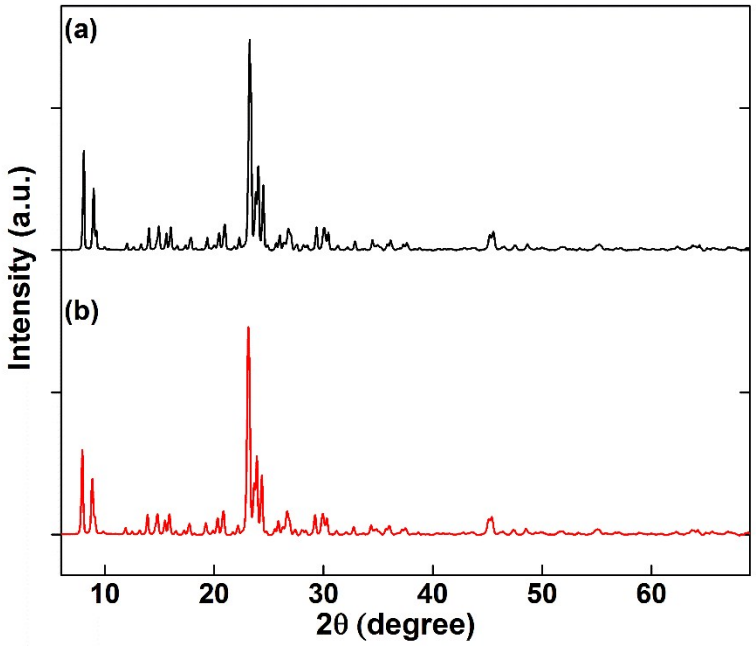

Figure S1. XRD pattern of (a) HZSM-5 and (b) [BA] HZSM-5.

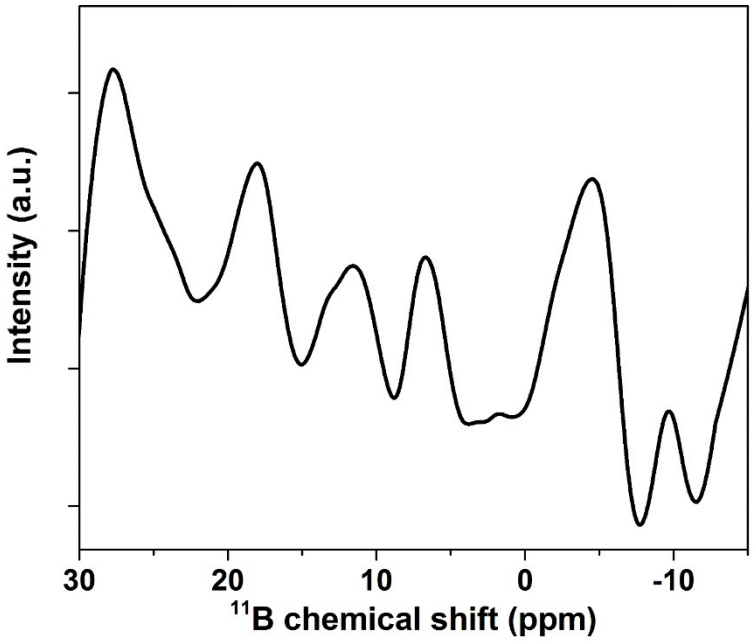

Figure S2. ^{11}B MAS NMR spectra of HZSM-5.

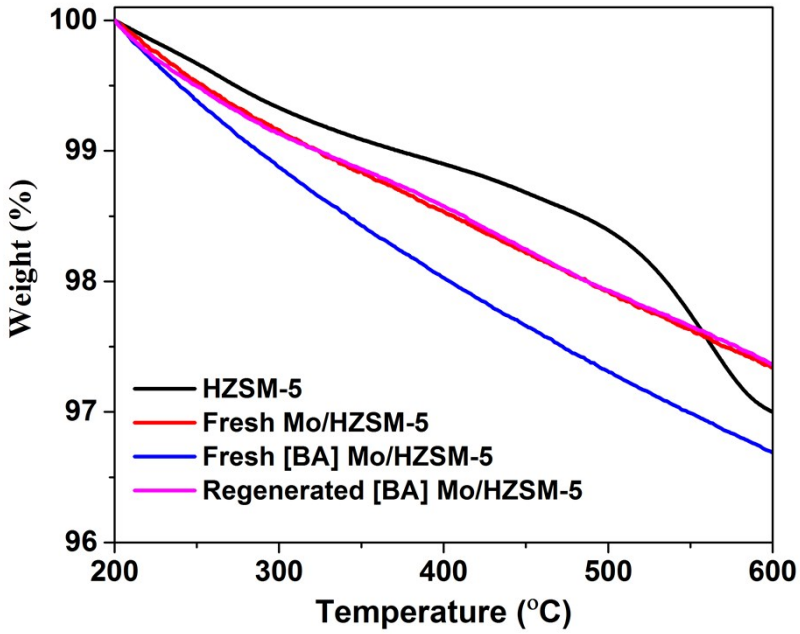

Figure S3. TGA graph of HZSM, fresh Mo/HZSM-5, fresh [BA] Mo/HZSM-5, and regenerated Mo/HZSM-5 cataltyst.

From the graph it is clear that the regenerated protocol followed in the method setion is able to completely remove the coke deposited over the used [BA] Mo/HZSM-5 catalyst. The weight loss in the regenerated [BA] Mo/HZSM-5 is showing similar trend as that of calcined fresh Mo loaded prostine and BA treated HZSM-5 with 2.95 wt % loss. For Mo/HZSM-5 and [BA] Mo/HZMS-5 the weight loss are 2.97 and 3.58 wt % respectively.

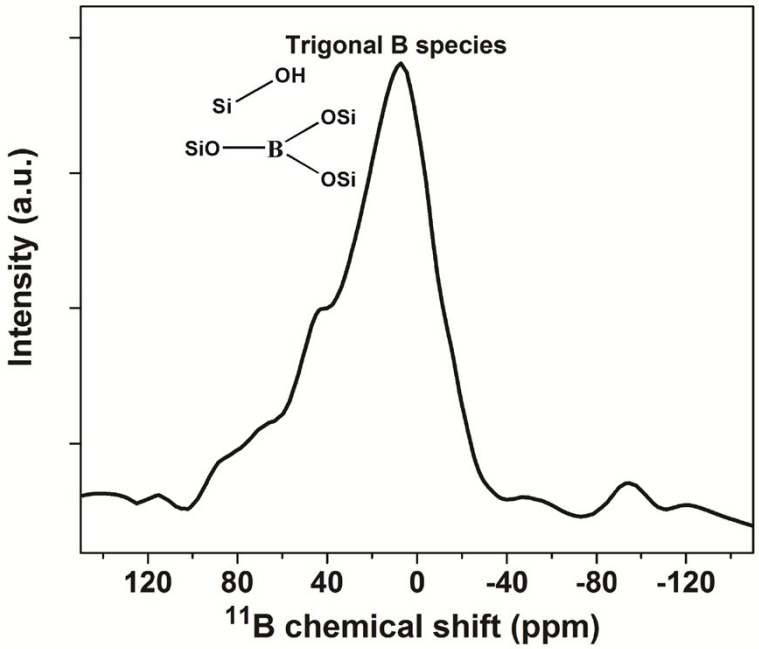

Figure S4. ^{11}B MAS NMR spectra of regenerated [BA] Mo/HZSM-5.

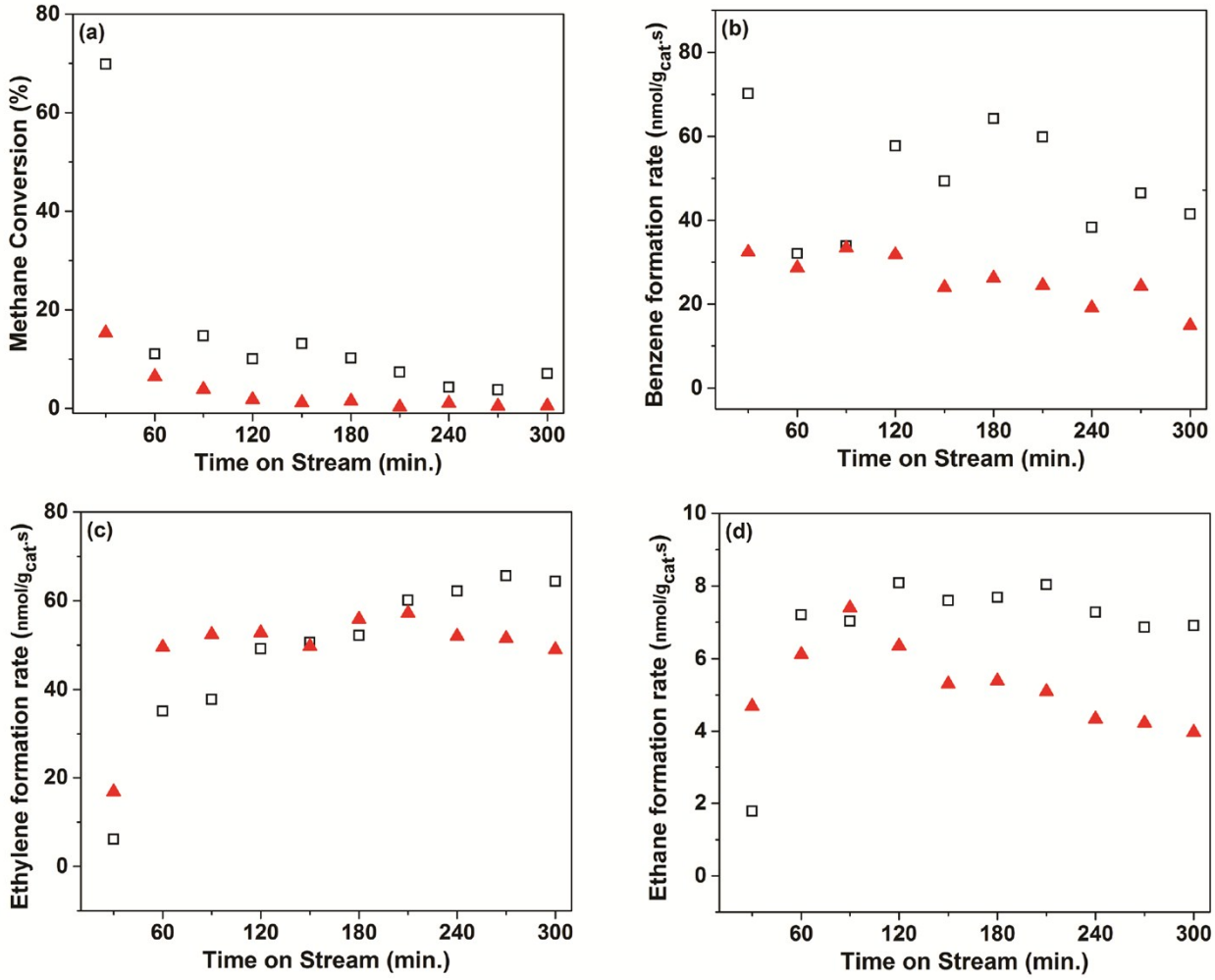

Figure S5. (a) Methane conversion and product formation rate of (b) benzene, (c) ethylene and (d) ethane measured over time on stream for 1% Mo/HZSM-5 (□) and [BA] 1% Mo/HZSM-5 (▲) catalyst at 700 ºC.

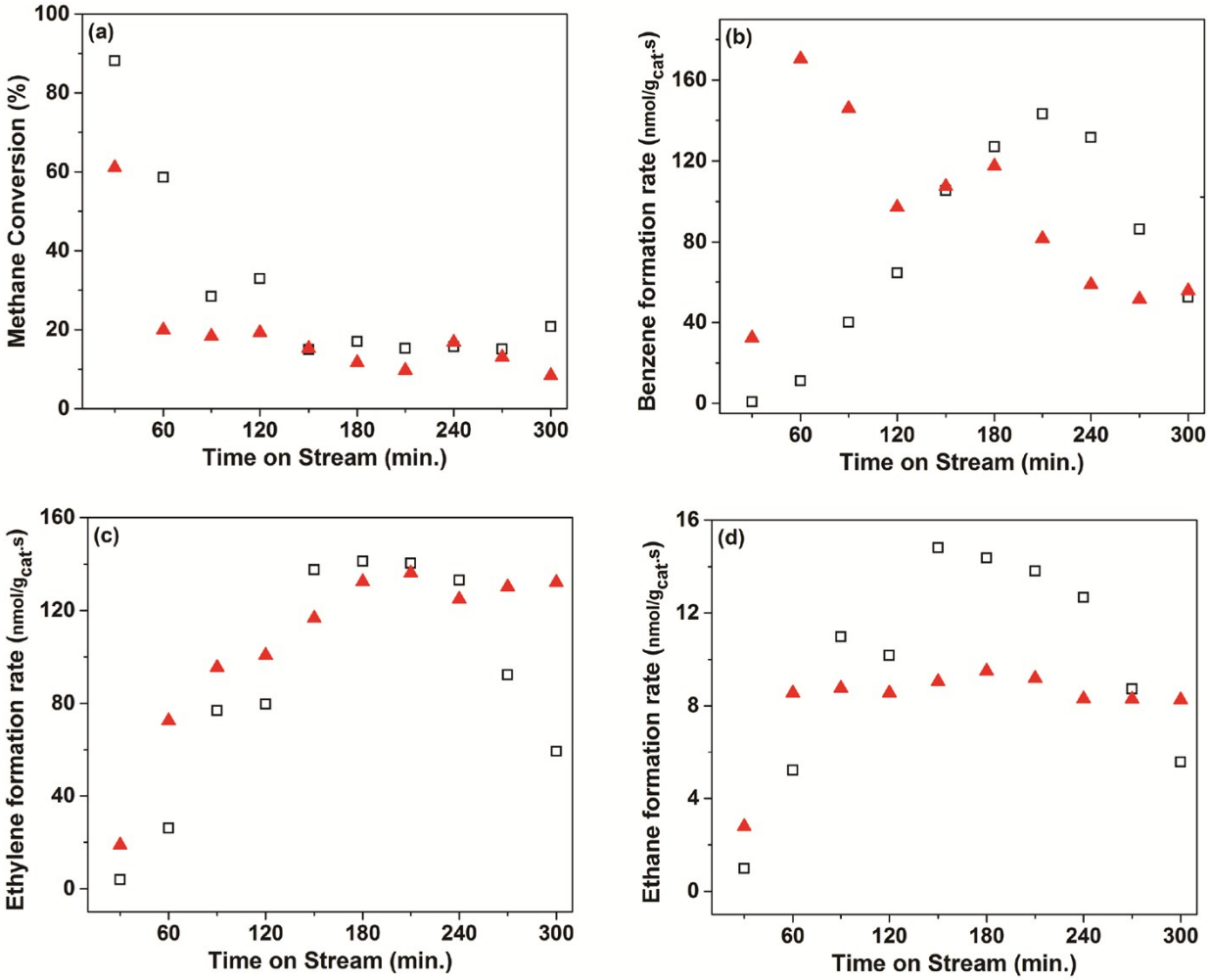

Figure S6. (a) Methane conversion and product formation rate of (b) benzene, (c) ethylene and (d) ethane measured over time on stream for 2% Mo/HZSM-5 (□) and [BA] 2% Mo/HZSM-5 (▲) catalyst at 700 ºC.

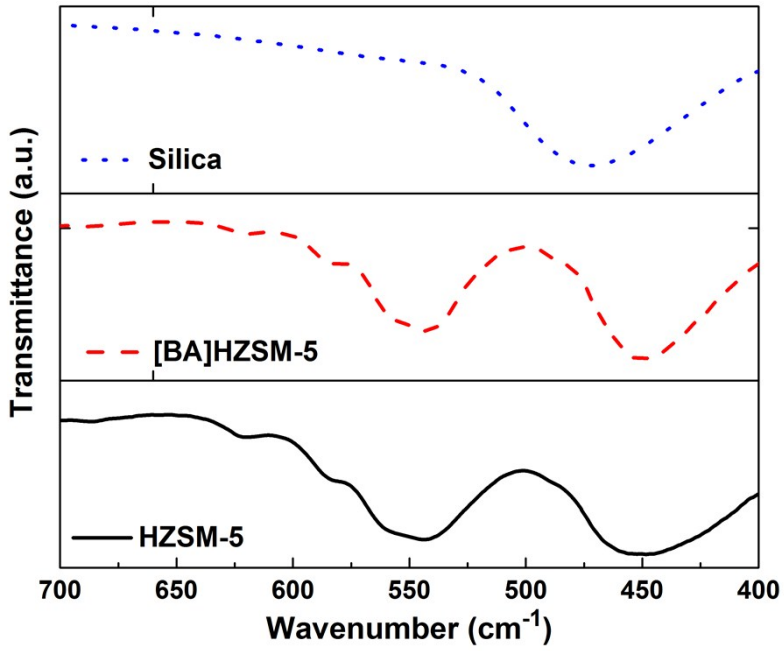

Figure S7. Infrared spectra of the framework region (700-400 cm^{-1}) of HZSM-5, [BA] HZSM-5, and silica. The IR spectra is used to check the crystallinity.

Studies conducted by Verdine and co-workers[1] and Pandya and co-worker[2] estimates the crystalline phase in ZSM-5 using IR spectroscopy. Determination of purity in ZSM-5 is checked by IR optical density ratio of band at 550 cm^{-1} and 450 cm^{-1} in the mid-IR region of structural spectra. Optical density ratio ~ 0.72-0.8 shows the presence of pure zeolite. If amorphous silica is present in zeolite this optical density ratio is likely to be less than 0.7 for ZSM-5. In our study we utilized these benchmark to confirm the crystallinity of [BA] HZMS-5 w.r.t HZSM-5. From IR analysis, the ratio of optical density for [BA] HZMS-5 and HZSM-5 are 0.78 and 0.72 respectively.

Table S1. Quantitative estimation of H_2 consumption in TPR over as-synthesized catalysts.

Catalyst	H_2 consumption (mmol/g)		
	Peak II	Peak III	Peak IV
Mo/HZSM-5	0.58 (492 °C)	0.42 (598 °C)	1.37 (858 °C)
[BA] Mo/HZSM-5	1.01 (484 °C)	0.79 (721 °C)	

Table S2. Measured acidity of parent and impregnated HZSM-5.

Catalyst	NH_3 consumption (mmol/g)	
	Total	Weak acid/strong acid
HZSM-5	1.67	0.97
[BA] HZSM-5	2.12	1.49
Mo/HZSM-5	1.39	0.75
[BA] Mo/HZSM-5	2.05	0.94

References

1 G. Coudurier, C. Naccache and J. C. Vedrine, *J. Chem, Soc., Chem. Commun*, 1982, 1413–1415.

2 D. B. Shukla and V. P. Pandya, *J. Chem. Technol. Biotechnol.*, 1989, **44**, 147–154.