Supporting Information

Title: Organic-free synthesis of CHA-type zeolite catalysts for the methanol-to-olefins reaction

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Study on the effect of steam treatment on SSZ-13 for MTO

SSZ-13 was synthesized following the method reported in literature[13] at a Si/Al ratio of 5 using the N,N,N-trimethyladamantylammonium hydroxide SDA. The product was calcined, NH_4^+-exchanged and then steamed for 24 h at 750°C under a flow of water vapor/inert mixture, which was accomplished by bubbling inert through a water saturator held at 75°C. Reaction testing of the samples was conducted at 400°C using a 10% methanol/inert feed at a WHSV of 1.3 h^{-1}. The MTO reaction profiles for the fresh (unsteamed) SSZ-13 with Si/Al = 5 and steamed SSZ-13 are shown in Figures S1-S2, respectively. The unsteamed SSZ-13 initially converts methanol at 100% but deactivates rapidly after approximately 45 min TOS. Both the catalyst lifetime and olefin selectivities are improved after steam treatment. Methanol conversion remains above 80% for more than 200 min TOS for the steamed SSZ-13. Further, whereas the unsteamed SSZ-13 shows a transient period at the start of the reaction in which a significant amount of propane is observed in addition to rising olefin selectivities, the steamed material has a more stable reaction profile, similar to SAPO-34 (Figure 9F).

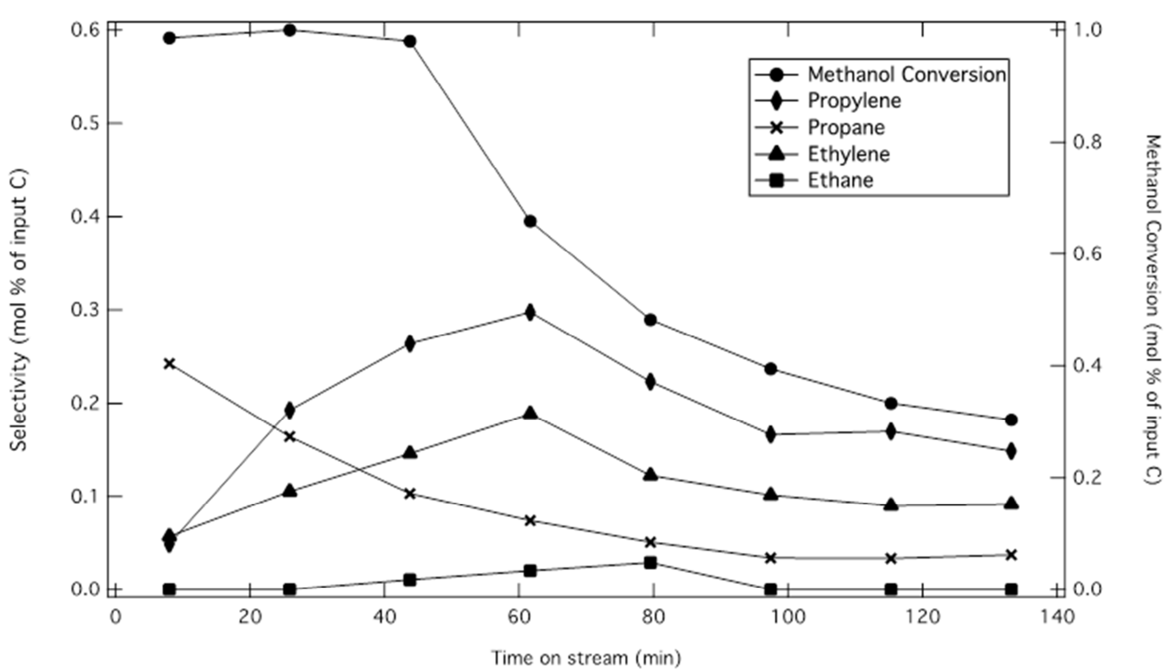

Figure S1. MTO reaction data for fresh (unsteamed) H-SSZ-13 Si/Al=5

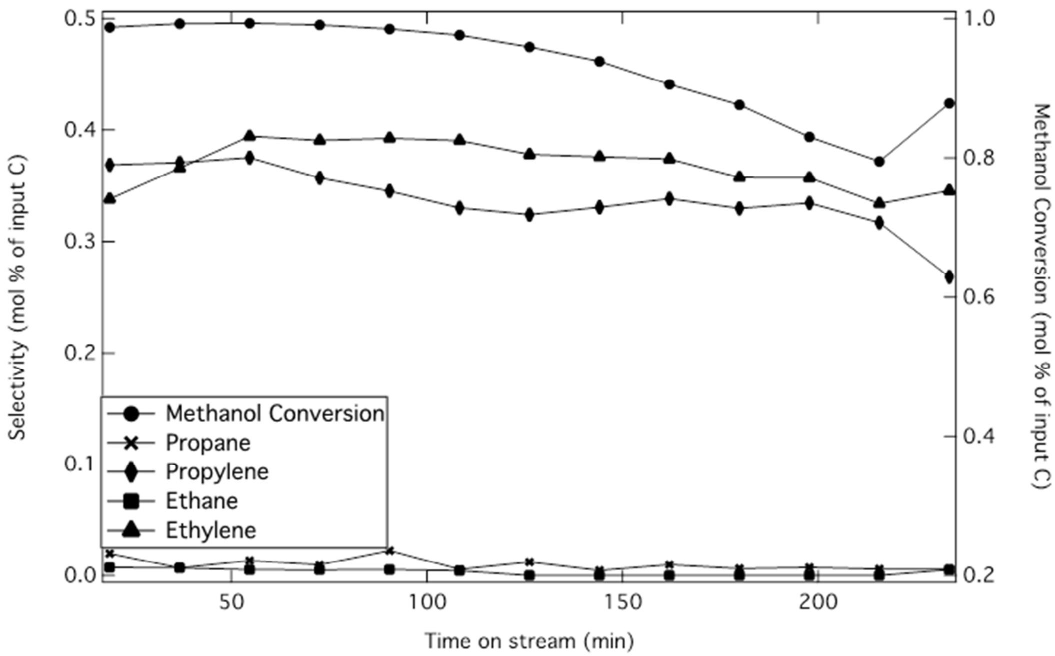

Figure S2. MTO reaction data for steamed H-SSZ-13 Si/Al=5

Further Characterization of Catalysts

A ^{27}Al MAS NMR spectrum of the as-synthesized K-CHA was obtained and is shown in Figure S3. The spectrum contains only a single sharp peak centered at approximately 55 ppm, corresponding to tetrahedral aluminum, and indicates that all aluminum is initially incorporated in the framework.

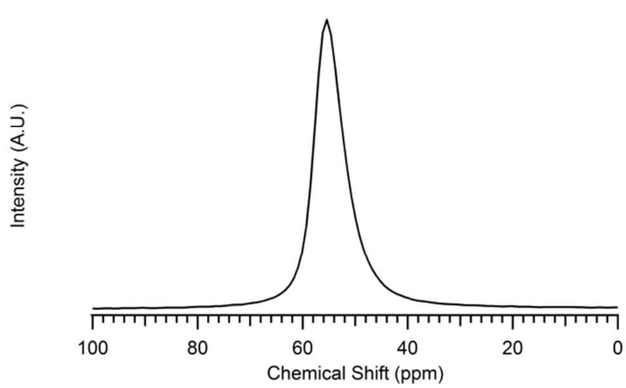

Figure S3. ^{27}Al MAS NMR of as-synthesized K-CHA

Steaming Experiments with Zeolite Y and CHA

Three series of steaming experiments were conducted using zeolite Y (FAU) for the purposes of verifying that the steaming and dry calcination results previously reported in the literature on Y can be reproduced as well as determining whether the trend observed with CHA under varying partial pressures is also observed in Y when steamed using the same procedure. For all of the Y steaming experiments, the starting zeolite was a commercial NaY with Si/Al=2.97 that had been NH_4^+ exchanged three times for 2 h at 90°C with 1 M NH_4NO_3. The NH_4^+ exchanged Y, designated NH_4NaY, had a Na/Al ratio of 0.28 (measured by EDS) and was steamed using the same tube furnace set up as that used for the CHA samples.

A summary of the steaming conditions is provided in Table S1. Two sets of steaming experiments were conducted at 550°C and 650°C under similar conditions reported by Wang et al.[19], who investigated the effect of the water partial pressure on steaming of zeolite Y. Samples were heated at 5°C/min to the steaming temperature (550°C or 650°C) under 50 cc/min of dry air and then subjected to flowing steam (created by bubbling 50 cc/min of dry air through a heated water saturator) for 3 h at the steaming temperature. Samples were cooled under 50 cc/min of dry air flow at the end of the 3 h steaming period. Steaming experiments were conducted with the bubbler (providing approximately a 50% saturated air and water vapor mixture) held at 60°C, 80°C and 90°C, for which the water saturation pressures are 19.9 kPa, 47.3 kPa and 70.1 kPa, respectively. An additional dry calcination was carried out on the NH_4NaY using the same temperature profile under flowing dry air (50 cc/min).

In the third set of steaming experiments, NH_4NaY samples were steamed under more severe conditions using the same procedure that was used for the CHA samples steamed at 600°C under varying steam partial pressures. Samples were heated at 1°C/min to 800°C and held for 8 h at the steaming temperature. The entire process, including heating and cooling, was carried out under flowing air. An additional dry calcination was conducted under 50 cc/min of dry air using the same temperature profile.

To determine whether CHA would also show the same trend that was observed with Y steamed at 550°C and 650°C, an additional series of steaming experiments was conducted with CHA using the same steaming procedures that were used for the 550°C and 650°C zeolite Y steaming experiments, where NH_4-CHA samples were steamed for 3 h at 500°C under varying steam partial pressures. The furnace was ramped at 5°C/min to 500°C under 50 cc/min of dry air, steam was introduced for 3 h at 500°C only, and the sample was then allowed to cool under flowing dry air (50 cc/min).

Table S1. Summary of zeolite Y steaming conditions

Sample	Heating Ramp Rate	Steaming Time	Steaming Temperature	Bubbler Temperature	Duration of Flowing Steam	Al_T/Al_{Total}
NH_4NaY-S550B90	5°C/min	3 h	550°C	90°C	At steaming temperature only	0.144
NH_4NaY-S550B80	5°C/min	3 h	550°C	80°C	At steaming temperature only	0.288
NH_4NaY-S550B60	5°C/min	3 h	550°C	60°C	At steaming temperature only	0.387
NH_4NaY-C550	5°C/min	3 h	550°C	-	Dry calcination	0.822
NH_4NaY-S650B90	5°C/min	3 h	650°C	90°C	At steaming temperature only	0.394
NH_4NaY-S650B80	5°C/min	3 h	650°C	80°C	At steaming temperature only	0.325
NH_4NaY-S650B60	5°C/min	3 h	650°C	60°C	At steaming temperature only	0.308
NH_4NaY-C650	5°C/min	3 h	650°C	-	Dry calcination	0.444
NH_4NaY-S800B90	1°C/min	8 h	800°C	90°C	Entire period	0.230
NH_4NaY-S800B80	1°C/min	8 h	800°C	80°C	Entire period	0.670
NH_4NaY-S800B60	1°C/min	8 h	800°C	60°C	Entire period	0.713
NH_4NaY-C800	1°C/min	8 h	800°C	-	Dry calcination	0.234
CHA-S500B90	5°C/min	3 h	500°C	90°C	At steaming temperature only	0.139
CHA-S500B60	5°C/min	3 h	500°C	60°C	At steaming temperature only	0.156
CHA-C500	5°C/min	3 h	500°C	-	Dry calcination	0.201

Figures S4 and S5 show the powder XRD patterns of the NH_4NaY samples steamed at 550°C and 650°C, respectively. ^{27}Al MAS NMR spectra of the 550°C and 650°C steamed samples are shown in Figures S6 and S7. At both steaming temperatures, the ^{27}Al NMR indicates that a greater fraction of tetrahedral aluminum is converted to pentacoordinated and octahedral aluminum for the steamed

NH_4NaY samples compared to the dry calcined samples, consistent with what has been reported by Wang et al.

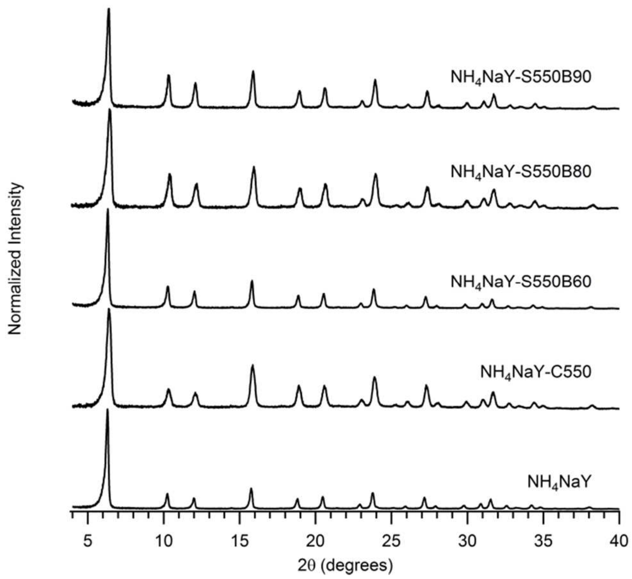

Figure S4. Powder XRD patterns of unsteamed NH_4NaY and NH_4,NaY samples steamed for 3 h at 550°C in order of increasing steam partial pressure (bottom to top).

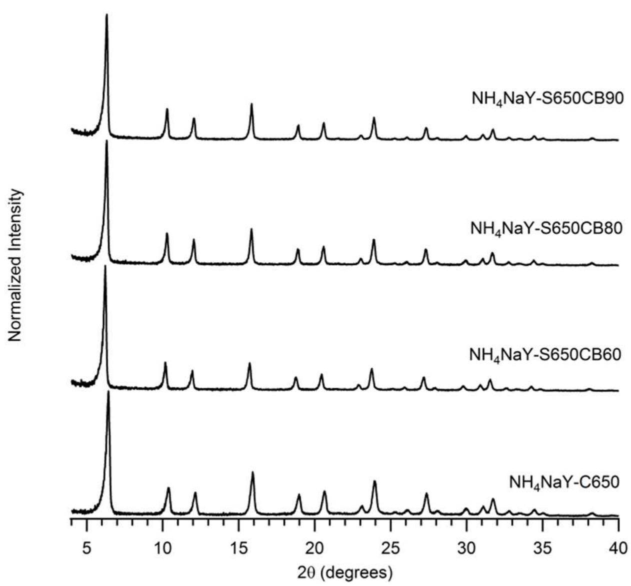

Figure S5. Powder XRD patterns of NH_4NaY samples steamed for 3 h at 650°C in order of increasing steam partial pressure (bottom to top).

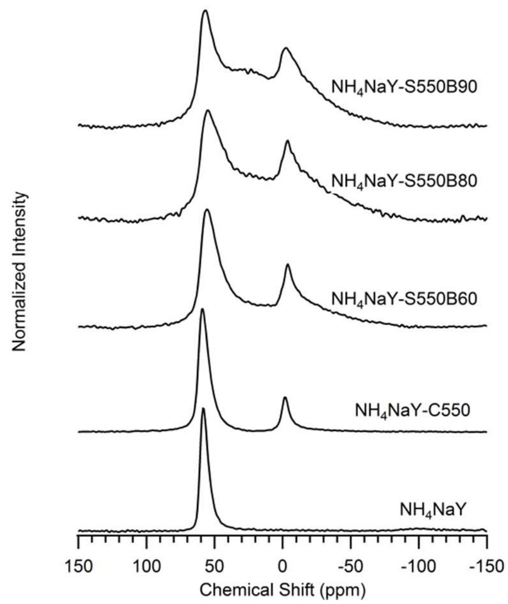

Figure S6. ^{27}Al NMR spectra of unsteamed NH_4NaY and NH_4NaY samples steamed for 3 h at 550°C in order of increasing steam partial pressure (bottom to top).

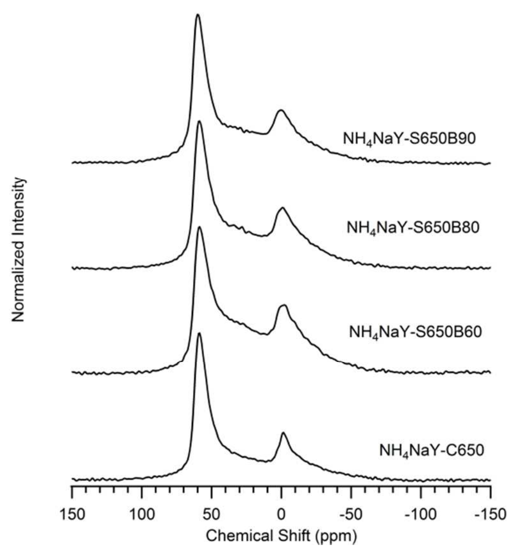

Figure S7. ^{27}Al NMR spectra of NH_4NaY samples steamed for 3 h at 650°C in order of increasing steam partial pressure (bottom to top).

The powder XRD patterns and ^{27}Al NMR spectra of the NH_4,Na-Y samples steamed at 800°C are shown in Figures S8 and S9, respectively. At these conditions, the NH_4NaY samples show increased degradation when the water partial pressure is lowered, with the sample calcined under dry air showing the greatest degradation. The ^{27}Al NMR is consistent with the XRD data in that the amount of pentacoordinated and octahedral aluminum increase relative to the tetrahedral aluminum as the water partial pressure is lowered. This trend is opposite of what was observed for the 550°C and 650°C steamed NH_4NaY but consistent with the behavior of CHA steamed at 600°C under varying steam partial pressures. The similarity in the behavior of steamed Y compared to CHA at these conditions suggests that the trend of increased degradation with decreasing steam partial pressure is not unique to CHA.

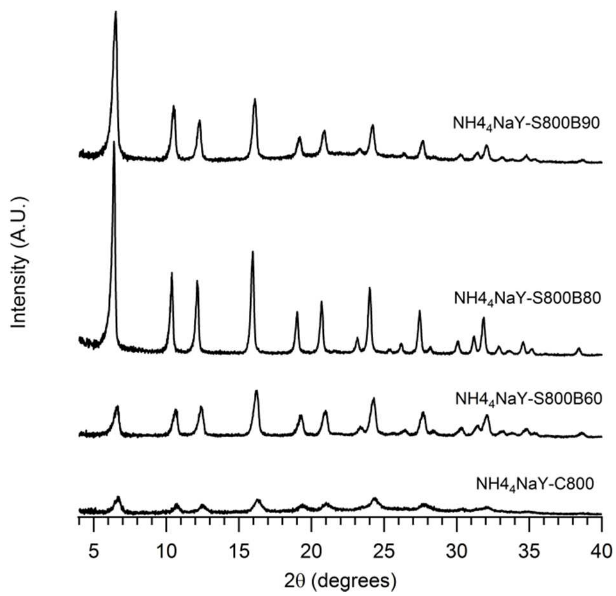

Figure S8. Powder XRD patterns of NH_4Na-Y samples steamed for 8 h at 800°C in order of increasing steam partial pressure (bottom to top).

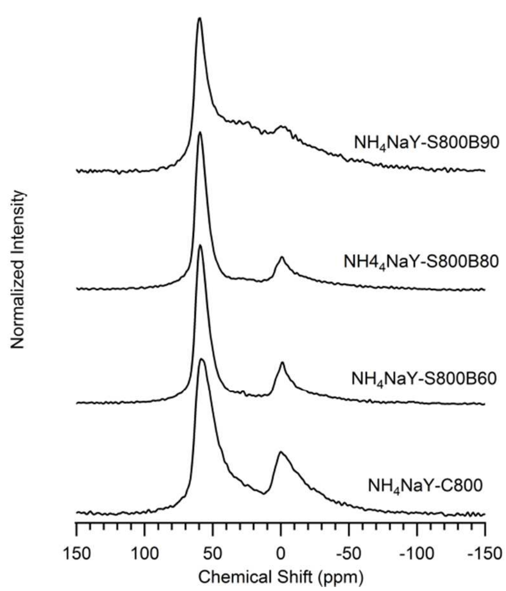

Figure S9. ^{27}Al MAS NMR of NH_4Na-Y samples steamed for 8 h at 800°C in order of increasing steam partial pressure (bottom to top).

Figures S10 and S11 show the powder XRD patterns and ^{27}Al MAS NMR, respectively, of the CHA samples steamed at 500°C where steam is introduced at 500°C only. While the powder XRD patterns of the steamed samples are very similar to each other, the ^{27}Al NMR spectra indicate that as the steam partial pressure is increased, an increasing portion of the tetrahedral aluminum is converted to pentacoordinated and octahedral aluminum and is consistent with what was observed for the 550°C and 650°C steamed Y.

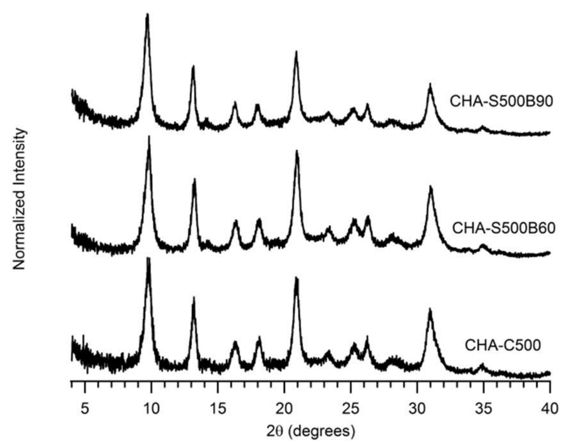

Figure S10. Powder XRD patterns of CHA samples steamed for 3 h at 500°C in order of increasing steam partial pressure (bottom to top).

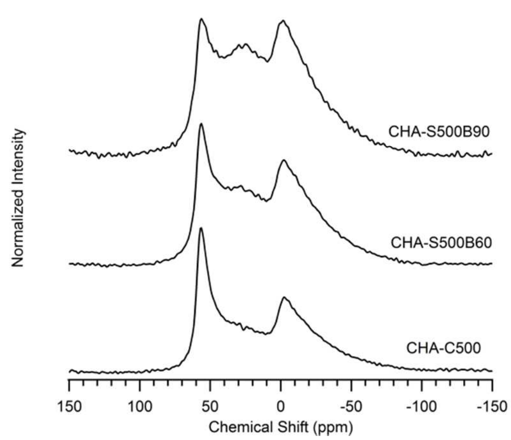

Figure S11. ^{27}Al MAS NMR of CHA samples steamed for 3 h at 500°C in order of increasing steam partial pressure (bottom to top).

MTO Reaction Data for Fresh and Regenerated Steamed CHA

An additional batch of steamed CHA was prepared to determine whether the activity could be recovered by regeneration. CHA was steamed for 8 h at 600°C under a steam partial pressure of 47.3 kPa, and a portion of the steamed material was acid washed in the same manner as described in the Experimental section. Reaction testing was conducted using a 10% methanol/inert feed at a WHSV of 1.3 h^{-1}. The reaction profiles at 400°C of the fresh and regenerated 600°C steamed CHA are shown in Figures S12 and S13, respectively. The activity of the 600°C steamed and acid washed CHA was evaluated over two reaction cycles at 450°C and the reaction profiles are shown in Figures S14 and S15.

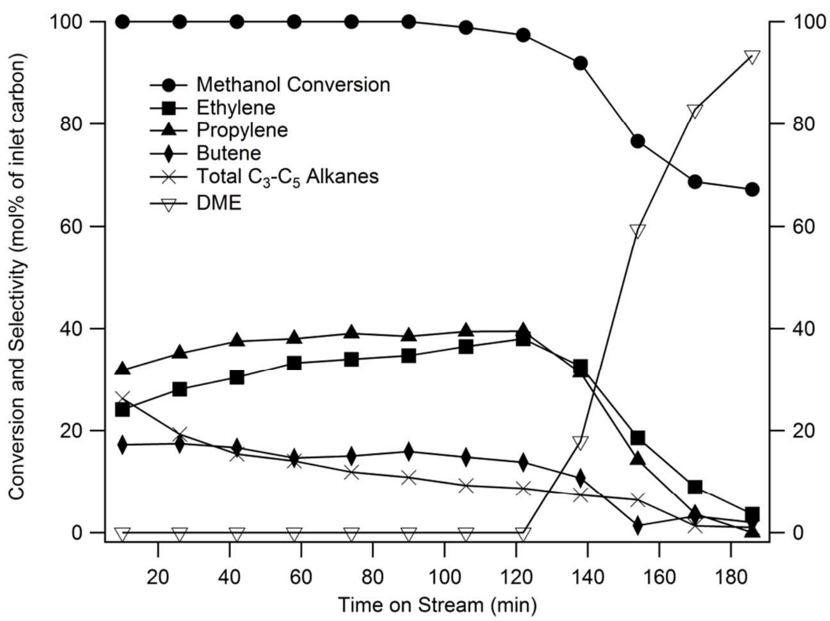

Figure S12. MTO reaction data obtained at 400°C for 600°C steamed CHA during the initial reaction run

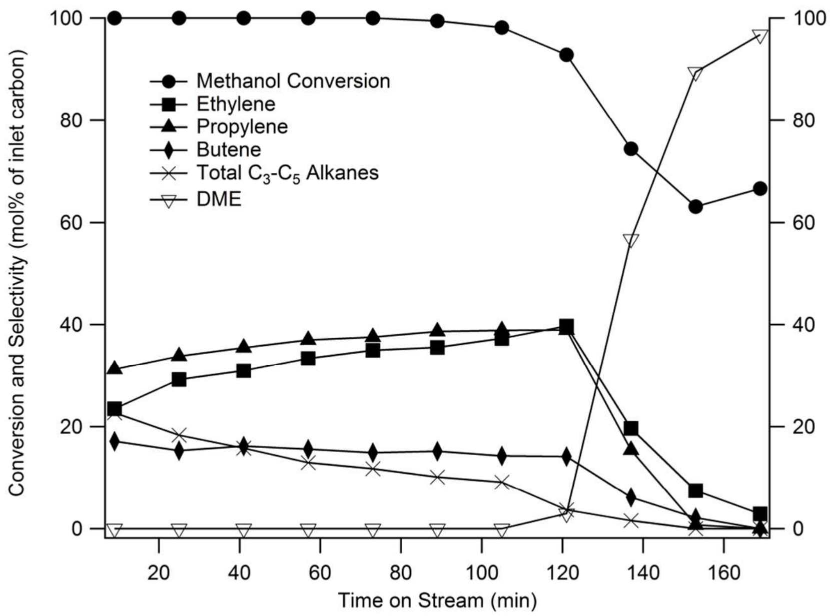

Figure S13. MTO reaction data obtained at 400°C for 600°C steamed CHA after regeneration of spent catalyst

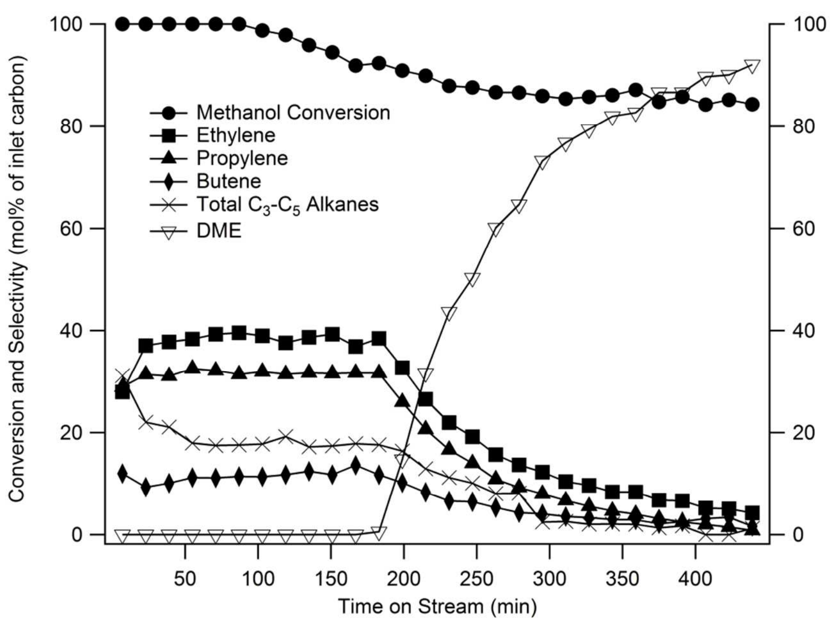

Figure S14. MTO reaction data obtained at 450°C for 600°C steamed and acid washed CHA during the initial reaction test

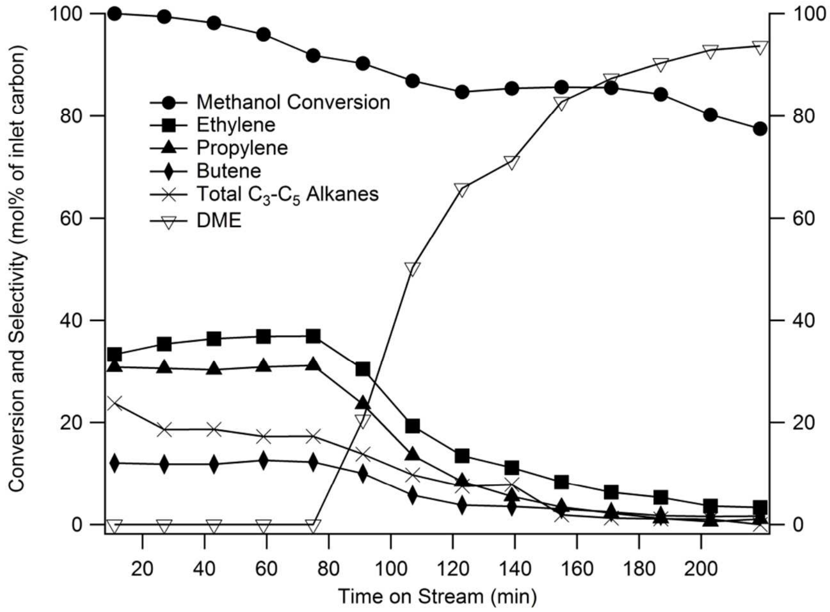

Figure S15. MTO reaction data obtained at 450°C for 600°C steamed and acid washed CHA after regeneration of spent catalyst