

Supplementary Materials

High-silica KFI zeolite: highly efficient synthesis and catalysis in methanol amination reaction

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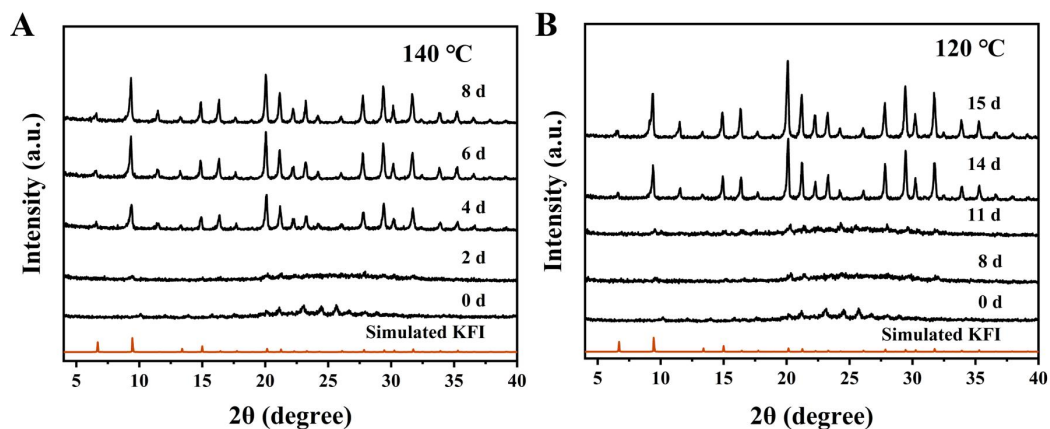
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Synthesis of low-silica KFI zeolite (KFI-3.8) seed

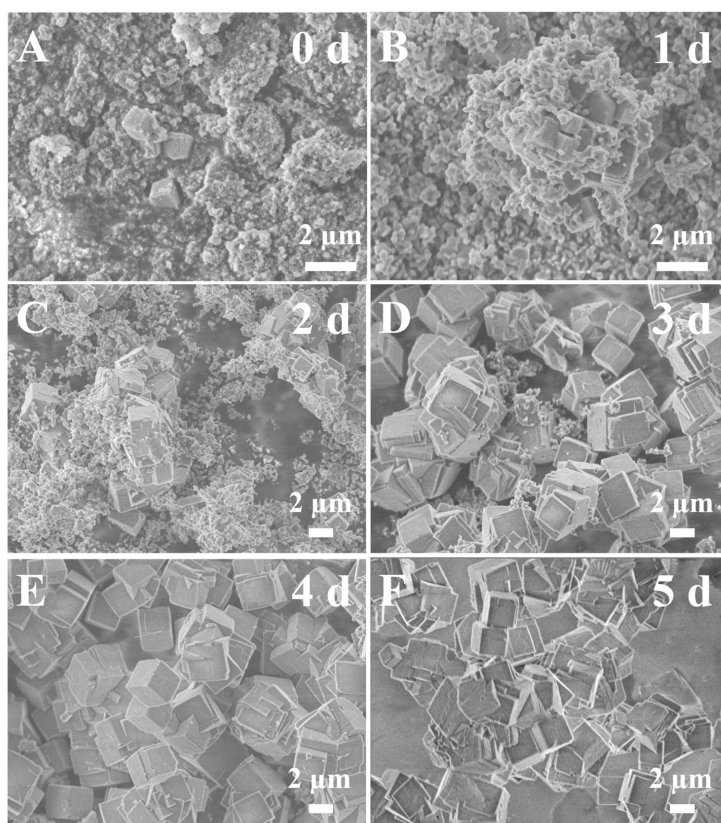
Materials and chemicals for the synthesis of low-silica **KFI** zeolite (KFI-3.8): Phosphoric acid (Beijing Chemical Works, 85 wt.% H₃PO₄), pseudoboehmite (Sasol, 72.7% Al₂O₃), fumed silica (Xuzhou Tiancheng Chlor_alkali Co., Ltd), and morpholine (Tianjin Fuchen Chemical Reagents Factory, C₄H₉NO ≥ 98.5%) were used to synthesize SAPO-34 seed that was used to synthesize low-silica KFI-3.8 zeolite. Fumed silica (Xuzhou Tiancheng Chlor_alkali Co., Ltd), sodium aluminate (Sinopharm Chemical Reagent Co., Ltd, Al₂O₃ ≥ 41.0%), and potassium hydroxide (Beijing Chemical Works; KOH ≥ 85%) were used to synthesize the low-silica KFI-3.8 zeolite in the presence of SAPO-34 seed. All chemicals were used without further purification.

The low-silica **KFI** zeolite (KFI-3.8) was synthesized with SAPO-34 seed substantially according to our previous work^[1]. Firstly, SAPO-34 was synthesized according to “verified synthesis of zeolitic materials third revised edition” released by the Synthesis Commission of the International Zeolite Association (IZA)^[2]. In detail, a mixture was obtained by mixing 11.53 g phosphoric acid, 6.9 g pseudoboehmite, and 21.0 g deionized (DI) water. Another mixture was obtained by mixing 3.07 g fumed silica, 8.72 g morpholine, and 11.25 g DI water, and added to the former mixture with 18.0 DI water. After stirring for few hours at the room temperature, the mixture was transferred into a stainless-steel autoclave, incubated for 24 h at 38 °C, and heated for 24 h at 200 °C. Finally, after the autoclave was cooled to room temperature, the solid sample of SAPO-34 seed was filtered, washed with distilled water, and dried at 80 °C overnight.

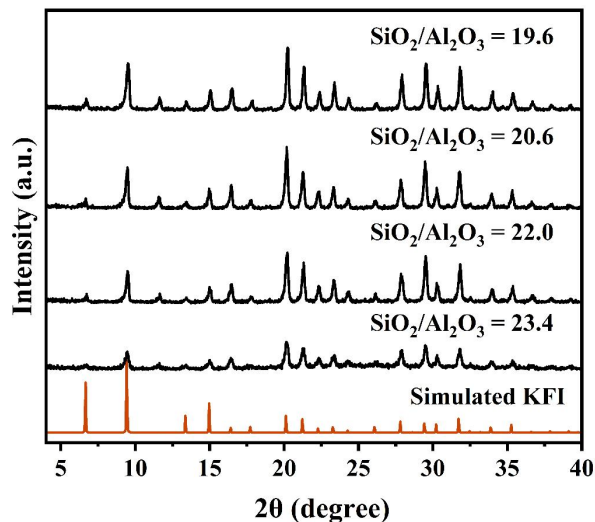
For the KFI-3.8 synthesis, 0.39 g potassium hydroxide and 0.075 g sodium aluminate were first dissolved in 8.0 g DI water. 0.5 g fumed silica was then added and stirred for few hours until a homogeneous mixture was obtained. 0.05 g SAPO-34 seed was added to the mixture, and subsequently transferred into a 10 mL stainless-steel autoclave and crystallized at 100 °C for 5 days. The solid product KFI-3.8 zeolite was filtered, washed with DI water, and dried at 80 °C overnight.



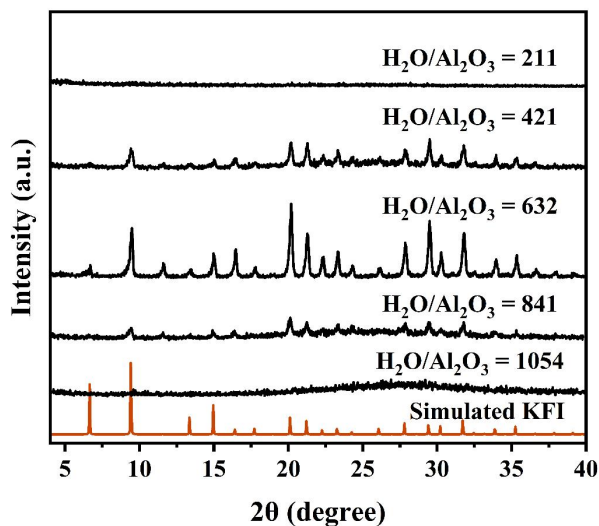
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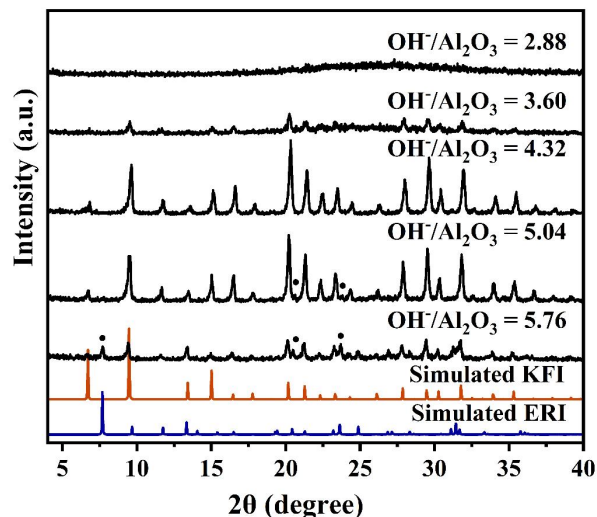
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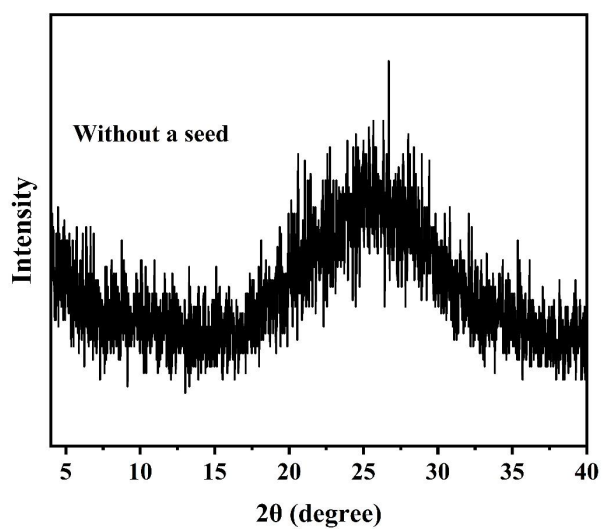
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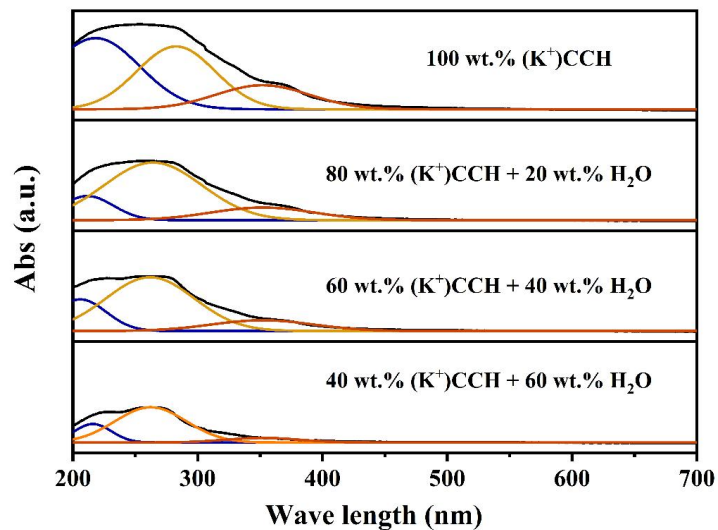
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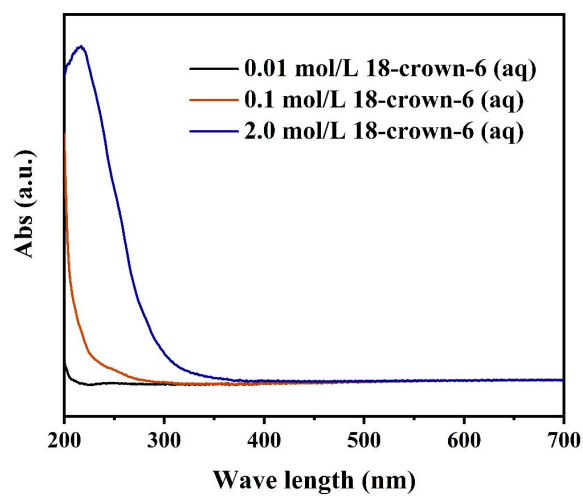
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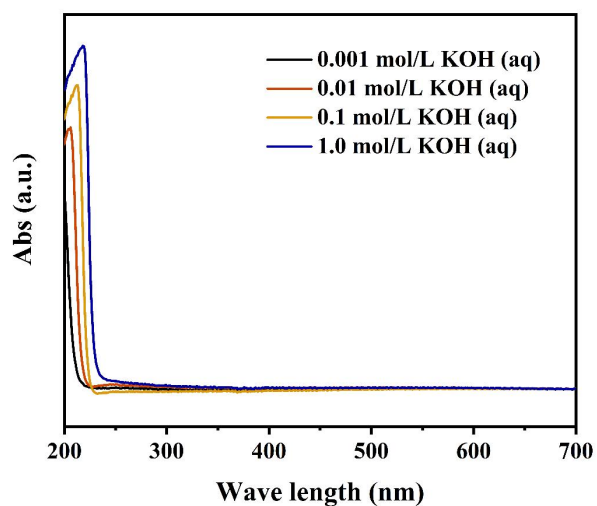
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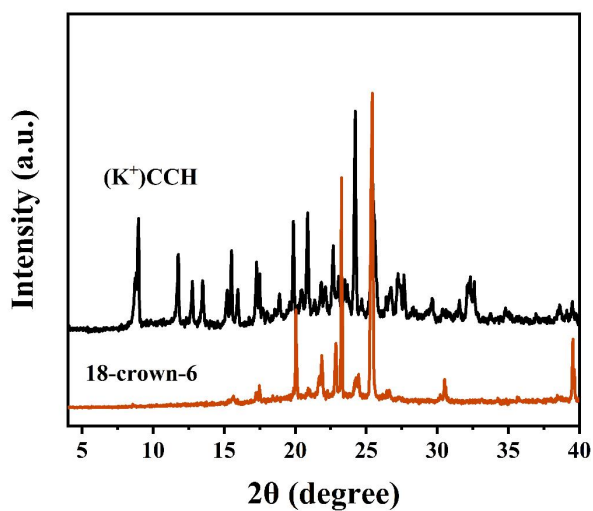
Supplementary Figure 7. UV-Vis spectra deconvolution of $(K^+)CCH$ diluted with different fraction of DI water.



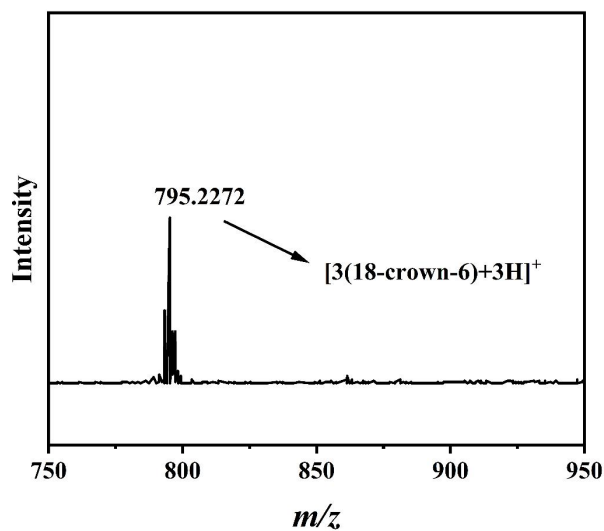
Supplementary Figure 8. UV-Vis adsorption spectra of 18-crown-6 aqueous solutions with different concentrations.



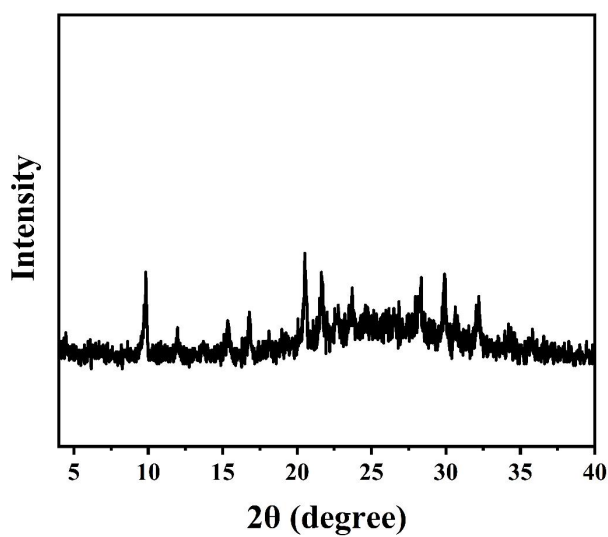
Supplementary Figure 9. UV-Vis adsorption spectra of KOH aqueous solutions with different concentrations.



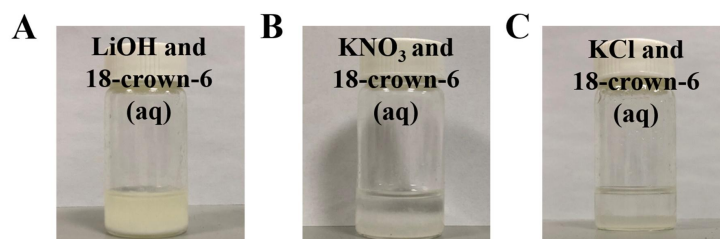
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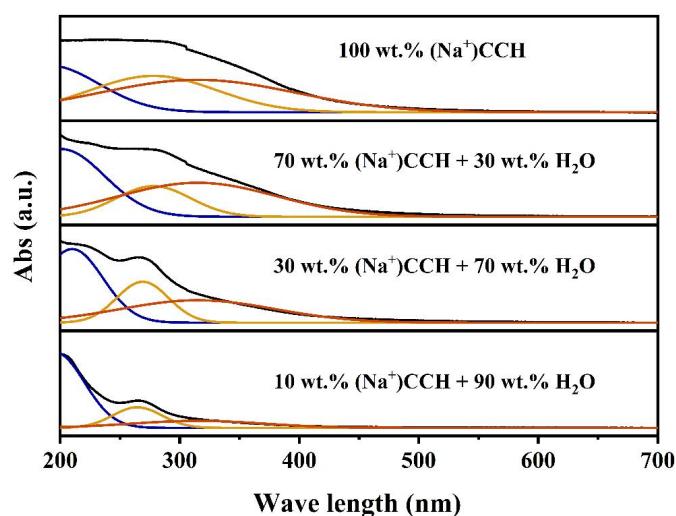
Supplementary Figure 11. Mass spectrum of $(\text{K}^+)\text{CCH}$.



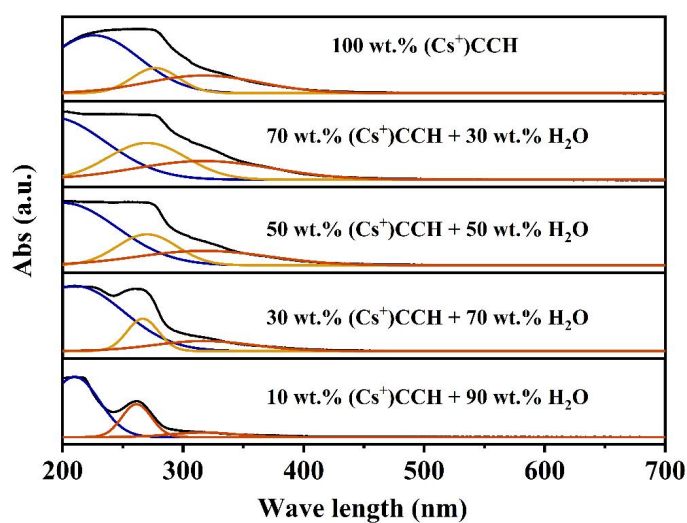
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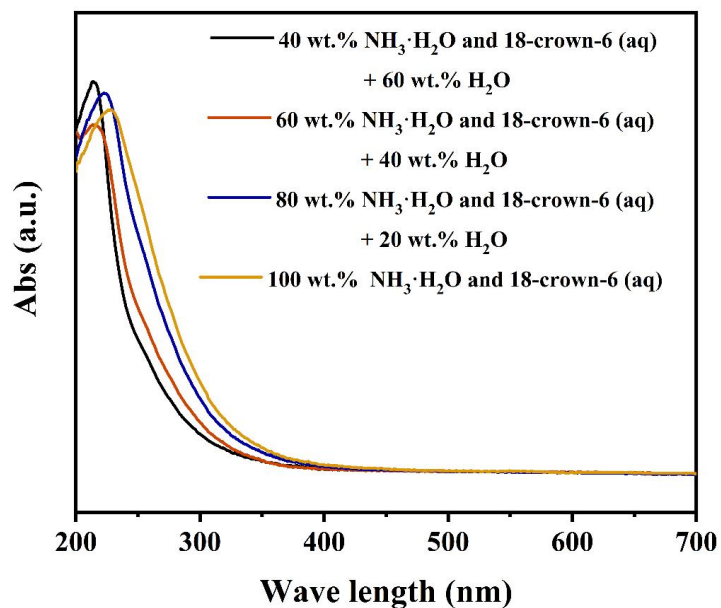
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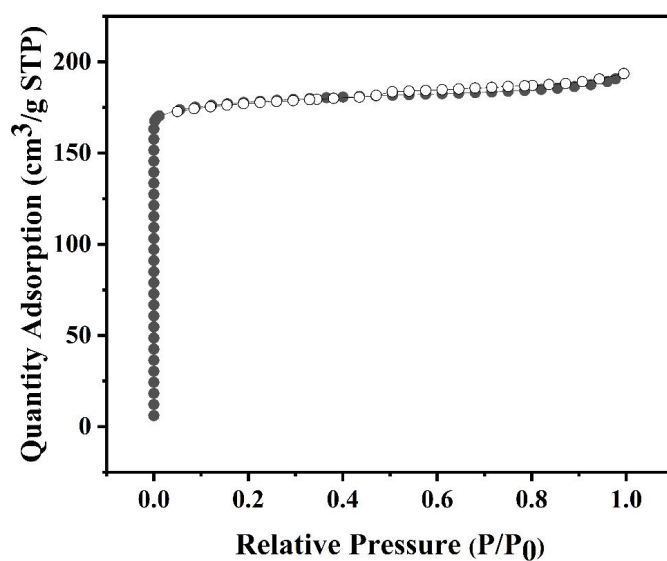
Supplementary Figure 14. UV-Vis spectra deconvolution of (Na⁺)CCH diluted with different fraction of DI water.



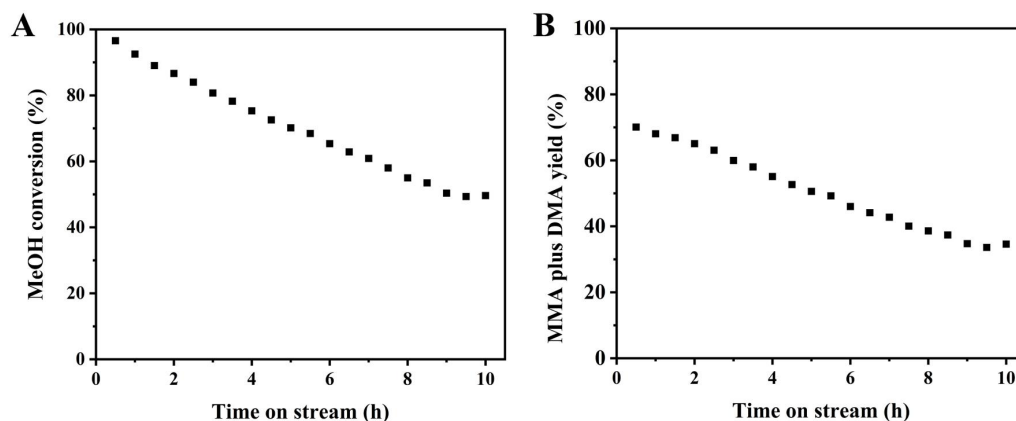
Supplementary Figure 15. UV-Vis spectra deconvolution of (Cs⁺)CCH diluted with different fraction of DI water.



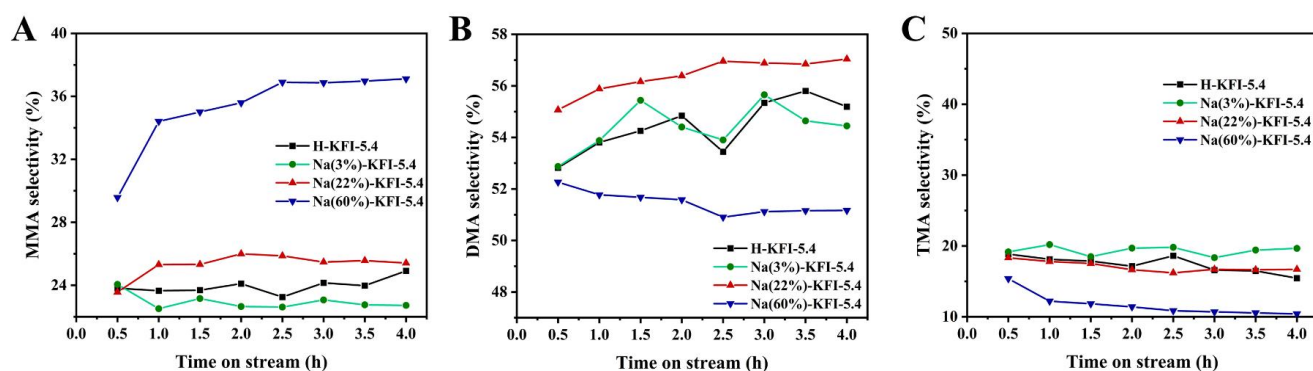
Supplementary Figure 16. UV-Vis adsorption spectra of $\text{NH}_3 \cdot \text{H}_2\text{O}$ and 18-crown-6 (aq) mixture diluted with different fraction of DI water.



Supplementary Figure 17. N_2 adsorption (●) and desorption (○) isotherms of H-KFI-5.4 zeolite synthesized at the crystallization temperature of $150\text{ }^\circ\text{C}$ and time of 5 days.



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Supplementary Table 1. Composition details of (K⁺)CCH.

Sample	K ⁺ (g/L) ^a	Weight percentage of H ₂ O (%) ^b	Weight percentage of 18-crown-6 (%) ^c	Chemical composition
(K ⁺)CCH	78.54	23.21	71.46	[(KOH) _{1.0} ·(18-crown-6) _{2.85} ·(H ₂ O) _{13.57}]

^aThe concentration of K⁺ determined by ICP; ^bWeight percentage of H₂O (%) = (weight of the (K⁺)CCH - weight of the (K⁺)CCH after vacuum freeze-drying) / weight of the (K⁺)CCH × 100%; ^cWeight percentage of 18-crown-6 (%) = (weight of the (K⁺)CCH - weight of the H₂O - weight of the KOH) / weight of the (K⁺)CCH × 100%.

References

1. Wu R, Han JF, Wang YZ, et al. Exclusive SAPO-seeded synthesis of ZK-5 zeolite for selective synthesis of methylamines. *Inorg Chem Front* 2022;9:5766-73.[DOI: 10.1039/d2qi01544g]
2. Mintova S. Verified syntheses of zeolitic materials third revised edition. Available from: http://www.iza-online.org/synthesis/VS_3rdEd.pdf. [Last accessed on 17 Apr 2024]