

***This is the preprint of the following article:***

Bajec D, Kostyniuk A, Huš M, Grom M, Pohar A, Likozar B. Catalytic methane halogenation by bromine over microporous SAPO-34 zeolite material towards methyl bromide, dibromomethane and hydrogen bromide. Journal of the Taiwan Institute of Chemical Engineers. 2023; (142): 1–11.

doi: 10.1016/j.jtice.2022.104645

***which has been published in final form at:***

<http://dx.doi.org/10.1016/j.jtice.2022.104645>

## Appendix A. Supplementary info



Figure S1: Photograph of quartz reactor containing 1 g of SAPO-34 after 30 h on stream with remaining volume filled with SiC.

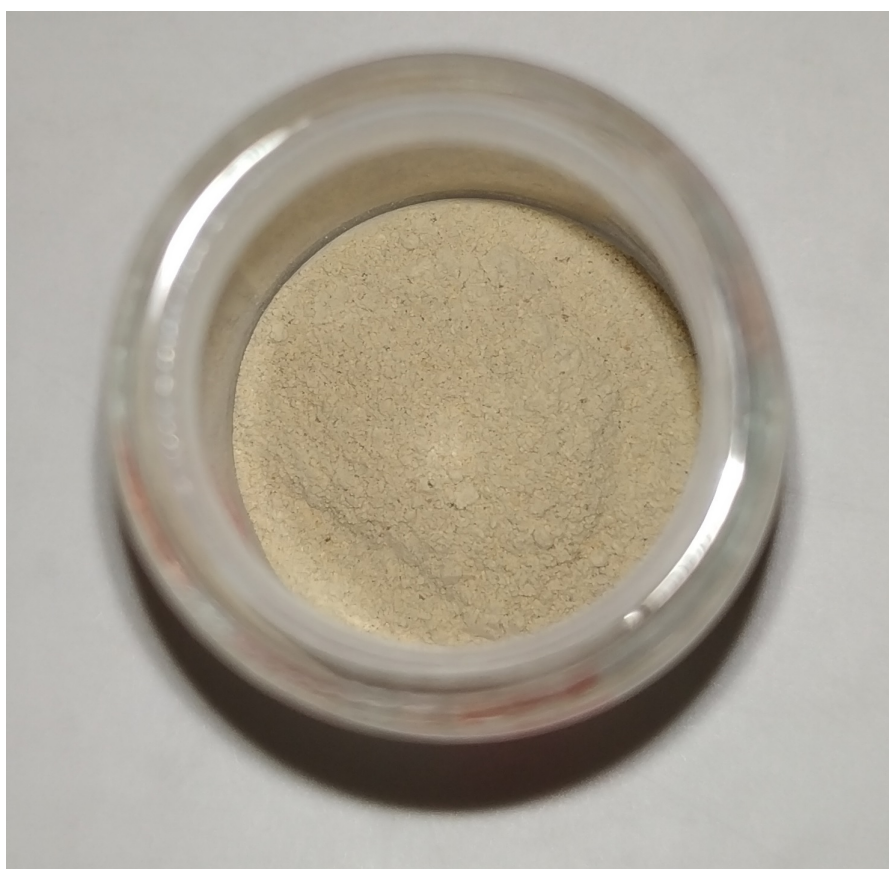


Figure S2: Photograph of used SAPO-34 after 30 h on stream and after evacuating the sample at 120 °C.



Figure S3: Photograph of quartz reactor containing 1 g of coked SAPO-34.



Figure S4: Used SAPO-34 after 20 h on stream at 380 °C and WHSV = 2 h<sup>-1</sup>, with 15 mol.% of Br<sub>2</sub> in inlet gas mixture.

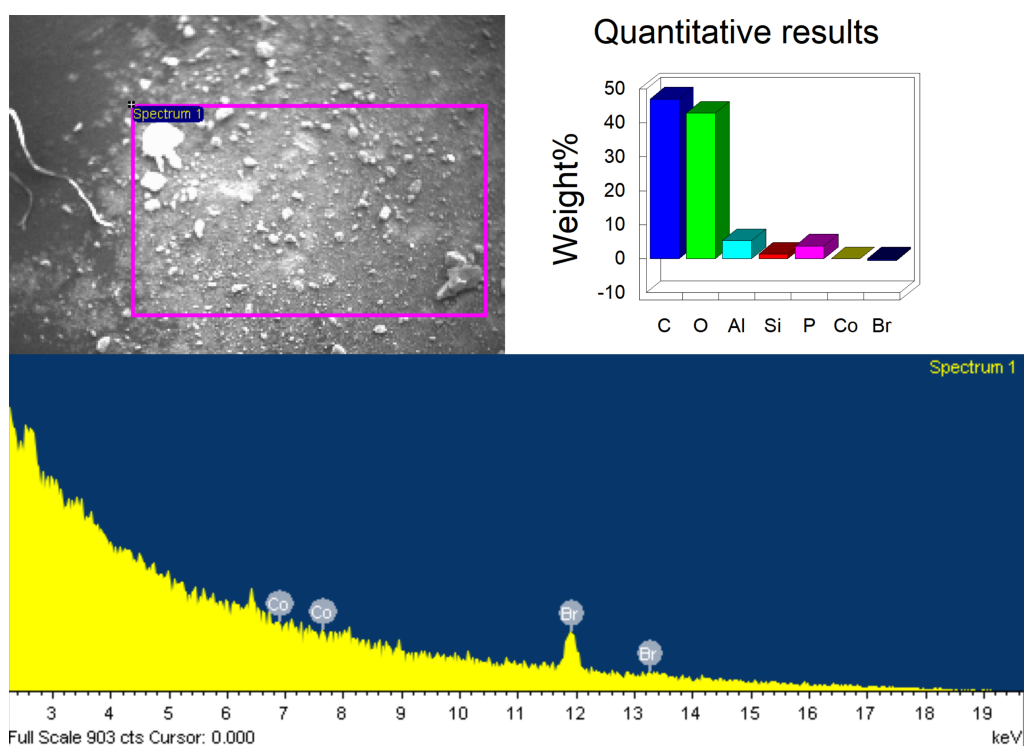


Figure S5: SEM-EDX analysis of the spent SAPO-34. Reaction conditions: WHSV = 0.6 h<sup>-1</sup>, T = 300–365 °C, TOS = 30 h.

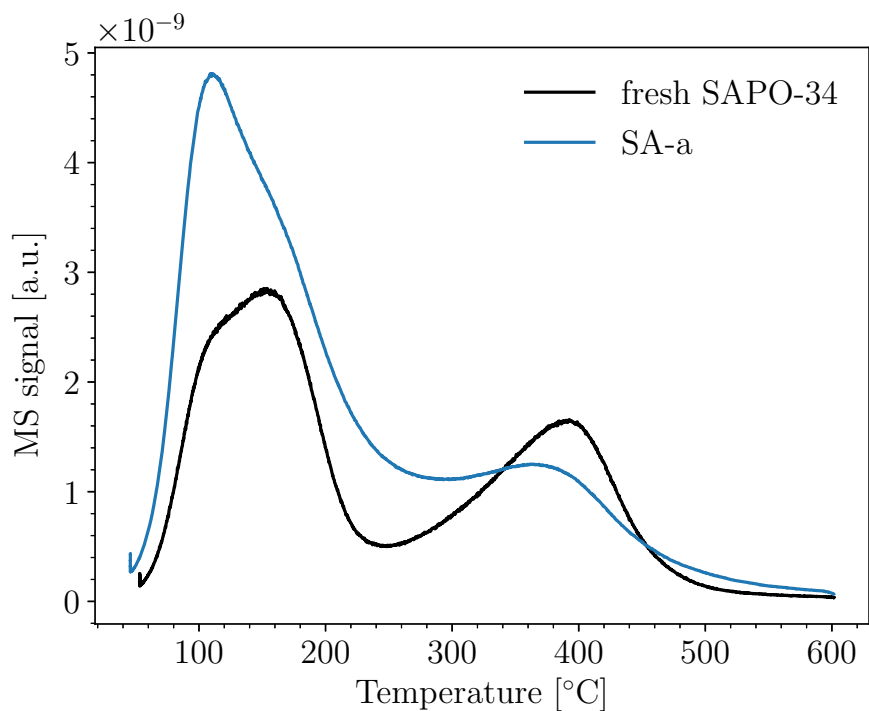


Figure S6: Comparison of  $\text{NH}_3$ -TPD-MS ( $m/Z = 17$ ) profiles of fresh SAPO-34 with used sample SA-a.

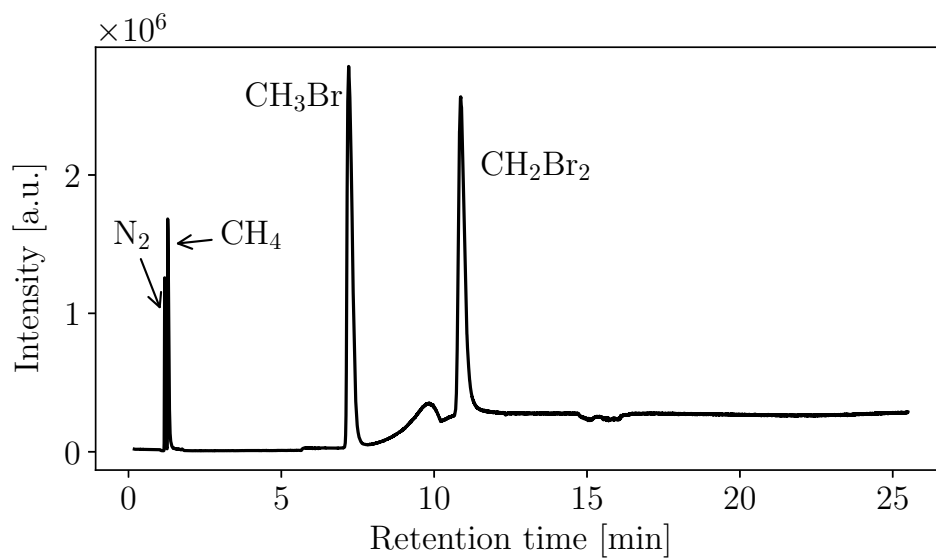
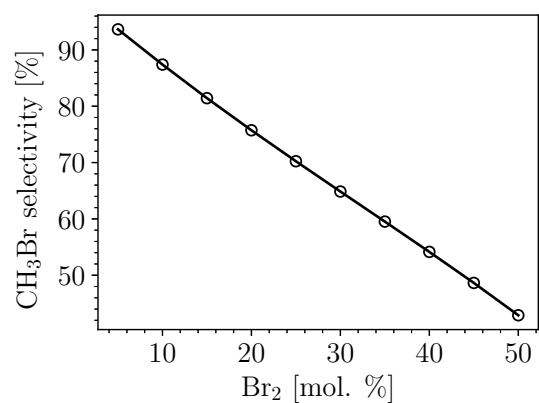
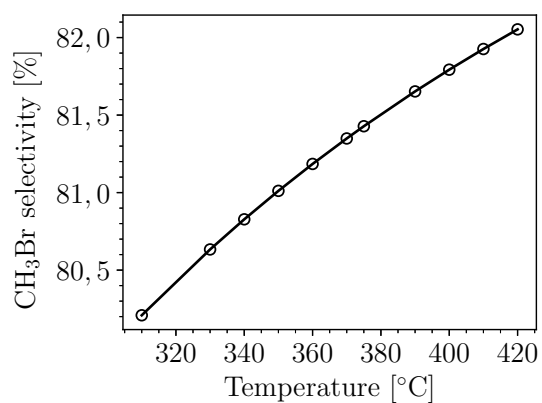


Figure S7: Example of a chromatogram (total ion) from the middle of methane bromination over SAPO-34 at 390  $^{\circ}\text{C}$  and  $\text{WHSV} = 0.22 \text{ h}^{-1}$ .



Figure S8: Photograph of quartz reactor containing 1 g of used SAPO-34 after 4.5 h reaction with  $\text{CH}_2\text{Br}_2$  at  $410\text{ }^\circ\text{C}$ .



(a)  $\text{CH}_3\text{Br}$  selectivity at different temperatures with 15 mol. %  $\text{Br}_2$  in the reaction mixture.

(b)  $\text{CH}_3\text{Br}$  selectivity at different content of  $\text{Br}_2$  in the reaction mixture at  $375\text{ }^\circ\text{C}$ .

Figure S9: Equilibrium selectivity for  $\text{CH}_3\text{Br}$  at 1 bar.