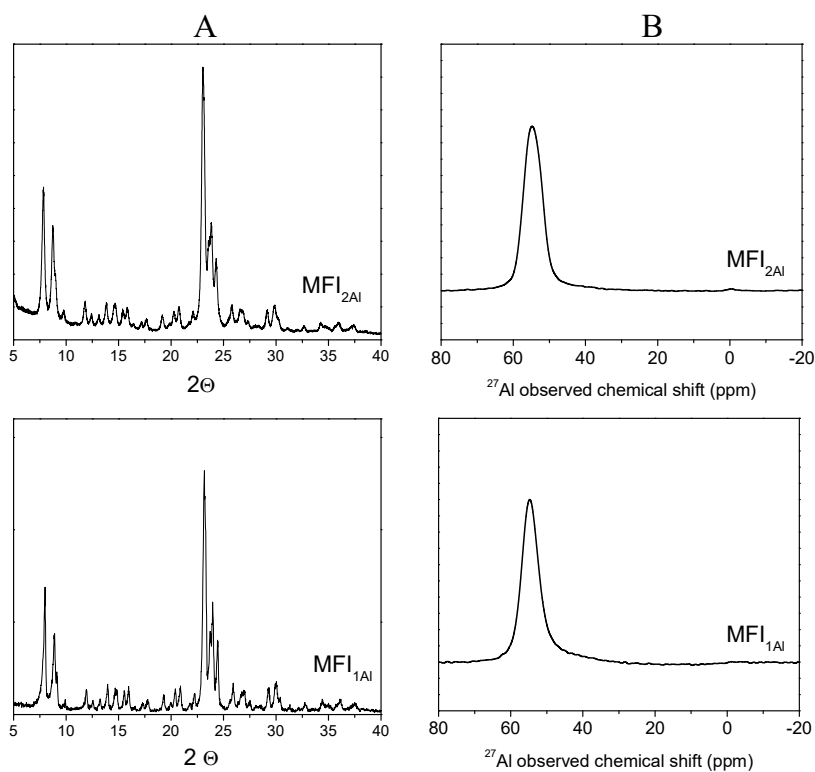


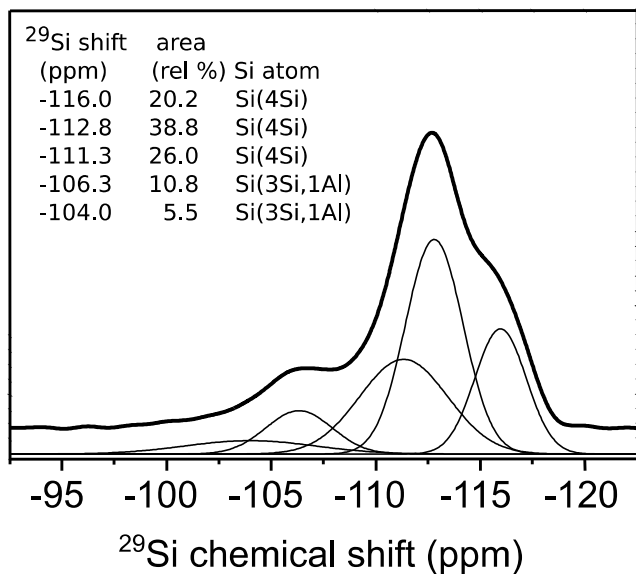
## Electronic Supplementary Information (ESI)

### S-1 Protocols for synthesis of $\text{MFI}_{2\text{Al}}$ and $\text{MFI}_{1\text{Al}}$ zeolites.

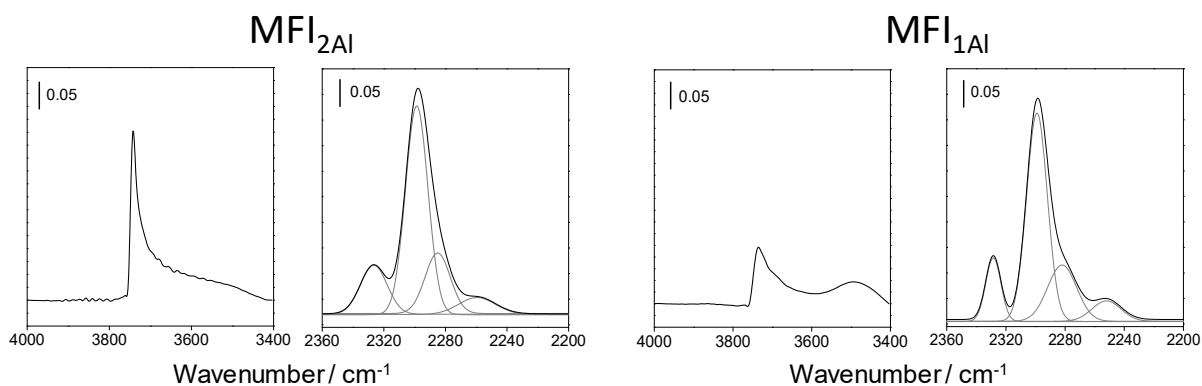
For hydrothermal synthesis of the  $\text{MFI}_{1\text{Al}}$  sample,  $\text{Al}(\text{NO}_3)_3$  in an amount of 1.63 g was added to 10 ml of distilled water and then 22.6 g TEOS (Aldrich 99) in 5 ml of ethanol was added and stirred for 90 min. In another beaker, 20.4 ml of 40 % TPAOH (Fluka, 20% TPAOH in water) was mixed with 60 ml of distilled water and stirred for 90 min. Then a resulting TPAOH solution and a mixture containing Al and Si were put together and stirred for further 90 min. In the case of synthesis of  $\text{MFI}_{2\text{Al}}$  0.098 g of metallic Al were at first added to the TPAOH solution (20.4 ml of 40 % TPAOH mixed with 60 ml of distilled water and 5 ml of ethanol) to enhance metal dissolution, and stirred for 90 min, then 6.5 g of Tixosil (Solvay) was added and stirred for further 90 min.



### S-2 XRD patterns (A) and $^{27}\text{Al}$ MAS NMR spectra (B) of Na- $\text{MFI}_{2\text{Al}}$ and Na- $\text{MFI}_{1\text{Al}}$ .



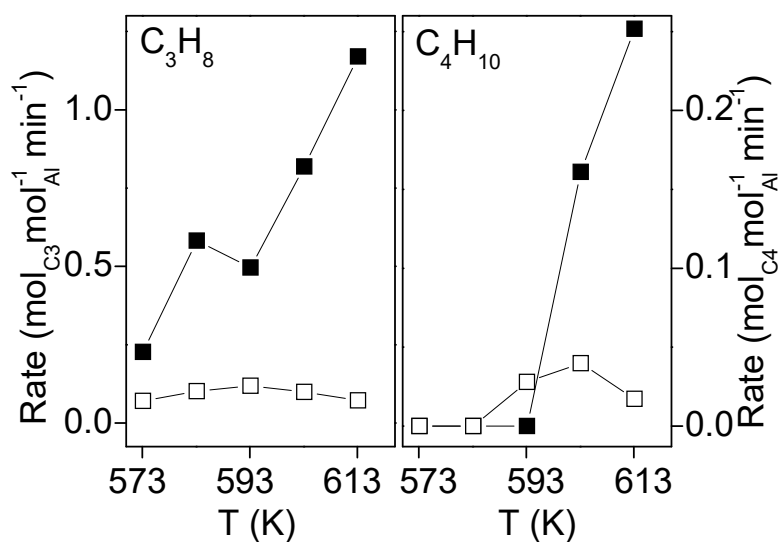
S-3 <sup>29</sup>Si MAS NMR spectrum of MFI<sub>2Al</sub>.



S-4 FTIR spectra of MFI<sub>2Al</sub> and MFI<sub>1Al</sub> dehydrated at 720 K in vacuum after interaction of 1.3 kPa CD<sub>3</sub>CN (30 min at RT and 30 min evacuation at RT), and spectra deconvolution. Extinction coefficients for C≡N groups interacting with Brønsted (2 297 cm<sup>-1</sup>) sites, ε<sub>B</sub> = 2.05 cm μmol<sup>-1</sup>, and Lewis (2 325 cm<sup>-1</sup>) sites, ε<sub>L</sub> = 3.62 cm μmol<sup>-1</sup> (B. Wichterlová et al. Microporous Mesoporous Mater. 24 (1998) 223-233).

**S-5** Vis band frequencies and absorption coefficients for  $\alpha$ -,  $\beta$ - and  $\gamma$ -Co(II) ions in MFI zeolites (J. Dedecek et al. Microporous Mesoporous Mater. 35-6 (2000) 483-494).

| Co(II) ions | Wavenumber<br>$\text{cm}^{-1}$   | Absorption coefficient<br>$\text{mmol.cm.g}^{-1}$ |
|-------------|--|---|
| $\alpha$    | $15\,100 \pm 100$  | $3.7 \pm 1.1$                                     |
| $\beta$     | $16\,000 \pm 150$<br>$17\,150 \pm 150$<br>$18\,600 \pm 100$<br>$21\,200 \pm 200$ | $2.7 \pm 0.7$                                     |
| $\gamma$    | $20\,100 \pm 50$<br>$22\,000 \pm 50$   | $0.9 \pm 0.6$                                     |



**S-6** Turnover rates of formation of propane and isobutane over MFI<sub>2Al</sub> (full symbols) and MFI<sub>1A</sub> (open symbols) depending on temperature.

## S-7 Apparent activation entropy and enthalpy

The apparent activation entropy ( $\Delta S_{\text{app}}^{\#}$ ) and apparent activation enthalpy ( $\Delta H_{\text{app}}^{\#}$ ) were calculated based on transition state theory (TST)

Assuming first order reaction and the reaction rate ( $r_{C_3}$ ) expressed as turnover frequency (TOF), the Eyring-Polanyi equation can be expressed

$$r_{C_3} = \frac{k_b T}{h} \exp\left\{\frac{\Delta S_{\text{app}}^{\#}}{R}\right\} \exp\left\{-\frac{\Delta H_{\text{app}}^{\#}}{RT}\right\} y_{C_3},$$

where  $y_{C_3}$  is the propene molar fraction,  $k_b$  is Boltzmann constant,  $h$  is Planck constant.  $\Delta S_{\text{app}}^{\#}$ ,  $\Delta H_{\text{app}}^{\#}$  were estimated by nonlinear regression procedure minimizing following function

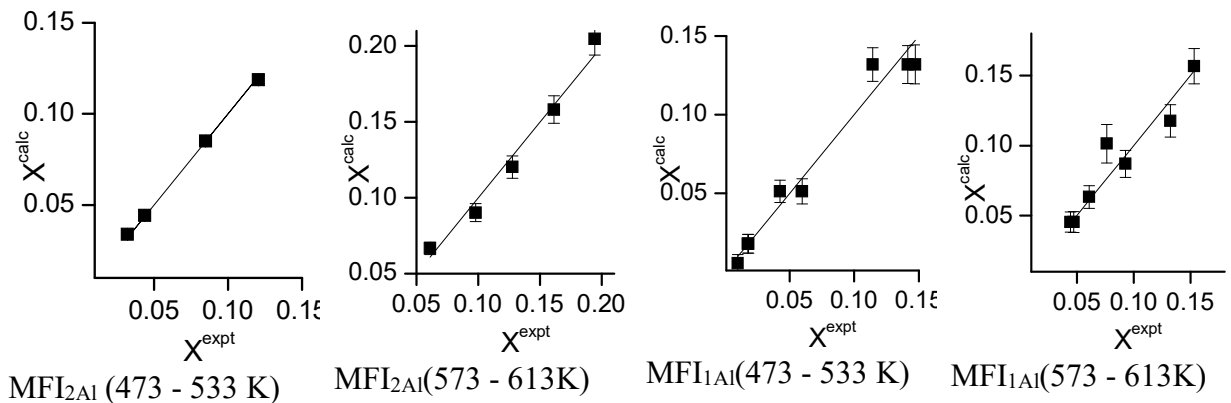
$$S = \min \sum_j \left( \frac{X_{C_3,j}^{\text{calc}} - X_{C_3,j}^{\text{expt}}}{s(X_{C_3,j}^{\text{expt}})} \right)^2,$$

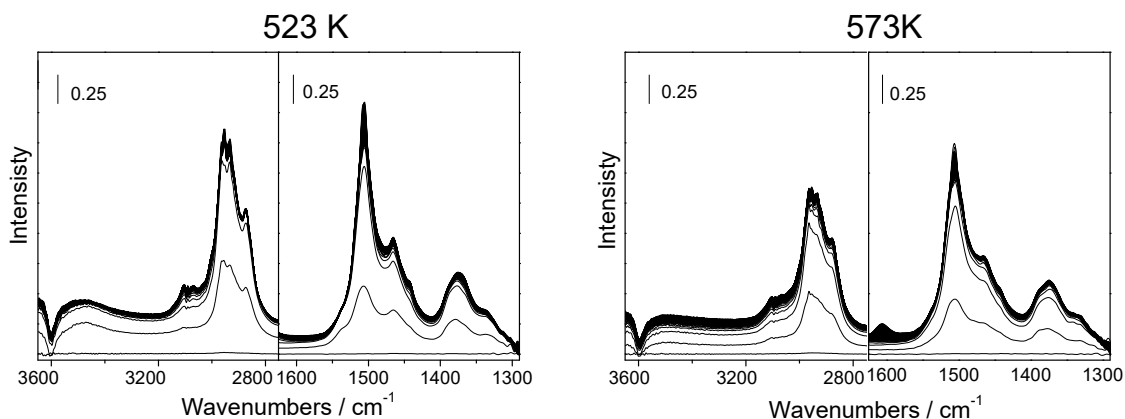
where  $X_{C_3,j}^{\text{calc}}$ ,  $X_{C_3,j}^{\text{expt}}$  are calculated and experimental propene conversion, respectively, and  $s(X_{C_3,j}^{\text{expt}})$  is the standard experimental uncertainty of the experimental propene conversion. The  $X_{C_3,j}^{\text{calc}}$  was calculated by numerical solution of following differential equation describing the material balance inside the catalyst bed.

$$\frac{dX_{C_3}}{dn_{Al}} = k \frac{p^o}{F_{C_3}^0} y_{C_3},$$

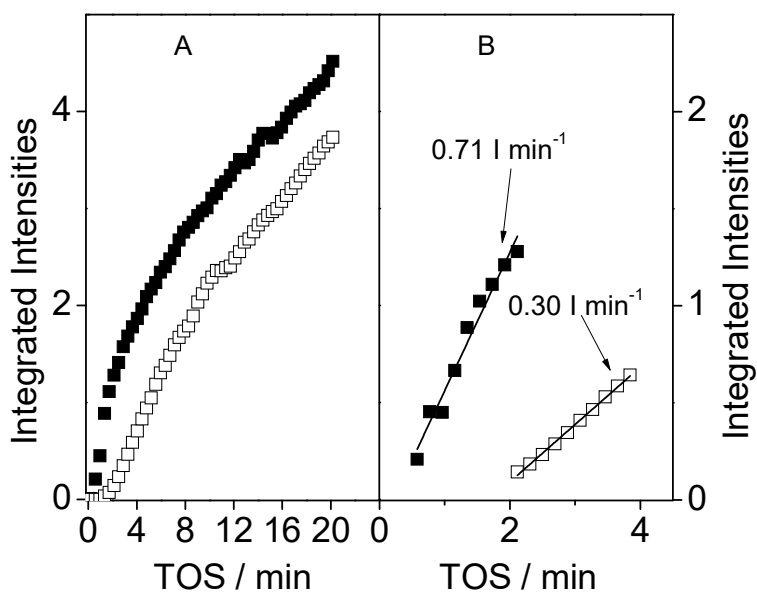
where  $n_{Al}$  is the molar amount of Al sites,  $p^o$  is the reaction pressure,  $F_{C_3}^0$  is the propene molar feed rate.

The fit goodness was checked by chi-square test (*N. Balakrishnan, et al. in Chi-Squared Goodness of Fit Tests with Applications, Academic Press, 2013*). The results are depicted as follows:

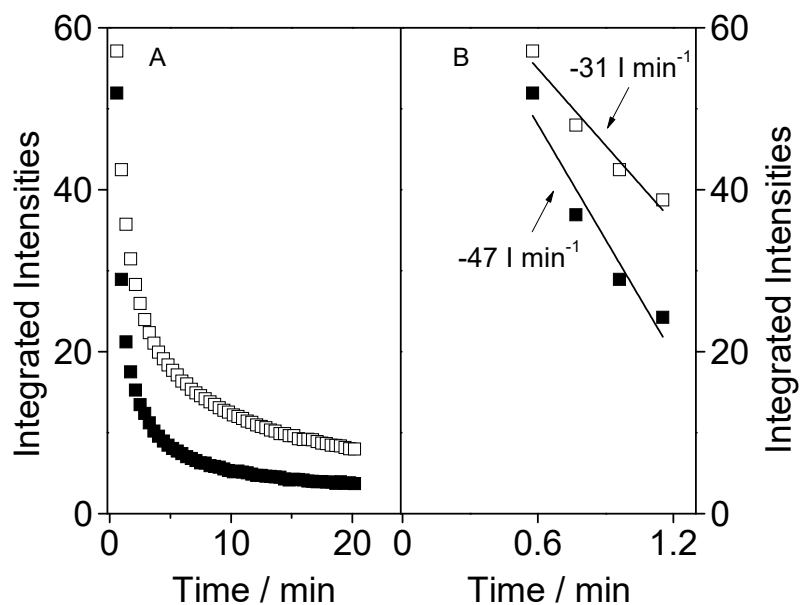




**S-8** Development of *in situ* time-resolved FTIR spectra for  $\text{MFI}_{2\text{Al}}$  at space-time  $200 \text{ mol}_{\text{C}_3} \text{ mol}_{\text{Al}}^{-1} \text{ min}^{-1}$  at 523 K and 573 depending on TOS.



**S-9** Integrated intensities of aromatic carbenium ions ( $1607 \text{ cm}^{-1}$ ) for  $\text{MFI}_{2\text{Al}}$  (full squares) and  $\text{MFI}_{1\text{Al}}$  (empty squares) formed at propene reaction at space time  $200 \text{ mol}_{\text{C}_3} \text{ mol}_{\text{Al}}^{-1} \text{ min}^{-1}$  at 613 K in TOS (A) and estimated initial rates of formation of aromatic carbenium ions (B).



**S-10** Decrease of integrated intensities of saturated carbenium ions ( $3050\text{-}2700 \text{ cm}^{-1}$ ) for MFI<sub>2Al</sub> (full squares) and MFI<sub>1Al</sub> (empty squares) obtained when propene reaction at space time  $200 \text{ mol}_{\text{C}_3} \text{ mol}_{\text{Al}}^{-1} \text{ min}^{-1}$  at 613 K after 20 min of TOS was switched to a He stream kept for 20 min (A) and estimated initial rates of deprotonation of saturated carbenium ions (B).