

**SUPPORTING INFORMATION for**

**Zeolite-Catalyzed Isobutene Amination: Mechanism and Kinetics**

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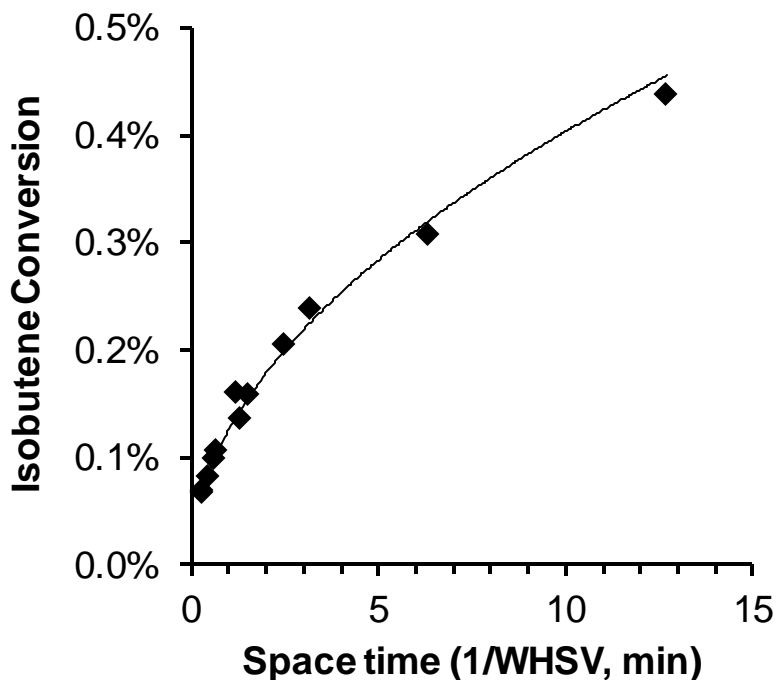
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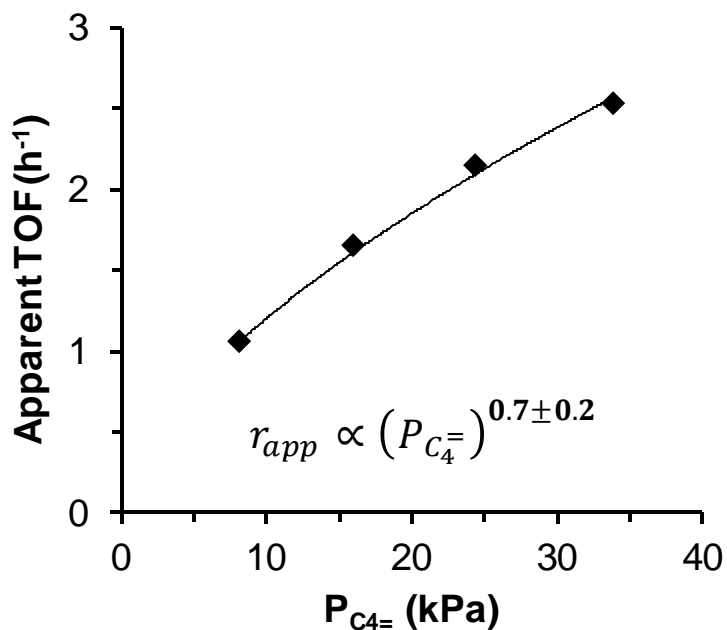
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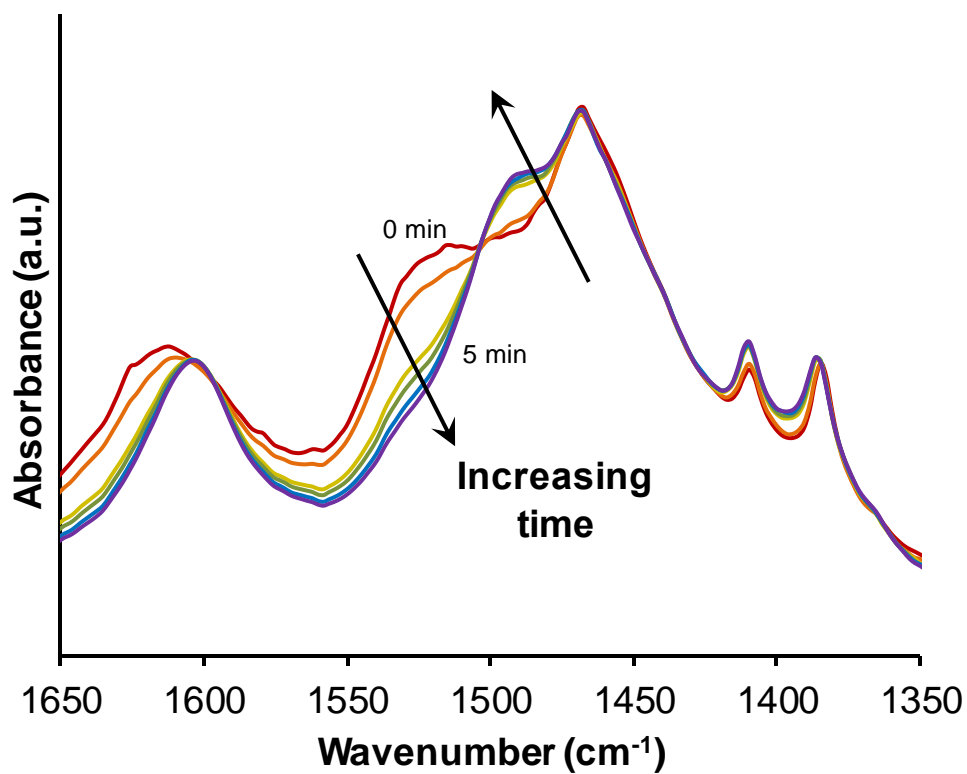
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**Figure S1:** Effects of space time on isobutene conversion over MFI-15. T = 473 K; P = 1 atm;  $P_{C_4=}$  = 32 kPa;  $P_{NH_3}$  = 69 kPa.



**Figure S2:** Effect of isobutene partial pressure on amination rates over MFI-15. T = 473 K; P = 1 atm;  $P_{NH_3}$  = 69 kPa;  $m_{cat}$  = 0.01 g.



**Figure S3:** FTIR spectra of MFI at 433 K after stopping NH<sub>3</sub>/t-BuNH<sub>2</sub> flow. Spectra were taken once per minute up to 5 minutes. The perturbed band around 1520 cm<sup>-1</sup> disappears over the course of several minutes, indicating that NH<sub>3</sub> is desorbing from the surface tert-butylammonium ions.

## Energetic span model considering reactant and product partial pressures

We employ the total expression for turnover frequency as derived in the energetic span model, which considers all intermediate states, transition states, and effects of reactant and product partial pressures:<sup>26</sup>

$$\begin{aligned} \text{TOF} &= \frac{k_B T}{h} \frac{e^{-\Delta G_{\text{rxn}}/RT} \prod_h [R_h] - \prod_h [P_h]}{\sum_{ij} e^{(T_i - I_j - \delta G'_{ij})/RT} \prod_h \delta R'_{h,ij} \delta P_{h,ij}} \\ &= \frac{k_B T}{h} \frac{e^{-\Delta G_{\text{rxn}}/RT} p_{\text{NH}_3} p_{\text{C}_4=} - p_{t\text{-BuNH}_2}}{\sum_{i,j=1}^4 e^{(T_i - I_j - \delta G'_{ij})/RT} \prod_h \delta R'_{h,ij} \delta P_{h,ij}} \quad (\text{S1}) \end{aligned}$$

$$\delta G'_{ij} = \begin{cases} 0 & \text{if } i \leq j \\ \Delta G_{\text{rxn}} & \text{if } i > j \end{cases}$$

Here,  $T_i$  refers to the  $i^{\text{th}}$  transition state before the  $i^{\text{th}}$  intermediate, and  $I_j$  refers to the  $j^{\text{th}}$  intermediate state after the  $j^{\text{th}}$  transition state. All values of  $T_i$  and  $I_j$  are energies with respect to a single reference state. Where there is no explicit transition state for  $T_i$ , the transition state is considered to be the higher of the previous intermediate  $I_{i-1}$  and the following intermediate  $I_i$ .

The term  $\delta R'_{h,ij}$  is equal to the partial pressure of reactant  $h$  if, between intermediate  $I_j$  and  $T_i$ , the reactant is not consumed, and is equal to unity otherwise. The term  $\delta P_{h,ij}$ , on the other hand, is equal to the partial pressure of product  $h$  if, between intermediate  $I_j$  and  $T_i$ , the reactant is consumed, and is equal to unity otherwise. Reactants that enter the catalytic cycle are considered to do so on the uphill of the relevant transition state's formation, while products that leave the catalytic cycle are considered to do so on the downhill from the relevant transition state. The result for the partial pressure term in the denominator for all  $i$  and  $j$  in this reaction is:

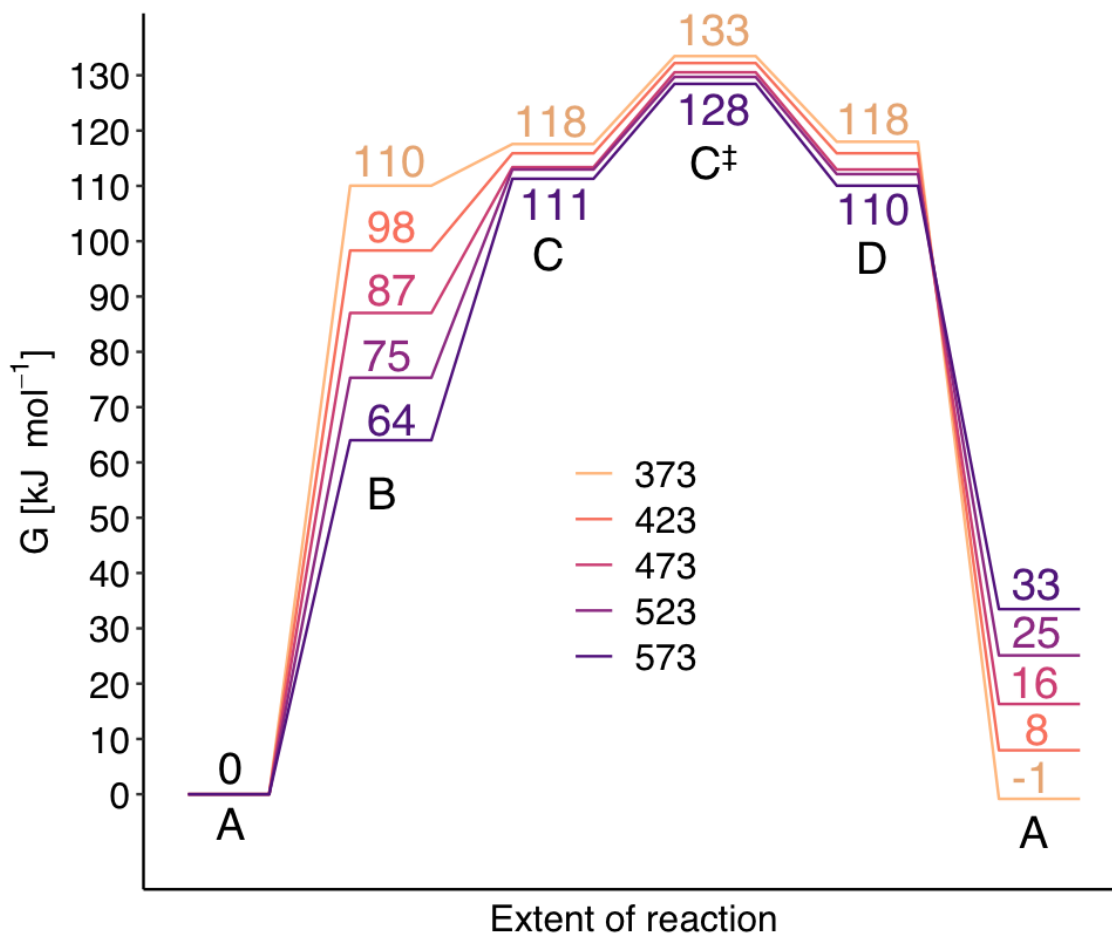
$$\prod_h \delta R'_{h,ij} \delta P_{h,ij} = \begin{bmatrix} 1 & p_{\text{C}_4=} & p_{\text{C}_4=} & p_{\text{C}_4=} p_{\text{NH}_3} \\ p_{\text{NH}_3} & p_{t\text{-BuNH}_2} & p_{t\text{-BuNH}_2} & p_{t\text{-BuNH}_2} p_{\text{NH}_3} \\ p_{\text{NH}_3} & p_{\text{C}_4=} p_{\text{NH}_3} & p_{t\text{-BuNH}_2} & p_{t\text{-BuNH}_2} p_{\text{NH}_3} \\ 1 & p_{\text{C}_4=} & p_{\text{C}_4=} & p_{t\text{-BuNH}_2} \end{bmatrix} \quad (\text{S2})$$

From this expression, we calculated TOF at reaction partial pressures and temperatures. Free energy profiles for a range of temperatures were generated, from which Arrhenius analysis was used to predict apparent activation energies. The free

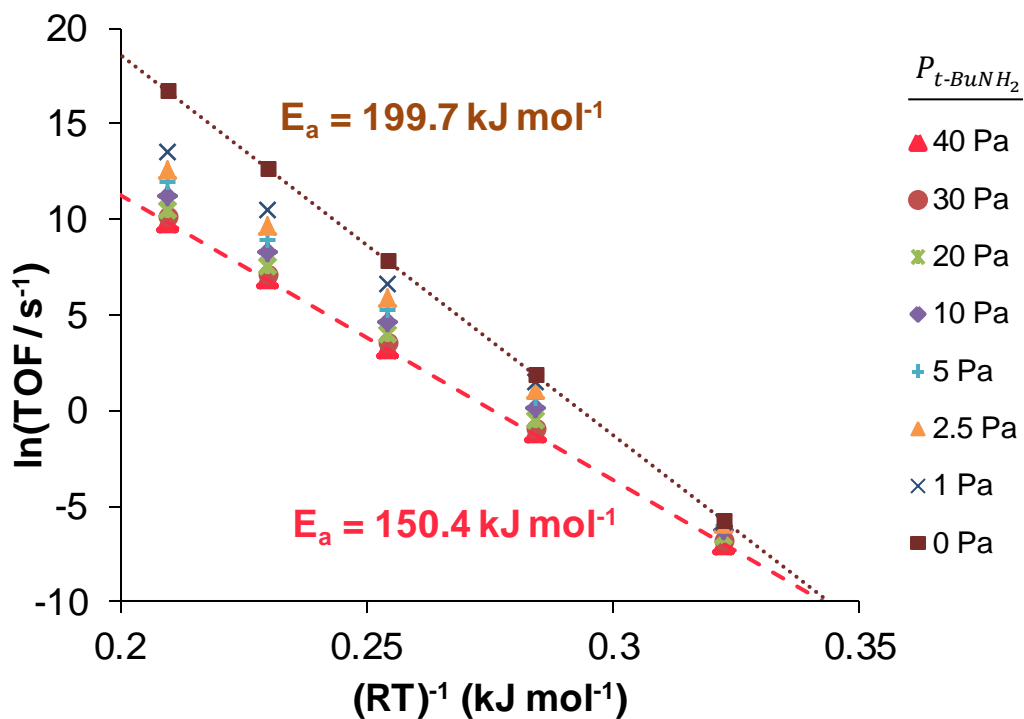
energies of reaction at each temperature interrogated are reported in Table S1, and the free energy profiles at each reaction temperature in Figure S4.

**Table S1:** Effect of temperature on free energy of reaction. Experimental reaction temperature is highlighted.

$T$ (K)	$\Delta G_{\text{rxn}}$ (kJ mol <sup>-1</sup> )
373	-0.87
423	7.8
473	16.4
523	25.0
573	33.6



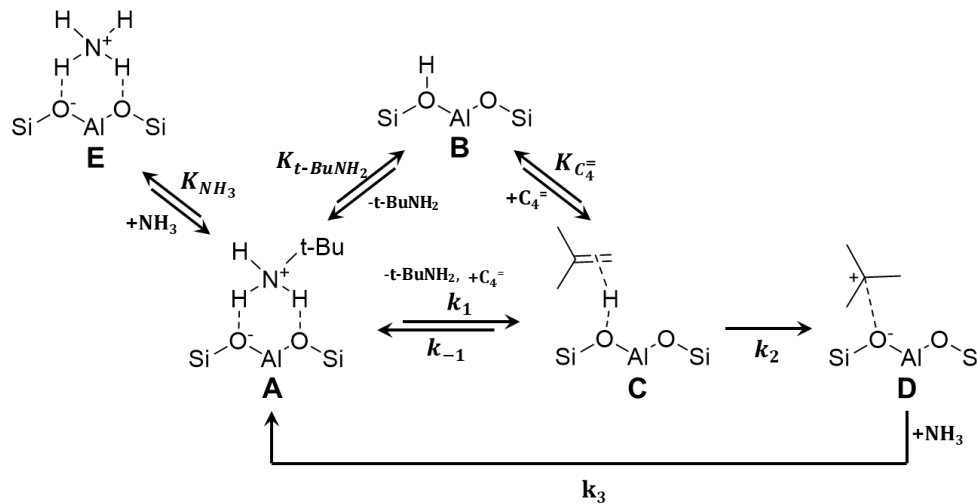
**Figure S4:** Predicted free energy profile of the amination of isobutene at different temperatures.  $P = 1$  atm. Intermediate states are labeled according to Scheme 2. The transition state for carbenium formation is denoted by  $C^\ddagger$ .



**Figure S5:** Arrhenius plots from energetic span model predictions of TOF, varying partial pressure of t-BuNH<sub>2</sub>.  $P = 1 \text{ atm}$ ;  $P_{\text{C}_4\text{=}} = 35 \text{ kPa}$ ;  $P_{\text{NH}_3} = 69 \text{ kPa}$ . The associated apparent activation barriers are shown for the highest and lowest partial pressures of t-BuNH<sub>2</sub>.

## Concentration gradients in reactor and choice of a one-parameter model:

Although kinetic measurements were conducted at low isobutene conversions (<0.4%), the system cannot be treated as a differential reactor because the rate is a function of  $t\text{-BuNH}_2$  partial pressure, which varies along the length of the reactor.



The rate expression for this mechanism is,

$$r_{int} = \frac{k_1 k_2 [C_4^=]}{k_{-1} [t\text{-BuNH}_2] + k_2}$$

This equation is a simplified form of the rate expression derived from the energetic span model, where only the two largest terms in the denominator are retained. The apparent rate of reaction can be obtained by using the mathematical definition of an average and integrating the rate expression along the length of the reactor.

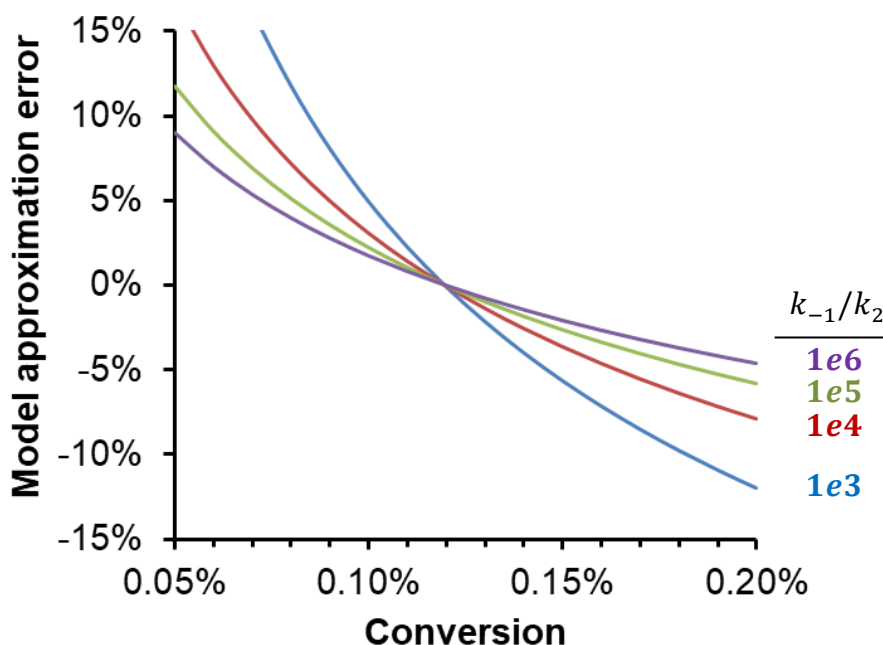
$$r_{app} = \frac{\int_0^{X_f} r dX}{X_f} = \frac{k_1 k_2 [C_4^=]}{k_{-1}} \frac{\ln \left( 1 + \frac{k_{-1}}{k_2} [t\text{-BuNH}_2]_f \right)}{[t\text{-BuNH}_2]_f} \quad (S3)$$

where  $r_{app}$  is the apparent reaction rate,  $r$  is the intrinsic reaction rate,  $X_f$  is the conversion at the outlet of the reactor,  $[C_4^=]$  is the partial pressure of isobutene, and  $[t\text{-BuNH}_2]_f$  is the partial pressure of  $t\text{-BuNH}_2$  in the product stream. The apparent rate expression can be simplified to a one-parameter model if we assume that  $t\text{-BuNH}_2$  desorption is pseudo-equilibrated.

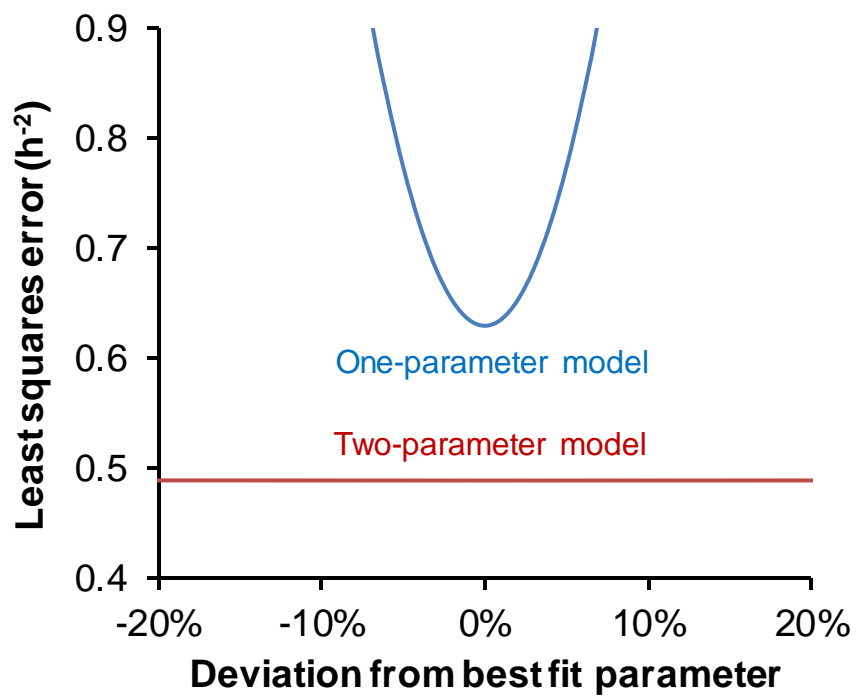
$$r_{app} \approx \frac{k_{app} [C_4^=]}{[t\text{-BuNH}_2]_f}$$



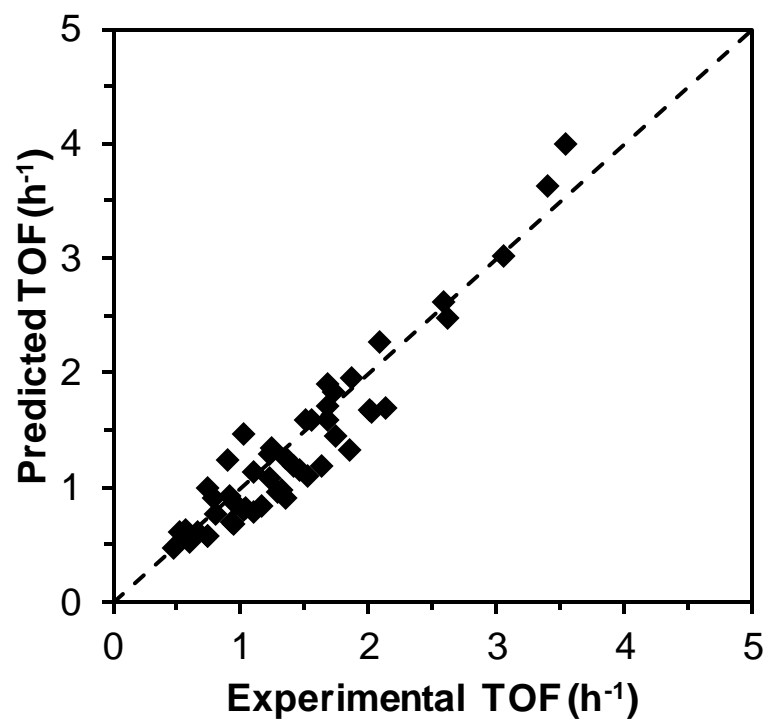
The relative error in this approximation decreases with increasing surface coverage of t-BuNH<sub>2</sub>. If the adsorption constant for t-BuNH<sub>2</sub> is much higher than that of ammonia ( $k_{-1}/k_2 > 1e4$ ), the relative error is less than 20% for the range of conditions used in this study (Figure S6). Furthermore, one-parameter model has a much higher sensitivity to the input variable compared to the two-parameter model, which translates to higher confidence in the value of the apparent rate constant (Figure S7). For these reasons, the kinetic data were fitted using the one-parameter model. Since the model error depends on the final t-BuNH<sub>2</sub> partial pressure (and hence conversion), kinetic measurements of all catalysts were conducted at a similar range of conversions (0.05 – 0.2%).



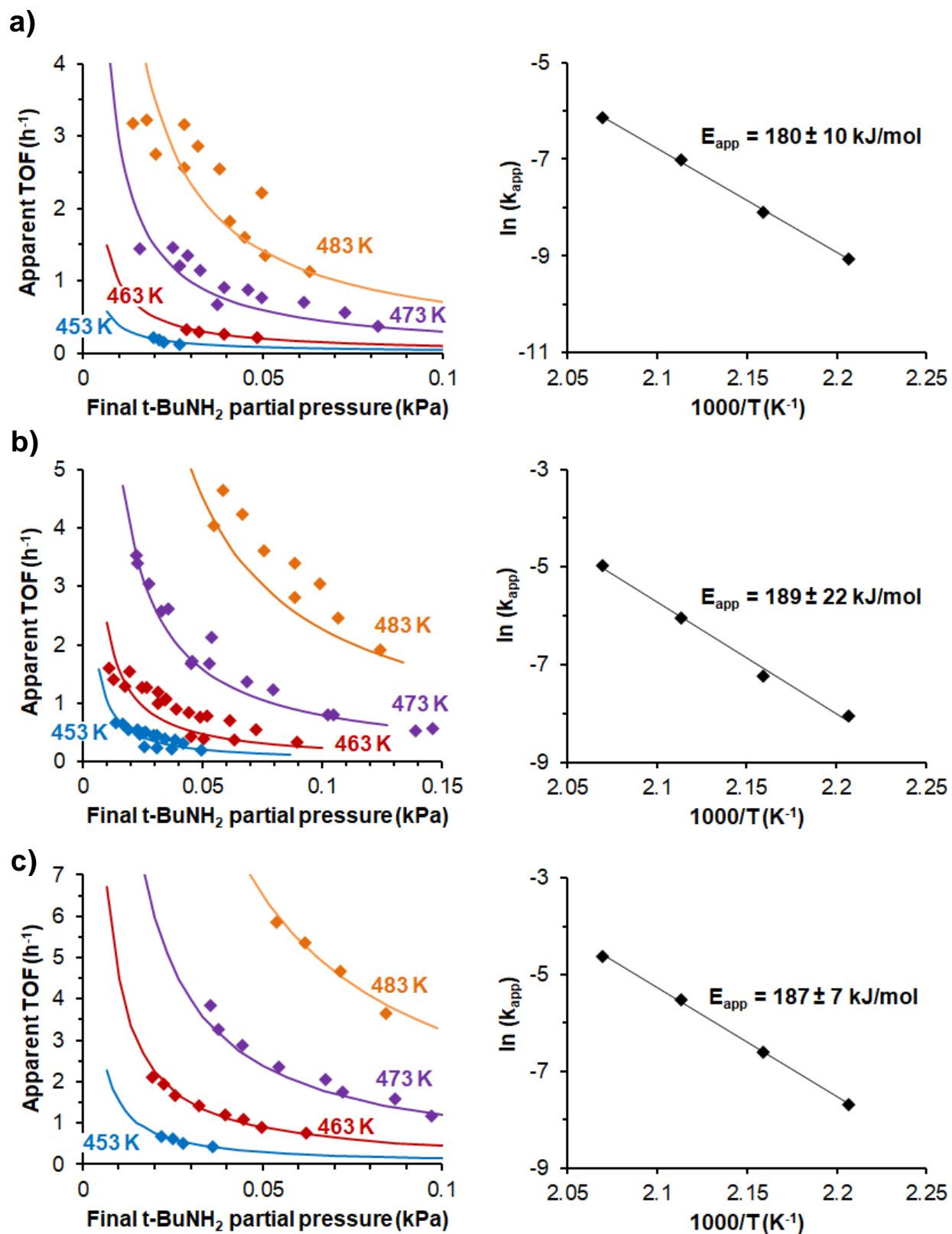
**Figure S6:** Relative error of the pseudo-equilibrium assumption as a function of different  $k_{-1}/k_2$  ratios.



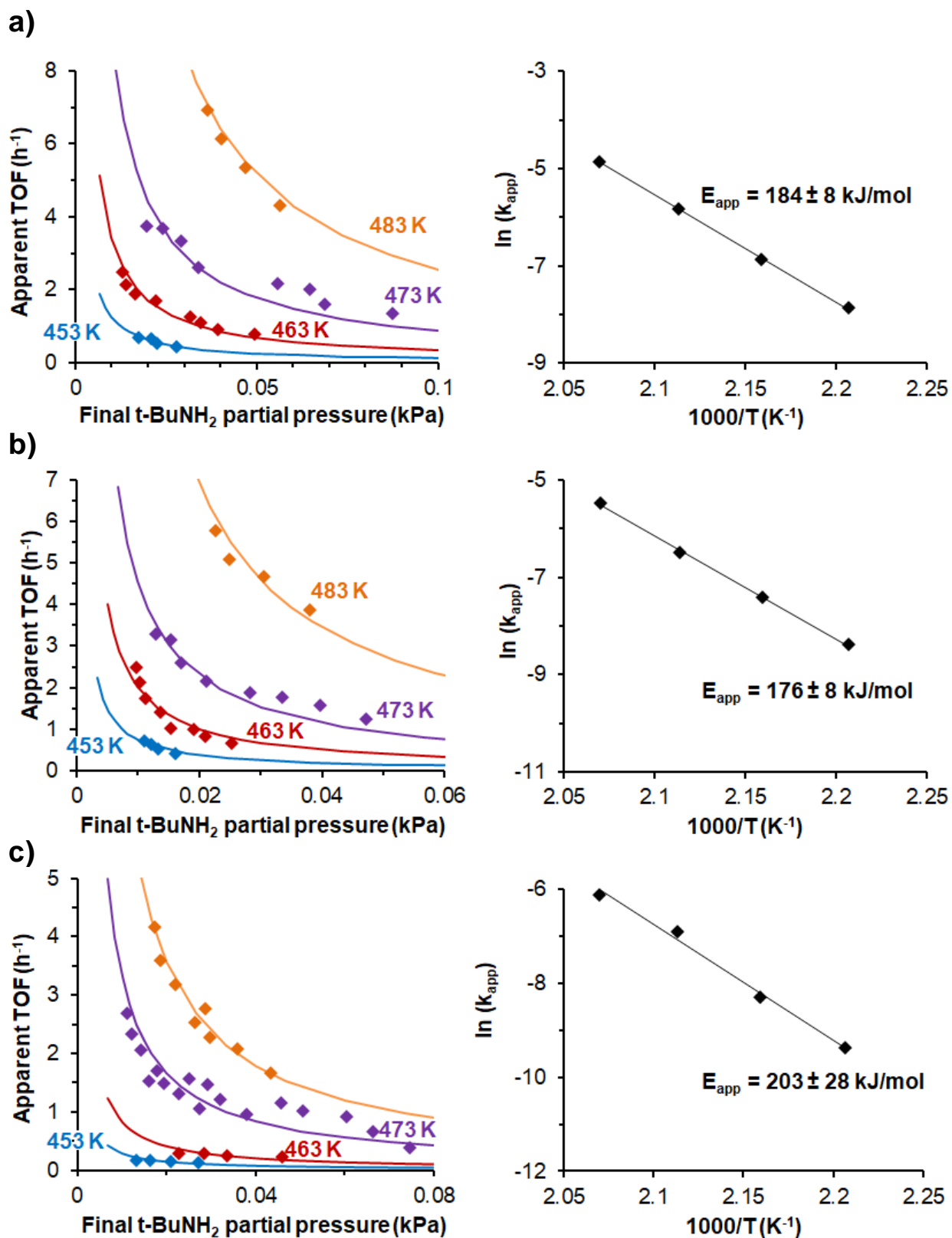
**Figure S7:** Sensitivity analysis for the one-parameter (pseudo-equilibrium) and two-parameter (pseudo steady-state) model fits.



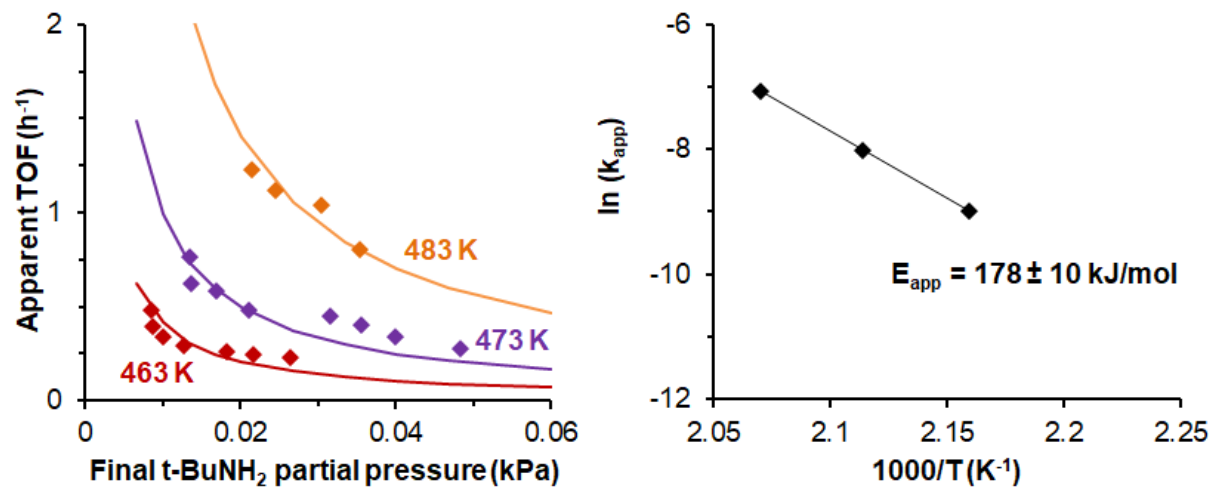
**Figure S8:** Parity plot for the apparent turnover frequency of isobutene amination over MFI. T = 473 K; P = 1 atm; P<sub>NH<sub>3</sub></sub> = 69 kPa. The predicted TOF was determined using Eqn. 1.



**Figure S9:** Temperature dependence and Arrhenius plots for a) MFI-11.5 b) MFI-15 c) MFI-25.  $P = 1 \text{ atm}$ ;  $P_{\text{C}_4} = 35 \text{ kPa}$ ;  $P_{\text{NH}_3} = 69 \text{ kPa}$ .



**Figure S10:** Temperature dependence and Arrhenius plots for a) MFI-40 b) MFI-140 c) MOR-10.  $P = 1 \text{ atm}$ ;  $P_{\text{C}_4} = 35 \text{ kPa}$ ;  $P_{\text{NH}_3} = 69 \text{ kPa}$ .



**Figure S11:** Temperature dependence and Arrhenius plots for FAU-15. P = 1 atm; P<sub>C4=</sub> = 35 kPa; P<sub>NH3</sub> = 69 kPa.