

Supplementary Information

Effects of Transport Limitations on Rates of Acid-Catalyzed Alkene Oligomerization

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S1. Synthesis of zeolite samples with different crystal sizes

ZSM-5, ZSM-12, and ZSM-22 samples with different crystal sizes were synthesized hydrothermally. Control of crystallite size was achieved by varying the dissolution rate of silica or modifying the nature of the structure-directing agent. ZSM-5 samples were synthesized using different water-to-silica ratios (see gel compositions in Table 1 of manuscript). In a typical synthesis of ZSM-5, TEOS was mixed with appropriate amounts of TPAOH and deionized water, and the resulting mixture was aged at 353 K for 24 h. Subsequently, an aqueous solution containing aluminum nitrate nonahydrate and sodium hydroxide was added to the aged mixture. Thus formed gel was crystallized at 443 K for 24 h under rotation (60 rpm). The solid product was then washed with deionized water, dried, and calcined at 823 K for 5 h under static air. Na⁺-form samples were converted to H⁺-form by ion exchange with a 1 M ammonium nitrate aqueous solution twice at 353 K for 3 h followed by calcination under static air at 823 K.

ZSM-12 samples were synthesized using two different structure-directing agents, namely TEAOH and TEABr. Since ZSM-12 crystallizes in TEABr at much narrower gel compositions than in TEAOH, the TEA⁺/SiO₂ and OH⁻/SiO₂ ratios were varied as well.¹ In a typical synthesis of ZSM-12, TEAOH or TEABr were mixed with appropriate amounts of sodium aluminate and deionized water until dissolved. To this mixture, colloidal silica and deionized water were added under stirring. The resulting gel was crystallized at 433 K for 120-132 h under static conditions. The solid product was subsequently washed with deionized water, dried, and calcined at 823 K for 5 h under air flow. Na⁺-form samples were converted to H⁺-form following the same procedure used in ZSM-5 synthesis.

In similarity with ZSM-5 synthesis, ZSM-22 samples were synthesized using different water-to-silica ratios. In a typical synthesis of ZSM-22, colloidal silica was diluted in an appropriate amount of deionized water and mixed with an aqueous solution containing aluminum sulfate octadecahydrate, potassium hydroxide, and 1,6-hexanediamine. The resulting gel was crystallized at 453 K for 48 h under rotation (50 rpm). The solid product was then washed with deionized water,

dried, and calcined at 823 K for 5 h under static air. K^+ -form samples were converted to H^+ -form following the same ion exchange procedure used in ZSM-5 synthesis.

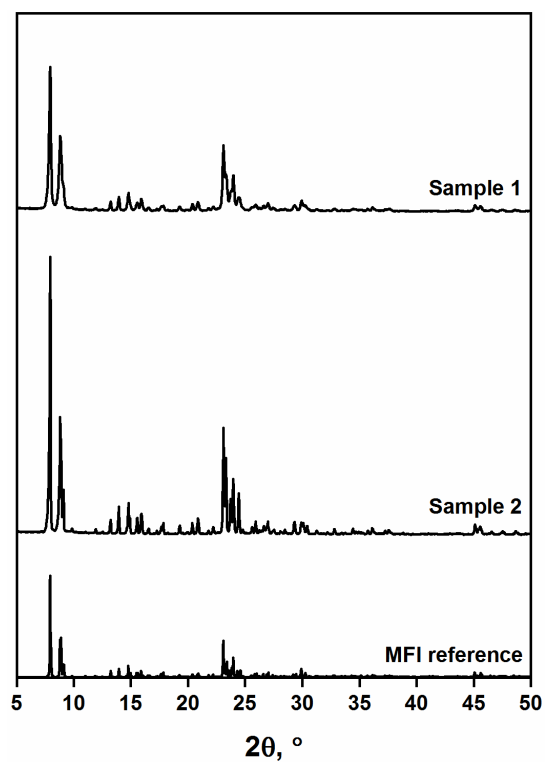


Fig. S1. XRD patterns of ZSM-5 samples compared to MFI reference.

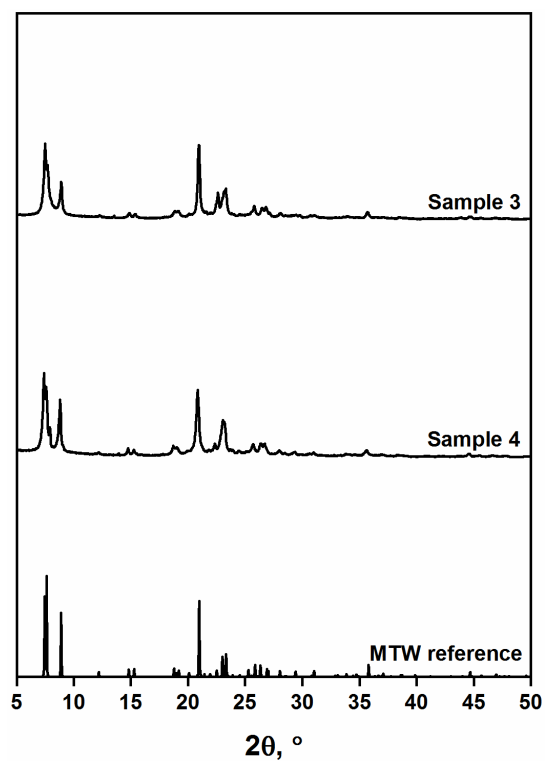


Fig. S2. XRD patterns of ZSM-12 samples compared to MTW reference.

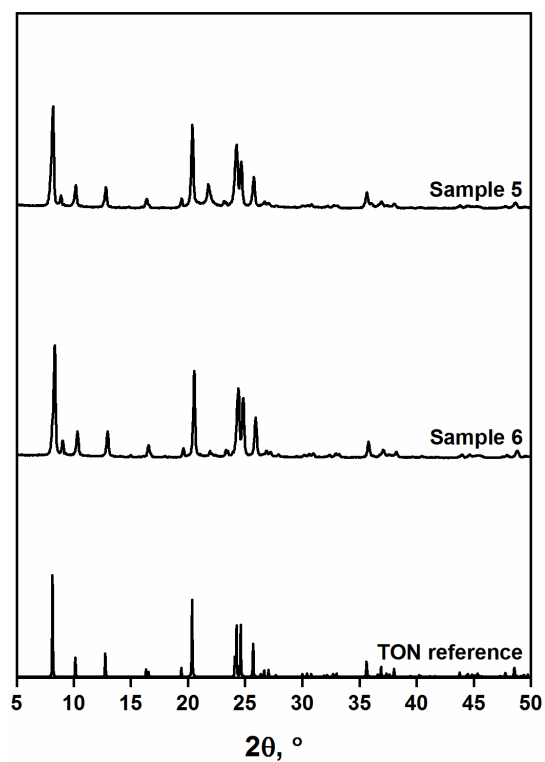


Fig. S3. XRD patterns of ZSM-22 samples compared to TON reference.

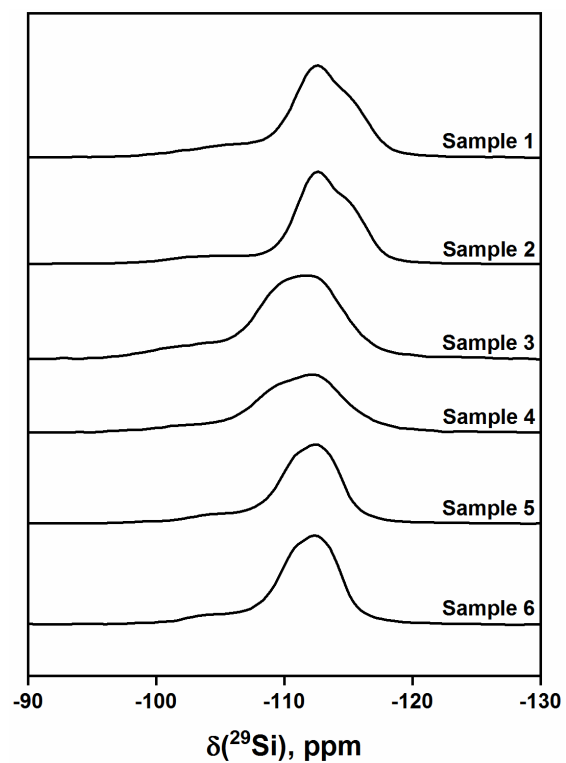


Fig. S4. ^{29}Si MAS NMR spectra of Samples 1-6 (Table 2 of manuscript).

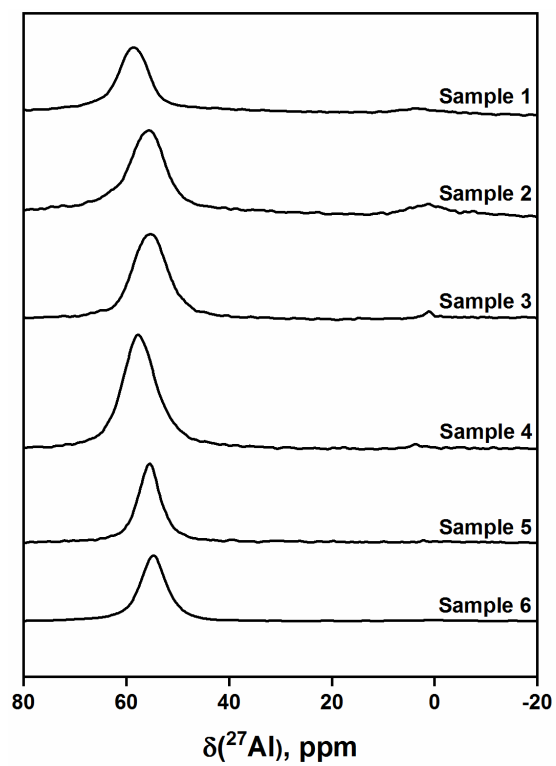


Fig. S5. ^{27}Al MAS NMR spectra of Samples 1-6 (Table 2 of manuscript).

S2. Measurement of alkene oligomerization turnover rates and selectivity

Alkene oligomerization was performed in fixed bed reactors operating isothermally. The flow was assumed to conform to plug behavior where no mixing takes place in the axial or radial directions. This assumption is valid as the ratio of bed length to particle diameter was kept above 50.² For a first-order, deactivating reaction where molar expansion/contraction is neglected, a plug flow reactor model is solved³ as follows:

$$\ln \ln \frac{1}{1 - X_A} = \ln(k\tau) - k_d t \quad (\text{S1})$$

where X_A is the fractional conversion of reactant A, k is the kinetic rate constant, τ is the residence time, k_d is the deactivation rate constant, and t is time-on-stream (TOS). Eqn (S1) was linearly regressed against tabulated data of conversion (calculated based on product formation) versus TOS to estimate first-order rate constants. Measurement of turnover rates was conducted in the absence of intraparticle and extraparticle transport limitations. This was confirmed by observing no change in conversion while varying the flow rate (while keeping residence time the same) and particle size.

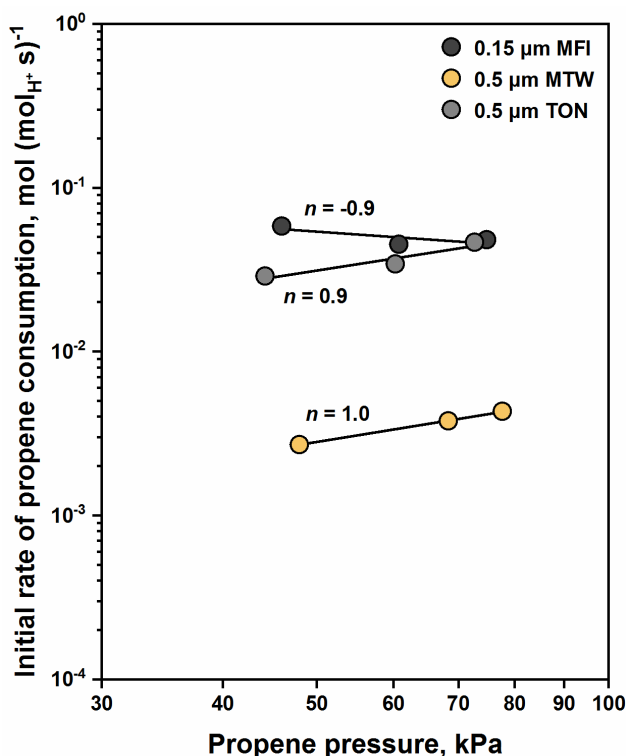


Fig. S6. Initial rates of propene consumption as a function of propene pressure. [$T = 523$ K, $X_{C_3H_6} = 0.01-0.1$].

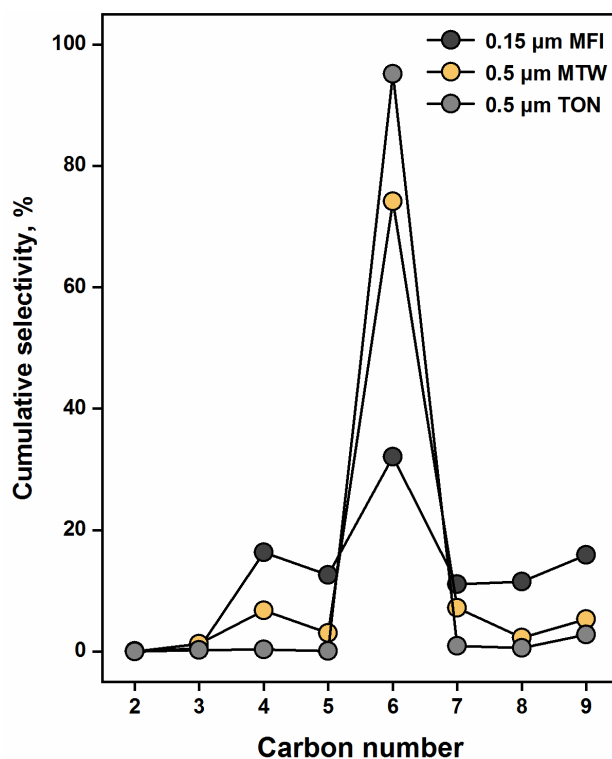


Fig. S7. Cumulative selectivity to hydrocarbons measured over 16 h of TOS. [$T = 523$ K, $P_{C_3H_6} = 50$ kPa, $X_{C_3H_6} = 0.01-0.1$].

Propylene (20%, AHG) was reacted over zeolite samples at 523 K to perform a detailed analysis of product distribution. The reactor (5 mm ID) was held in a resistively heated oven where temperature is controlled by a K-type thermocouple. The flow was regulated by a Bronkhorst EL-FLOW Select mass flow controller. The reactor effluent was analyzed by a Bruker 450 GC equipped with a DB-Petro column (see manuscript for specifications) operated at constant flow (1.0 mL min^{-1}) and temperature-programmed at 1 K min^{-1} .⁴

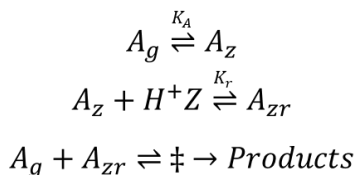
Table S1. Product selectivity (in %) for propene reactions on Samples 1-6. [$T = 523$ K, $P_{C_3H_6} = 20$ kPa, TOS = 1 h].

Sample	1	2	3	4	5	6
Framework	MFI	MFI	MTW	MTW	TON	TON
Crystallite size, μm	0.15	1.5	0.5	2.5	0.5	5.0
Conversion ^a , %	5.6	9.3	5.4	5.2	10.0	8.4
C ₄	9.1	4.5	4.2	6.3	0.4	0.4
C ₅	15.9	7.7	5.6	7.2	0.5	0.5
C ₆	18.2	10.8	14.3	33.7	66.2	67.7
C ₇	10.8	7.8	8.1	9.2	0.4	0.3
C ₈	9.5	10.6	10.9	10.8	2.2	1.5
C ₉	19.0	23.4	23.4	17.6	17.2	15.2
C ₁₀₊	17.6	35.1	33.6	15.2	13.1	14.4

^a Calculated based on reactant consumption

S3. Transition state theory treatments of bimolecular Eley-Rideal reactions

Bimolecular Eley-Rideal reactions of alkene species on Brønsted acid sites is proposed to proceed through the following pathway:



Scheme 1. Proposed reaction sequence for bimolecular Eley-Rideal reactions.

Alkene species in the gas phase (A_g) adsorb onto zeolite channels in a quasi-equilibrated step. Adsorbed alkene species (A_z) react with Brønsted acid sites (H^+Z) located within zeolite channels to form a precursor state in a subsequent quasi-equilibrated step. Alkene species in the precursor state (A_{zr}) react with those in the gas phase via transition states to form oligomerization products. Transition state theory treatments of the latter step lead to the following rate expression:

$$r = \frac{k_b T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(\frac{-\Delta H^\ddagger}{RT}\right) \frac{\gamma_A C_A K_r \gamma_{A_z} C_{A_z} \gamma_{H^+} C_{H^+}}{\gamma^\ddagger} \quad (\text{S2})$$

where k_B is the Boltzmann constant, T is absolute temperature, h is the Planck constant, ΔS^\ddagger is the entropy of activation, R is the universal gas constant, and ΔH^\ddagger is the enthalpy of activation. The terms γ , C , and K refer to the activity coefficient, concentration, and equilibrium constant, respectively, of a given species or step. The activity coefficient of gaseous alkene species (γ_A) is considered as unity, while the activity coefficient of adsorbed alkene species (γ_{A_z}) cancels with that of the transition state (γ^\ddagger) since transition states and their precursors reside at the same site. The concentration of adsorbed alkene species is related to their gas-phase pressures through Langmuir isotherms:

$$C_{A_z} = \frac{K_A P_A}{1 + \sum_i K_i P_i} \quad (\text{S3})$$

Combining eqns (S2) and (S3), and assuming surface coverage of alkene species, the rate of reaction can be rewritten as

$$r = \frac{k_b T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(\frac{-\Delta H^\ddagger}{RT}\right) K_r \gamma_{H^+} C_{H^+} C_A = k C_A \quad (\text{S4})$$

which is consistent with a rate that is directly proportional to alkene pressure (see Section 3.2 of manuscript). The terms K_r and γ_{H^+} reflect effects of the acid environment on the pre-exponential

factor, as defined by Bhan et al.⁵ The activation entropies reported in Table 3 were calculated using the following equation:

$$\Delta S_{act} = R[\ln(A) - \ln\left(\frac{k_B T}{h}\right)] \quad (S5)$$

where A is the pre-exponential factor determined from Arrhenius relations.

S4. Sorption isotherms

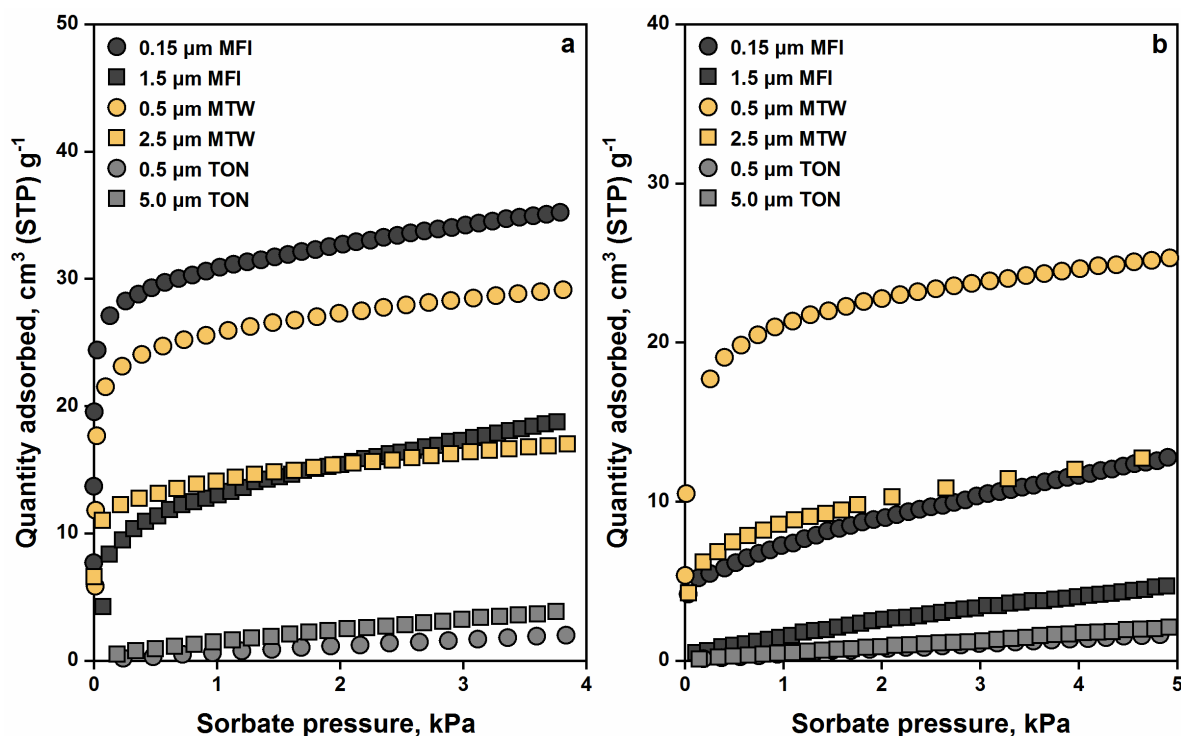


Fig. S8. Sorption isotherms of (a) 2,3-dimethylbutane and (b) 2,2-dimethylbutane on MFI, MTW, and TON samples at 303 K.

References

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