

Consequences of Al Location and of Partial Confinement for Transition State Selectivity in Monomolecular Alkane Reactions on Zeolites

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Introduction

Intrachannel environments around Brønsted acid sites influence reaction rates and selectivities in acid catalysis through their solvation of reactants and cationic transition states. These effects of channel location on free energies are most consequential for highly-charged transition states stabilized by electrostatic interactions with the zeolite framework, but much weaker for uncharged transition states predominantly stabilized by covalent interactions. As a result, CO insertion into surface methyl groups, an elementary step involving significant charge separation at the transition state, occurs with remarkable enzyme-like specificity within eight-member ring (8-MR) channels in MOR zeolites [1]. In contrast, exchange between CD₄ and OH groups, which occurs via uncharged transition states, occurs at similar rates on 8-MR and 12-MR OH groups in MOR [1]. We show here that these strong effects of location are also critical in alkane activation reactions involving late cationic transition states and provide evidence for the role of partial confinement in stabilizing the required transition states.

Materials and Methods

Catalytic rates for monomolecular reactions of alkanes (C₃H₈, n-C₄H₁₀) on H-zeolites (MFI, FER, MOR) were measured at 718-778 K and low alkane pressures (<2 kPa) and differential conversions (<2%). The location of Brønsted acid sites in 8-MR and 12-MR channels of MOR was determined using deconvolution methods and infrared spectra [1].

Results and Discussion

Alkane cracking and dehydrogenation turnover rates (per H⁺) and cracking-to-dehydrogenation (C/D) rate ratios differed among zeolites (by factors of ~4) and even for a given zeolite (MOR) between acid sites located within 8-MR side pockets and 12-MR channels. Activation barriers depend on properties of acid sites and reactants, specifically deprotonation enthalpies and proton affinities, respectively, as shown by thermochemical cycles that define these relations for acid catalysis [2]. For each reaction, measured barriers were higher on 8-MR than 12-MR acid sites (Table 1) due to losses of van der Waals contacts as a result of partial containment within side pockets. Yet, turnovers were much higher for both cracking and dehydrogenation on 8-MR than on 12-MR acid sites, because partial confinement leads to higher transition state entropies, which compensate enthalpy losses and decrease transition state free energies (Table 1).

Table 1. Rate constants (k_{meas}) and measured activation energies (E_{meas}) and entropies (ΔS_{meas}) for monomolecular C₃H₈ cracking at 748 K within 8-MR and 12-MR locations of MOR.

	k_{meas} (/ $10^{-3} \text{ mol (mol H}^+)^{-1} \text{ s}^{-1} \text{ bar}^{-1}$)	E_{meas} (/ kJ mol^{-1})	ΔS_{meas} (/ $\text{J mol}^{-1} \text{ K}^{-1}$)
8-MR	2.0 ± 0.5	164 ± 5	-91 ± 9
12-MR	0.7 ± 0.4	151 ± 5	-117 ± 14

These dominant effects of entropy on transition state stability were stronger for dehydrogenation than for cracking (Figure 1), because of later and looser transition states; thus, cracking-to-dehydrogenation rate ratios depend sensitively on the location of protons within H-MOR (Figure 1, inset), as we show by the selective titration of 8-MR protons with Na⁺. Partial confinement also led to the preferential cracking of terminal C-C bonds in n-C₄H₁₀ on 8-MR sites (Figure 1, inset). Similar effects of acid site location may account for alkane cracking and dehydrogenation rates that differ (by factors of ~5) among on MFI samples of varying provenance, Al density, and Na⁺ content, for which Al location cannot be assessed by titration or spectroscopic methods; these findings contrast previous studies, which reported that Al content and, by inference, location did not influence alkane cracking rates on MFI [3].

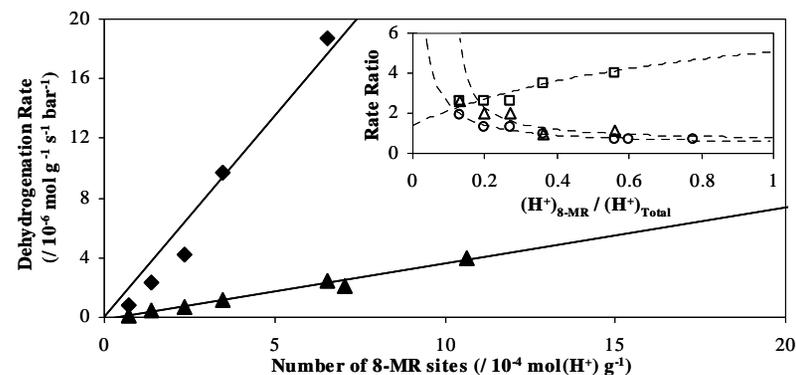


Figure 1. Rates of C₃H₈ (▲) and n-C₄H₁₀ (◆) dehydrogenation at 748 K plotted against the number of 8-MR sites in H-MOR. Inset shows C/D rate ratios of C₃H₈ (○), C/D rate ratios of n-C₄H₁₀ (△), and terminal-to-central cracking rate ratios of n-C₄H₁₀ (□) at 748 K plotted against the fraction of Brønsted acid sites in 8-MR pockets of H-MOR; rate constants estimated for 8-MR and 12-MR acid sites were used to predict rate ratios (dashed curves).

Significance

These findings and concepts provide rigorous strategies for controlling transition state selectivity by selective titration of OH groups within specific locations and for the design of materials with void structure or site location that provide entropic preferences for specific transition states.

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- Bhan, A., Allian, A. D., Sunley, G. J., Law, D. J., Iglesia, E., *J. Am. Chem. Soc.* 129, 4919 (2007); Bhan, A., Iglesia, E. *Acc. Chem. Res.* 41, 559 (2008).
- Aronson, M. T., Gorte, R. J., Farneth, W. E., *J. Catal.*, 98, 434 (1986); Macht, J., Janik, M. J., Neurock, M., Iglesia, E., *J. Am. Chem. Soc.* 130, 10369 (2008).
- Olson, D. H., Haag, W. O., Lago, R. M., *J. Catal.*, 61, 390 (1980).