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Impact of Zeolite Structure on Entropic-Enthalpic Contributions to Alkane Monomolecular Cracking, an IR *Operando* study

Shashikant A. Kadam,^[a] Haoguang Li,^[a] Richard F. Wormsbecher,^[a] Arnaud Travert^{*[a]}

Abstract: The monomolecular cracking rates of propane and *n*-butane over MFI, CHA, FER and TON zeolites were determined simultaneously with the coverage of active sites at reaction condition using IR *operando* spectroscopy. This allowed direct determination of adsorption thermodynamics and intrinsic rate parameters. The results show that the zeolite confinement mediates enthalpy-entropy trade-offs only at the adsorbed state, leaving the true activation energy insensitive to the zeolite or alkane structure while the activation entropy was found to increase with the confinement. Hence, relative cracking rates of alkanes within zeolite pores are mostly governed by activation entropy.

Acidic zeolites are catalysts of prime importance due to their use in petroleum refineries and chemical manufacturing.^[1] Their catalytic activity is strongly influenced by the local environment of Brønsted acid sites which depends on the zeolite framework type and Al sitting.^[2] Alkane monomolecular cracking is a reaction sensitive to the environment of the active site.^[3-7] The variations in the apparent cracking rate coefficients (k_{app}) are not only dependent on the alkane chain length^[3-4, 8-12] but also on the zeolite type.^[7, 9-11, 13-16] The origin of this sensitivity is still under debate as the environment of the acid site changes both adsorption and intrinsic reactivity. In particular, an accurate determination of adsorption parameters at reaction conditions is required to extract the activation parameters. Until recently, these adsorption parameters were either estimated by extrapolation of low temperature measurements,^[4, 14, 17-18] or by molecular simulations.^[19-26] The intrinsic activation energy E_a derived from low temperature adsorption parameters was found insensitive to the alkane or zeolite structure. On this ground, the variations in apparent rate coefficients were initially accounted by changes in adsorption parameters, K_{ads}^o ^[9-11, 14-15, 27], and more recently by changes in the pre-exponential factor of the intrinsic rate constant, and hence activation entropy ΔS^\ddagger .^[4, 12, 16, 28] However, state of the art simulations predict a strong influence of temperature on the adsorption entropy, $\Delta_{ads}S^\ddagger$ ^[7, 20, 25, 29-31] which was assumed to be negligible in previous studies. This temperature dependence has a large influence on the estimates of alkane coverage and hence the estimates of intrinsic rates.^[20, 29] Accounting for such temperature effects, the latest studies combining molecular simulations and cracking rate measurements suggest that structure-activity trends are neither explained by the adsorption parameters, nor by activation entropy, but by changes in activation energies E_a that would be affected by the alkane chain length, or the zeolite topology.^[7, 25, 31-32] A key to resolve these discrepancies is the simultaneous determination of active site coverage and apparent rates at reaction conditions. We have recently shown that the use of IR

operando spectroscopy allowed such measurements and that the variations of cracking rates with alkane chain length in H-MFI zeolites are primarily accounted for by an increase of the activation entropy ΔS^\ddagger .^[33]

We present here a study on the influence of zeolite structure (FER, TON, MFI and CHA) on the monomolecular cracking of light alkanes (propane and *n*-butane). To this aim, the reaction was carried out at various temperatures (580-710K), partial pressures and contact times, while recording the corresponding IR spectra (See ESI section S1 for experimental details). These spectroscopic data, combined with simultaneous activity measurements, were used to derive the intrinsic rate parameters, E_a and ΔS^\ddagger , as well as the thermodynamic adsorption parameters, $\Delta_{ads}H$ and $\Delta_{ads}S$ at reaction conditions.

Figure 1a shows the difference IR spectra (spectra recorded during the reaction minus spectrum of the bare zeolite) at constant temperature, variable partial pressure and space times for propane cracking over MFI, CHA, FER and TON. The difference IR spectra characterize the hydrogen bond formation between the acidic OH groups and the feed, leading to the negative ν OH band at 3600 cm^{-1} and a broad positive band at \sim 3530 cm^{-1} . At a fixed temperature and variable pressure, the cracking yields increased linearly with contact time (Figure 1b) while no significant variation in ν OH spectra with contact time was observed. This observation validates the usual assumption of negligible adsorption of reaction products at monomolecular cracking reaction conditions. The area of negative ν OH band at 3600 cm^{-1} , which absorption coefficient have been determined (see ESI section S1), can thus be used to determine the active site coverage by reactants and hence the adsorption constants $K_{ads}^o(T)$. The corresponding adsorption isotherms and van't Hoff plots are shown in ESI section S2. They were used to determine adsorption thermodynamic parameters at reaction conditions (Table 1).

Table 1. Adsorption parameters of propane and *n*-butane

zeolite	propane				n-butane			
	This work		Previous work ^{a,b}		This work		Previous work ^a	
	$\Delta_{ads}H$	$\Delta_{ads}S$	$\Delta_{ads}H$	$\Delta_{ads}S$	$\Delta_{ads}H$	$\Delta_{ads}S$	$\Delta_{ads}H$	$\Delta_{ads}S$
FER	-49(2)	-117(4)	-49 ^a	-112 ^a	-65(1)	-142(2)	-59	-130
TON	-51(2)	-119(3)	-49 ^a	-104 ^a	-68(2)	-145(3)	-60	-136
CHA	-36(1)	-93(2)	-38 ^b	-88 ^b	-64(4)	-123(6)	-	-
MFI	-38(2)	-91(3)	-45 ^a	-102 ^a	-51(3)	-105(4)	-58	-119

Standard errors from the linear regression are reported in parenthesis, ($\Delta_{ads}H$ and $\Delta_{ads}S$ are reported in kJ mol^{-1} and $\text{J K}^{-1} \text{mol}^{-1}$ respectively)

^a Eder et al.^[18, 34] The values of $\Delta_{ads}S$ are calculated using total concentration of the acidic OH groups as reference state reported by Eder et al. ($T = 333 \text{ K}$).

^b Piccini et al.^[35]

The magnitudes of adsorption parameters are larger for *n*-butane than propane for a given zeolite and clearly follow the

[a] Dr. S.A. Kadam, Dr. H. Li, Dr. R.F. Wormsbecher, Pr. A. Travert
Normandie Univ, ENSICAEN, UNICAEN, CNRS, Laboratoire
Catalyse et Spectrochimie, 14000 Caen, France
E-mail: arnaud.travert@ensicaen.fr

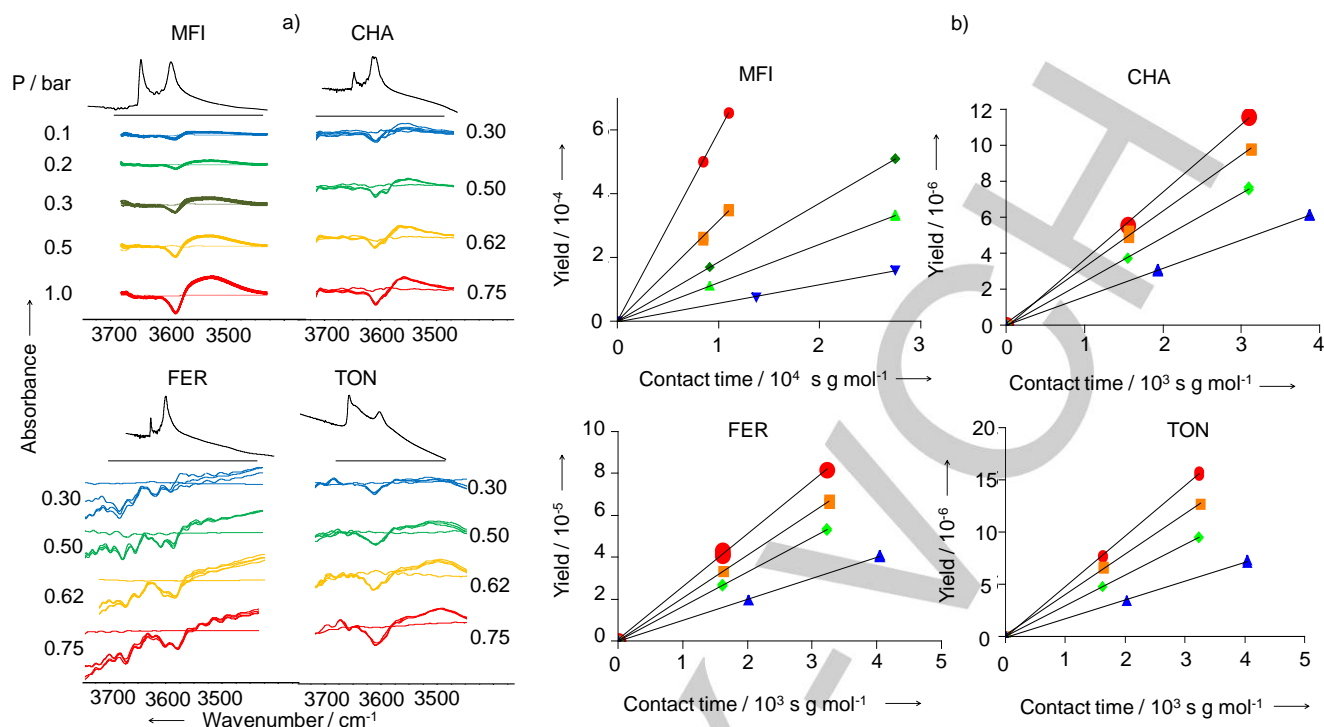


Figure 1. a) Difference IR spectra in the νOH range of H-MFI, H-CHA, H-FER and H-TON at increasing partial pressures of propane. The flat spectra were obtained after propane shut-off. b) Cracking yields versus contact time on increasing partial pressures of propane over MFI at pressures 1.0 bar (●), 0.5 bar (■), 0.3 bar (◆), 0.2 bar (▲), 0.1 bar (▼) at 698K, and for CHA, FER and TON at pressures 0.75 bar (●), 0.62 bar (■), 0.5 bar (◆), 0.3 bar (▲) at 605K.

trend $\text{FER} \equiv \text{TON} > \text{CHA} \equiv \text{MFI}$ for a given alkane. This ranking parallels the decrease of the corresponding effective pore radii (see section S3 in ESI) whereby the 8MR (3.4 Å) and 10MR channels (3.7 Å) in FER are only slightly smaller than the 10MR 1-dimensional channel (3.9 Å) in TON, while the MFI intersections and CHA cages are larger and have similar radii (4.6 Å).

The apparent cracking rates (r_{app}) were found directly correlated to the alkane coverage (see section S4 in ESI). These correlations at a common temperature for each alkane on the different zeolites are displayed in Figure 2. It shows that at given coverage the cracking rates of both alkanes significantly increase with the increase of confinement i.e. in the order: $\text{FER} \geq \text{TON} > \text{CHA} \equiv \text{MFI}$.

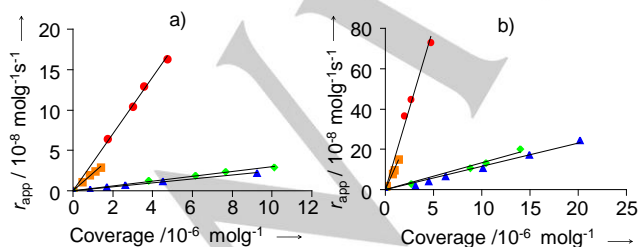


Figure 2. Apparent cracking rates (r_{app}) versus Coverage for (a) propane and (b) n-butane at 649K (641K for MFI); MFI (▲), CHA (◆), TON (■), FER (●) (●)

Following the approach of Janda et al.^[7], Figure 3 displays the apparent rate constants k_{app} against the intrinsic rate constants k_{int} and adsorption equilibrium constants K_{ads}° at a common temperature. A significant correlation was only observed between k_{app} and k_{int} for propane ($p = 0.010$) and n-butane ($p = 3 \times 10^{-5}$) while such significance was not found for K_{ads}° ($p = 0.59$ and 0.27 for propane and n-butane respectively).

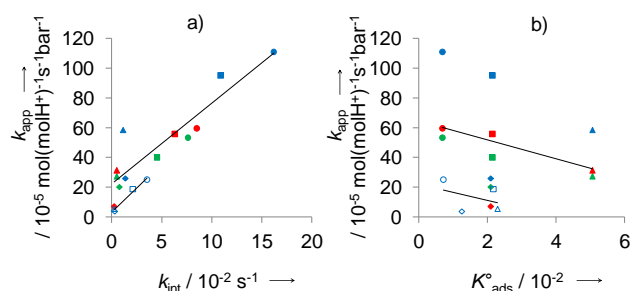


Figure 3. Dependence of k_{app} on a) k_{int} and b) K_{ads}° with zeolite structures for propane (open symbols) and n-butane (closed symbols) at $T = 649\text{K}$ (641K for MFI); MFI (▲), CHA (◆), TON (■), FER (●), blue – overall cracking, green – terminal cracking and red – central cracking

This confirms that the variations in apparent cracking rates are mostly accounted for by changes in intrinsic rates and not in coverage.

Figure 4a and 4b show the Arrhenius plots of the apparent rate constants and the intrinsic rate constants of propane cracking

over the four zeolites. Similar shifts along the ordinate axis are observed in both Arrhenius plots, confirming that the differences in apparent turnover rates are essentially due to changes in the intrinsic rate constants. The intrinsic activation energies derived from the individual Arrhenius plots (Fig. 4b) were very close for both reactants over the four zeolites (185–190 kJ mol⁻¹). A statistical comparison of linear regression models (see ESI section S5) allowed determining a single activation energy (187 kJ mol⁻¹) and distinct activation entropies which are reported in Table 2.

Table 2. Activation entropies determined by *Operando* IR spectroscopy.

Zeolite	Effective pore radii (Å)	Propane	n-butane
		ΔS^\ddagger	ΔS^\ddagger
FER	3.4–3.7	2 (2)	12 (2)
TON	3.9	-3 (2)	10 (2)
CHA	4.5	-19 (1)	-6 (1)
MFI	3.9 (ZC), 4.1 (SC), 4.6 intersection	-18 (1)	-5 (1)

ZC-zigzag, SC-straight channel. Standard errors are reported in parenthesis. Entropies are reported in J K⁻¹ mol⁻¹.

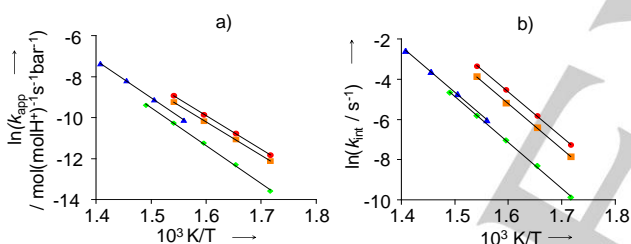


Figure 4. Arrhenius plots of the (a) apparent turnover rates and (b) intrinsic rate constants of propane cracking over MFI (▲), CHA (◆), TON (■), FER (●).

Table 2 shows significant increases of activation entropies with the increase of the alkane chain length on the one hand, and the decrease of the zeolite effective pore radii, on the other hand. These changes of activation entropy directly affect the pre-exponential factor of the intrinsic rate constant according to:

$$A = \nu \exp\left(\frac{\Delta S^\ddagger}{R}\right) \quad (1)$$

where, $\nu = ek_B T/h$ is a universal frequency factor.

For each alkane/zeolite system investigated, the contributions of the enthalpic and entropic terms to the total apparent rates can be obtained by the logarithm of the apparent cracking rate constant divided by the frequency factor ν :

$$\ln \frac{k_{app}}{\nu} = -\frac{\Delta_{ads}H}{RT} + \frac{\Delta_{ads}S}{R} - \frac{E_a}{RT} + \frac{\Delta S^\ddagger}{R} \quad (2)$$

The positive and negative influence of these contributions to the apparent rate constant is shown sequentially in the waterfall

charts in Figure 5 for propane cracking. For adsorption terms, it shows that the zeolitic confinement leads to partial enthalpy-entropy compensation at the adsorbed state which results in a limited variation of the equilibrium adsorption constant, the latter being lower for the small pore zeolites (TON, and FER). The activation energy is the main and largest contributor but is insensitive to the zeolite structure. Finally, the activation entropy is the smallest contribution to the apparent rate constant. However, this term leads to an increase of the apparent rate constant k_{app} despite the slight decrease of the adsorption equilibrium constant. A similar plot was obtained for butane (see ESI section S6).

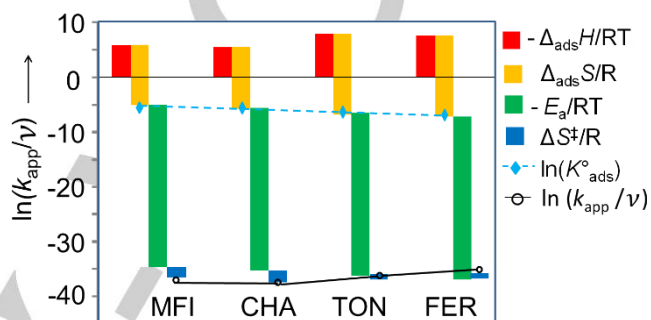


Figure 5. Waterfall plots of the adsorption and kinetic terms contributing to the adsorption constant and apparent rate constant for propane at T = 700K

The activation entropy is thus at the origin of the confinement effect observed for this reaction. Examination of the entropic balance (see ESI section S7) shows that the confinement primarily decreases the entropy of the adsorbed state while the entropy of the transition states is much less affected. For instance, the entropy of adsorbed propane is lowered by ~ 26 J mol⁻¹ K⁻¹ in H-FER with respect to H-MFI, while the entropy of the corresponding transition states differs by only ~ 6 J mol⁻¹ K⁻¹.

These data are qualitatively consistent with estimates derived from low temperature measurements.^[4, 12, 16, 28] However the small values of activation entropy obtained here are not in favour of a late transition state as often suggested.^[4, 12, 16, 28] With this respect, these data are in line with molecular simulations that also predict small activation entropy.^[7, 25]

On the other hand, they do not confirm the predictions that the alkane chain length and zeolite topology primarily influence the intrinsic activation energy and not the activation entropy.^[7, 20–21, 25] A first explanation accounting for this discrepancy could lie in the harmonic approximation used to compute entropies as it is known to overestimate the contribution of low frequency modes.^[35] Second, while our measurements explicitly probe the alkane – acid site complexes, the reactant state taken into account in simulations is defined by the Al - C atoms distance being lower than a given cut-off radius. This might not correctly describe the hydrogen bonded states for which the distance from the oxygen atom bearing the proton and the directionality of the H-bond has a substantial influence.^[33, 36] The consideration of explicit models for the hydrogen bond could improve the

agreement with experiments. While such developments go beyond the present work, the experimental data obtained using operando spectroscopy present the advantages of being self-consistent (adsorption and intrinsic kinetics parameters are determined for the same adsorbed/reactant state) and obtained at relevant temperature (hence allowing minimizing extrapolation errors over large temperature ranges). In this respect, the present data could provide a reliable benchmark for such developments.

In conclusion, this work shows that the changes in monomolecular cracking rates observed for distinct zeolite structures are driven by the activation entropy. This generalizes previous conclusions relative to the influence of the alkane structure.^[33]

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Keywords: Zeolites • Alkanes • Adsorption • IR Operando Spectroscopy • Activation entropy

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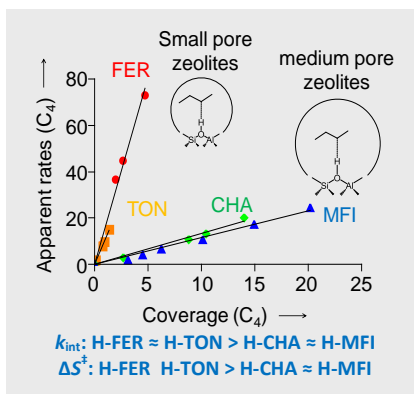
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Layout 1:

COMMUNICATION

In the search of the reactant state:

The determination of the concentration of acid site-alkane complexes within zeolite pores at reaction conditions allows for a consistent determination of adsorption and intrinsic rate terms governing the monomolecular cracking activity.



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