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IR OPERANDO STUDY OF THE DYNAMICS, THERMODYNAMICS AND INTRINSIC CRACKING KINETICS OF ALCANES IN ZEOLITES

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INTRODUCTION

The monomolecular cracking of alkanes over zeolites, discovered by Dessau and Haag thirty five years ago [1], can be considered as archetypal of acid-catalyzed reactions. Because of the interplay between adsorption and surface kinetics, the interpretation of structure – activity trends have long been subject to discussion. It is now generally admitted that the variations of apparent cracking rates are primarily governed by the intrinsic kinetics [2-6]. However, strong discrepancies still persist as to the rate parameter which determines these changes, i.e. activation entropy [2-4] vs. activation energy [5], as well as the magnitude of these parameters, in particular entropic factors. Overall, depending on the studies, the estimates of the coverage of active sites and of the intrinsic kinetics span several order of magnitude [2-7]. The origin of these huge discrepancies lies in the absence of experimental measurement of the coverage prevailing at reaction conditions, which up to now could only be assessed by extrapolation of low temperature measurements [2,3] or state of the art simulations [3-7]. In this lecture, we will show how infrared *operando* spectroscopy can be used to determine the coverage of active sites by alkanes in transient or steady state conditions, thus allowing determining alkane diffusion coefficients in micropores, adsorption equilibrium constants and intrinsic cracking kinetics of the alkane-acid sites complexes by IR operando spectroscopy [8,9,10].

RESULTS AND DISCUSSION

It will be shown that the reactive state of the alkanes in the zeolite, hydrogen bonded OH – alkane complexes, can be identified unambiguously and quantified at reaction conditions using IR operand spectroscopy. Further, we have been able to study the contribution of the two types of weak interactions prevailing in the zeolite pores - H-bonding vs. van der Waals - on the adsorption parameters of n-alkanes. This was achieved by employing a new experimental technique combining gravimetric analysis and IR spectroscopy.

The determination of the coverage can in turn be used to determine the intrinsic cracking kinetic parameters by correlating the apparent rates with the coverage of the bridged OH groups. Our results show that the intrinsic activation energies are constant for all the alkanes and zeolites investigated in this study ($187 \pm 4 \text{ kJ mol}^{-1}$) lying in the lower range of values currently predicted by from low temperature adsorption experiments or molecular simulations. On the other hand, significant differences were found in activation entropies which consistently increased with the alkane chain length and the decrease of characteristic pore or cage size of the zeolite. Examination of the entropic balance 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 $\sim 25 \text{ J mol}^{-1} \text{ K}^{-1}$ in H-FER with respect to HMFI, whereas the entropy of the corresponding transition states differs by only $\sim 5 \text{ J mol}^{-1} \text{ K}^{-1}$.

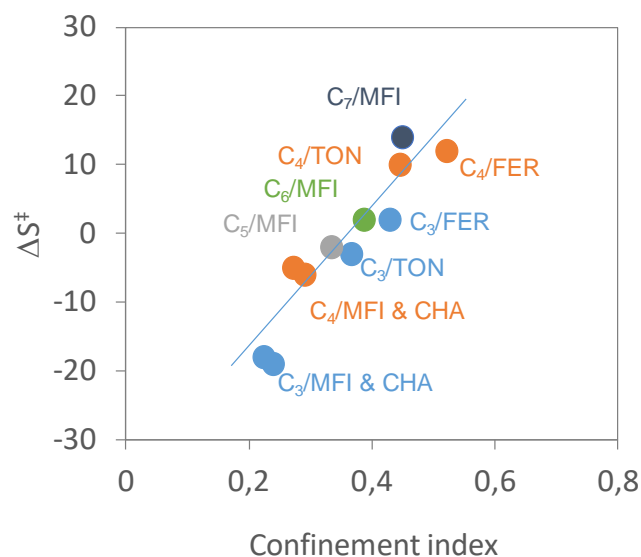


Figure 1: Relationship between monomolecular cracking activation entropy and confinement index.

Analysis of the selectivities of these reactions shows that they are also ruled by entropic parameters, leading to a symmetric, pairwise distribution of lower alkane products. It will be shown that a model where adjacent CC bonds involved in the cracking reaction equally contribute to the activation entropy through the loss of their torsional degrees of freedom at the transition state consistently accounts for the activity trends *and* the observed symmetric distribution of products.

CONCLUSIONS

In summary, the application of IR *operando* methodology to the study of protolytic cracking of alkanes has allowed for the first direct experimental assessment of the intrinsic parameters of this reaction with unprecedented precision. Our data confirm that the relative monomolecular cracking rates of alkanes over zeolites are chiefly controlled by their intrinsic activation entropies at high temperature. IR spectroscopy allows for unambiguous definition and quantification of the initial state of the reaction, namely alkane–acid site hydrogen bond complexes at reaction conditions, which is key to properly quantify adsorption and activation entropic terms. Further, the confidence intervals of activation parameters determined by *operando* spectroscopy were found lower than those currently predicted by state of the art calculations. In this respect, the present work could provide guidelines for theoretical predictions of alkane adsorption and reactivity on zeolites acid sites at elevated temperatures. The applicability of the methodology and concepts developed here to other zeolite types and reactions will be discussed.

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