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Monomolecular cracking of alkanes over zeolites : activity vs. adsorption properties

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The protolytic cracking of alkanes over zeolites, discovered by Dessau and Haag thirty years ago[1], can be considered as archetypal of acid-catalyzed reactions. Because of the interplay between adsorption and surface kinetics, the main structure – activity trends, such as the increase of apparent rates with the alkane chain length or the narrowness of the zeolite pores, have long been subject to discussion [2-6]. While it is now generally admitted that the variations of apparent cracking rates are primarily governed by the intrinsic kinetics, strong discrepancies still persist as to the rate parameter which determines these changes (activation entropy vs. activation energy), 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 [2-5]. 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 [4, 5].

Here, 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 operando 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 Analysis by Gravimetry and IR spectroscopy (AGIR), which allowed a better understanding of the discrepancies between experimental and theoretical studies.

This determination of the coverage at reaction conditions was 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 ± 4 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. Analysis of the selectivities of these reactions shown 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 allows rationalizing structure-activity relationshiops and the impact of the adsorbed state on the intrinsic activities.

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