Journal of Catalysis 345 (2017) 53–69

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Effect of temperature and branching on the nature and stability of alkene cracking intermediates in H-ZSM-5 ☆

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ARTICLE INFO

Article history:
Received 12 August 2016
Revised 7 November 2016
Accepted 8 November 2016
Available online 18 December 2016

Keywords:
Metadynamics
Molecular dynamics
Density functional theory
Zeolite ZSM-5
Catalysis
Alkene adsorption

ABSTRACT

Catalytic cracking of alkenes takes place at elevated temperatures in the order of 773–833 K. In this work, the nature of the reactive intermediates at typical reaction conditions is studied in H-ZSM-5 using a complementary set of modeling tools. Ab initio static and molecular dynamics simulations are performed on different C_4— C_5 alkene cracking intermediates to identify the reactive species in terms of temperature. At 323 K, the prevalent intermediates are linear alkoxides, alkene π-complexes and tertiary carbenium ions. At a typical cracking temperature of 773 K, however, both secondary and tertiary alkoxides are unlikely to exist in the zeolite channels. Instead, more stable carbenium ion intermediates are found. Branched tertiary carbenium ions are very stable, while linear carbenium ions are predicted to be metastable at high temperature. Our findings confirm that carbenium ions, rather than alkoxides, are reactive intermediates in catalytic alkene cracking at 773 K.

1. Introduction

Acid zeolite catalyzed alkene cracking processes are widely applied in chemical industry for the production of gasoline and light olefins, e.g., fluid catalytic cracking (FCC), methanol-to-olefins (MTO), . . . [1–6]. Recently, the expanding shale gas recovery and rising interest in sustainable chemical processes, based on alternative feedstocks, have seriously impacted the light olefin economy. To meet the increasing propene and (to a lesser extent) ethene demand, on-purpose producing technologies have become economically interesting [7–10]. A promising technology is zeolite-catalyzed cracking of the less valuable C_4 through C_8 alkene fraction. Although cracking is generally accepted to occur through a β-scission mechanism of carbenium ions [5,11–15], the precise nature of the adsorbed intermediates remains unresolved up to date. Especially at operating conditions (773–833 K), limited information is known on the nature of alkene cracking intermediates.

Upon adsorption of the olefin in the zeolite channels, four possible intermediates (Scheme 1) can be formed, namely (1) a physisorbed van der Waals complex characterized by only dispersion interactions between the alkene and the zeolite wall; (2) a physisorbed π-complex in which the C═C double bond interacts with the Brønsted acid site (BAS) of the catalyst; (3) a chemisorbed carbenium ion formed upon protonation of the alkene; and (4) a chemisorbed alkoxide, covalently bound to a framework oxygen. While the existence of a stable physisorbed π-complex has been generally accepted [16–18], the nature of the chemisorbed state upon alkene protonation – a free carbenium ion or an alkoxide – is still debated. Many studies presume that covalently bound alkoxide intermediates are formed as cracking reactants [18–25].

Because of the high reactivity of alkenes, even at low temperature, studying olefin adsorption is challenging and experimentally tracking the often short-lived intermediates is extremely hard [26,27]. To date, the existence of small linear alkyl carbenium ions could not be proven by spectroscopic techniques due to their fleeting nature. In the 1990s, several ^{13}C NMR [28–34] and FT-IR spectroscopy studies [35–41] were carried out to identify alkene intermediates in H-ZSM-5 and other acid zeolites. In all of these, alkoxide species were observed as long-living intermediates. No non-aromatic carbenium ions were found freely in the zeolite pores in a temperature range of 150–370 K. Therefore carbenium ions were suggested to behave as short-living transition states rather than reaction intermediates [28,31]. Kondo et al. showed the existence of branched C_8 alkoxide dimers below room temperature by IR spectroscopy on adsorption and dimerization of isobutene in H-ZSM-5, although formation of secondary C_8-alkoxides prevailed over tertiary ones because of steric constraints [40,41]. Interestingly, no t-butoxide nor t-butyl cation intermediate could be identified. However, at actual cracking temperatures, the

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☆ This contribution is part of the virtual issue "30 years of the International Conferences on Theoretical Aspects of Catalysis (ICTAC)".

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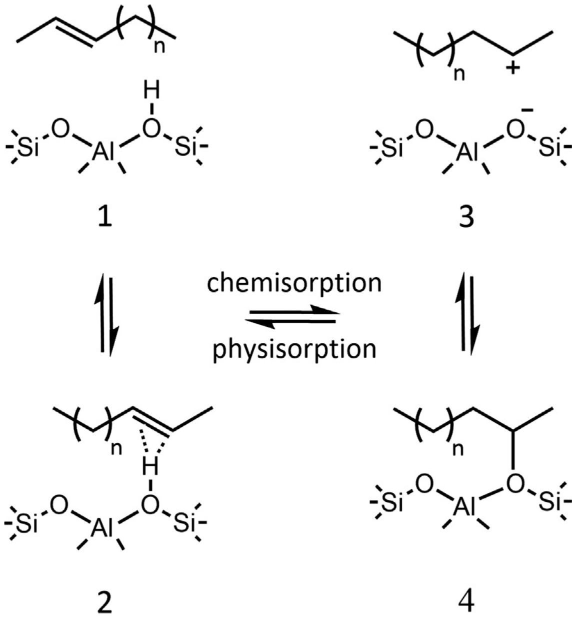
http://dx.doi.org/10.1016/j.jcat.2016.11.010
0021-9517/



Scheme 1. Four adsorption states of a 2-alkene – 1: Van der Waals complex, 2: π-complex, 3: carbenium ion, 4: alkoxide.

situation may be different than at the relatively low temperatures employed in these spectroscopy studies.

Apart from these experimental studies, alkene adsorption has been mainly addressed theoretically. Early quantum chemical studies, carried out on small cluster models consisting of only a few T atoms, supported the hypothesis that chemisorbed alkoxides are highly stable, while secondary or tertiary carbenium ions are non-existent in the zeolite pores except as transition states [21,42–48]. However, these small cluster models lack a proper description of long-range interactions and the zeolite confinement. Studies on larger clusters or periodic models that account for the zeolite cavity concluded that C_3—C_6 alkoxides indeed exist as the most stable adsorption state, although their relative stability compared to physisorbed states at 0 K may not be as high as initially expected [18,20,49–53]. This observation resulted in the assumption that alkoxides can act as reactive intermediates, which rearrange over transition states of ionic nature [20,49].

The zeolite topology and local geometry of the active site can complicate alkoxide and facilitate carbenium ion pair formation since the stability of alkoxides is influenced by steric constraints introduced by the pore dimensions [54–58]. Some computational studies rationalized the possibility of persistent carbenium ions in the zeolite pores [55,59–63]. Nicholas and Haw established an empirical relationship stating a stable carbenium ion can exist in an H-zeolite if the neutral compound has a gas-phase proton affinity (PA) of 874 kJ/mol or higher [64,65]. The authors also suggested that at high temperature, species with a PA around the critical value are likely to form transient, short-living cations. Later studies confirmed for different zeolites that the proton affinity of the neutral alkene correlates with the energy difference between the carbenium ion and the alkene [57,66]. Furthermore, Benco et al. showed that the relative stability of protonated olefins also depends on the carbon number [60]. Carbenium ions may be stabilized from a certain length of the olefin, resulting from a proper accommodation of the positive charge in the zeolite environment [60,67,68]. In a recent study, we identified pentyl carbenium ions as metastable intermediates on the free energy surface at 323 K using a combination of static and dynamic methods [69].

Isobutene adsorption is an ideal benchmark system that received special attention in a series of theoretical studies [54,58,61,70–72]. Alkoxide stability was found to diminish from very stable primary to less stable tertiary alkoxides, which is opposite to the stability order of carbenium ions. It has been argued that due to steric constraints between the methyl groups and the zeolite wall, the *tert*-butyl carbenium ion can become relatively more stable than *tert*-butoxide [19,54,55,72–74]. Tuma and Sauer were the first to perform periodic DFT calculations on H-FER including entropy effects at finite temperature [70]. They concluded that although the *tert*-butyl carbenium ion is electronically least favored, the entropic penalty for *tert*-butoxide formation renders the tertiary cation more stable than the alkoxide for temperatures higher than 120 K. Later, the authors extended their study using a hybrid MP2:DFT method to re-evaluate the stability of the C_4 species when dispersion interactions are included [61,74]. The observed behavior of *tert*-butyl species on H-ZSM-5 in function of temperature has been confirmed by Nguyen et al. while accounting for dispersion interactions and entropy effects [58]. Recently, Dai et al. found additional evidence for the existence of the *tert*-butyl cation by combining NMR spectroscopy with DFT calculations [71].

To the best of our knowledge, the nature of linear and branched alkene intermediates at process temperatures has not yet been unraveled. Nevertheless, such insight is mandatory for further optimizing the process and catalyst. In this work, we aim to clarify the precise nature of adsorbed linear and branched C_4—C_5 intermediates at actual alkene cracking conditions. As a catalyst, we chose H-ZSM-5, which was proven to be one of the most effective industrial catalysts in light olefin production due to its optimal balance between conversion, selectivity and coke formation stability [13,75,76]. Schemes 2a and 2b depict the possible intermediates upon adsorption of C_4 and C_5 alkenes respectively. Primary carbenium ions are not considered as candidate intermediates in this work due to their highly unstable nature [12,22,77,78]. We investigate the differences in stability between linear and branched adsorbate states and the influence of temperature by comparing three different cases – 323 K, a typical temperature for spectroscopy experiments, 573 K, an intermediate temperature and 773 K, a typical cracking temperature. To this end, we applied a combination of static DFT calculations and molecular dynamics simulations which inherently account for entropy and finite temperature effects as well as the mobility of the adsorbates. Metadynamics simulations were performed to sample transitions between the different intermediate states, separated by non-negligible free energy barriers. Using the advantages of these three techniques allows assessing the stability differences at operating conditions both qualitatively and quantitatively. MD simulations have been successfully combined with static calculations and free energy methods to study adsorption properties and reactions of hydrocarbons in zeolite materials [27,68,79–86]. For the problem at hand, a complementary approach between static and dynamic techniques is applied to acquire detailed knowledge on the nature of the intermediates.

2. Methodology

2.1. Zeolite model

All static and dynamic density functional theory (DFT) calculations are performed on a periodic model of the H-ZSM-5 catalyst, fully accounting for the confinement in the zeolite pores. H-ZSM-5 exhibits the MFI topology which consists of intersecting straight (5.3 Å × 5.6 Å) and sinusoidal (5.1 Å × 5.5 Å) channels. The orthorhombic unit cell contains 289 atoms (96T atoms) and a single Brønsted acid site. The substitutional Al defect is situated at the T12 position, i.e. at the intersection of the straight and sinusoidal