The cracking of n-heptane in the gas phase state and in the HZSM-5 zeolite: a quantum molecular dynamics study

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Quantum molecular dynamics is used to investigate the cracking of a representative hydrocarbon of the paraffin family (n-heptane), analysing the effects of temperature in the fragmentation of n-heptane when this compound is in the gas phase and inside a typical industrial catalyst (zeolite HZSM-5). The hydrocarbon structural and electronic features in the two environments are determined and compared. The results substantiate current views and exhibit the basic aspects in the cracking of n-heptane.

1. Introduction

The cracking of heavy oils into smaller compounds has traditionally involved the combination of different techniques. Thermal cracking in conjunction with catalytic conversion has shown one of the best performances and is an economic way to manufacture liquid fuels [1]. Thermal cracking (with no inclusion of catalysts) demands the use of high temperatures for the decomposition of large hydrocarbons. The recombination of smaller fragments requires high temperatures too. In principle, the thermal degradation of hydrocarbons needs no catalysts and temperature, pressure and time represent the key factors that determine product types. For instance, different boiling temperatures may lead to major portions of hydrocarbon gases, gasoline in the boiling range, or coke [2]. Although the use of heat is one of the oldest forms of crude oil conversion, thermal cracking takes no account of the explicit nature of compounds and can lead to undesirable products, like major concentrations of olefinic compounds. In this context, the use of catalysts has been of particular help to achieve size and shape selectivity in the cracking of hydrocarbons [3, 4]. Catalysts in the form of crystal structures are not easily degraded under intense heat and favour the formation of energetic products, which give better engine combustion rates with a minimum quantity of residuum. The key factors in the catalytic process are similarly the temperature, pressure and time. The catalytic materials have become so effective that their use has been extended to other scientific areas.

Given the important roles that the temperature and catalysts have in the fragmentation of hydrocarbons, it is our goal to study the thermal cracking of hydrocarbons in the gas phase as well as the combined role that the temperature and catalysts, like zeolites, play in the conversion of hydrocarbons. For this, we have recourse to systems such as zeolite HZSM-5 and n-heptane. HZSM-5 is one of the major catalysts used in industry, while n-heptane is a representative compound of the paraffin family [4]. The physical features of HZSM-5 and n-heptane have been described [5], but only a few efforts have been concentrated in analysing from a molecular and dynamic point of view the interplay between temperature and catalyst in the precise moments of hydrocarbon conversion.

2. Theoretical approach

We resort to density functional theory (DFT) to compute the quantum forces among atoms because it has been shown that DFT is capable of predicting structures and energetics reasonably close to experiment [6]. The generalized gradient formulation (GGA) of DFT gives accurate results for reaction energies and the thermochemistry of bonded and even weakly bonded systems like those studied here. Thus, we use the Becke (1988) and Lee–Yang–Parr (1988) GGA expressions for the calculation of exchange and correlation, respectively. These terms demand modest computational efforts, especially for calculations of an all-electron type. The molecular orbitals are expanded in terms of Gaussian basis sets of double-zeta quality (DZVP), which minimize basis set superposition errors and account for polarization effects of valence electrons. We additionally
resort to Gaussian auxiliary basis sets to evaluate the energy terms and electronic potentials that depend on the electron density. They are also of DZVP quality, and their use aims at a rapid evaluation of matrix elements in the time-consuming self-consistent field process that determines the DFT wavefunction.

Given the dynamic character of the thermal and catalytic cracking of hydrocarbons [7], we combine the DFT approach with molecular dynamics to introduce temperature effects [8]. We assume the Born–Oppenheimer approximation, which separates in parametric form the electronic motion from the nuclear. In this form the Newtonian equations of motion are integrated with atomic forces computed from DFT potentials [5, 9]. We use the leap-frog finite difference algorithm to generate atomic trajectories, with timesteps of 2 fs that avoid numerical divergence. All the dynamics are evolved under an isotherm constraint as in the experimental reactor, so atomic velocities are negligible with respect to relativistic speeds. The simulations are limited to the femtosecond regime due to the small number of particles involved in our model system. The computations are performed with NWChem [9] in a supercomputer of eight processors.

3. Results and discussion

3.1. Thermal cracking

A large hydrocarbon like n-heptane can fragment in many ways, leading to different types of product. The fragment types depend not only on environmental forces, but also on the temperature. Initially, n-heptane is resistant to breaking, but the temperature forces nuclear conformations where electron repulsion effects become the dominant forces that promote fragmentation. In order to study temperature effects, we performed several simulations of n-heptane in the gas phase at different temperatures (300, 800, 1200, 1250, 1280, 1400 and 1600 K). Our results should be reliable for low density gases because at such densities the interaction among n-heptane molecules is weak. The products of the thermal cracking, sketched in figure 1, are intermediate compounds, chemically active, with short lifetimes. Clearly, the instability of these intermediates complicates their experimental detection [10], nonetheless, our results should be of help in elucidating the fundamental aspects involved in the thermal cracking.

All the simulations except for that at room temperature (300 K) show common behaviour, namely, the folding of the hydrocarbon chain and release of hydrides (negatively charged hydrogens). At 800 K only one hydride is released (H14), but at higher temperatures (like 1200 K and 1600 K) two or more may be ejected, in agreement with experimental evidence [11]. Hydride release is shown as a resonant effect, where the similar vibrating fields of nearby hydrogens produce the resonance. The resonance may be favoured or dissuaded by the carbon chain conformation, which depends on the temperature. In the higher temperature range we observe CC bond breaking. The breaking of carbon bonds in n-heptane starts between 1250 K and 1280 K. At 1280 K the C2C3 and C5C6 bonds break slightly after the release of H16. The breaks occur in symmetric bonds of the molecule and are characterized as beta-type scissions [12, 13] because the CC bond that is broken is always the second adjacent bond to the atom that releases the hydride. At 1600 K we obtain similar results to those at 1400 and even at 1280 K; they all lead to the same chain fragments with a minimum difference in the number of released hydrides. The formation of smaller carbon chains and the number of released hydrides as we increase the temperature let us predict the formation of coke at such high temperatures.
Thus far, the preferred mechanism of n-heptane to fragment in a vacuum is through the release of hydrides, but still need to investigate the charged nature of the products to assess their reactivity. We investigate the electronic charge of these products obtained at 1280 K (for our lowest temperature simulation that shows the breaking of n-heptane). In figure 2 we sketch the evolution of the charge and correlate it with distances of relevant atoms that participate in the fragmentation. The population charges have been computed according to the Mulliken approximation. The initial breaking of the C4H16 bond (267 fs after starting the simulation) is a heterolytic process as it produces two oppositely charged species, where H16 subtracts electronic charge from the rest of the molecule. The fragmentation of the C2C3 and C5C6 bonds, which occurs approximately 7–8 fs later, leads to two (CH3CH2) ethane- and one (CH2CHCH2) propane-type fragments. The proximity of the fragments yields a continuous polarization of electron clouds. This is the reason that all fragments appear with fractional charges, making a conclusion about the possible formation of ions or radicals difficult. Nevertheless, we observe a tendency for the propane-type fragment to become neutral by subtracting charge from the ethane-type compounds, which tend to stay positively charged. H16 is the hydrogen that compensates the charged state of the two ethane molecules for the range of distances shown in the plot.

Note that the computations are based on a spin compensated density functional method, and the neglect of spin polarization could in principle produce a fictitious charge stabilization of the products. However, the spin
is a global property of the system and cannot be localized on atoms or fragments. Therefore, the neglect of spin polarization should not prevent the formation of ionic fragments or compounds with unpaired electrons, even when the system as a whole may be in a spin compensated state.

Energy plots are presented in figure 3 (a). At 300, 800 and 1200 K the ejection of charged protons produces a sudden increase in the energy, which is stabilized after a short period (when the particles are far away from the rest of the molecule and the interaction is small). These curves increase with increase in temperature. However, at higher temperatures the expected increment in the electronic energy that should in principle correspond to an increment in the temperature is not observed. Presumably, electronic effects dominate by temperature range. This can be explained based on the way the hydrocarbon breaks. At 1280 K or 1400 K, for instance, n-heptane shows breaking of carbon bonds, which brings the whole system into lower energies than those achieved at 1200 K where the molecule still remains as a single carbon-chain entity and the electronic cloud is under stress. The fragmentation of n-heptane simulates a change of phase state, and energy plots indicate it as a

Figure 3. Electronic energies (in au) and dipole moment curves (in D) of n-heptane in the gas phase at different temperatures. The energy curves at 1280 K and 1400 K are very close to each other. The sudden rise in the energy and dipole curves is attributed to the release of hydrides. Their ejection speeds (taken at the end of the simulations when the particles were well apart) appear in parentheses (in km s$^{-1}$). Note the correlation between the curves of the two parts for a given temperature.
nonlinear phenomenon. At higher temperatures the breaking of both (CC and many CH) bonds again makes the energy curves increase.

In figure 3(b) we show plots of the dipole moment at different temperatures. The release of one or several hydrides leaves n-heptane in a charged state, producing an abrupt increase in the dipole. Then the dipole curves exhibit different timescales, due to the different temperatures at which the breaking of CH bonds takes place. On the other hand, the slope of the dipole plots represents an indirect measure of the number and ejection speeds of the hydrides.

3.2. Catalytic cracking

We have performed molecular dynamics simulations of n-heptane inside a HZSM-5 model cavity, which represents one of the many rings that build the HZSM-5 pores (figure 4). Inside these pores the catalysis takes place due to the presence of cationic transition metals like Al$^{3+}$. Since metals may be positioned in or out of the crystal framework [14], we have assumed that the catalytic centre is located in the lattice [15]. Contrary to the simulations in the gas phase, n-heptane in the ring shows less twisting due to cavity confinement forces. These forces in conjunction with the cationic metal pro-
mote the fragmentation of the carbon chain at much lower temperatures than in the gas phase. For instance, at 300 K (almost room temperature) we already observe cracking of the hydrocarbon with the usual release of a hydride. In general, the products of catalytic cracking (figure 4) differ from those obtained in thermal cracking.

Differences also appear in the electronic energy curves (figure 5(a)). In the catalytic cracking the energy does not show sigmoidal behaviour, but energy barriers like dynamic analogues of transition states. In the catalytic cracking case, barrier heights diminish with increase in temperature. Thus, at 800 K the formation of products is greatly facilitated in comparison with the 300 K temperature. In addition, at the ends of our simulations, the products of catalytic cracking at 800 K are in a higher energetic state than these at 300 K.

As in the gas phase, the dipole moments of the n-heptane/HZSM-5 complex indicate the departure of hydrides (figure 5(b)). However, departure times are shorter in the catalytic cracking case. In addition,
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hydrides ejected from n-heptane in the zeolite show lower speeds than those achieved in the gas phase. Therefore, inside the HZSM-5 ring cavity, where the torsion of the carbon chain is limited, the electronic cloud seems to be under less stress, thus releasing particles with slower speeds.

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References
