



Effect of Confinement on Chemical Reactions

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Abstract. Molecular simulation studies of chemical equilibrium for several reactions in pores of slit-like and cylindrical geometry have shown a significant effect of the confinement on the equilibrium compositions, with differences of several orders of magnitude with respect to the bulk fluid phase in some cases. As a first step towards the calculation of rate constants in confinement, we have studied the reaction mechanisms for several reactions involving small organic molecules in slit-like pores. We show results for the rotational isomerization of 1,3-butadiene and the unimolecular decomposition of formaldehyde obtained using plane wave pseudopotential density functional theory (DFT). These examples show the influence that confinement can have through both geometrical constraints and fluid-wall interactions.

Keywords: chemical reactions, confinement, porous carbon, density functional theory

1. Introduction

Chemical reactions are often carried out in micro- and nanoporous materials, which can enhance reaction rates and equilibrium yields through a host of different effects. Some of these effects include an increase in the contact area between the catalyst and the reac-

tive mixture, additional catalytic effects due to interactions with the support, selective adsorption of the reactants and/or products and geometric constraints, among others. Despite many years of research in the area of heterogeneous catalysis, it still remains a problem to elucidate the relative importance of each of these factors on a given reaction. A major reason for this is the fact that experimental measurements often reflect the influence of several effects at a time, and it is costly

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and time-consuming to design experiments to study the influence of each one separately. Furthermore, the relative importance of each effect is likely to be dependent on the particular reaction considered. Due to the difficulties and costs associated with a purely experimental approach, this problem is a good candidate for molecular simulation studies.

In recent years, there have been several studies of the effect of confinement on both equilibrium yields and rate constants for several reactions (Byl et al., 2003; Halls and Schlegel, 2002; Turner et al., 2001a, 2001b, 2002a; Turner et al., 2002b; Turner and Gubbins, 2003). Although equilibrium yields are relatively easy to obtain, the calculation of rate constants requires knowledge of how the environment affects the reaction mechanism. In sufficiently small pores, or in materials that can interact strongly with the reactive mixture, the reaction mechanism may be very different from that in the bulk. Hence, an understanding of the effect of confinement on reaction rates requires a prior study of the effect of each of the factors mentioned above on different reaction mechanisms. A clear understanding of these factors could lead to the design of much improved catalytic systems, and it may be possible to optimize both the yield and rate of the reaction, while achieving partial or complete separation of the products.

As a first step towards an understanding of the effects mentioned above, we have chosen to study two simple chemical reactions confined in carbon nanopores. The first example is the rotational isomerization of 1,3-butadiene. This reaction is a good candidate to study the effect of the geometrical constraints imposed by the pore walls for several reasons: (1) it has an easily identifiable reaction coordinate (the dihedral angle between the four carbon atoms); (2) the mechanism involves a three-dimensional motion of the molecule, which is likely to be affected by the reduced dimensionality of the porous environment, and (3) the reaction in the bulk has been extensively studied both experimentally (Arnold et al., 1990; Fisher and Michl, 1987; Squillacote et al., 1979; Engeln et al., 1992; Carreira, 1975; Lipnick and Garbisch, 1973) and through simulations (Murcko et al., 1996; De Maré et al., 1997; Sancho-García et al., 2001a; Sancho-García et al., 2001b), and hence there is data available for comparison. The reaction is also made interesting by the fact that the structure of the high-energy rotamer is determined by an interplay between the steric impediment of the methylene end groups and the stabilization due to sp^2 - sp^2 conjugation. Therefore, the confinement by

the porous material can potentially affect not only the energy barrier for the reaction, but also the nature of one of the equilibrium states.

The second example we consider is the unimolecular decomposition of formaldehyde in carbon nanopores. This reaction is a good candidate to study the influence of the pore-wall interactions on the reaction mechanism, and later the possibility of a separation of the products due to preferential adsorption. The relative charge on the oxygen and carbon atoms changes as the reaction progresses, and the presence of a large polarizable graphene wall nearby can potentially reduce the reaction energy barrier. An example of this kind of effect is discussed by Halls and Schlegel (Halls and Schlegel, 2002). In addition, the relative affinity of the decomposition products (carbon monoxide and hydrogen) for the carbon wall is quite different, allowing for the possibility of a simultaneous separation of the products.

2. Methodology

All the results presented in this work were obtained using density functional theory (DFT) with the Becke-Lee-Yang-Parr (BLYP) exchange-correlation functional (Becke, 1988; Lee et al., 1988). The calculations for the rotational isomerization of 1,3-butadiene were carried out using the CPMD code, and the calculations for the formaldehyde decomposition were carried out using the pwscf code. Both CPMD and pwscf use the plane-wave pseudopotential approach, where the electronic states are represented by 3-dimensional Fourier expansions. For our calculations, we used ultrasoft pseudopotentials (Vanderbilt, 1990) with an energy cutoff of 35 Ry.

For both the bulk and pore simulations of the 1,3-butadiene isomerization, we constructed the potential energy surface by a two-step procedure. First we performed a series of simulations with the dihedral angle between the four carbon atoms constrained to values ranging from 0 to 180 degrees in steps of 15 degrees. All other degrees of freedom in the molecule were allowed to relax, and the final energy was recorded. Then, in order to improve the resolution on the interesting parts of the curve, we performed additional simulations with different torsional constraints. The transition state for the *s-trans-s-gauche* conversion was optimized in CPMD using the rational function optimization (RFO) method (Banerjee et al., 1985; Billeter et al., 2002). For the simulations in confinement, we represented the pore as a set of two graphene sheets

containing 32 carbon atoms each, in a hexagonal cell. We optimized the cell parameter of the graphene sheets before the simulations, yielding an optimal carbon-carbon bond length of 1.43 Å. The carbon atoms on the graphene sheets were constrained during the simulations. In some of the highest-energy conformations we allowed the carbon atoms to relax in order to estimate the effect of this constraint. The structure of the graphene sheet in these calculations remained essentially the same, and the maximum energy change was ~ 0.15 kcal/mol, about 2% of the energy barrier for rotation.

We obtained the reaction path for the unimolecular decomposition of formaldehyde using the nudged elastic band (NEB) method (Mills et al., 1995, Jónsson et al., 1998) with the climbing image modification to find the transition state (Henkelman et al., 2000). In order to estimate the possible catalytic effect of the carbon surface, we did NEB calculations for the decomposition close to a graphene sheet. The carbon atoms in the sheet were allowed to relax during the calculations.

3. Results and Discussion

Figure 1 shows the torsional profile for isolated 1,3-butadiene as obtained from our DFT-BLYP calculations. The transition state for the *s-trans-s-gauche* conversion corresponds to a dihedral angle of 100.4 degrees, and the energy barrier is 7.49 kcal/mol. Calculations using the coupled-cluster CCSD(T) method have obtained a dihedral angle for the transition state of 100.7 degrees, and an energy barrier of 6.30 kcal/mol (Sancho-García et al., 2001b). The difference

of 1.19 kcal/mol in the energy barrier can be explained by the poor representation of conjugated bond breaking given by the Becke exchange functional (Sancho-García et al., 2001b; Choi et al., 1997). We obtained an energy difference between the *s-cis* and the *s-gauche* conformers of 0.34 kcal/mol, in reasonable agreement with the CCSD(T) value of 0.42 kcal/mol (Sancho-García et al., 2001b).

The effect of confinement on the torsional energy profile of 1,3-butadiene, as predicted by DFT-BLYP, is shown in Fig. 2. For pore sizes greater than ~ 10 Å the effect in the torsional profile is negligible. As the pore width becomes comparable to the molecular size, two significant changes occur. First, as shown in Fig. 3(a), the energy barrier for the *s-trans-s-gauche* conversion increases sharply, becoming almost twice the value in the bulk for a pore size of 6.9 Å. Second, as shown in Fig. 3(b), the energy difference between the *s-cis* and *s-gauche* conformers, i.e. the barrier for the conversion between the two symmetrically equivalent *s-gauche* conformations, is reduced, becoming smaller than 0.1 kcal/mol for the 6.9 Å-wide pore. The torsion angle between the four carbon atoms in the *s-gauche* conformation is also reduced for the smaller pore widths, to 24.5° in the 7.4 Å pore and 15.2° in the 6.9 Å pore. This suggests that the *s-cis* conformer may become stable for smaller pore widths. We are currently carrying out calculations to check whether this is the case.

The reaction path obtained from the nudged elastic band calculations for the decomposition of formaldehyde in the bulk is shown in Fig. 4. The activation energy obtained from the DFT-BLYP calculations is 80.3 kcal/mol, in excellent agreement with the

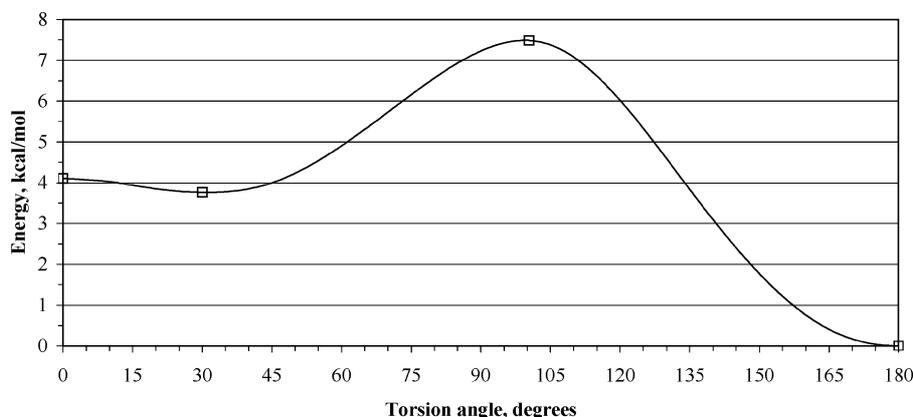


Figure 1. Torsional potential of 1,3-butadiene as obtained from the DFT-BLYP plane-wave calculations. The squares mark the stationary points: *s-cis* (maximum) at 0°, *s-gauche* (minimum) at 30.0°, transition state (maximum) at 100.4° and *s-trans* at 180°.

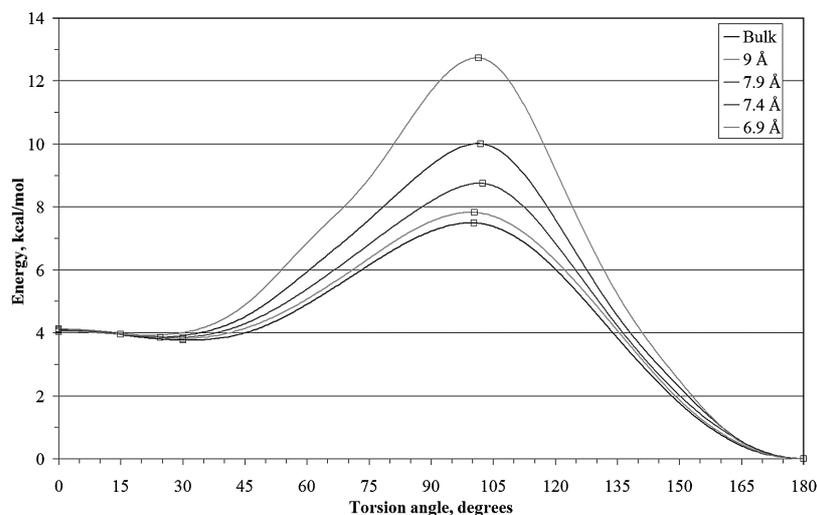


Figure 2. Effect of confinement on the torsional energy profile of 1,3-butadiene. Stationary points at each pore size are marked with squares. The legend shows the pore widths for each of the curves.

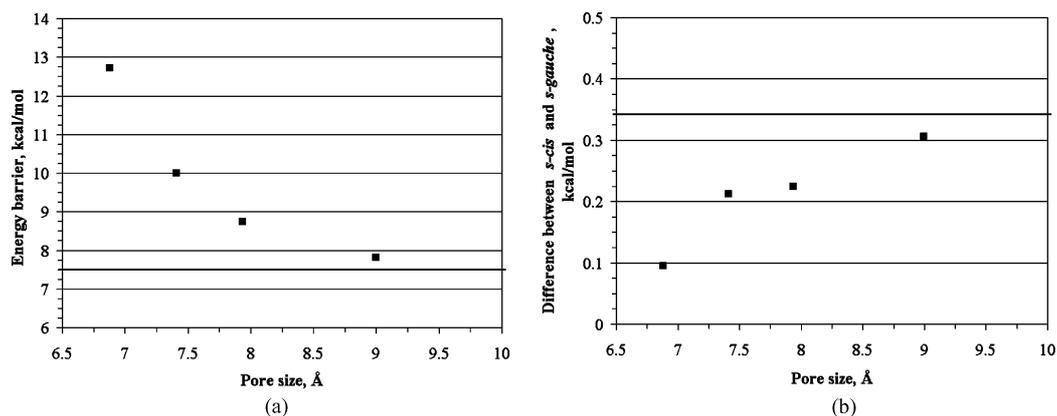


Figure 3. Effect of confinement on the barrier for the *s-trans-s-gauche* conversion (a) and the energy difference between the *s-cis* and *s-gauche* conformers (b). The horizontal line indicates the corresponding value for the bulk.

experimental value of 79.2 ± 0.8 kcal/mol (Guyer et al., 1990) and higher-level *ab initio* calculations (Dupuis et al., 1983; Bauerfeldt et al., 2002).

The reaction energy profile for the dissociation of formaldehyde close to a pore wall is depicted in Fig. 5. In this case the activation energy is 78.8 kcal/mol, i.e. 1.5 kcal/mol lower than the bulk value. This small reduction in the barrier for dissociation may be explained by the large polarizability of the graphene sheet, which facilitates the transport of charge along the C–O bond necessary for the dissociation. The products, CO and hydrogen, also become relatively

more stable (by 3.7 kcal/mol) in the proximity of the graphene sheet. The structure plots in Figs. 4 and 5 were made using the VMD code (Humphrey et al., 1996).

4. Concluding Remarks

Our results for the isomerization of 1,3-butadiene show that there is a significant effect of confinement on the potential energy profile for pore sizes comparable to the molecular size. For the *s-trans-s-gauche* conformational change, the energy barrier increases sharply

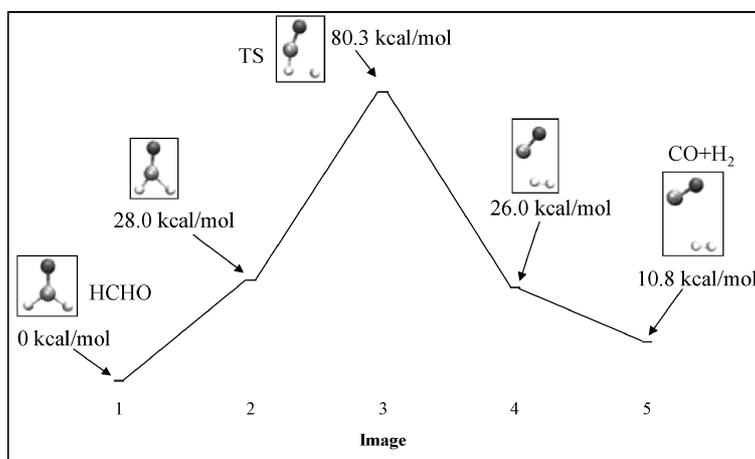


Figure 4. Energy profile for the dissociation of formaldehyde in the bulk as obtained from a NEB calculation with 5 images. The small spheres represent hydrogen, the large light gray sphere represents carbon, and the dark gray sphere represents oxygen.

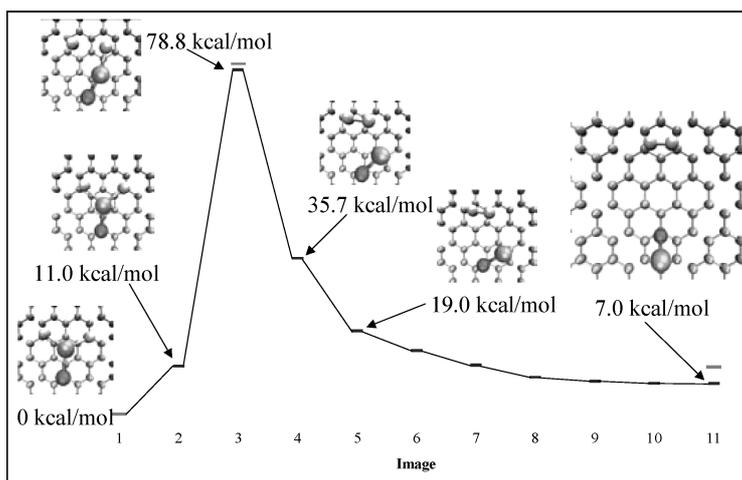


Figure 5. Energy profile for the dissociation of formaldehyde close to a graphene sheet as obtained from a NEB calculation with 11 images. The bulk values for the transition state and the products are indicated as horizontal lines above images 3 and 11.

with decreasing pore size, whereas for the interconversion between the two symmetric *s-gauche* images the energy barrier decreases as the pore width decreases. Calculations to refine the values of the energy barriers and to incorporate the effect of temperature are currently in progress.

The results presented for the decomposition of formaldehyde show that the proximity of the pore wall reduces somewhat the reaction barrier, although the change is relatively small. It would be interesting to examine the effect of a second graphene sheet (to explore the effect of geometric confinement) as well as study the effect of defects on the graphene structure. These calculations are currently underway.

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