MOLECULAR MODELING OF CHEMICAL REACTION EQUILIBRIA IN PORES; EFFECTS OF CONFINEMENT ON EQUILIBRIUM YIELD

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Introduction

Despite the widespread use of porous catalysts and catalyst supports in carrying out heterogeneous reactions industrially, there has been remarkably little fundamental work on the effects of confinement on chemical reaction equilibria. Molecular assemblies confined within narrow pores, with pore widths of a few molecular diameters, exhibit physical properties that are strikingly different from those of the bulk phase adsorbate. At a given temperature and bulk fluid pressure, the coexisting confined phase in a porous medium is usually at a considerably higher density than the bulk phase. Therefore we would anticipate that for any chemical reaction in which there is a change in the total number of moles, the confined phase would yield an equilibrium composition that is quite different from that of the bulk.

In this paper we apply the Reactive Canonical Monte Carlo (RCMC) method [1] to study the dimerization of nitric oxide, $2NO \leftrightarrow (NO)_2$, in activated carbon fibers, modeled as slit-shaped pores. We show that the effects of confinement on the yield of dimers is dramatic for this reaction.

Methods and Models

The RCMC algorithm consists of the usual Metropolis steps of displacement, reorientation, and volume changes but is modified to include forward and reverse reaction steps which preserve chemical equilibrium within the system. The reaction steps are performed by swapping particle identities so that the need to specify individual chemical potentials is eliminated.

RCMC simulations of the NO dimerization were performed with a constant number of atoms, pressure, and temperature (NPT) in both the liquid and gas phases. The potential cutoff was set at 3σ and standard long-range corrections were applied. The simulations were typically equilibrated for 10^6 moves and averages were taken for 10^7 moves. 512 particles were used in the simulations starting from an initial configuration of 100%

NO monomers. The typical probability of attempting each move was: movement/reorientation 39%, forward reaction 30%, reverse reaction 30%, volume change 1%. Forward and reverse reaction attempts must be chosen with equal probability in order to maintain microscopic reversability.

As a starting point, we used the models of NO and $(NO)_2$ from Johnson et al. [1] in our simulations and then compared with experimental results of NO dimerization in the bulk phase. In following Johnson, we adjusted the value of the dissociation energy, D_o, to match experimental mole fraction versus temperature data. We obtained close agreement between experiment and simulation with a value of $D_o = 17.7 kJ/mol$.

Figure 1 shows our simulated results of the liquid phase mole fraction of $(NO)_2$ compared to experimental measurements. The experimental data includes Guedes' extrapolation of the mole fractions beyond $120K$ using the thermodynamic properties of NO [2]. While the liquid phase is predominantly dimerized, the gas phase is almost entirely composed of unassociated NO particles. In the vapor phase at $T = 121.4K$ and a pressure of 1.01 bar ($P* = 0.0019$) we calculated the mole fraction of dimers to be 1%, which is in agreement with theoretical predictions of $1 - 2\%$.

Once we had confirmed our model with the NO dimerization in the bulk phase, we investigated the influence of confinement on the reaction. To do this, we implemented a constant (bulk) pressure Gibbs ensemble Monte Carlo technique [3]. This simulation scheme allows the bulk system pressure to be specified while maintaining equilibrium between the bulk phase and the pore via particle exchanges. The pressure is controlled by varying only the bulk volume while the pore volume remains fixed. The overall effect is that the confined system can be easily compared to a bulk phase system without needing an equation of state or chemical potentials.

We simulated the nitric oxide dimerization in a slit-shaped carbon pore, using a structureless 10-4-3 Steel potential to model the carbon walls. We measured the mole fraction of $(NO)_2$ as the slit width was varied from
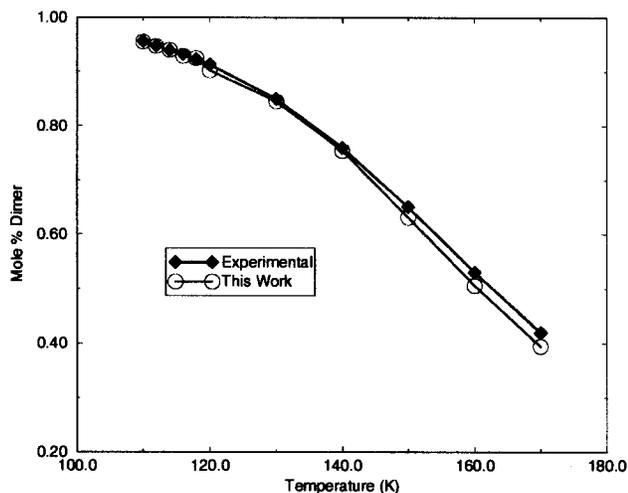
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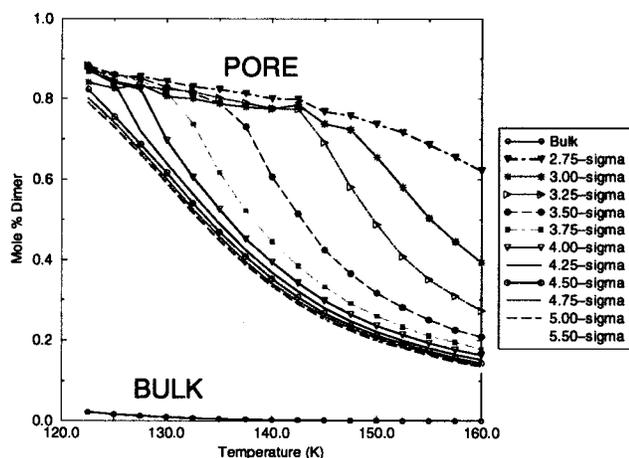Figure 1: Liquid Phase Dimerzation of NO in an Unconfined System

Figure 2: Dimerization of NO in Model Carbon Pores

2.25σ ($5\mathring{A}$) to 5.5σ ($12.3\mathring{A}$) in temperatures ranging from $122.5K$ to $160K$. The pressure was held constant at a value of 0.16 bar ($P* = 3 \times 10^{-4}$). With the inclusion of a second phase (the pore), the system size was increased to 1000 particles. Also the lengths of the simulations were increased to between 1×10^7 and 3×10^7 Monte Carlo moves following 5×10^6 moves for equilibration. The potential cutoff was extended to 5σ and long-range corrections were applied exclusively to the bulk phase.

Figure 2 shows the simulated mole fractions of $(NO)_2$ within pores of varying size along with the bulk mole fraction in equilibrium with the pores. As expected, the most noticeable effect of confinement is a dramatic shift in equibrium from almost 100% monomers in the

bulk phase to a highly dimerized system in the pore. The bulk phase mole fraction is identical for all runs at a given temperature and pressure, regardless of the pore size, consistent with our expectations.

While only selected slit widths are shown, all pore sizes investigated exhibit similar behavior. After reaching a pore size of about 4σ, the simulated mole fractions become very closely spaced. This can be attributed to the fact that the influence of the pore on the equilibrium is most strongly felt in the first adsorbed layer. As the pore size is increased above 4σ, the middle of the pore becomes increasingly similar to the bulk phase and the slit width becomes less influential.

Conclusions

We find a dramatic increase in the fraction of dimers for the confined system in activated carbon fibers, which is in agreement with the experimental findings of Kaneko et al. [4]. This confinement effect is strongly dependent on temperature, the temperature dependence being greater in the pore than for the bulk fluid. There is also a strong dependence on the pore width, dimerization being enhanced in smaller pores; this strong width dependence decreases for pores of width much larger than 4σ.

References

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Acknowledgements