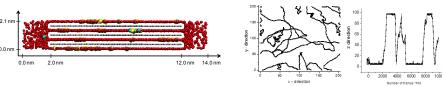# Adsorption of mixtures of methane and methyl mercaptan in nanoporous carbon

Carlos Wexler, Monika Gołębiowska, and Peter Pfeifer, University of Missouri, United States; Michael Roth, University of Northern Iowa, United States; Bogdan Kuchta, Université de Provence, France; Lucyna Firlej, Université Montpellier 2, France;

Natural gas (NG) is a widely-available but underutilized fuel, in particular for vehicular applications. NG consists mainly of methane, which has a hydrogen to carbon ratio higher than any other molecule used as a fuel. Such a property yields low CO_2 emission and high energy per unit mass. A major problem is that methane, the principal component of NG, requires bulky high-pressure tanks to store sufficient compressed natural gas (CNG) to have hundreds of kilometers of autonomy. An attractive alternative is to store methane by physisorption into a suitable substrate (adsorbed natural gas, ANG). Currently there exists several materials that store methane efficiently at room temperature at moderate pressures, e.g., nanoporous carbon.[1,2] However, a significant concern is the safety of such ANG system against gas leaks. For easy detection low concentrations of highly odorant gases such as thiols (mercaptans) are utilized since their threshold for detection by humans is in the parts per billion. Whereas pure methane adsorption has been extensively studied, a full understanding of the behaviour of methane-mercaptane mixtures is required for the development of ANG systems. Given the different fugacities of the two components, we are in interested on how reversible the mercaptan adsorption is, and the minimum mercaptan concentration in the adsorbate so as to still achieve a concentration in the desorbed phase above the human threshold for detection. Here we present results of extensive molecular dynamics computer simulations of adsorption of methane-methylmercaptan and methane-ethylmercaptan mixtures on reasonable models for activated carbon (single graphene surface and graphene-based slit pores). Adsorption is simulated directly in a two-phase system (gas in equilibrium with adsorbate). The simulations were carried out in the temperature range 150–350 K for a large range of pressures, up to the saturation pressure of methane. We focus on the thiols diffusion (trajectories) during the adsorption-desorption cycle of methane and the reversibility of their adsorption in the presence of methane (this can be only be observed with the two-phase system where the molecules can easily be transferred between adsorbed and gas phases). This is a large, multiscale problem because such situation requires big simulation box where the interface can be represented in an accurate way. As a result of our simulations we conclude that, for normal ANG operating conditions, thiols adsorb preferentially but still reversible and that only a modest increase in mercaptane's concentration in the NG is necessary to provide for human detectable admixtures in the gas phase.

Left: adsorption of thiols and CH_4. Right: diffusion of thiols at $T = 298$ K, $P_{NG} = 70$ bar.

[1] P. Pfeifer, *et al.,* Mater. Res. Soc. Symp. Proc. **1041**, R02-02 (2008), and references therein.
[2] X. D. Dai, X. M. Liu, L. Qian, K. Qiao and Z. F. Yan, Energy & Fuels **22**, 3420–3423 (2008).