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# GCMC Simulations in Zeolite MFI and Activated Carbon for Benzene Removal from Exhaust Gaseous Streams

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## GCMC Simulations in Zeolite MFI and Activated Carbon for Benzene Removal from Exhaust Gaseous Streams

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Keywords:	GCMC simulation, benzene removal, adsorption, zeolite, activated carbon

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60**Table1.** 3D periodic cells characteristics.

Structure	Dimensions x, y, z [Å]	Composition [% in weight]	Density [kg/m <sup>3</sup> ]
Zeolite MFI	40.044, 39.798, 26.766	Si 46.7%, O 53.3%	1796
Zeolite FAU (NaY)	25.104, 25.104, 25.104	Si 30.1%, O 48.3%, Al 11.7%, Na <sup>+</sup> 9.9%	1337
Cs1000a	25.000 x 25.000 x 25.000	C 99.2%, H 0.8%	728

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**Table 2.** Isosteric heats for multicomponent adsorption in zeolite MFI and activated carbon cs1000a.

		Benzene [kcal/mol]	H <sub>2</sub> O [kcal/mol]	CO <sub>2</sub> [kcal/mol]	N <sub>2</sub> [kcal/mol]	O <sub>2</sub> [kcal/mol]
MFI (101.3 kPa)	500 K	24.46 (0.12)	10.46 (0.63)	10.99 (0.34)	[-]	[-]
	750 K	24.30 (0.17)	7.98 (0.16)	9.64 (0.15)	[-]	[-]
	1000 K	24.27 (0.17)	7.68 (0.17)	9.68 (0.10)	[-]	[-]
MFI (202.6 kPa)	500 K	24.59 (0.13)	10.32 (0.52)	10.91 (0.40)	[-]	[-]
	750 K	24.35 (0.06)	8.22 (0.26)	9.67 (0.18)	[-]	[-]
	1000 K	24.29 (0.19)	7.75 (0.11)	9.71 (0.06)	[-]	[-]
MFI (506.5 kPa)	500 K	24.39 (0.12)	7.65 (0.12)	9.30 (0.07)	[-]	[-]
	750 K	24.30 (0.15)	8.49 (0.36)	9.96 (0.32)	[-]	[-]
	1000 K	24.03 (0.14)	7.64 (0.07)	9.27 (0.07)	6.45 (0.01)	5.65 (0.04)
Cs1000a (101.3 kPa)	500 K	19.75 (0.20)	3.47 (0.05)	5.32 (0.14)	3.14 (0.05)	2.71 (0.05)
	750 K	16.80 (0.23)	3.38 (0.04)	4.64 (0.03)	3.26 (0.02)	2.97 (0.03)
	1000 K	14.26 (0.49)	3.59 (0.04)	4.62 (0.06)	3.51 (0.01)	3.31 (0.03)
Cs1000a (202.6 kPa)	500 K	19.50 (0.33)	3.53 (0.04)	5.18 (0.14)	3.12 (0.06)	2.68 (0.05)
	750 K	16.98 (0.18)	3.37 (0.04)	4.66 (0.04)	3.27 (0.02)	2.97 (0.02)
	1000 K	14.11 (0.48)	3.60 (0.03)	4.62 (0.04)	3.51 (0.01)	3.30 (0.02)
Cs1000a (506.5 kPa)	500 K	19.21 (0.43)	3.53 (0.07)	5.17 (0.06)	3.08 (0.05)	2.64 (0.03)
	750 K	16.95 (0.16)	3.40 (0.02)	4.67 (0.04)	3.26 (0.01)	2.96 (0.01)
	1000 K	14.26 (0.29)	3.60 (0.02)	4.61 (0.05)	3.52 (0.01)	3.30 (0.02)

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# GCMC Simulations in Zeolite MFI and Activated Carbon for Benzene Removal from Exhaust Gaseous Streams

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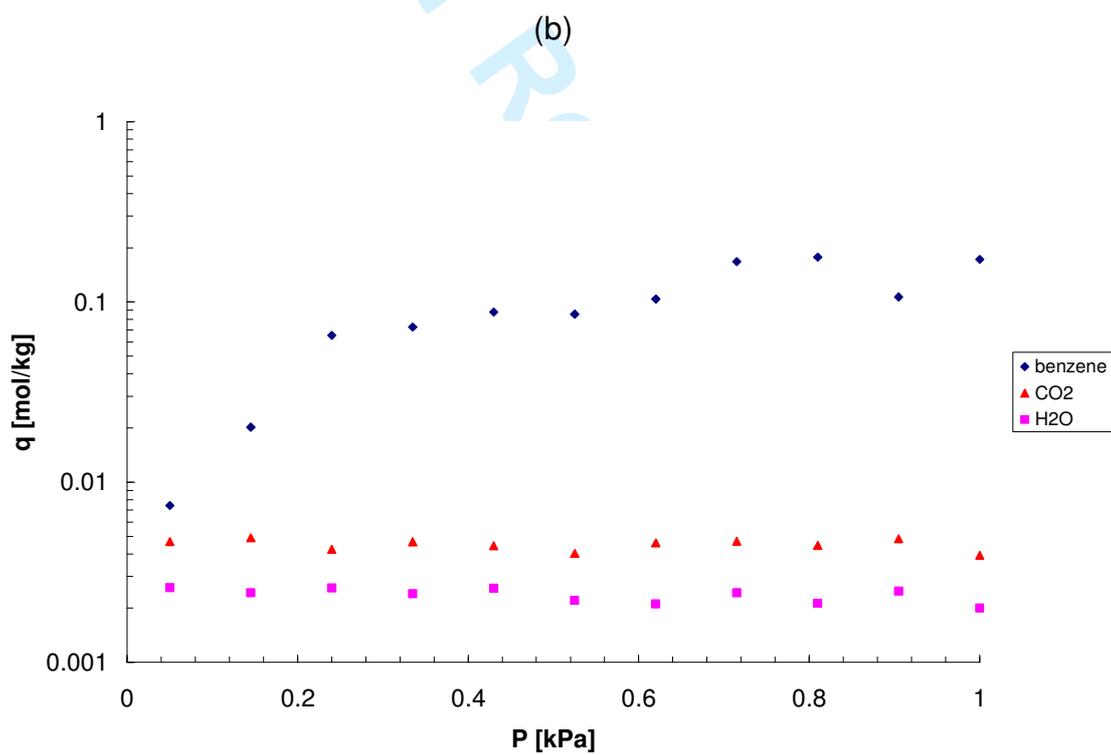
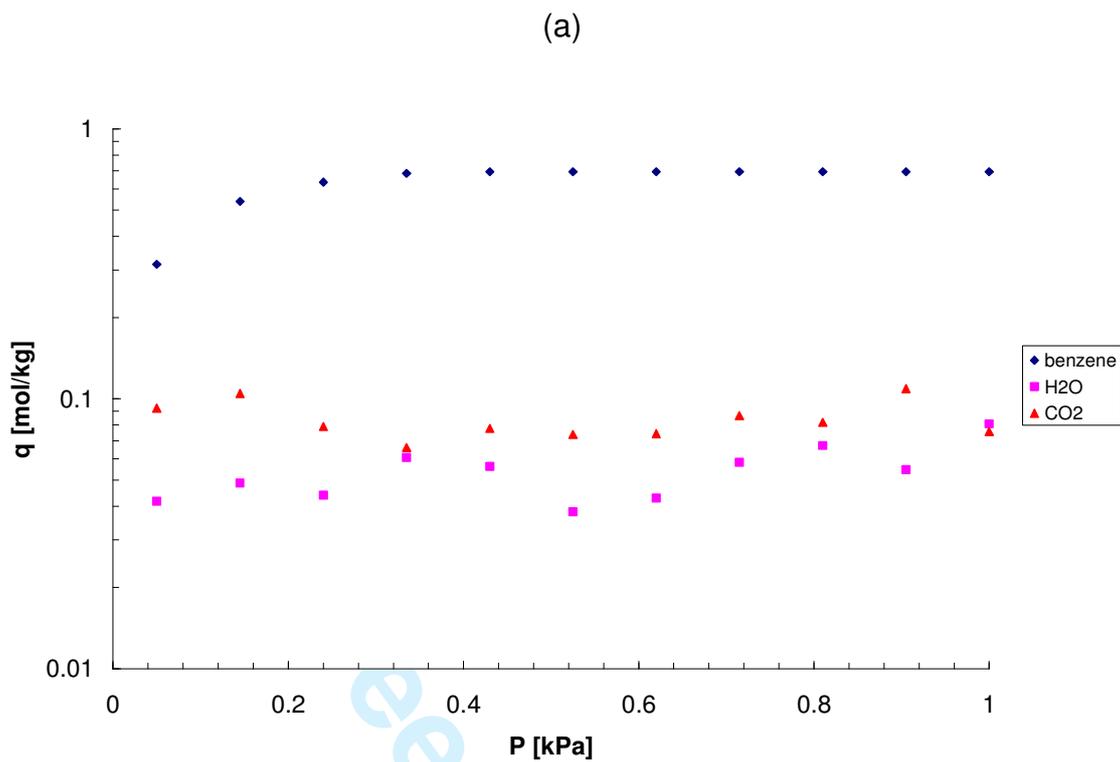
## *Additional information*

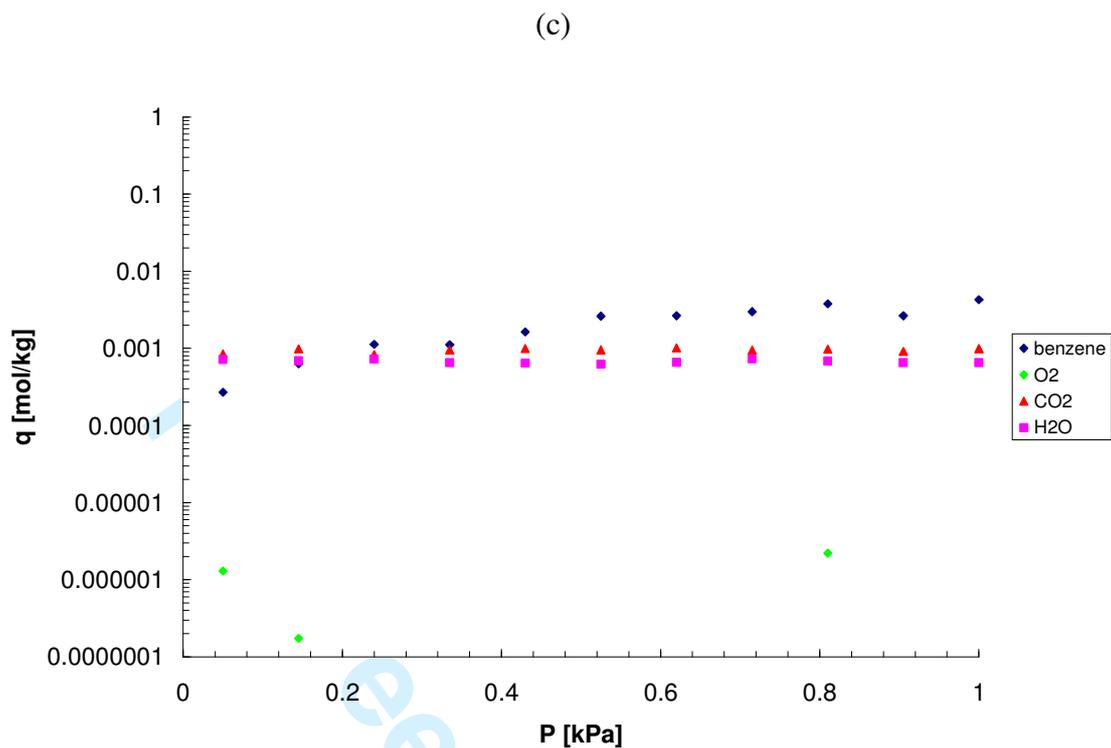
In this additional section we provide some of the intermediate results for the data fitting with the Sips model; in Table 1 fitting coefficients for pure gas adsorption (Langmuir-Freundlich model) are given.

Table 1: Langmuir-Freundlich coefficients obtained from GCMC simulations for pure gases.

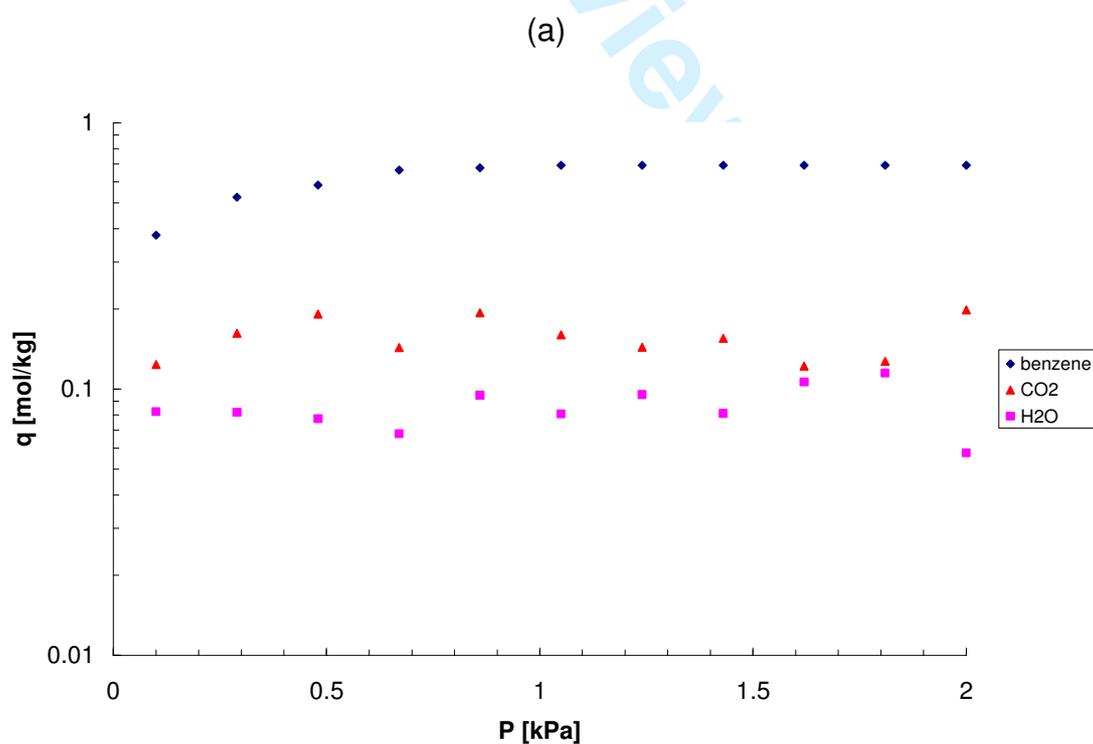
	Component	$q_0$	$b$	$\alpha$
MFI 500 K	C <sub>6</sub> H <sub>6</sub>	0.694891	1720.402	1.697132
	CO <sub>2</sub>	2.256095	0.004879	0.996195
	H <sub>2</sub> O	2.50333	0.000924	1.157638
	N <sub>2</sub>	2.996174	0.001264	0.794164
	O <sub>2</sub>	2.167964	0.000162	1.081247
MFI 750 K	C <sub>6</sub> H <sub>6</sub>	0.5777	0.4892	1.201978
	CO <sub>2</sub>	2.619929	0.0016	0.708732
	H <sub>2</sub> O	4.010516	0.000431	0.778028
	N <sub>2</sub>	3.094037	0.000141	0.855976
	O <sub>2</sub>	2.624987	5.62E-05	0.948991
MFI 1000 K	C <sub>6</sub> H <sub>6</sub>	0.6124	0.030372	0.635486
	CO <sub>2</sub>	2.181992	0.000131	0.88384
	H <sub>2</sub> O	2.744951	1.64E-05	1.061462
	N <sub>2</sub>	3.171256	4.56E-05	0.87837
	O <sub>2</sub>	2.598625	1.98E-05	0.970649
Cs1000a 500 K	C <sub>6</sub> H <sub>6</sub>	5.548263	0.160656	0.49089
	CO <sub>2</sub>	15.15991	0.000329	0.785837
	H <sub>2</sub> O	19.56613	2.11E-06	1.376407
	N <sub>2</sub>	13.38064	4.68E-05	0.959993
	O <sub>2</sub>	16.36275	2.76E-05	0.954396
Cs1000a 750 K	C <sub>6</sub> H <sub>6</sub>	3.862232	0.002408	0.970701
	CO <sub>2</sub>	18.62218	9.5E-07	1.254696
	H <sub>2</sub> O	19.6067	0.0007	1.036259
	N <sub>2</sub>	13.2514	1.89E-05	0.946193
	O <sub>2</sub>	18.18576	1.78E-05	0.89834
Cs1000a 1000K	C <sub>6</sub> H <sub>6</sub>	4.052317	2.69E-05	1.188316
	CO <sub>2</sub>	1.026116	1.11E-05	1.059579
	H <sub>2</sub> O	2.582858	4.34E-06	1.048639
	N <sub>2</sub>	5.546026	8.37E-06	0.858746
	O <sub>2</sub>	2.145528	7.38E-06	0.9716

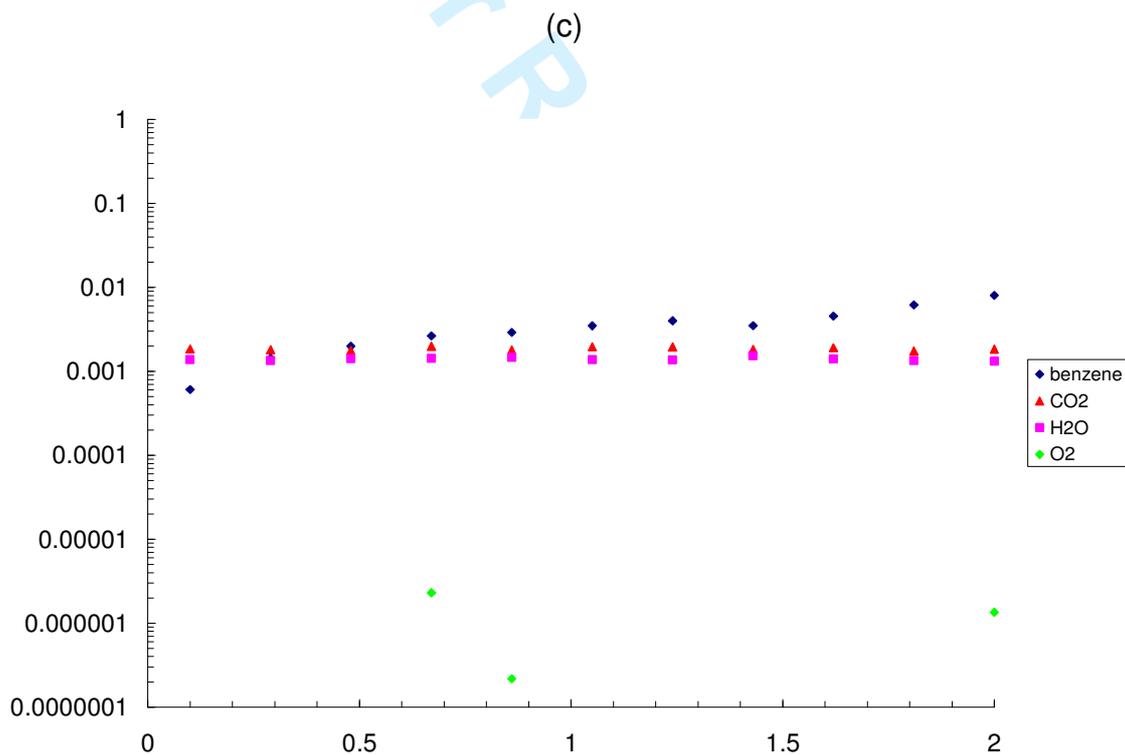
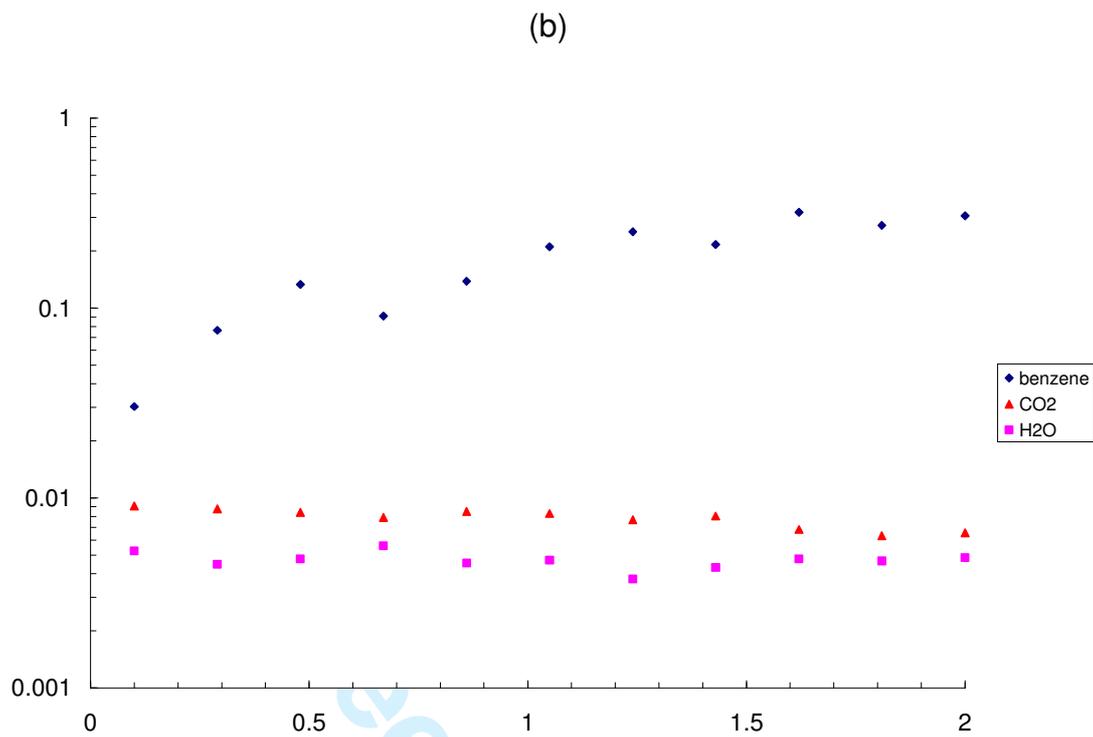
In Figure 2 - 7, adsorption isotherms for all adsorbed gases in the mixtures and for zeolite MFI and activated carbon cs1000a are given; loading is expressed as a function of benzene partial pressure. It can be seen how the coverage of the other components is very limited. In Figure 8 adsorption isotherms for the mixture at 500 K, 101.3 kPa (1 atm) for zeolite NaY are given; loading is expressed as a function of benzene partial pressure. It can be noticed how benzene loading is significantly lower than water or oxygen.



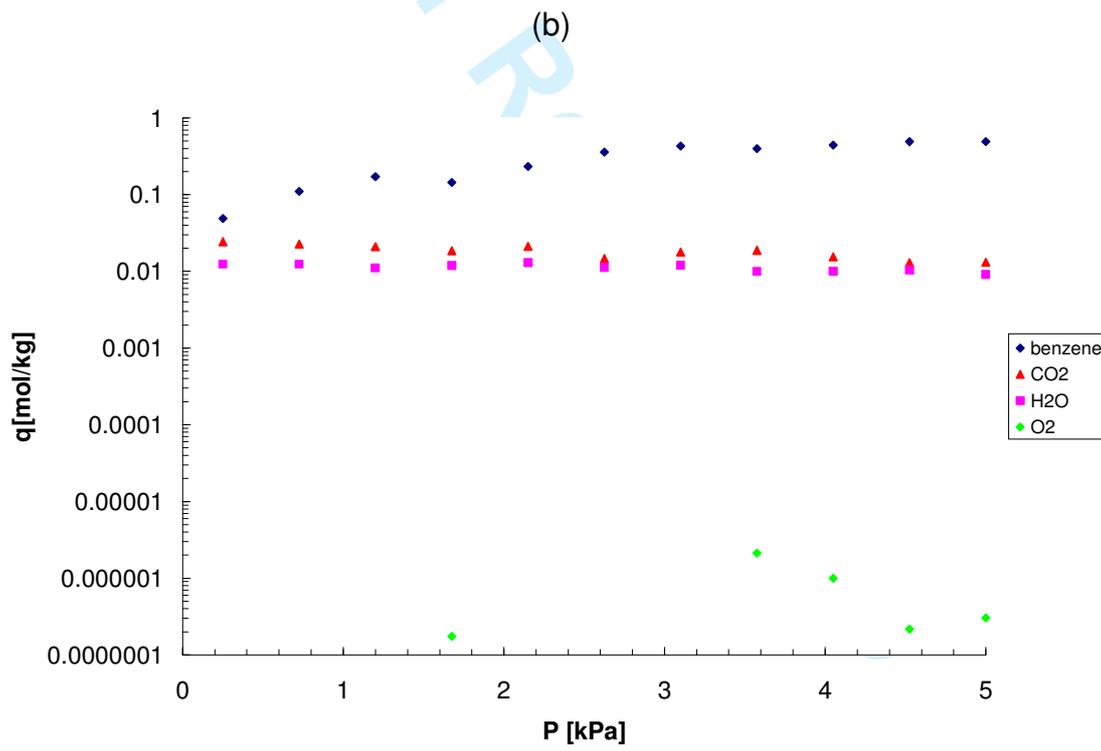
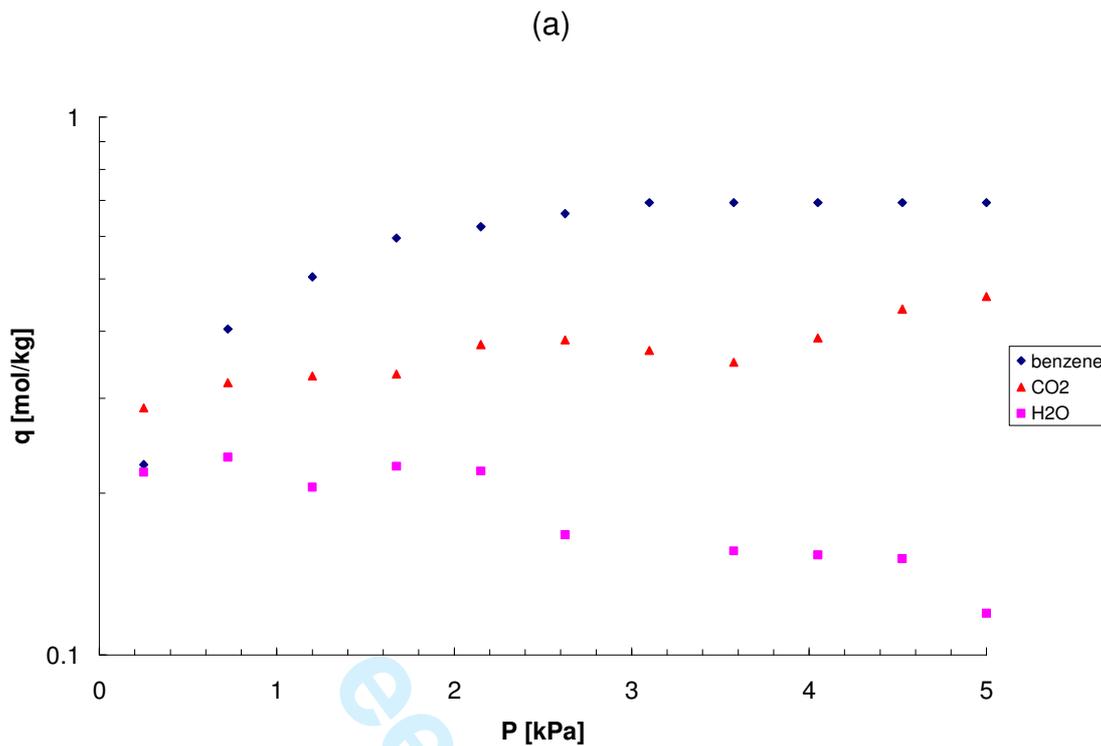


29 Figure 2. Adsorption isotherms for all components in zeolite MFI at a total pressure of  
30 101.3 kPa (a: 500 K, b: 750K, c: 1000K). Blue: benzene, red: CO<sub>2</sub>, pink: H<sub>2</sub>O, green: O<sub>2</sub>.  
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55 Figure 3. Adsorption isotherms for all components in zeolite MFI at a total pressure of  
56 202.6 kPa (a: 500 K, b: 750K, c: 1000K). Blue: benzene, red: CO<sub>2</sub>, pink: H<sub>2</sub>O, green: O<sub>2</sub>.  
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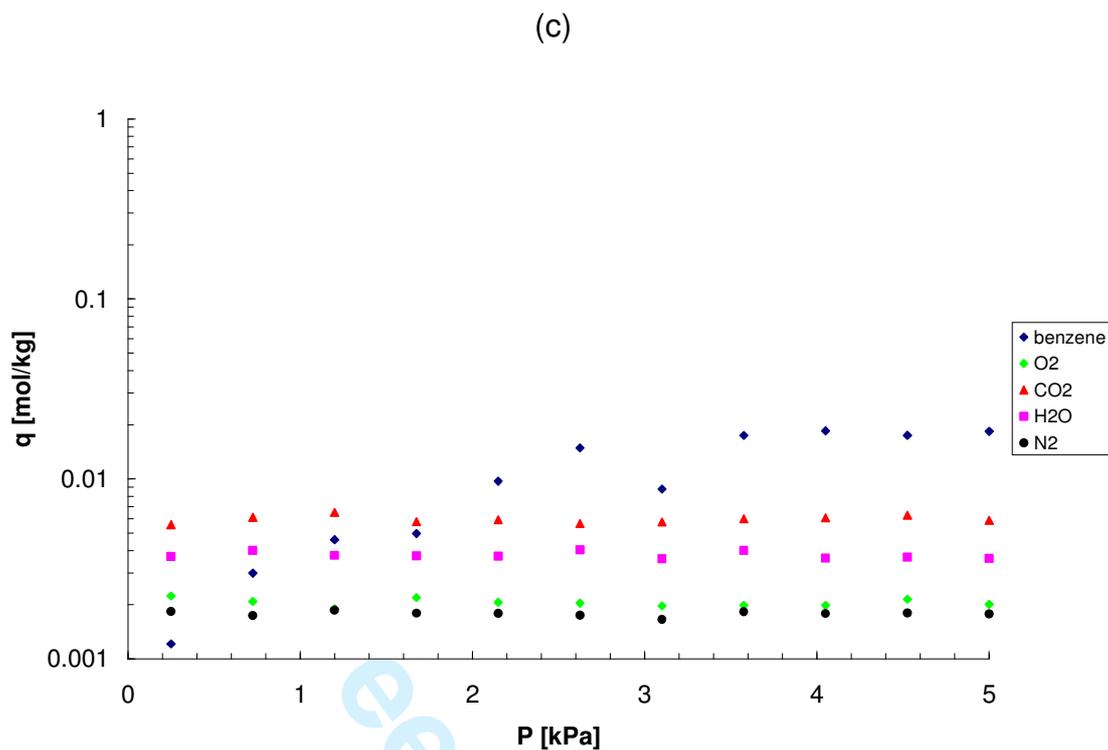
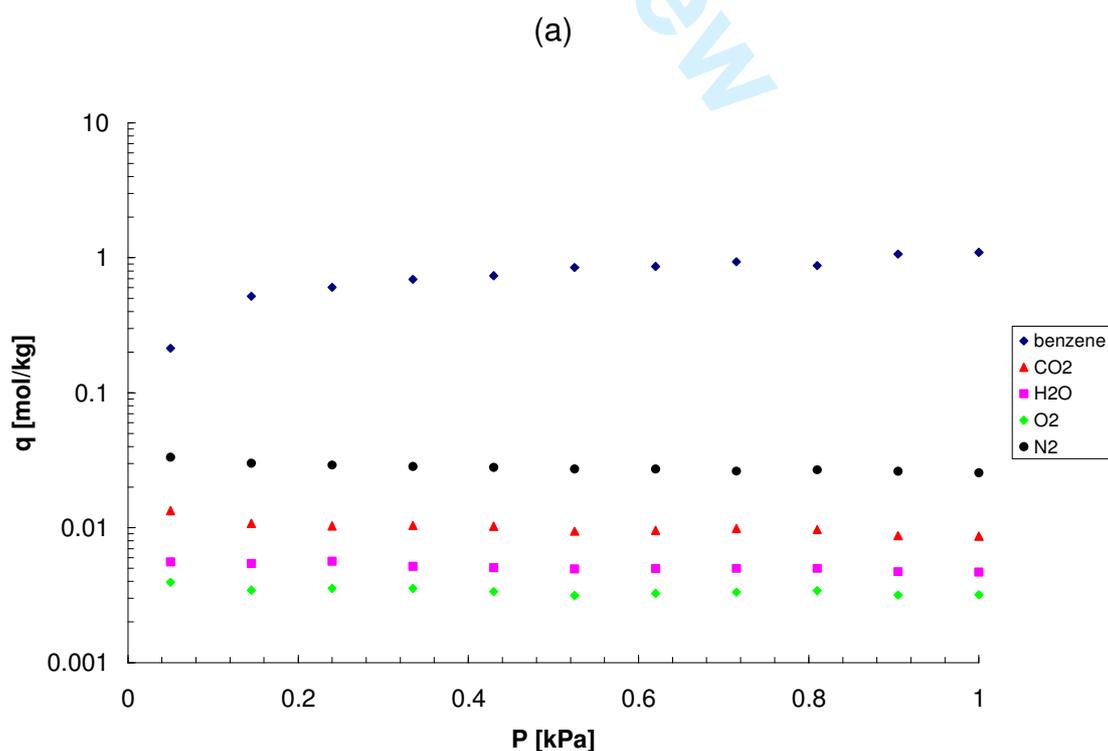
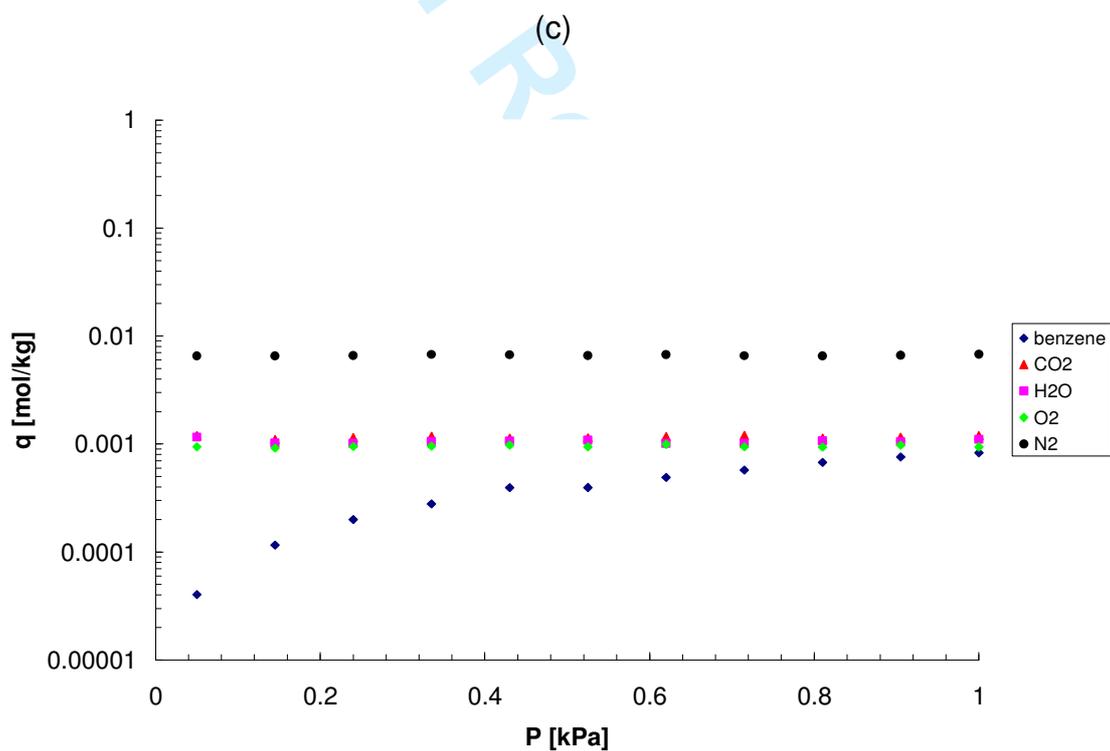
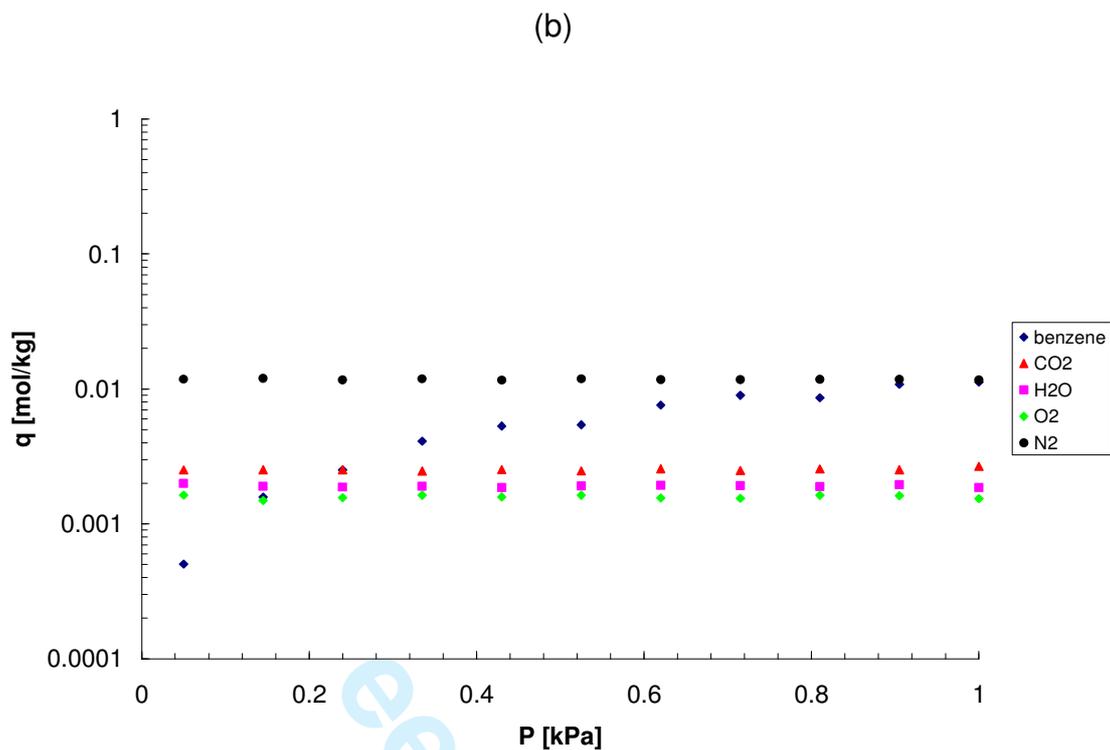
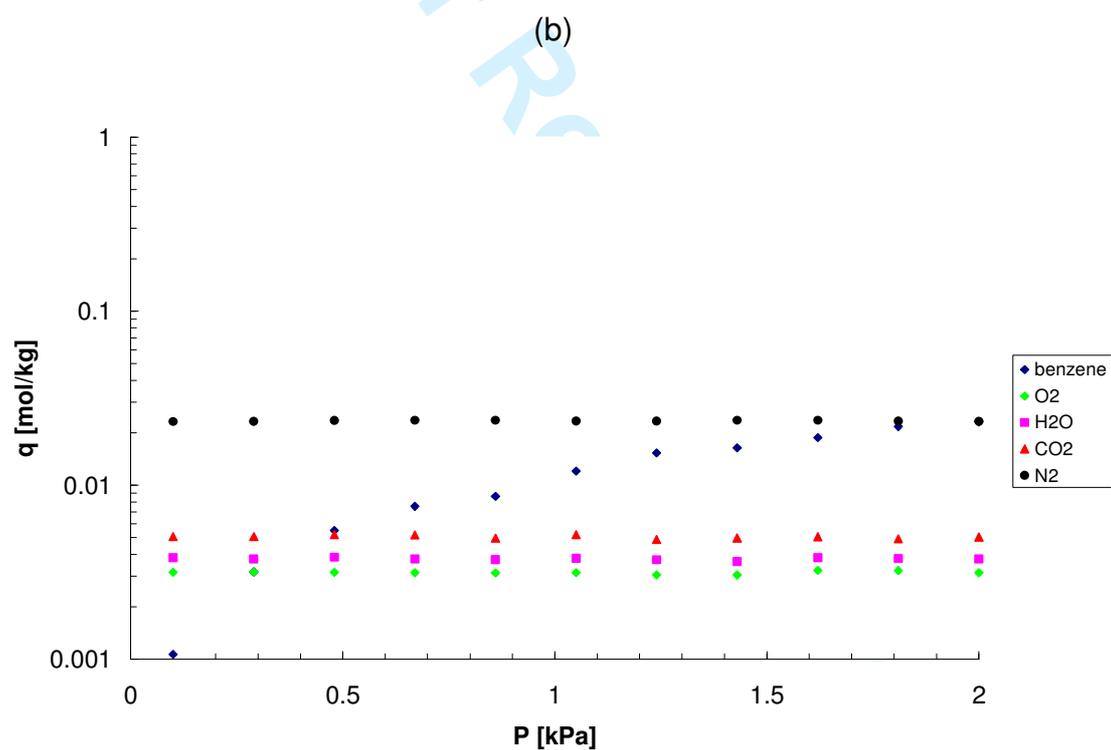
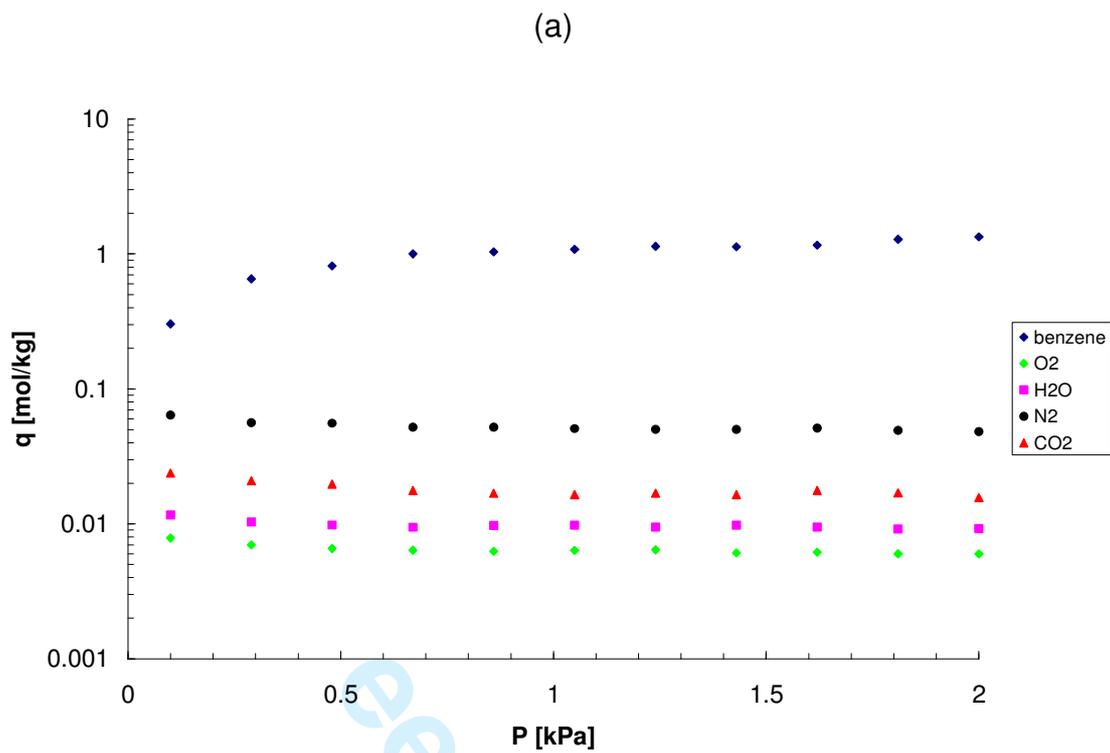


Figure 4. Adsorption isotherms for all components in zeolite MFI at a total pressure of 506.5 kPa (a: 500 K, b: 750K, c: 1000K). Blue: benzene, red: CO<sub>2</sub>, pink: H<sub>2</sub>O, green: O<sub>2</sub>, black: N<sub>2</sub>.





55 Figure 5. Adsorption isotherms for all components in cs1000a at a total pressure of 101.3  
56 kPa (a: 500 K, b: 750K, c: 1000K). Blue: benzene, red: CO<sub>2</sub>, pink: H<sub>2</sub>O, green: O<sub>2</sub>, black:  
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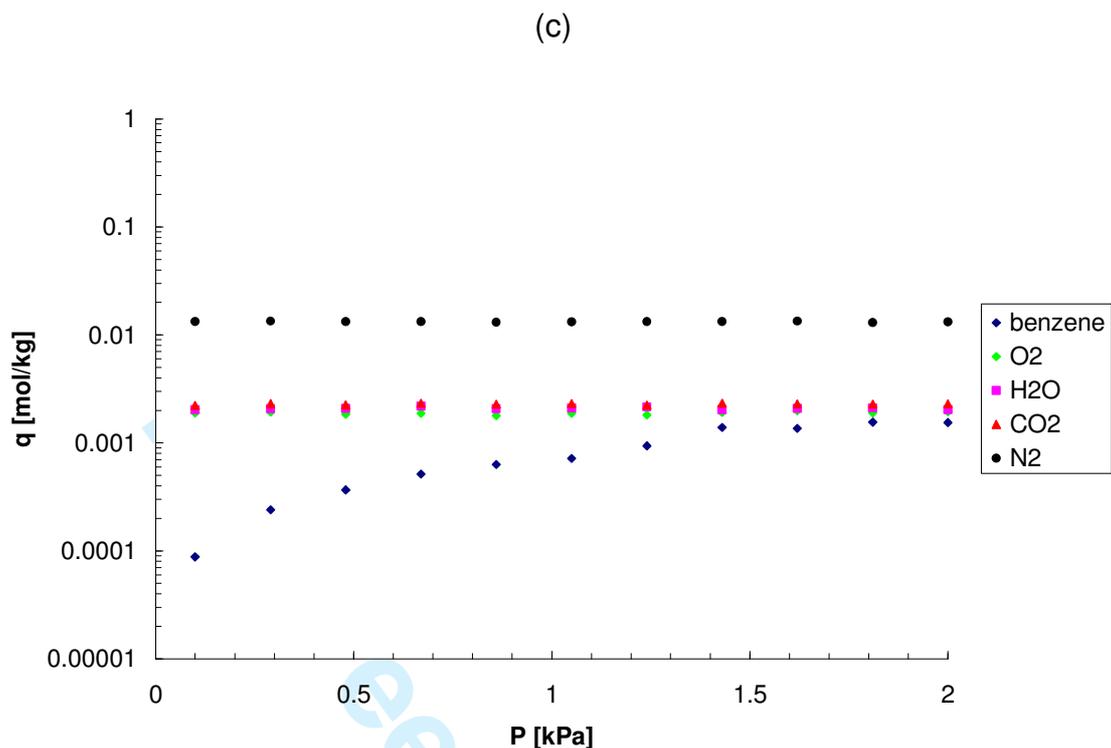
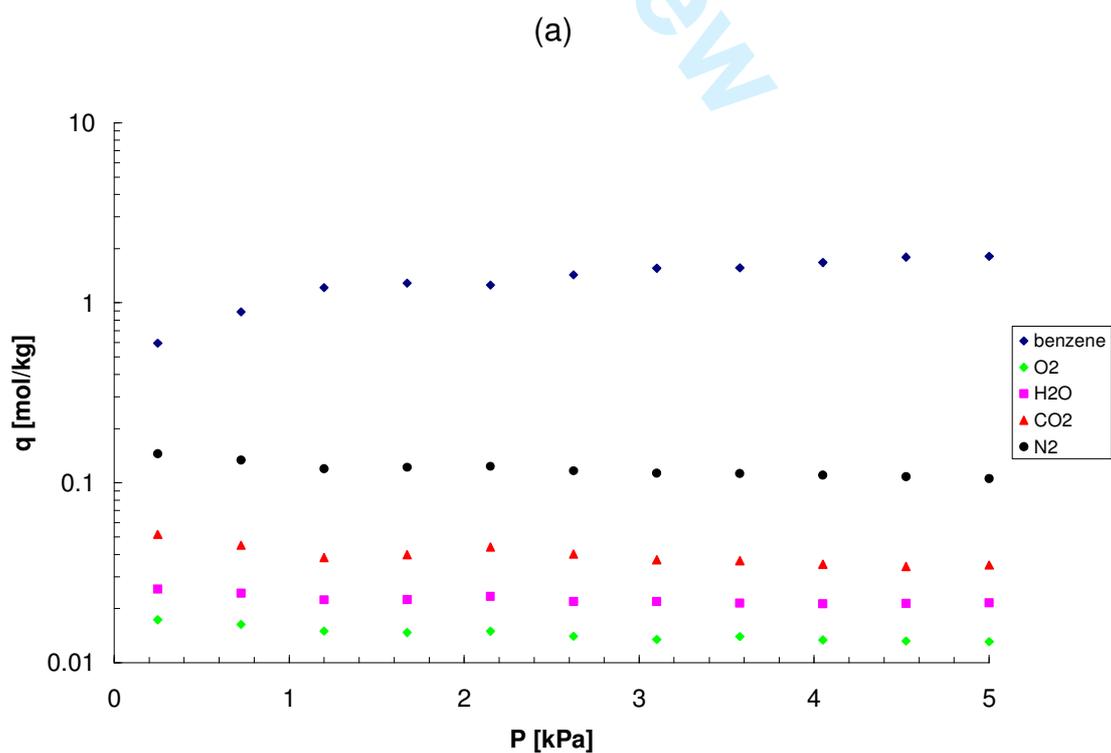
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Figure 6. Adsorption isotherms for all components in cs1000a at a total pressure of 202.6 kPa (a: 500 K, b: 750K, c: 1000K). Blue: benzene, red: CO<sub>2</sub>, pink: H<sub>2</sub>O, green: O<sub>2</sub>, black: N<sub>2</sub>.



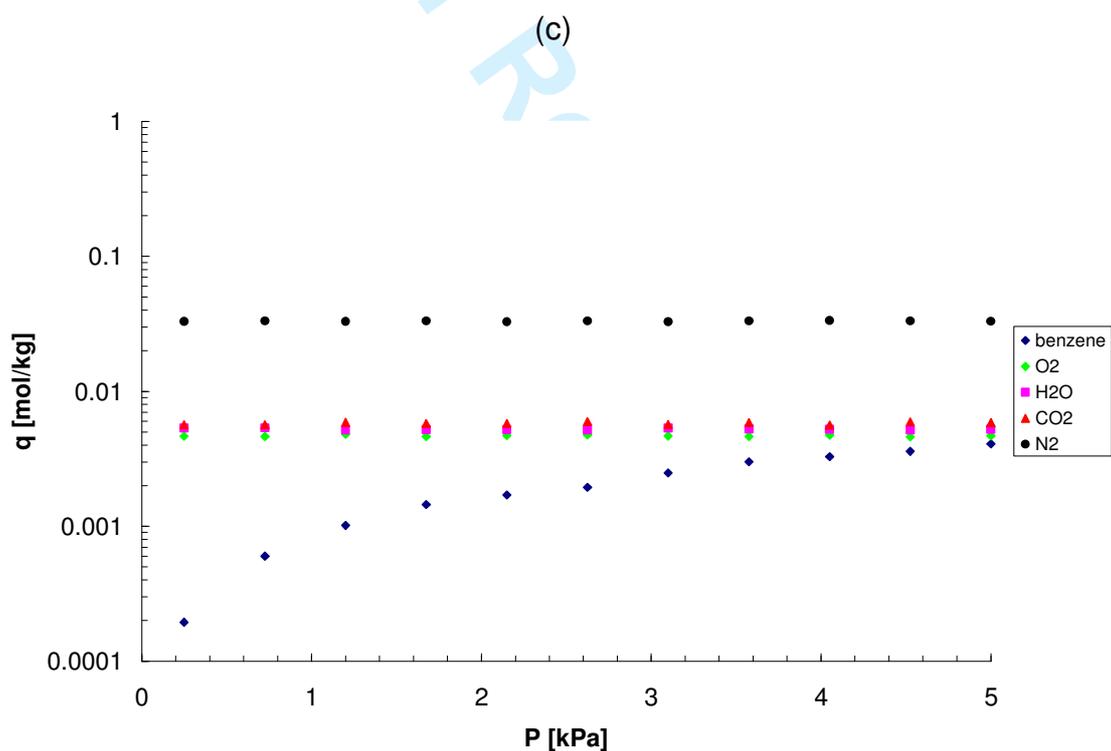
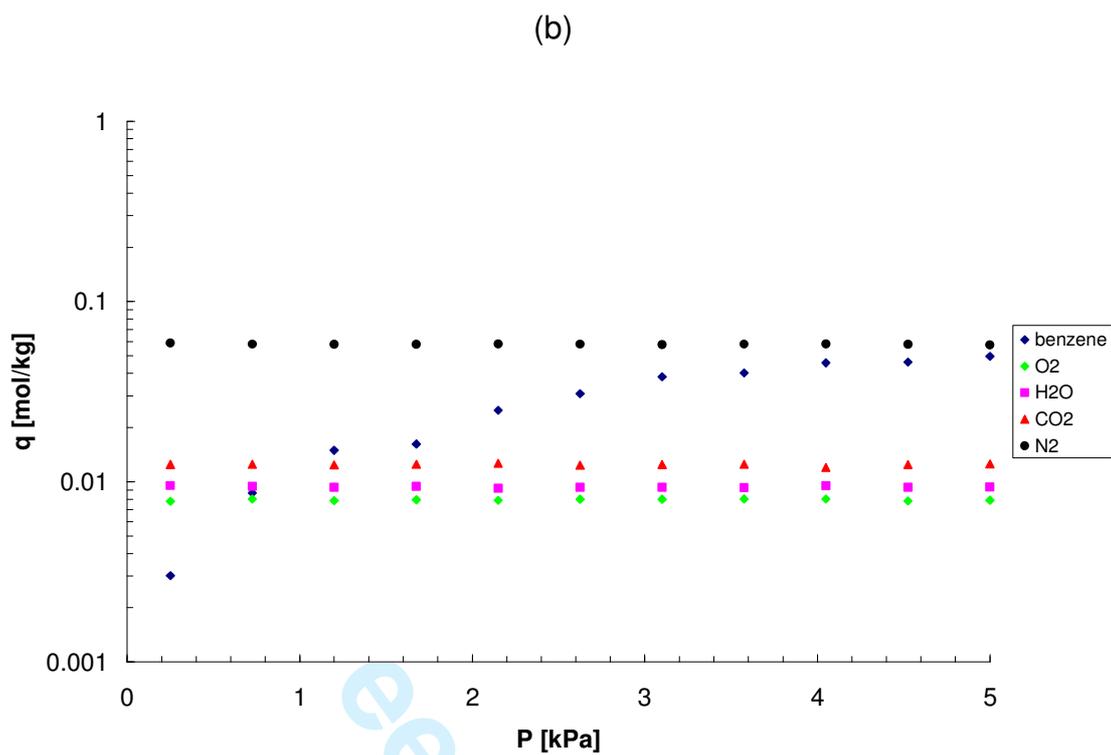


Figure 7. Adsorption isotherms for all components in cs1000a at a total pressure of 506.5 kPa (a: 500 K, b: 750K, c: 1000K). Blue: benzene, red: CO<sub>2</sub>, pink: H<sub>2</sub>O, green: O<sub>2</sub>, black: N<sub>2</sub>.

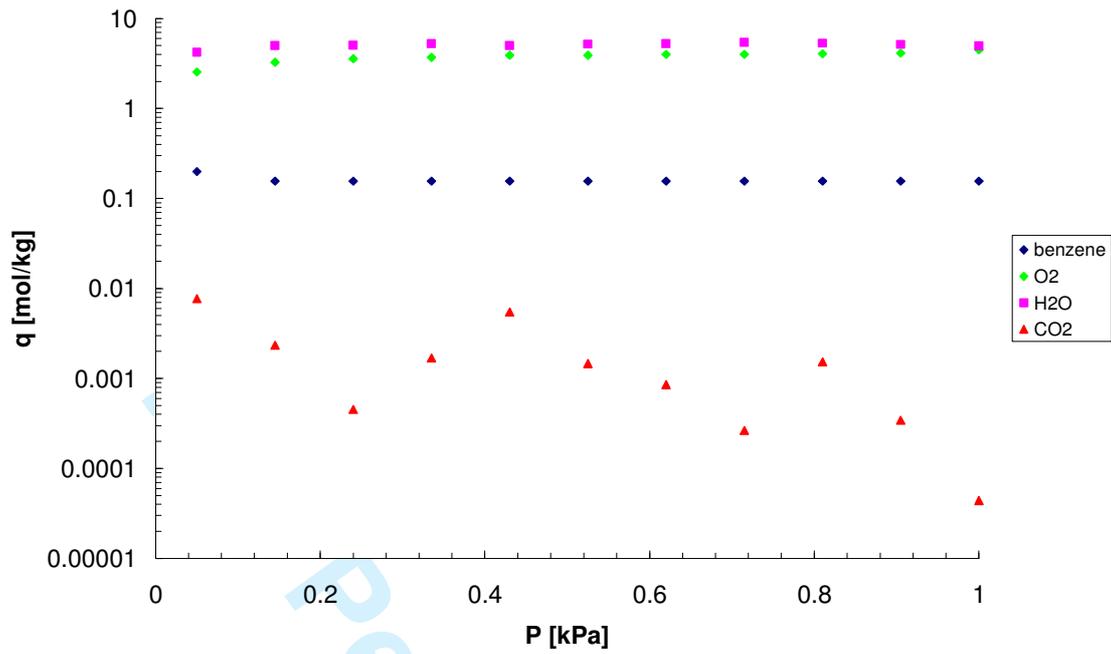
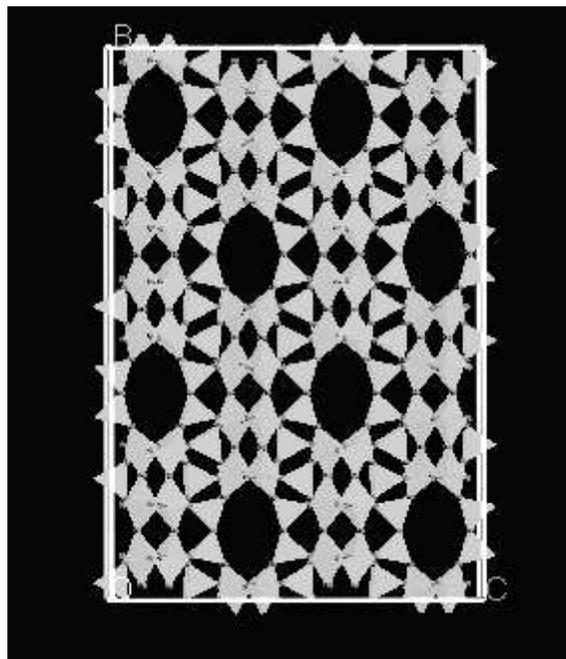


Figure 8. Adsorption isotherms for all components in NaY at a total pressure of 101.3 kPa and 500 K. Blue: benzene, red: CO<sub>2</sub>, pink: H<sub>2</sub>O, green: O<sub>2</sub>.

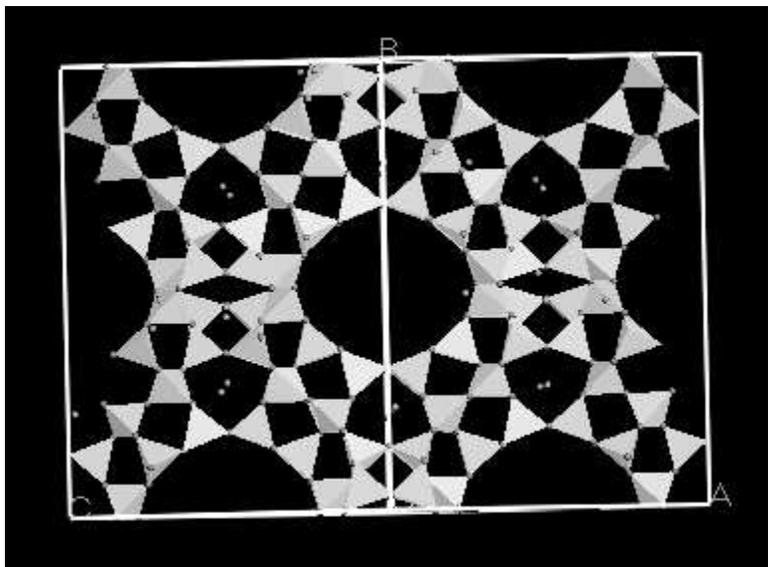
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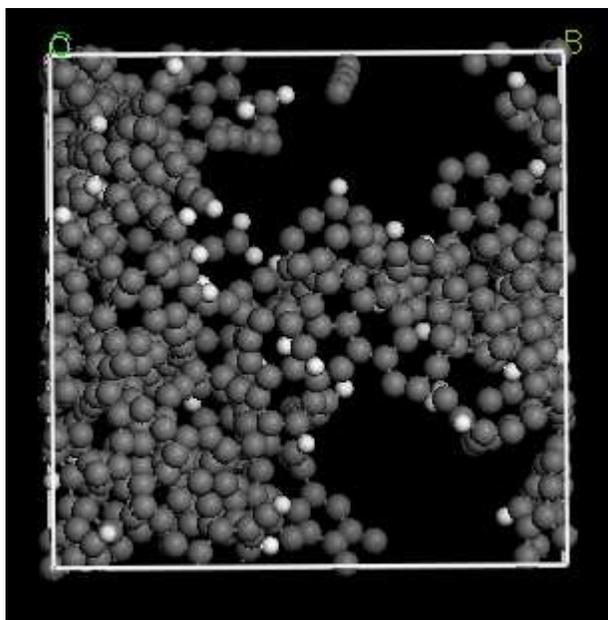
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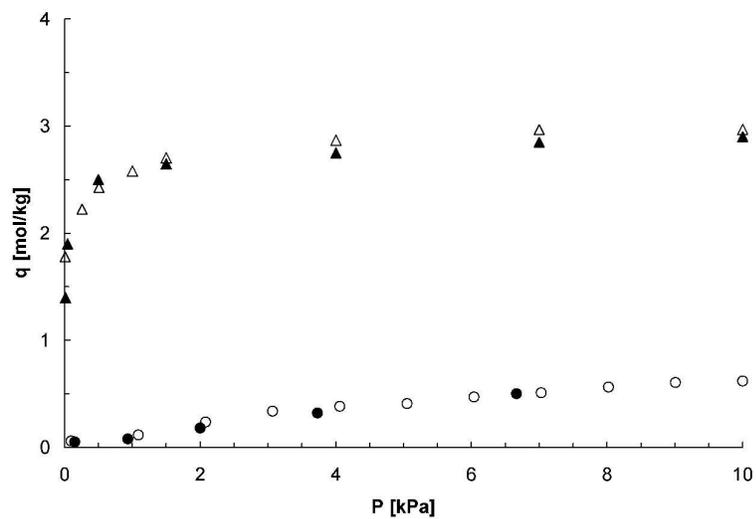
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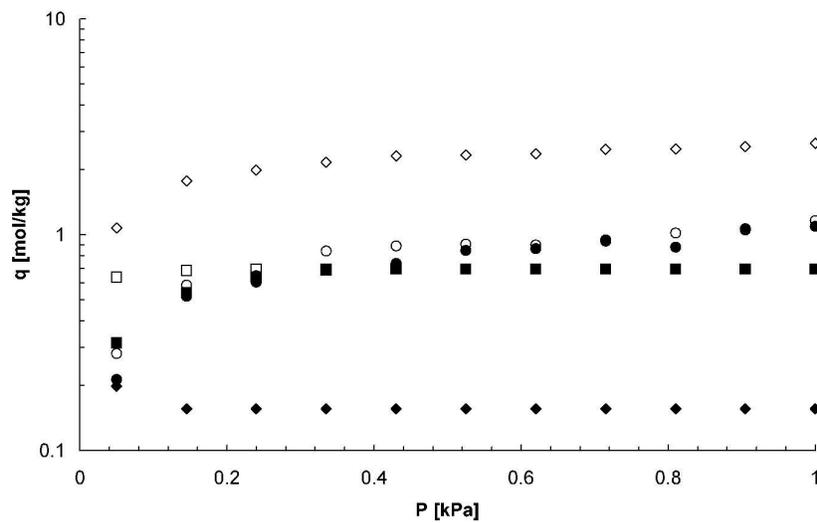
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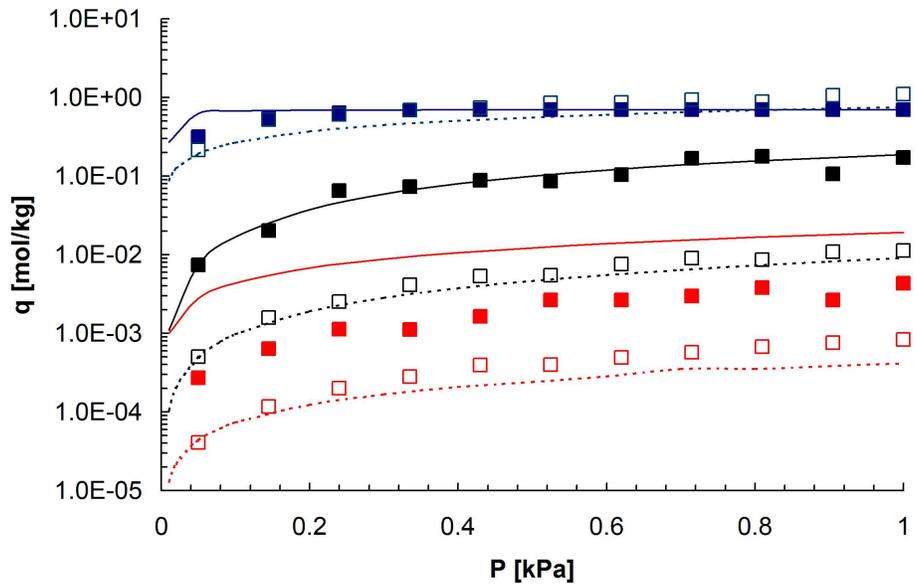
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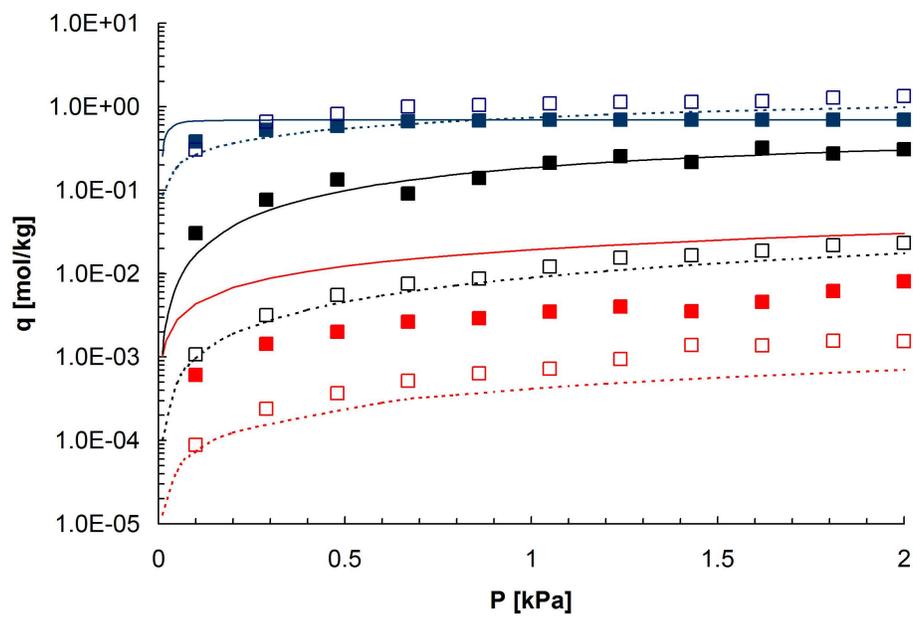
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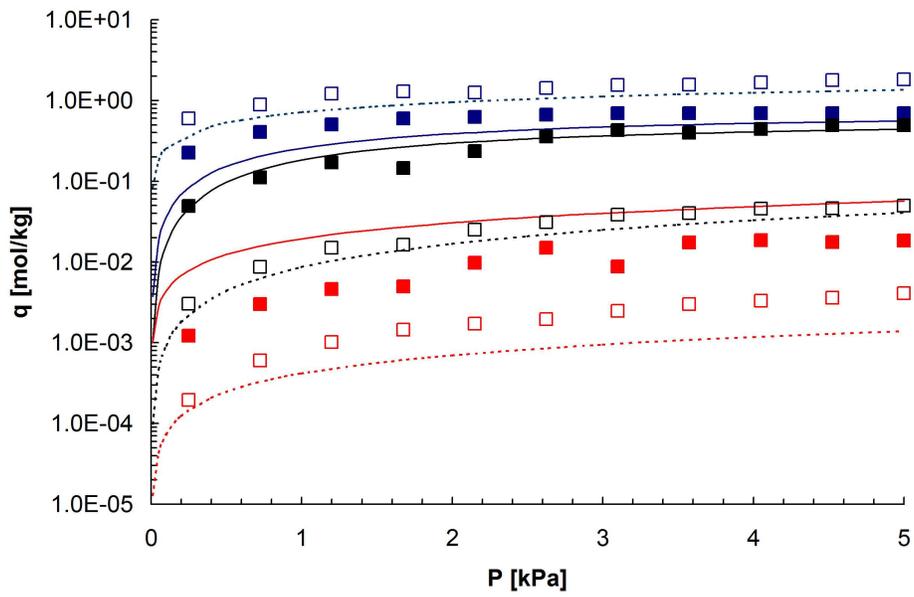
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# GCMC Simulations in Zeolite MFI and Activated Carbon for Benzene Removal from Exhaust Gaseous Streams

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# GCMC Simulations in Zeolite MFI and Activated Carbon for Benzene Removal from Exhaust Gaseous Streams

For Peer Review Only

## ABSTRACT

A set of GCMC molecular simulations has been performed over zeolite MFI and disordered, activated carbon structures, to determine adsorption isotherms and thermodynamic characteristics of a gaseous mixture adsorbed into porous structures, activated carbon, all-silica MFI and hydrophilic FAU-NaY zeolites. Simulations have been carried out over a multicomponent mixture, in order to mimic a more realistic gaseous emission, when benzene has to be removed. Validation of the model has been obtained by comparison with available experimental data. Different conditions, as temperature and total pressure of the stream have been taken into account. Results give a ranking for the most appropriate process conditions, and for the best materials to be employed for the separation process. Data fitting with the Sips thermodynamic model has also been provided for benzene isotherms. Our procedure is simple and may be adapted to different temperature and pressure conditions, adsorbate or adsorbent characteristics, and gas composition.

## KEYWORDS

GCMC simulation, benzene removal, adsorption, zeolite, activated carbon.

## INTRODUCTION

Volatile organic compounds (VOC) removal is a necessary operation to respect imposed standard limits in exhaust gaseous streams [1, 2]. It is well known how the presence of even small amounts of these components can be detrimental to environment and human health. **VOC are chemical compounds**

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3 with a high vapour pressure to vaporise at normal conditions, and usually  
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5 have a low water solubility. A large amount of carbon-based compounds, such  
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7 light hydrocarbons, aldehydes, ketons, are considered as VOC.  
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10 VOC can originate from different sources, such as petrochemical processes,  
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12 vehicle emissions, combustions and, in general, from all kinds of industrial  
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14 processes [3]. Among all the others VOC, one of the most hazardous ones is  
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16 the benzene, as its effects, even at typical very low concentrations in  
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18 emissions, are nowadays well documented [4, 5]. One possible way of VOC  
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20 removal is the selective adsorption into porous media [6].  
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25 In this work we aim at examining possible ways of benzene removal  
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27 from gaseous streams by adsorption into zeolites or activated carbons, taking  
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29 into account different operation conditions, such as temperature and pressure,  
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31 which may be encountered in gaseous streams exiting from a plant. This has  
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33 been done with the aid of molecular simulation techniques, in particular the  
34  
35 well known Grand Canonical Monte Carlo method [7].  
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39 Two kinds of zeolites, hydrophobic, dealumined MFI and hydrophilic  
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41 FAU NaY (Si/Al= 2.5) [8] have been tested in our work, and then dealumined  
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43 MFI was used. We also tested and used one disordered structure, called  
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45 cs1000a, which reproduces an activated carbon fibre, obtained from the  
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47 pyrolysis of pure saccharose at 1000 °C for 20 hours in a CO<sub>2</sub> atmosphere.  
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49 This was one of the disordered structures obtained by the group of Keith  
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51 Gubbins using the Hybrid Reverse Monte Carlo method (HRMC), and is now  
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53 freely available in literature [9, 10]. In Figure 1 the 3D structures used in this  
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55 work are shown: zeolites MFI and NaY, and disordered, activated carbon  
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57 cs1000a. Both activated carbon and zeolites have been commonly  
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3 investigated, and frequently employed, in processes of purification  
4 technologies, in particular for VOC and benzene separation [11 – 22].  
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8 The aim of the work is mainly to establish a flexible and simple  
9 procedure to estimate the efficacy of different adsorbents in different  
10 conditions, to give more insights to the adsorption process at molecular level,  
11 and to understand how the presence of a gaseous mixture, which is usually  
12 encountered in these kinds of processes, will affect the predicted adsorption  
13 isotherms. In fact adsorption experiments have been performed in different  
14 conditions and for a huge kind of matrices and adsorbates, as there is a  
15 considerable interest in adsorption processes and technologies, as testified by  
16 a huge literature [23]. Nevertheless, in the case complex multicomponent  
17 mixtures, especially when the component to be separated is very dilute, data  
18 are absent or still very scarce [24], due to the difficulties of experimental  
19 procedures. Experimental sessions are often tedious and rather expensive;  
20 moreover, difficulties for multi-component adsorption experiments and very  
21 low partial pressure of some components increase. Although, it is known how  
22 competition for pore sites in multi-component adsorption may substantially  
23 affect the adsorption mechanism [25].  
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46 In our example, we decided to mimic in a simplified way a composition  
47 which can be an example of a stream from waste incinerator processes, or  
48 from combustions due to industrial processes, or from residual streams of  
49 chemical plants. In this way the choice of benzene as pollutant and the  
50 specific gaseous composition, are merely exemplificative, and should be  
51 intended as a specific case study to explore the effectiveness of the  
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3 procedure, which may be also adapted to different conditions or changed in  
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5 the case of a different pollutant removal.  
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8 This work is organized as follows: in the materials and methods section  
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10 we define Hardware and Software characteristics, we briefly describe the  
11  
12 GCMC method and then we give computational details of our simulations. In  
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14 the Results and discussion section, we provide a validation of our procedure  
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16 against available data; then we compare results of pure benzene adsorption  
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18 isotherms at 500 K with the ones in the multicomponent gaseous mixture,  
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20 and, finally, we analyze and discuss the results for multicomponent mixtures  
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22 at different total pressures and temperatures, comparing the obtained results  
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24 with a simple thermodynamic model for gaseous mixtures.  
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### 31 COMPUTATIONAL DETAILS

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34 Calculations were carried out on an Intel quad-core bi-processor Xeon x5355  
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36 with a 6GB RAM.  
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39 The Sorption module of *Materials Studio*® (v. 4.2, Accelrys, San Diego,  
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41 CA, USA) has been employed in this work [26]. It is a Monte Carlo method  
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43 which is particularly suitable for adsorption phenomena estimation over  
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45 defined adsorbents.  
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48 A mixture of O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub> and benzene has been used to  
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50 approximate and mimic an exhaust gaseous stream from a combustion  
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52 process. Due to the relatively low pressures considered for all simulations,  
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54 and accordingly to the aim of our work, we decided to approximate fugacity  
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56 with partial pressure.  
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3 The frameworks of the chosen zeolites, MFI and FAU (NaY, Si/Al= 2.5),  
4 are available in the database of the platform; the Na<sup>+</sup> ions added to balance  
5 the total charge have been placed into the NaY cell with a cation locator  
6 option, provided in the Sorption module. This allows performing a Metropolis  
7 Monte Carlo location of the ions in the cell, according to the lowest energy  
8 configuration; acceptance criteria are similar to the ones used for Canonical  
9 Monte Carlo simulations [7] but in this case a specified number of annealing  
10 cycles (called simulated annealing) is used to slowly freeze the system, in  
11 order to repetitively explore the configurational space determined by the  
12 adsorbate (sorbent) and adsorbate (Na<sup>+</sup>) system, and to avoid local minima  
13 [27, 28].  
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29 The atom positions of the disordered structure cs1000a, have been  
30 obtained with the HRMC method [9, 10]. This method uses an algorithm which  
31 attempts to simultaneously minimize the error in the radial distribution function  
32 and also the total energy of the system, thus matching the experimental data  
33 obtained for the real structure, such as structure factor, porosity and density.  
34 Further, a simulated annealing minimization method is also employed to avoid  
35 the system to be trapped in local minima.  
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46 The core of this work is the GCMC application with the stochastic  
47 Metropolis method [29] for multicomponent gas adsorption. The method is  
48 well known and described in several books, as in [7]; references to some  
49 specific applications both to pure gases and to mixtures can be found  
50 elsewhere, thus in this paper we provide a short description.  
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57 Generally speaking, the stochastic Monte Carlo (MC) method, which  
58 uses statistical mechanical principles to calculate properties of a given  
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3 system, has been employed to perform the simulations. In brief, MC  
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5 simulations generate configurations of a system by making random changes  
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7 to the positions of the present species, together with their orientation and  
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9 conformations, where appropriate [30]. The Metropolis sampling method  
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11 generates chains of configurations with the ensemble probability.  
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13 Transforming a configuration involves a random displacement of each atom in  
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15 the system from its actual position. A trial move is accepted if it lowers the  
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17 configuration energy of the system. If the configuration energy is increased,  
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19 trials are accepted with a probability proportional to a Boltzmann factor:  $P =$   
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21  $e^{-\Delta U/kT}$ , where  $\Delta U$  is the configuration energy difference. Sampling techniques  
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23 [31] are used to generate states of low energy, and enabling accurate  
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25 property calculations. In this work, the simulations were carried out using the  
26  
27 Grand Canonical Monte Carlo ensemble (GCMC), which creates, destroys,  
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29 translates, and rotates molecules in order to obtain thermodynamic  
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31 equilibrium in an open system. Accordingly, in a GCMC calculation the system  
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33 chemical potential  $\mu$ , volume  $V$ , and temperature  $T$  are kept constant, as if the  
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35 framework is in open contact with an infinite adsorbate reservoir at a given  
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37 temperature. The reservoir is completely described by temperature and  
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39 fugacity (or partial pressure) of all components, and does not have to be  
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41 simulated explicitly. Chemical potential  $\mu$  is transformed into the partial  
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43 pressure (or fugacity) of each component. Equilibrium is achieved when the  
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45 temperature and the chemical potential of the gas inside the framework are  
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47 equal to the temperature and chemical potential of the free gas outside the  
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49 framework. The adsorption isotherms were computed by calculating the mean  
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51 loading of the adsorbate in the framework at a specific vapour pressure.  
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The probability of a configuration,  $m$ , in the grand canonical ensemble is given by:

$$\rho_m = C \cdot F(\{N_m\}) e^{-\beta E_m} \quad (1)$$

Where

$$\beta = \frac{1}{k_B T} \quad (2)$$

$C$  is an arbitrary normalization constant;  $E_m$  is the total energy of configuration  $m$ :

$$E_m = E_m^{SS} + E_m^{SF} + U_m^S \quad (3)$$

where  $E_m^{SS}$  is the intermolecular energy between the adsorbate molecules,  $E_m^{SF}$  is the interaction energy between the adsorbate molecules and the framework, and  $U_m^S$  is the total intramolecular energy of the adsorbate molecules (which is equal to 0 if only translational and rotational degrees of freedom are present). The set of adsorbate loadings of all components in configuration  $m$  is denoted by  $\{N\}_m$ . For a single component, the function  $F(N)$  is given by:

$$F = \left[ \frac{(\beta f V)^N}{N!} \right] e^{-\beta N \mu_{int}} \quad (4)$$

where  $f$  is the fugacity (equal to the partial pressure for ideal gases),  $\mu_{int}$  is the intramolecular chemical potential, and  $N$  is the loading of the component. For

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3 a mixture of components,  $F(\{N\}_m)$  factorizes to a product of functions (1) for  
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5 each component. The intramolecular chemical potential in (4) follows from  
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$$\exp[-\beta\mu_{\text{int}}] = \langle \exp[-\beta\mu_{\text{int}}] \rangle_u \quad (5)$$

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13 The average is taken over a uniform ensemble, which means that every  
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15 configuration has the same probability. If the adsorbate has one conformation  
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17 with no degrees of freedom other than translation and orientation, the  
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19 intramolecular chemical potential reduces to the intramolecular energy.  
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23 The thermodynamics of adsorption have been further investigated  
24  
25 analyzing the values of the isosteric heat of adsorption  $h_{RF}$ , a measure of  
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27 adsorption capabilities of an adsorbate in an adsorbent framework.  $h_{RF}$  is  
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29 defined as the difference between the partial molar enthalpy of the adsorbate  
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31 component in the external reservoir (i.e., free gas) and in the framework;  
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33 accordingly, it is a measure of the enthalpy change involved in the transfer of  
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35 a solute from the reference state to the adsorbed state at a constant solid  
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37 phase concentration [32]:  
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$$h_{RF} = h_R - h_F \quad (6)$$

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45 Evaluation of  $h_{RF}$  requires the application of Clausius-Clapeyron equation [31]:  
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$$h_{RF} = (v_S - v_F) \left[ \frac{dp}{d(\ln T)} \right] \cong RT \left[ \frac{d(\ln p)}{d(\ln T)} \right] \quad (7)$$

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53 where  $v_R$  and  $v_F$  are the adsorbate partial molar volumes in the reservoir and  
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55 in the framework, respectively,  $p$  the partial pressure, and  $T$  the temperature.  
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57 In the right-hand side term of equation (7), the partial molar volume of the gas  
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59 molecules in the framework is neglected with respect to that in the reservoir,  
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and the gas behavior in the reservoir is assumed to be ideal. This leads to the expression of  $h_{RF}$  in the Grand Canonical ensemble, where the free energy  $G$  can be calculated:

$$h_{RF} = RT - G \quad (8)$$

The characteristics of the 3D periodic cells are described in Table 1.

In these simulations we used a slightly modified Augmented Consistent-Valence Force Field (cvff\_aug) [33, 34], which is particularly suitable for small molecules adsorption calculations in solid or crystal frameworks. Modifications have been made to take into account the quadrupole moments of some molecules in a more accurate way. Thus, we used the Watanabe-Austin models [35] for  $N_2$ ,  $O_2$ ,  $CO_2$ , which introduce the presence of dummy atoms to simulate charge displacements. We used the standard TIP3P model for water [36]; the benzene molecule was constructed and then minimized with the cvff\_aug Force Field. Finally, in the activated carbon structure, hydrogen parameters have been set to the ones describing hydrogen bonded to  $sp^3$  carbons. Finally, we report the partial charges for adsorbates and frameworks: oxygen: -0.112 (O), 0.224 (dummy atom in the centre); nitrogen: -0.509 (N), 1.018 (dummy atom in the centre); carbon dioxide: 1.04 (C), -0.462 (O), 0.112 (external dummy atoms of Watanabe-Austin model); benzene: 0.1 (H), -0.100 (C), water: 0.417 (H), -0.834 (O); MFI: 2.400 (Si), -1.200 (O); NaY: 2.400 (Si), 1.400 (Al), -1.200 (O), 1.000 ( $Na^+$ ); Cs1000a: 0.100 (C linked to an H atom), 0.000 (C not linked to H atoms), -0.100 (H).

The representative mixture ( $N_2$  70%,  $CO_2$  10%,  $H_2O$  10% and  $O_2$  11%) contained also a variable amount of benzene (0.05 – 1%). We performed simulations at 500, 750 and 1000 K, and at a total pressure of 101.3, 202.6

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3 and 506.5 kPa (1, 2 and 5 atm, respectively), with the same mixture  
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5 composition. In this way we aim to establish the most convenient conditions  
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7 for benzene removal in terms of adsorption isotherms for the considered  
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9 structures.

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12 For all simulations, we performed 5000000 of Monte Carlo steps,  
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14 preceded by 1000000 of equilibration steps. Electrostatic interactions have  
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16 been taken into account with the Ewald and group summation method [7] with  
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18 a Ewald accuracy of 0.001 kcal/mol and a cut off distance of 12.5 Å, which is  
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20 half of the smaller considered cell width. Van der Waals interactions have  
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22 been described with an atom based summation method, with a cubic spline  
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24 truncation, splined for 1 Å; the cut off is 12.5 Å.  
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29 Finally, we used the common thermodynamic model developed by Sips  
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31 [37] to reproduce simulated data for mixtures. This is an extension of the  
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33 Langmuir-Freundlich model to mixtures; the equation for the component  $i$  is  
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35 written as:  
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$$q_i = q_{0,i} \cdot \frac{b_i \cdot P_i^{\alpha_i}}{1 + \sum_{i=1}^n b_i \cdot P_i^{\alpha_i}} \quad (9)$$

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44 in the case of  $n$  components, where  $q_{0,i}$  is the saturation value for  $i$ ,  $P$  is the  
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46 partial pressure of  $i$ ,  $\alpha_i$  and  $b_i$  are the coefficients of the Langmuir-Freundlich  
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48 model [38] which have been obtained from the fitting of simulated adsorption  
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50 isotherms of pure species (see Additional Information).  
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54 We performed a set of simulations to validate our procedure,  
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56 comparing adsorption isotherms with data available in literature. Then we  
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58 examined the differences between adsorption isotherms of pure benzene and  
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60 adsorption isotherms of benzene in the multicomponent mixture, i.e. the

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3 gaseous emission ( $N_2$  70%,  $CO_2$  10%,  $H_2O$  10% and  $O_2$  11% as partial  
4 pressures) to find a reasonable ranking of the most suitable adsorbent and the  
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6 most convenient thermodynamic conditions.  
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## 10 11 12 RESULTS AND DISCUSSION 13

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15 For validation, we tried to compare adsorption isotherms with data available in  
16 literature.  
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19 Figure 2 shows the comparison between our data for pure adsorption over  
20 MFI zeolite (a) and NaY zeolite (b) and, respectively, the adsorption isotherms  
21 of [19] and [39]. As expected, the agreement is fair for all the considered  
22 pressure range, bearing in mind the possible presence of impurities in the real  
23 zeolite MFI, and the slightly different Si/Al ratio (2.43 in the case of this  
24 publication). Analogously, for comparison we report the average isosteric heat  
25 of adsorption for pure benzene in MFI, 16.6 (kcal/mol), which is close to the  
26 values reported for pure benzene adsorption by Snurr et.al [40], bearing in  
27 mind some zeolite structural differences, and the temperature discrepancy (in  
28 this case, 328 K). In that case, isosteric heats are plotted as a function of  
29 loading and range between 13 and 17 kcal/mol. Finally, for NaY, we find an  
30 average isosteric heat value of 18.3 kcal/mol. This is also close to the ones  
31 reported by Takahashi and Yang [41], between 16.4 and 18 kcal/mol at the  
32 same temperature, and the one proposed by Auerbach et.al. [42] (18.8  
33 kcal/mol at 445 K).  
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55 Analogous data for activated carbons, although present in several  
56 works, are difficult to compare to our specific structure, due to the huge  
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3 differences which appear in disordered structures with different framework  
4 and porosity.  
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8 Figure 3 shows a comparison between pure benzene adsorption  
9 isotherms and benzene adsorption isotherms in the gaseous mixture (N<sub>2</sub> 70%,  
10 CO<sub>2</sub> 10%, H<sub>2</sub>O 10% and O<sub>2</sub> 11%) at 500 K and at a total pressure of 101.3  
11 kPa (1 atm). Benzene loading is expressed as a function of the benzene  
12 pressure.  
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20 Results show several differences, which are due to the adsorption site  
21 competition inside the pores. These differences are very pronounced at low  
22 benzene pressures and for the hydrophilic zeolite NaY, where the most polar  
23 groups and the Na<sup>+</sup> ions favour the adsorption of water and oxygen.  
24 Accordingly, benzene adsorption in NaY is very low. As expected, MFI and  
25 cs1000a are indicated for the non-polar VOC (in particular, benzene) removal,  
26 while NaY zeolite is not.  
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36 Thus, we proceeded by examining the isotherms for mixtures (N<sub>2</sub> 70%,  
37 CO<sub>2</sub> 10%, H<sub>2</sub>O 10% and O<sub>2</sub> 11%) in cs1000a and MFI. Figure 4 show the  
38 adsorption isotherms at 500, 750 and 1000 K for MFI and cs1000a, at a total  
39 pressure of the system of 101.3, 202.6 and 506.5 kPa (1, 2 and 5 atm,  
40 respectively), together with the fitting curves with the Sips model; benzene  
41 loading is expressed as a function of the benzene partial pressure. Additional  
42 information provides also the adsorption isotherms of all the other components  
43 for all structures.  
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55 In Table 2 we also show the isosteric heats of adsorption for all  
56 effectively adsorbed molecules. Values are averaged over all simulated point,  
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3 standard deviations are in brackets. Empty cells mean no adsorption for the  
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5 whole pressure range.  
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8 Examining isotherms and isosteric heats, it is clear how benzene is  
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10 favoured over all other components, confirming these structures as suitable  
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12 for benzene removal. The high benzene loading, even at low partial  
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14 pressures, corresponds to the other hand to a very low coverage of the other  
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16 gases (see Additional Information). Nevertheless, higher temperatures  
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18 influence negatively the adsorption for both structures in a quite dramatic way,  
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20 as differences are up to 3 orders of magnitude. Isosteric heats are quite  
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22 constant for all isotherms points; they are slightly temperature dependent,  
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24 especially for benzene adsorbed in the cs1000a structure.  
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29 Higher values for benzene isosteric heats are reached for mixtures. This can  
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31 be explained invoking the favourable adsorbate-adsorbate interactions that  
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33 take place in a more confined space. This is particularly evident if we consider  
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35 the narrow, zig-zag pores of MFI. In the single-component simulations,  
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37 benzene rings are regularly disposed in a “flat” configuration which is mainly  
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39 normal to the axe of straight, bigger pores. In multi component simulations,  
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41 the presence of new adsorbed molecules (mainly CO<sub>2</sub> and H<sub>2</sub>O) forces  
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43 benzene molecules to adsorb in a “close” and mainly randomly oriented  
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45 disposition, even in zig-zag pores.  
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51 In MFI saturation values at low temperatures are reached before the  
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53 maximum benzene partial pressure. When total pressure increases, benzene  
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55 adsorption is slightly decreasing, due to the effect of the higher partial  
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57 pressure of other components; then, at a total pressure of 506.5 kPa and  
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59 1000 K, we can observe how in practice the benzene adsorption is very  
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3 limited, and decreasing for a higher total pressure. A similar behaviour can be  
4 noticed for cs1000a; in this case saturation values, which are also higher,  
5 increase with the total pressure of the system. Generally speaking, both for  
6 MFI and cs1000a, adsorption is slightly influenced by total pressure. Although  
7 the choice of MFI will be favoured for higher temperatures, and lower total  
8 pressures, the most indicate and common situation, (moderate pressure and  
9 temperature, 101.3 kPa at 500 K) at the outlet of the stream, seems to  
10 suggest the use of the considered activated carbon model, with the exception  
11 of a very low benzene fraction. Finally, the considered Sips model show a  
12 rather acceptable behaviour, as it is able to reproduce qualitatively (and, with  
13 the exception of 1000 K, also quantitatively) the trends for both structures.  
14 The use of more sophisticated thermodynamic models to take into account  
15 non-idealities or framework heterogeneity for such a complex mixture was out  
16 of the scope of our work.  
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## 38 CONCLUSIONS

39 We used the GCMC molecular simulation technique to evaluate adsorptive  
40 potentialities of zeolites and activated carbon structures. We validated our  
41 procedure against available adsorption data; then we considered a simplified,  
42 ideal gaseous mixture to mimic an outlet stream (e.g. exhaust gas from  
43 combustion). Results show how hydrophobic zeolite MFI and the prototype of  
44 an activated carbon structure, cs1000a, are indicated for benzene removal.  
45 The adsorption isotherms dependence on the total pressure is weak, while it  
46 can be suggested to operate at relatively low temperatures, due to the strong  
47 influence of this parameter. In this case, the choice of the considered  
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3 activated carbon structure will be generally slightly favoured. Further, the Sips  
4 thermodynamic model showed to be able to fit calculated data in an  
5 acceptable way. The adopted methods and procedures have shown to be  
6 simple and suitable for further applications in the environmental-related fields,  
7 providing that porous adsorbent structures are known.  
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## 15 16 17 SUPPLEMENTARY MATERIAL

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19 Additional information is freely available as supplementary material.  
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## CAPTION TO FIGURES

Figure 1. From left to right: 3D structures of (a) zeolite MFI, (b) zeolite FAU (NaY), and (c) activated carbon cs1000a.

Figure 2. Comparison of simulated data (open symbols) with literature data (filled symbols) for benzene adsorption in NaY and MFI zeolites; ▲: NaY, 393 K; ●: MFI, 435 K; q is the loading, P the pressure.

Figure 3. Adsorption isotherms for pure benzene (open symbols) and for benzene in the mixture (filled symbols) at 500 K. ◇: NaY; □: MFI; ○: cs1000a; q is the loading, P is the pressure.

Figure 4. Adsorption isotherms for benzene in the multicomponent mixture at a total pressure of 101.3 kPa (a), 102.6 kPa (b) and 506.5 kPa (c). Filled symbols: zeolite MFI; open symbols: activated carbon cs1000a. Blue: 500 K; black: 750K; red: 1000 K. Continue lines: Sips model for MFI; dotted lines: Sips model for cs1000a; q is the loading, P is the pressure.