

# Combined Adsorption and Reaction in the Ternary Mixture $N_2$ , $N_2O_4$ , $NO_2$ on MIL-127 Examined by Computer Simulations

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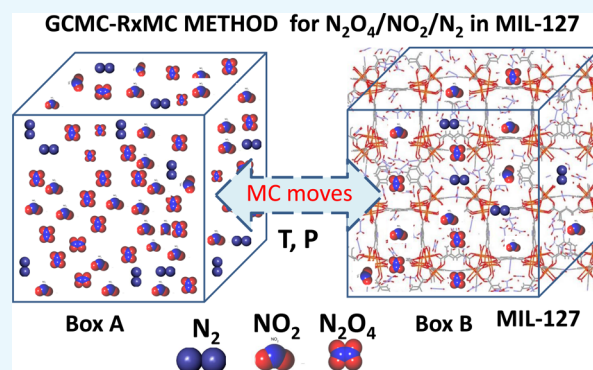
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**ABSTRACT:** A high selectivity of  $NO_x$  over  $N_2$  (simulating air) is found in silico when studying the adsorption of the ternary mixture  $N_2O_4/NO_2/N_2$  on the metal–organic framework MIL-127(Fe) by molecular simulations under consideration of the recombination reaction  $N_2O_4 \leftrightarrow 2NO_2$ . The number of N atoms in nitrogen oxides  $NO_x$  and that in  $N_2$  is used to define a selectivity of the combined adsorption and chemical recombination that can reach values of about 1000.



## 1. INTRODUCTION

Among other air pollutants like fine dust,  $CO_2$ , or  $CH_4$ , the toxic nitrogen oxides  $NO_x$  play an important role. They include nitrogen dioxide  $NO_2$ , nitrogen monoxide  $NO$ , and dinitrogen tetroxide  $N_2O_4$ , which pose a health risk for humans and animals.<sup>1</sup> In the presence of oxygen,  $NO$  can become oxidized to  $NO_2$ . Therefore, among the  $NO_x$ , the  $NO_2$  and  $N_2O_4$  are the most important air pollutants, and they can arise from natural sources like volcanos, lightning, or bacterial respiration, but they are also produced by combustion engines burning fossil fuels or by industrial processes.  $NO_x$  can be removed from mixtures of exhaust gases by selective catalytic reduction<sup>2</sup> or by storage as nitrates. However, these technologies require additional apparatus, materials, and energy. Thus, alternative techniques like selective adsorption deserve consideration.

Several experimental studies and a few simulation papers about the adsorption of  $NO_x$  (in many cases only  $NO_2$ ) on porous materials are already available.<sup>3–12</sup> It turns out that porous materials can serve to adsorb  $NO_x$  for separation purposes. However,  $N_2$  has only been examined in few studies.<sup>7,8,10,11</sup> Instead,  $N_2$  was sometimes only used to determine the porosity.<sup>6</sup> The mixture  $N_2/NO_x$  under simultaneous consideration of the chemical reaction  $N_2O_4 \leftrightarrow 2NO_2$ , which is the subject of this work, is not examined in any one of those previous papers. Moreover, among those papers, only Han *et al.*<sup>7</sup> and Matito-Martos *et al.*<sup>12</sup> mention and examine this chemical reaction that permanently happens among the  $NO_x$  under ambient conditions. In the paper of Han *et al.*,<sup>7</sup> the single component systems for  $NO_2$ ,  $SO_2$ ,  $CO_2$ ,  $CH_4$ ,  $CO$ ,  $CO_2$ ,  $Ar$ ,  $H_2$ ,  $N_2$ , and  $O_2$  are considered and also the

pressure dependence of the chemical reaction  $N_2O_4 \leftrightarrow 2NO_2$  is investigated. Although such a single component adsorption gives valuable trends about expected results of mixtures, the properties of competitive simultaneous adsorption cannot be forecasted with certainty if not really mixtures are examined (see e.g., effects reported by Tan *et al.*<sup>8</sup>). The selectivity of  $NO_2/CO_2$  and  $NO_2/CO_2$  but not of  $N_2/NO_x$  has been investigated by ideal adsorbed solution theory (IAST) from pure gas data reported by Han *et al.*<sup>7</sup> Tan and co-workers investigated the competitive co-adsorption of  $CO_2$  with  $H_2O$ ,  $NH_3$ ,  $SO_2$ ,  $NO$ ,  $NO_2$ ,  $N_2$ ,  $O_2$ , and  $CH_4$  in M-MOF-74 by infrared spectroscopy and density-functional theory calculations.<sup>8</sup> However, in contrast to the present paper,  $N_2O_4$  is not mentioned, and the mixture of  $NO_2/N_2O_4/N_2$  and the chemical reaction  $N_2O_4 \leftrightarrow 2NO_2$  have not been examined. A high selectivity as examined in the present paper is not reported. Ab initio studies about  $NO_x$  adsorption have been carried out by Fioretos *et al.*<sup>10</sup> where aromatic molecules were used as models for the ligands of metal–organic frameworks (MOFs). The binding energies of  $NO_x$  with respect to these molecules have been investigated and compared with those of several gas molecules, including  $N_2$ , but the mixtures or the chemical reaction  $N_2O_4 \leftrightarrow 2NO_2$  have not been examined.

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A gas mixture of  $N_2$ ,  $CO_2$ ,  $O_2$ ,  $SO_2$ , and  $NO_2$  forming a model of flue gas from combustion engines is examined at 1 bar by grand canonical Monte-Carlo (GCMC) by Sun *et al.*<sup>11</sup>  $N_2O_4$  and the chemical reaction  $N_2O_4 \leftrightarrow 2 NO_2$ , that are examined in the present paper, are not mentioned.

In the work of Matito-Martos *et al.*,<sup>12</sup> the adsorption and chemical reaction of  $NO_2$  and  $N_2O_4$  adsorbed in several zeolites have been studied by a combination of reactive MC (called RxMC, for a description of RxMC, see Section 4) and GCMC. This is, to our knowledge, the first simulation paper of combined adsorption and reaction of  $NO_x$  in a porous solid. In contrast to the present paper, they examine the  $NO_x$  without the presence of other guest molecules. The authors calculated the equilibrium constant for 1 bar (ideal gas) from the ideal gas partition functions, and it has been found to be in good agreement with the experimental equilibrium constant reported by Chao *et al.*,<sup>13</sup> and we also use the same in the present study. In accordance with the principle of Le Chatelier, it has been found that the confinement by the zeolite pores strongly favors the dimerization reaction.<sup>12</sup> By defining a selectivity between the two forms of nitrogen oxides, very large selectivities between  $N_2O_4$  and  $NO_2$  have been found by using different zeolite materials.

In some of the papers, the properties of mixtures (*e.g.*,  $SO_2/NO_2$  and  $CO_2/NO_2$ ) are concluded from single component systems by IAST from pure gas data.<sup>3,7</sup> In contrast to simulations or experiments with real mixtures, this is an approximation, and it can also not reproduce effects of competitive co-adsorption that are, for example, reported by Tan and co-workers<sup>8</sup> and mentioned in the Results and Discussion section of the present paper.

All these studies suggested that MOFs are promising materials for separation purposes. However, now the question arises, how will these remarkable findings influence the most important application of the combined adsorption and reaction on porous materials, that is, their use for separation purposes. Therefore, we intend, in this study, to investigate the details of  $NO_2$  and  $N_2O_4$  separation from  $N_2$  by molecular simulations under consideration of the equilibrium of the chemical reaction  $N_2O_4 \leftrightarrow 2 NO_2$  that determines the  $NO_2/N_2O_4$  composition of the mixture at a given temperature and pressure. For illustration, in the gas phase at 1 bar total pressure and room temperature, in the absence of other gases, the partial pressure of  $NO_2$  will be about 0.3 bar and that of  $N_2O_4$  will be about 0.7 bar. At 374.7 K and at 1 bar total pressure, the partial pressure of  $NO_2$  will be about 0.96 bar and that of  $N_2O_4$  will be about 0.04 bar. At higher pressures or within the restricted geometry of small pores, the equilibrium will be shifted in favor of the recombination reaction, as mentioned above. This means that adsorption of  $NO_2$  and  $N_2O_4$  must be considered with simultaneously taking into account the equilibrium of this chemical reaction (as it has been performed in the work of Matito-Martos *et al.*<sup>12</sup> and in the present paper). Only in special cases, the reaction can be neglected, for example, it could be neglected in the investigation at 374.7 K for the  $N_2/NO_2$  mixture in different MOFs, especially zeolitic imidazolate frameworks (ZIFs) because hardly any  $N_2O_4$  exists at this temperature.<sup>14</sup> The chemical reaction equilibrium can be treated by simulations using RxMC, a special version of MC simulations, which is explained briefly in Section Methodology and in Section S2 of the Supporting Information.

Air has been represented by  $N_2$  because in some investigations, it could be shown that the adsorption isotherms

of  $N_2$  and  $O_2$  for different porous materials are almost identical.<sup>14,15</sup> Therefore, we consider in this paper the separation of  $NO_x$  from  $N_2$ . However, in contrast to the system studied by Chokbunpiam and co-workers,<sup>14</sup> both  $NO_2$  and  $N_2O_4$  must now be considered.

Because of their size,  $N_2O_4$  molecules cannot penetrate into those ZIFs,<sup>14</sup> and if  $N_2O_4$  is formed by the chemical reaction inside the ZIF pores, it will not be able to diffuse out. Moreover, the equilibrium constant inside narrow pores will be changed by the strongly reduced degrees of freedom for rotation, which means that the ideal gas equilibrium constant cannot be used as an approximation for the equilibrium constant at high dilution within the porous solids with narrow pores. Hence, we had to find another material to include the big  $N_2O_4$  molecules. We have chosen a material from a class of porous solids called MOFs. These materials, that have been the subject of many experimental and simulation studies during the last decades, show remarkable features. Their most outstanding property is the desired on-demand fine-tuning of the pore system during their synthesis because the variety of possible MOF structures is almost unlimited. They are also widely used for separation purposes<sup>14–18</sup> or  $NO_2$  capture.<sup>3,4</sup>

Our aim was to investigate the influence of the chemical reaction  $N_2O_4 \leftrightarrow 2 NO_2$  on the selective adsorption of an  $NO_x/N_2$  mixture by molecular simulations. Therefore, we were searching for a material with pores of sizes that allow the  $N_2O_4$  molecule to be adsorbed, to migrate, and to rotate. In the Supporting Information, it is shown that this requires channel diameters of more than 5 Å. On the other hand, the channels should be small enough to observe the effects of the confinement on adsorption and on the chemical reaction. Both effects are discussed in the Results and Discussion section.

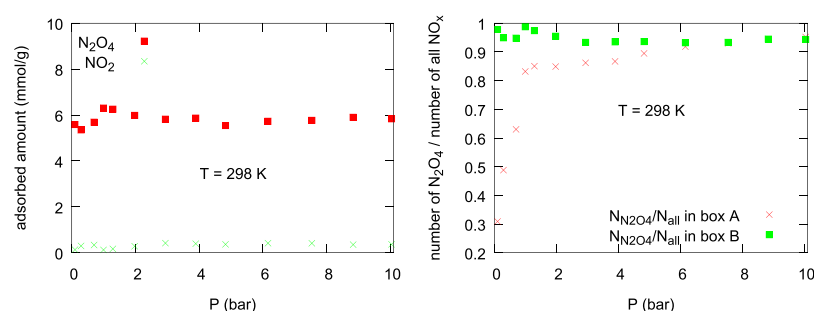
A material that fulfills these conditions is the MOF framework MIL-127(Fe) that means Material of Institut Lavoisier-127 (MIL-127). The lattice of MIL-127(Fe) is formed by trimers of iron(III) and 3,3',5,5'-azobenzene-tetracarboxylate anions. It is also called *soc*-MOF(Fe).<sup>19</sup> The average diameter of channels and pores of MIL-127(Fe) is around 10 Å. This material has also been found to be highly stable.<sup>20</sup> MIL-127(Fe) has, for example, been used already to examine the separation of  $CO_2$  from  $CO$ .<sup>17</sup>

Please note that the aim of this paper is not to compare materials to find the most effective one for the separation of  $NO_x$  from air. Instead, we intend to study the interplay of reaction, adsorption, and separation of the ternary system  $N_2O_4/NO_2/N_2$  for capture on a given example material.

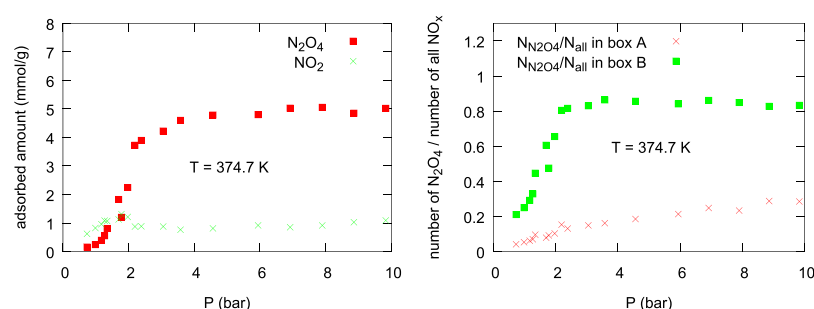
## 2. RESULTS AND DISCUSSION

**2.1.  $N_2O_4$ - $2 NO_2$  Equilibrium and the Adsorption of the Binary Mixture.** First, the binary system  $N_2O_4/NO_2$  was investigated. Because adsorption and reaction happen simultaneously, the single component systems of  $N_2O_4$  or  $NO_2$  cannot be studied. From the investigation of the binary system, we hope to gain insights that help to analyze the properties of the ternary system which is the main subject of this paper.

First, we checked in test RxMC simulations whether the equilibrium constant at 1 bar is really independent of the pressure and can be considered to be the one for the ideal gas that we need to know for our simulations. This was to be expected, and it could be confirmed, and it is reported in the Supporting Information.



**Figure 1.** Left: adsorption/reaction isotherm of pure  $NO_x$  in MIL-127 at 298 K. Note that the majority of the adsorbed  $NO_x$  is present as  $N_2O_4$ , and the saturation region of the isotherm is reached at low pressures. Right: ratio of  $N_2O_4$  molecules to all  $NO_x$  molecules in box A (gas phase) and in MIL-127 (box B, adsorbed phase) as a function of pressure at 298 K.



**Figure 2.** Left: adsorption/reaction isotherm of pure  $NO_x$  in MIL-127 at 374.7 K. Note that because of the endothermal splitting of  $N_2O_4$ , the  $NO_2$  concentration is enhanced at higher temperatures as compared to the one shown in Figure 1 (left). Right: ratio of  $N_2O_4/NO_x$  in MIL-127 in box A and in box B as a function of pressure at 374.7 K.

As shown in Figure 1, left hand side, the amounts of  $N_2O_4$  and of  $NO_2$  in MIL-127 are given at 298 K as a function of pressure. This figure shows the result of simultaneous adsorption and reaction and should therefore be called adsorption/reaction isotherm and not adsorption isotherm. The saturation loading of  $N_2O_4$  is reached already at very low pressure which means that the  $N_2O_4$  molecules are attracted by the channels and cavities of the MIL-127 very strongly. The maximum amount of adsorbed  $N_2O_4$  is about 6 mmol/g. For comparison: the highest amount of adsorbed  $N_2O_4$  for Faujasite was found to be 5 mmol/g, while other porous solids (*i.e.*, zeolites FER, MFI, MER, and TON) showed lower adsorption.<sup>12</sup> This capacity of adsorption is important for the effectivity of industrial applications.

As shown in Figure 1, right hand side, the ratio of the number of  $N_2O_4$  molecules to the number of all  $NO_x$  molecules, that is, all  $N_2O_4$  and  $NO_2$  molecules is given for the gas phase (box A) and in MIL-127 (box B, adsorbed phase) as a function of pressure at 298 K. While in the gas phase,  $NO_2$  is the dominating kind of  $NO_x$ , and the majority of  $NO_x$  in the adsorbed phase is  $N_2O_4$  because of the confinement. Such a high ratio within the porous solid has been found also in the simulations given in the previous work.<sup>12</sup> Interestingly, the  $N_2O_4/NO_x$  ratio for pressures larger than 5 bar is found to be almost the same for the gas and the adsorbed phase. The confinement strongly favors dimerization, which is in accordance with the principle of Le Chatelier.  $NO_x$  exists in the adsorbed phase mainly as  $N_2O_4$ . All these findings and the high ratio, as shown in Figure 1 (right), agree with the former simulations.<sup>12</sup>

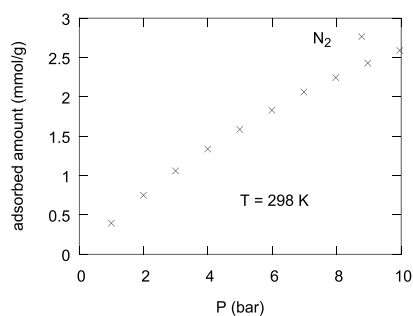
Figure 2 shows the same for 374.7 K. As it can be expected, the amount of adsorbed molecules in box B is smaller than that at 298 K. Also, the dimerization in the gas phase is reduced at

374.7 K in comparison to 298 K. Therefore, in the gas phase, now  $NO_2$  is the dominating species of  $NO_x$  molecules. While the saturation of  $NO_x$  uptake at 298 K is reached already at pressures far below 1 bar, saturation is reached above 2 bar at 374.7 K. Interestingly, the amount of adsorbed  $N_2O_4$  at 374.7 K is about 5 mmol/g, not much smaller than the 6 mmol/g at 298 K, while the amount of adsorbed  $NO_2$  is somewhat higher at 374.7 K.

Examination of the radial distribution functions (RDFs) for the binary mixture in MIL-127 seems not to be necessary because in the examination of the ternary mixture, it will turn out that the number of adsorbed  $N_2$  molecules is very low. This means that, within the limits of accuracy, the RDFs for  $NO_2$  and  $N_2O_4$  can be expected to be the same in the binary and in the ternary mixture. RDFs and number integrals in the ternary mixture are discussed below.

**2.2. Adsorption of  $N_2$  as Unary System.** The third kind of guest molecules that are involved into the process under investigation is  $N_2$ . This component is also investigated separately as single gas. The adsorption of  $N_2$  is lower than that of  $NO_x$ , and it is also decreasing with increasing temperature. Possible adsorption centers can more easily be identified at low temperatures. Moreover, the separation will not be carried out at higher temperatures in applications. Therefore, we restricted ourselves in the case of  $N_2$  adsorption at  $T = 298$  K.

Figure 3 shows the amount of adsorbed  $N_2$  in mmol/g at 298 K as a function of pressure for pure  $N_2$ . The adsorption isotherm for low pressure is a straight line directed toward the origin indicating that a Henry law will be valid. Without the competition with other guest molecules, the adsorbed amount of  $N_2$  reaches 2.5 mmol/g at 10 bar. It is to be checked whether in the ternary mixture the adsorbed amount will be



**Figure 3.** Amount of adsorbed  $\text{N}_2$  as a function of pressure at 298 K for pure  $\text{N}_2$ .

smaller. In order to see whether there are adsorption sites for  $\text{N}_2$ , the RDFs of  $\text{N}_2$  in the single component case have been examined.

Figure 4 shows the RDFs and number integrals of  $\text{N}_2$  with the lattice atoms for which the RDF reaches the largest values. The case  $\text{N}[\text{N}_2]\text{---CN}$  is the RDF of the N atom of  $\text{N}_2$  with the lattice atom of MIL-127 that is called CN. The names of the lattice atoms are explained in the Supporting Information. The minimum of the RDF is located at about 8 Å. This distance seems to be too long to be interpreted as the end of the first shell of neighbors. A weak inflection found in the number integral at 8 Å would yield a coordination number of about 2. In any case, CN cannot be considered to be an adsorption center for  $\text{N}_2$ . For  $\text{N}[\text{N}_2]\text{---O}[\text{Fe}]$ , it can clearly be seen that no shell of next neighbors can be identified. Thus, the conclusion is that in MIL-127 at  $T = 298$  K and  $P = 2$  bar, no adsorption centers for  $\text{N}_2$  exist. If this is not the case for 298 K, then the existence of adsorption centers at the higher temperature of 374.7 K needs not to be examined. With this knowledge about the pure gases  $\text{N}_2$  and  $\text{NO}_x$  without other guest molecules, the investigations about the ternary mixture could be started.

**2.3. Combined Adsorption and Chemical Reaction for the Ternary Mixture  $\text{N}_2\text{O}_4/\text{NO}_2/\text{N}_2$ .** The aim of this paper is to investigate the adsorption under the condition of simultaneously happening chemical reactions for the ternary mixture  $\text{N}_2\text{O}_4/\text{NO}_2/\text{N}_2$ . The equilibrium constant from studies of Chao *et al.*<sup>13</sup> and Roscoe *et al.*<sup>21</sup> was used for the reaction, but we have chosen the more common unit of bar instead of atm for pressure. In box B, the restricted space of the MOF will favor the recombination reaction, according to the principle of Le Chatelier. This holds true for the pure  $\text{NO}_x$  as well as for the mixture with  $\text{N}_2$ .

Figure 5 (left) shows the amount of the adsorbed species in mmol/g as a function of pressure at 298 K. The ratio of N

atoms in  $\text{NO}_x$  to N atoms in  $\text{N}_2$  in box A was 1:20. Interestingly, a straight line fitted to the first points of the  $\text{N}_2\text{O}_4$  curve would not point to the origin. This means that for low pressure, the adsorbed amount of  $\text{N}_2\text{O}_4$  is not a linear function of pressure like in the case of Henry's law of adsorption. This indicates that the interaction of already adsorbed  $\text{N}_2\text{O}_4$  with new ones enhances adsorption. Interestingly, the amount of  $\text{N}_2\text{O}_4$  within the MIL is relatively high and amounts about 5 mmol/g for pressures above 2 bar although about 95% of the N-atoms in the gas phase belong to  $\text{N}_2$  molecules. In the case of pure  $\text{NO}_x$ , it was about 6 mmol/g which is only 20% more than for the mixture with  $\text{N}_2$ . Hence, the presence of  $\text{N}_2$  does not reduce very much the amount of  $\text{N}_2\text{O}_4$  within the porous solid except at very low pressure where the adsorption of pure  $\text{N}_2\text{O}_4$  had already almost reached saturation at pressures below 1 bar as can be seen in Figure 1 (left). This difference between Figures 1 and 5 for  $\text{N}_2\text{O}_4$  at low pressure shows that the properties of the mixture cannot easily be concluded from the pure component behavior. In contrast to that, the amount of adsorbed  $\text{N}_2$  is much lower than for the pure  $\text{N}_2$  gas. At 10 bar, it is about 5 times lower. This is another example for competitive co-adsorption.

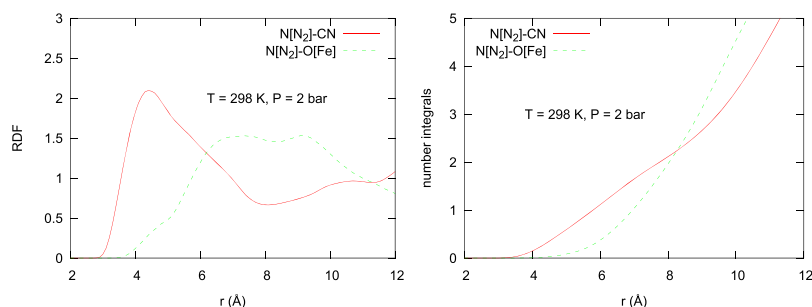
As shown in Figure 5 (right), the equilibrium ratio of the numbers of  $\text{N}_2\text{O}_4$  molecules to the number of  $\text{NO}_2$  molecules as a function of pressure in boxes A and B at 298 K can be seen. This ratio increases with increasing pressure, and it is higher in the restricted volume of the MIL than in the gas phase. Both findings can be expected because they agree with the principle of Le Chatelier.

It can be seen in Figure 5 (right) that for pressures larger than 1 bar, more than 90% of the  $\text{NO}_x$  molecules in the gas phase are present as  $\text{N}_2\text{O}_4$  molecules. Because one  $\text{N}_2\text{O}_4$  molecule requires less space than two  $\text{NO}_2$  molecules, this effect can also increase the amount of adsorbed  $\text{NO}_x$ , thus supporting a high selectivity of  $\text{NO}_2:\text{N}_2\text{O}_4$  in the paper of Matito-Martos *et al.*<sup>12</sup> and of  $\text{NO}_x/\text{N}_2$  in this present paper.

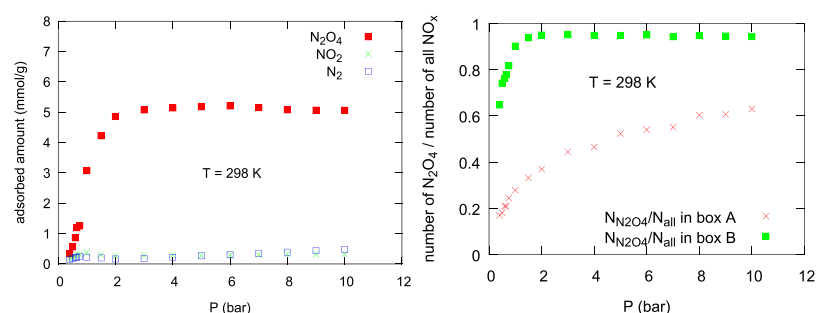
The most important property of the system, as far as the adsorptive separation of gases is considered, is the adsorption/reaction selectivity. Also, in order to check the concentration dependence of the selectivity, we have, additionally to the ratio of 1:20, carried out simulations for the ratio 1:40.

Figure 6 shows the selectivity  $S_{\text{ar}}$  as defined in eq 1 at 298 K and at different pressures. The ratio of N atoms in the  $\text{NO}_x$  to N atoms in  $\text{N}_2$  has been chosen to be 1:20 or 1:40. The selectivity  $S_{\text{ar}}$  obtained from the simulations is extraordinarily high, and it is higher for the lower concentration 1:40.

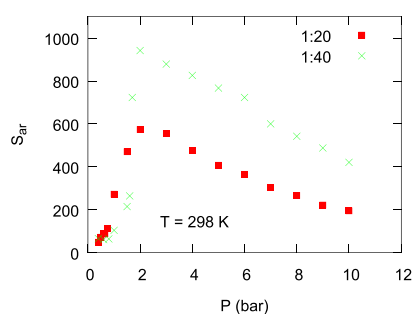
In order to understand the interplay of adsorption and reaction, we used the advantage of computer simulations that even systems can be simulated that do not exist in reality. In



**Figure 4.** RDFs and number integrals of a single component  $\text{N}_2$  adsorbed in MIL-127 at  $T = 298$  K,  $P = 2$  bar with two selected lattice atoms.



**Figure 5.** Left: amount of the adsorbed species in the ternary mixture  $\text{N}_2\text{O}_4/\text{NO}_2/\text{N}_2$  in mmol/g as a function of pressure at 298 K at a ratio of 1:20 of N molecules in  $\text{NO}_x$  to N molecules in  $\text{N}_2$ . Right: equilibrium ratio of the numbers of  $\text{N}_2\text{O}_4$  molecules to the number of all  $\text{NO}_x$  molecules as a function of pressure in box A (gas) and box B (adsorbed) at 298 K.



**Figure 6.** Adsorption/reaction selectivity  $S_{ar}$  resulting from both adsorption and  $\text{NO}_x$  reaction at 298 K at ratios 1:20 and 1:40 of N atoms in  $\text{NO}_x$  ( $\text{N}_2\text{O}_4 + \text{NO}_2$ ) to N atoms in  $\text{N}_2$ .

order to check whether adsorption in the absence of the reaction would also result in a high selectivity, we have carried out a simulation in which the reaction was switched off in contrast to reality.

We considered the run with highest selectivity at 298 K, 2 bar for the ratio 1:40 of the number of N atoms in  $\text{NO}_x$  to the N atoms in  $\text{N}_2$ . We simply omitted the reactive steps in the MC simulations thus reducing the particle exchange to only adsorption. The concentration ratios between the different molecule sorts in the gas phase (box A) have been kept like those in the run with the reaction that led to the high selectivity, as shown in Figure 6.

It turned out that without the chemical reaction, the selectivity became even higher. The selectivity increased up to about 2400, going down immediately after switching on the reaction again. Thus, not the chemical reaction but the strong adsorption of  $\text{N}_2\text{O}_4$  is the reason for the high selectivity.

Table 1 shows the average potential energy per molecule of the guest molecules in MIL-127 at 298 K and 2 bar. This potential energy of a molecule of a given sort in a solid is the sum of all pair interactions of molecules of this sort with lattice atoms and with other guest molecules. This includes van der

**Table 1. Average Potential Energy of a Guest Molecule within the Porous MOF MIL-127 at 298 K and 2 bar in kJ/mol as Found in Runs under Different Conditions**

	$\text{N}_2\text{O}_4$	$\text{NO}_2$	$\text{N}_2$
ternary mixture, 1:20	-48.22	-25.01	-14.65
ternary mixture, 1:40	-48.24	-25.19	-14.27
ternary fictive, 1:20	-48.78	-26.99	-15.65
ternary fictive, 1:40	-48.46	-26.81	-15.21
$\text{NO}_x$ binary	-49.05	-27.50	

Waals energies and Coulomb energies. This potential energy is equal to the amount of kinetic energy that would be needed for the particle to escape from the adsorbed phase to zero potential energy that it would have in the diluted gas phase outside of the solid.

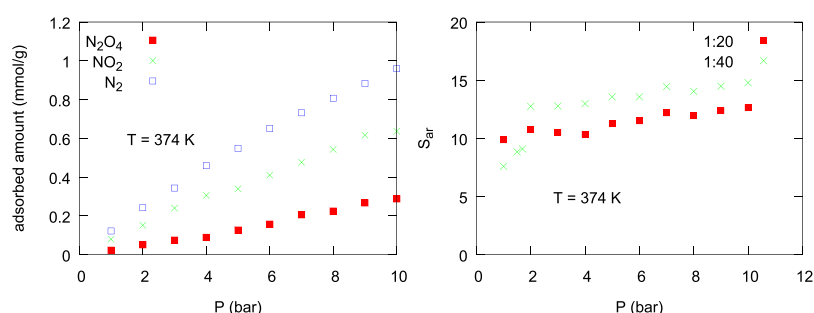
In this table, ternary mixture is the ternary system with combined adsorption and reaction. Ternary fictive is the simulation with the same concentration ratios in the gas phase at 298 K and 2 bar like in the real case but without the chemical reaction in the gas phase and also without the chemical reaction in the adsorbed phase.  $\text{NO}_x$  binary is the  $\text{NO}_2/\text{N}_2\text{O}_4$  mixture without any third component but with both adsorption and reaction.

It turns out that the average potential energy of  $\text{N}_2\text{O}_4$  is the same within the range of fluctuations in all considered cases. Only in the case without  $\text{N}_2$ , the potential energy of  $\text{N}_2\text{O}_4$  may be somewhat lower but the difference is still comparable with the fluctuations of the calculations. The potential energy of  $\text{NO}_2$  in the fictive case is lower than in the real ternary mixture. However, it is somewhat higher than in the case without  $\text{N}_2$ . The negative average potential energy of the adsorbed  $\text{N}_2\text{O}_4$  is almost twice that of  $\text{NO}_2$  and 3 times that of  $\text{N}_2$ . This explains the strong adsorption of  $\text{N}_2\text{O}_4$  and is the main reason for the high selectivity. Such high values of negative potential energy arise if a guest molecule is attracted by lattice atoms from several directions simultaneously. Hence, it is crucial that channels and cavities have diameters not much larger than the guest molecule.

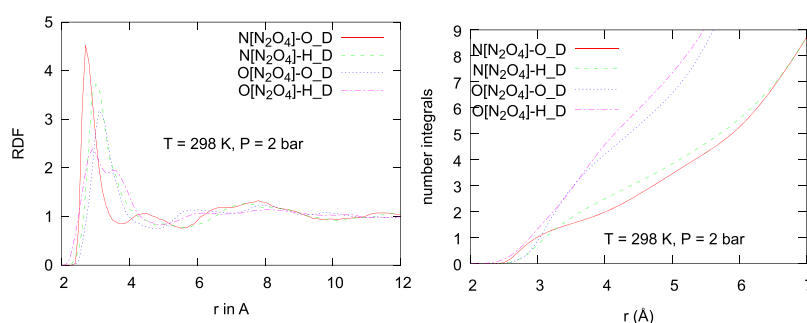
These potential energies are very low. This may be shown by comparison with the average kinetic energy of translation of a molecule, that is,  $3/2k_B T = 3.717$  kJ/mol at 298 K. This very low potential energy may explain why the maximum amount of adsorbed  $\text{N}_2\text{O}_4$  is reached already at very low pressure, as shown in Figure 2. Taking into account, that in the partition function, the potential energy appears in the exponent of the Boltzmann factor  $\exp(-U/k_B T)$ , the comparison of the potential energy values of the different species explains the high selectivity.

A possible explanation why the selectivity is higher at a low concentration is that the adsorbed amount of  $\text{N}_2\text{O}_4$  does not depend much upon the concentration of  $\text{NO}_x$  in the gas phase. Thus, lower concentration of  $\text{NO}_x$  in the gas phase means higher selectivity, according to eq 1. The fact that the maximum adsorbed amount of  $\text{N}_2\text{O}_4$  in the binary mixture  $\text{NO}_2/\text{N}_2\text{O}_4$  is almost the same as in the ternary mixture  $\text{NO}_2/\text{N}_2\text{O}_4/\text{N}_2$  supports this interpretation.

Figure 7 (left) shows the amounts of  $\text{NO}_x$  and  $\text{N}_2$  found within the MIL at 374.7 K and at various pressures. These



**Figure 7.** Left: the amount of molecules found in the MIL for the three particle sorts at 374.7 K as a function of pressure. The ratio of N atoms in  $\text{NO}_x$  ( $\text{N}_2\text{O}_4 + \text{NO}_2$ ) to N atoms in  $\text{N}_2$  is 1:20 in this case. Right: the adsorption/reaction selectivity  $S_{\text{ar}}$  resulting from simultaneous adsorption and reaction at 374.7 K at ratios 1:20 and 1:40 of N atoms in  $\text{NO}_x$  to N atoms in  $\text{N}_2$ .



**Figure 8.** Left: RDFs of the N and O atoms of  $\text{N}_2\text{O}_4$  with the strongest adsorption centers of the lattice, the  $\text{O}_{\text{D}}$  and  $\text{H}_{\text{D}}$  lattice atoms. Right: number integrals of the N and O atoms of  $\text{N}_2\text{O}_4$  with the strongest adsorption centers of the lattice, the  $\text{O}_{\text{D}}$  and  $\text{H}_{\text{D}}$  lattice atoms.

amounts are small, and hence, recycling the MIL after the highly selective adsorption at 298 K can easily be carried out by heating at low pressure. Figure 7 (right) shows the selectivity resulting from simultaneous adsorption and reaction at 374.7 K for N/N ratios of 1:20 and 1:40. It can be seen that the influence of the ratio of N in  $\text{NO}_x$  to the N in  $\text{N}_2$  at 374.7 K is much smaller than at 298 K.

Pressures lower than 1 bar have not been considered because the numbers of particles in the MIL become too small for a reasonable statistic. The selectivity at 374.7 K is much smaller than at 298 K. This has the advantage that the  $\text{NO}_x$  which was adsorbed at 298 K can quite easily be removed from the MIL by heating before the MIL is used again for adsorption. Thus, a temperature swing technique seems to be promising.

In order to gain deeper insights into the adsorption of the  $\text{NO}_x$  within the MIL-127 crystal, we have examined the RDFs that give the probability to find a given atom in a given distance from another given atom and the number integrals to obtain coordination numbers that correspond to the average numbers of neighbors in the first shell. These evaluations have been carried out at 298 K and 2 bar and for an N/N ratio 1:20. From the isobars shown in Figure 5 (left), it can be seen that for all three kinds of guest molecules, the saturation region has been reached already at 298 K and 2 bar.

The atom-type names in the lattice have been introduced taking into account not only the kind of the atom but also its surrounding because this influences the parameters of the interaction with guest molecules. These names are explained in Figure S5 of the Supporting Information.

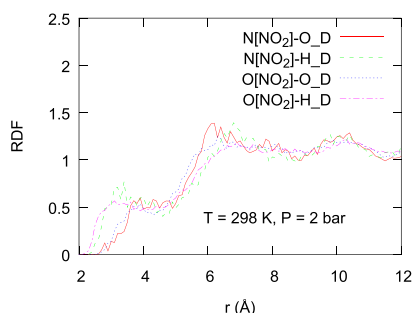
The highest peaks in an RDF of  $\text{N}_2\text{O}_4$  with a lattice atom was found for the lattice atoms  $\text{O}_{\text{D}}$  and  $\text{H}_{\text{D}}$ . Hence, we checked these RDFs and the corresponding coordination numbers. Figure 8 shows that the atom-type  $\text{O}_{\text{D}}$  is attractive

for  $\text{N}_2\text{O}_4$ . The peak of the N is higher and somewhat closer to the  $\text{O}_{\text{D}}$  than the peak for the O atom of  $\text{N}_2\text{O}_4$  indicating the favorite geometrical arrangement. For more information, we checked also the number integrals.

For  $\text{N}_2\text{O}_4$  with  $\text{O}_{\text{D}}$ , we find an inflection in the number integral at about 3.8 Å and a coordination number of about 1.8. This means that on an average 1.8 N atoms of  $\text{N}_2\text{O}_4$  are situated close to each  $\text{O}_{\text{D}}$  atom. This corresponds to 0.9  $\text{N}_2\text{O}_4$  molecules because each  $\text{N}_2\text{O}_4$  molecule contains two N atoms. For the O atom in  $\text{N}_2\text{O}_4$ , the inflection with respect to  $\text{O}_{\text{D}}$  is found to be also at about 3.8 Å, and the coordination number is about 3.6. Because there are four oxygen atoms in each  $\text{N}_2\text{O}_4$ , this corresponds also to 0.9  $\text{N}_2\text{O}_4$  molecules within the first shell of neighbors. Hence, these lattice atoms are not really adsorption centers.

For the N in  $\text{N}_2\text{O}_4$  with  $\text{H}_{\text{D}}$ , an inflection can be identified at 4.7 Å, and the coordination number would be 3.4. However, the distance of 4.7 Å is quite long, and the identification of a limited shell over such a distance is ambiguous. The  $\text{N}_2\text{O}_4$  which contributes to this apparent coordination number might be freely moving or might be adsorbed at other places than the lattice atom to which the evaluation has been carried out. The coordination number of 3.4 for N would correspond to a coordination number of 1.7 for the  $\text{N}_2\text{O}_4$  molecule. For the O in  $\text{N}_2\text{O}_4$  with  $\text{H}_{\text{D}}$ , an inflection can be identified also at around 4.7 Å, and the coordination number would be about 6.5, which divided by 4 gives about 1.6.

Figure 9 shows the RDFs of the N and O atoms in  $\text{NO}_2$  with the  $\text{O}_{\text{D}}$  and  $\text{H}_{\text{D}}$  lattice atoms. Interestingly, the probability density to find the N atom of  $\text{NO}_2$  close to the  $\text{O}_{\text{D}}$  is much smaller than 1.0, which is in contrast to the N atom in  $\text{N}_2\text{O}_4$ . This is obviously because these sites are mostly occupied by  $\text{N}_2\text{O}_4$  molecules. For  $\text{NO}_2$ , no such strong peaks are found in the RDFs as those for  $\text{N}_2\text{O}_4$  shown in Figure 8. The evaluation



**Figure 9.** RDFs of the N and O atoms in  $\text{NO}_2$  with the  $\text{O}_D$  and  $\text{H}_D$  lattice atoms.

of the corresponding number integrals does not make sense because the first shells of neighbors can hardly be defined because peaks at distances smaller than 6 Å are missing.

Guest–guest RDFs within the pores and channels do not give much useful information because—in contrast to a liquid—the formation of shells of other molecules around a given guest molecule is strongly disturbed by the confinement. Moreover, the space around a given particle within channels and pores depends strongly on the size of this molecule. This is particularly true for the big  $\text{N}_2\text{O}_4$  that fills a large part of each channel or pore. Thus, comparison of guest–guest RDFs between different guests does not make much sense. Therefore, we show only the RDF of the N in  $\text{N}_2\text{O}_4$  with all other atoms in guest molecules in order to see whether some of them, particularly  $\text{NO}_2$ , form clusters with the  $\text{N}_2\text{O}_4$ .

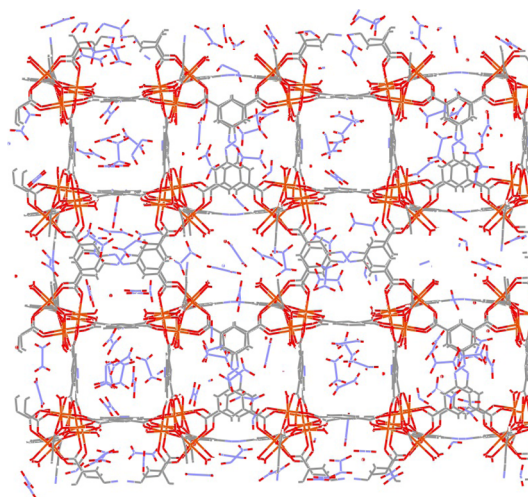
As shown in Figure 10, left side, the RDFs of the N atom of  $\text{N}_2\text{O}_4$  with all atoms in guest molecules are given. Of course, the RDF of N in  $\text{N}_2\text{O}_4$  with N in  $\text{N}_2\text{O}_4$  is the RDF with N of another  $\text{N}_2\text{O}_4$  molecule, not those of the same one. The highest peaks, as shown in Figure 10, correspond to the N atoms in  $\text{N}_2\text{O}_4$ , in  $\text{NO}_2$ , and even to the N in  $\text{N}_2$ . The number integrals, as shown in Figure 10, right hand side, do not show inflections. The reason is that the first minima in the RDFs appears at distances of more than 6 Å, and the weighting factor  $r^2$  in the number integral increases strongly with the distance.

From Figure 10, it is observed that the affinity of the atoms of  $\text{N}_2\text{O}_4$  with the atoms of another  $\text{N}_2\text{O}_4$  is not very strong. Thus, clustering between  $\text{N}_2\text{O}_4$  molecules can be excluded. Moreover, there is no indication for any clustering among guest molecules, but it is remarkable that the highest maximum in the RDF of the N atom in  $\text{N}_2\text{O}_4$  is that with N in  $\text{NO}_2$  and also the one between the N atoms in different  $\text{N}_2\text{O}_4$  has almost the same height and position in spite of the large size of the

$\text{N}_2\text{O}_4$  molecule. However, the peaks of the other atoms in guest molecules are not much smaller.

To gain more insights into the structure of the adsorbed gases within the MIL-127, we have plotted a pseudo-three-dimensional (3D) picture of a snapshot from the simulation.

Figure 11 shows a part of the MIL-127 lattice with adsorbed molecules. Only few  $\text{NO}_2$  and  $\text{N}_2$  can be seen. For example,



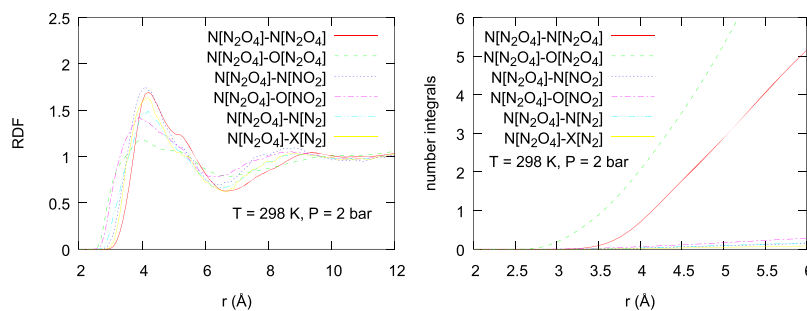
**Figure 11.** MIL-127 with adsorbed molecules. The molecules and lattice bonds are indicated by sticks.  $\text{NO}_2$  molecules have the shape of a V. The  $\text{N}_2\text{O}_4$  molecules have the shape of two connected Y, and  $\text{N}_2$  is linear.

there is one  $\text{N}_2$  and one  $\text{NO}_2$  in the rightmost part in the middle of the picture.  $\text{N}_2\text{O}_4$  molecules are mostly located in the middle of the cavity rather than close to any lattice atom. This can clearly be seen in some of the cavities, while in other cavities, the projection of the 3D lattice with guests on a plane makes the interpretation more difficult.

The conclusion is that the molecule positions are not concentrated at specific adsorption sites. This is in agreement with the RDFs and number integrals that do not show shells with significant coordination numbers. Instead, all kinds of guest molecules seem to have positions close to the middle of the channels and cavities.

### 3. CONCLUSIONS

Adsorption of  $\text{NO}_x$  in MIL-127 from a ternary mixture  $\text{N}_2/\text{N}_2\text{O}_4/\text{NO}_2$  results in an extraordinary high adsorption selectivity of  $\text{NO}_x$  over  $\text{N}_2$ . A selectivity, defined with respect to the number of N atoms in both  $\text{NO}_x$  and in  $\text{N}_2$ , can reach



**Figure 10.** Left: the guest–guest RDFs of the N atom of  $\text{N}_2\text{O}_4$  with all kinds of atoms in guest molecules. Right: number integrals of the N atom of  $\text{N}_2\text{O}_4$  with all kinds of atoms in guest molecules.

values up to about 1000. Simultaneously with adsorption, the chemical reaction  $\text{N}_2\text{O}_4 \leftrightarrow 2 \text{NO}_2$  takes place and has to be considered.

In the free gas phase, the  $\text{NO}_x$  exists mainly as  $\text{NO}_2$  even at 10 bar because of its low partial pressure. However, for the adsorbed phase, the restricted space within the porous MOF enhances the conversion of  $\text{NO}_2$  into  $\text{N}_2\text{O}_4$ , which is in accordance with the principle of Le Chatelier.

The  $\text{N}_2\text{O}_4$  molecules are strongly attracted by the lattice, much more than  $\text{NO}_2$ . The strong attraction of  $\text{N}_2\text{O}_4$  is the major reason for the high selectivity. This could be confirmed by an additional test simulation without the chemical reaction  $\text{N}_2\text{O}_4 \leftrightarrow 2 \text{NO}_2$ . In this situation, that is not possible in nature, the few  $\text{N}_2\text{O}_4$  that exist in the gas phase, were strongly adsorbed leading to even higher adsorption selectivity than in the real system with the reaction.

The selectivity increases with the decreasing concentration of  $\text{NO}_x$  in the mixture. This may be explained by the finding that the maximum of the adsorbed amount of  $\text{N}_2\text{O}_4$  does not depend much upon the concentration of  $\text{NO}_x$  in the gas phase. Thus, the lower concentration of  $\text{NO}_x$  in the gas phase means higher selectivity, according to eq 1.

The uptake of  $\text{NO}_x$  is strongly depending on the temperature. Thus, the  $\text{NO}_x$ -loaded MIL can easily be recycled by heating in a temperature swing procedure.

Because of the large and long-lasting fluctuations and also because of the particularly large computational effort for the adjustment of the  $\text{NO}_x/\text{N}_2$  ratio, our simulations have been restricted to only one material, namely, the MOF MIL-127 and have not been extended to other porous materials. However, it is the aim of this paper to prove the existence of the surprisingly large effect of the combined adsorption/reaction. Because of the reasons for the effect of the combined adsorption/reaction and corresponding to  $\text{NO}_2/\text{N}_2\text{O}_4$  separation in zeolites,<sup>12</sup> similar high  $\text{NO}_x/\text{N}_2$  selectivities can be expected for other porous materials particularly for ones with non-negligible partial charges on the lattice atoms.

#### 4. METHODOLOGY: GIBBS ENSEMBLE MC AND RXMC SIMULATIONS

Equilibrium between a gas phase in simulation box A and molecules adsorbed in MIL-127 in simulation box B is examined by Gibbs ensemble Monte-Carlo (GEMC), including the chemical reaction equilibrium between  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$ . Some information about GEMC for adsorption is given in Section S1 of the Supporting Information. The GEMC method and the home-made software Gibbon have already been used in the previous papers<sup>14,16,17,22–24</sup> for the treatment of adsorption equilibria. The RxMC method has been introduced in pioneering studies,<sup>25,26</sup> and a good description of both techniques, GEMC and RxMC, is given in the overviews,<sup>27,28</sup> while in Section S2 of the Supporting Information of this paper, details about the chemical reaction in the gas phase and its treatment by RxMC in this paper are given.

The basic concept of RxMC is predicated on the fact that the classical partition function is the phase space integral over the equilibrium probability density of the possible states of the system. The probability density for an ideal gas state can be calculated from the degrees of freedom of the gas molecules. This is also true for chemical reacting systems, and in this way, the ideal gas equilibrium constant can be calculated. Mutual interactions of the molecules and interactions with pore walls

are then involved explicitly in the RxMC method. Some more information about RxMC are given in Section S2 of the Supporting Information.

An overview over many successful applications of RxMC till 2008 can be found by Turner *et al.*<sup>29</sup> For example, the combination of adsorption in a restricted geometry (different zeolites and slit pore) and chemical reaction has been investigated by RxMC methods.<sup>12,30,31</sup> In a work of Fetisov *et al.*,<sup>31</sup> the reactive adsorption of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  in  $\text{Na}^+$ -exchanged zeolites has been examined. The simulations show that the presence of  $\text{Na}^+$  cations may change the equilibrium constant by orders of magnitude in comparison with the gas phase or the cation-free all-silica zeolite beta. This strongly supports the idea to use porous materials for separation purposes.

In the pioneering simulation paper of Matito-Martos *et al.*,<sup>12</sup> the same chemical reaction between  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  is considered which is the subject of the present paper. However, in the work of Matito-Martos *et al.*,<sup>12</sup> the  $\text{NO}_x$  reaction and adsorption are treated without the presence of other guest molecules such as  $\text{N}_2$ . A high selectivity between the two species of  $\text{NO}_x$  by combined adsorption and reaction has been found. Because almost only  $\text{N}_2\text{O}_4$  exists in the zeolite, this selectivity consequently can reach values above 1000.

One point that deserves special thoughtfulness is the fact that the internal degrees of freedom or the rotational degrees of freedom of molecules in confined space can be influenced by the confinement, even at high dilution of the guest molecules, which means that the high dilution equilibrium constant within the pore can differ from that of the ideal gas.<sup>32</sup> However, the equilibrium constant within the pores can hardly be measured directly, and partition functions of molecules in pores are also difficult to calculate. Thus, in most of the RxMC papers, like in Matito-Martos *et al.*,<sup>12</sup> the ideal gas partition functions or equilibrium constants of the ideal gas are used as approximation for the reaction within the pores at high dilution. Of course, the pore diameters must be larger than the molecule diameters of all involved species in order to allow rotation.

The question to be answered is now, how both kinds of  $\text{NO}_x$ , namely  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$ , can be separated from  $\text{N}_2$ . However, these two  $\text{NO}_x$  species are not only adsorbed from the gas phase outside the MOF but they are also reacting with each other. Hence, it is not straightforward how to find a measure for the removal of  $\text{NO}_x$  from the gas mixture. The ratio  $\text{NO}_2/\text{N}_2\text{O}_4$  in the ternary mixture with  $\text{N}_2$  is not easy to forecast; moreover, it fluctuates permanently. However, there is a conserved quantity: in the chemical reaction, the total sum of N atoms and also the total sum of O atoms are conserved, and the reaction takes place only between the both kinds of  $\text{NO}_x$  molecules. Therefore, we decided to consider the total amount of N atoms in all  $\text{NO}_x$  and calculate their ratio to the number of N atoms in all  $\text{N}_2$  molecules. We define a selectivity  $S_{\text{ar}}$  (the subscript <sub>ar</sub> means selectivity resulting from simultaneous adsorption and reaction) by the equation

$$S_{\text{ar}} = \frac{N_{\text{NO}_x, \text{B}} N_{\text{N}_2, \text{A}}}{N_{\text{N}_2, \text{B}} N_{\text{NO}_x, \text{A}}} \quad (1)$$

In eq 1,  $N_{\text{NO}_x, \text{A}}$  and  $N_{\text{NO}_x, \text{B}}$  are the sum of the numbers of all N atoms contained in  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  in box A or in box B, respectively.  $N_{\text{N}_2, \text{A}}$  is the number of N atoms in  $\text{N}_2$  in box A and so forth.



**4.1. Technical Details.** The guest–guest and guest–lattice interactions are calculated as a sum of two-body interactions between the atoms of guest molecules and atoms of guest molecules with the lattice atoms. A review article gives a comprehensive treatise over all kinds of interactions between adsorbed species and the lattice of MOFs or zeolites.<sup>33</sup> Here, we use Lennard-Jones potentials and additional Coulomb terms for the calculations. Formulas and the molecular interaction parameters can be found in Section S3 of the [Supporting Information](#).

The main advantage of MC simulations over molecular dynamics (MD) simulations is the much larger shift of the molecules per simulation step. This advantage would be lost if the lattice flexibility is taken into account because of the high frequencies of lattice vibrations. Therefore, MC simulations are usually performed with rigid lattice and rigid molecules. Moreover, this is justified for the investigation of adsorption equilibria because the changes of the size of the transport bottlenecks by oscillations, that are crucial for diffusion for example,<sup>34–37</sup> will possibly influence only the time scale of approach to the adsorption equilibrium rather than the adsorption equilibrium itself. Of course, the passage of all molecules through the bottlenecks must be at least possible in order to allow a homogeneously equilibrated system. Moreover, structural changes in the lattice caused by guest molecules, such as gate opening,<sup>18,22,38–41</sup> must not appear. Whether or not they appear can be examined, for example, by MD.

The common concentration of  $\text{NO}_x$  in air is too small to be treated by molecular simulations. We have decided, therefore, that the number of N-atoms that belong to the  $\text{NO}_x$  divided by the number of N atoms in  $\text{N}_2$  in box A (gas phase) should be 1:20. In order to check the concentration dependence, we also performed runs with a ratio of 1:40. In reality, the  $\text{NO}_x$  content of air is usually much less than 1:40; however, in the simulations, very small numbers of  $\text{NO}_x$  are infeasible because of the bad statistics. The particle numbers in box A that result in these ratios are corrected, if necessary, after each continuation run by adding or removing particles in gas box A before a new continuation run starts. Then, the equilibrium must be established newly during the next continuation run. It may be noted that the fluctuations are strong, particularly for higher dilution, and require run lengths of up to 500 million of simulation steps. Some fluctuations have very long persistence.

The runs are isobaric in box A following the algorithm of Berendsen *et al.*<sup>42</sup> We decided to do it isobaric with respect to the ideal gas pressure. This is the pressure that the gas would have if the ideal gas equation of state would be valid. At low pressure (up to a few bar, depending upon the gas mixture), the ideal gas pressure agrees with the real pressure. For the presentation of the results at higher densities, the corresponding real gas pressure for each data point was also calculated by the Peng–Robinson equation of state.<sup>43</sup> The difference to the ideal gas pressure was small in all cases considered in the present paper. Thus, the pressures given in the [Results and Discussion](#) section are the real gas pressures. However, these real gas pressures do not need to be known during the simulation. They are only calculated for a proper presentation of the results.

The technical reason for the adjustment to the ideal gas pressure, not to the real gas pressure, during the run, is that the pressure is calculated very often in isobaric simulations. This is carried out much more easily with less computer time

consuming for the ideal gas pressure. Moreover, doing it in this way, the simulations are independent of the choice of an equation of state and its parameters.

We examined the adsorption and reaction at two different temperatures 298 and 374.7 K in order to find the temperature dependence of the observed effects. In particular, it is an interesting question whether the porous solid can be loaded with  $\text{NO}_x$  at ambient temperature, and then, the loading can be removed at higher temperature. Thus, a temperature swing procedure would be possible. The temperature of 374.7 K has been chosen as the higher temperature because for this temperature, the equilibrium constant is given in the paper of Chao *et al.*<sup>13</sup> For an ideal gas, the equilibrium constant does not depend upon the pressure.

Adsorption and reaction happen simultaneously and interfere with each other. This makes the equilibration and the adjustment of a certain and fixed ratio of molecules difficult. For some data points at 298 K, more than 25 continuation runs of 10 million steps were necessary for equilibration not only to reach equilibrium but also to get the desired ratios of 20:1 or 40:1 of N atoms in  $\text{N}_2$  to those in  $\text{NO}_x$  by trial and error. Sometimes, the equilibrium and the desired concentration ratio seem to be reached after 15 runs, each with 10 million steps. To be sure, we checked this quick result by conducting an additional run of 100 million steps, and in some cases, we found that the results changed. Equilibrium has, of course, been reached after such an extremely long run but the ratio of 20:1 or 40:1 of N atoms in  $\text{N}_2$  to those in  $\text{NO}_x$  was not fulfilled anymore. Hence, adjusting particle numbers and more simulations have been necessary.

For low pressure and at 374.7 K, the number of  $\text{N}_2\text{O}_4$  molecules in the gas phase is almost zero, that is, close to the range of fluctuations. Thus, the value is not accurate. However, this is no real problem because first, this corresponds to the real situation, and second, the influence of such a small tracer of  $\text{N}_2\text{O}_4$  within the  $\text{NO}_2$  on the behavior of the system is negligible. Moreover, at 374.7 K, the amount of molecules of all kinds that are adsorbed in the MIL-127 is quite small. This results in fluctuations which are large in comparison to these small particle numbers.

Because of these difficulties and the large computational efforts for the adjustment of the ratio of different N-species, we decided not to compare different porous materials for this very special separation process. Instead, we wanted to prove the effect of the combined adsorption and reaction as quick as possible. The basic separation effect that will be demonstrated in this paper for MIL-127 should also show in other porous materials. This assumption is supported by the examination of  $\text{NO}_2/\text{N}_2\text{O}_4$  adsorption and reaction within several zeolites.<sup>12</sup> The authors defined a selectivity between  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$ —that means between educts and products of the reaction—which reached large values up to more than 1000 in the MFI zeolite.

For comparison with experiments, the real gas pressure can be found from the gas phase density by, for example, the Peng–Robinson equation of state.<sup>43</sup> However, material constants (e.g., critical data) are needed for this. Under ambient conditions,  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  only coexist and are in permanent reaction. Therefore, the measurement of thermodynamic properties of one of them separately is difficult, if at all possible, and therefore, parameters can normally not be found in the literature. This problem is solved by McCarthy *et al.*,<sup>44</sup> where fictive critical data for the single components have been

fitted to thermodynamic measurements of the mixture. Parameters for  $N_2$  can be found in the standard literature.<sup>45</sup>

For the random trial moves in the GEMC simulations, the relative frequencies of shifts, rotations, and swaps between boxes have been chosen to be 5:5:1. As long as microscopic reversibility is ensured, these ratios are only important for the duration of the equilibration of the run and do not influence the results. For the trial shifts, random changes of the coordinates between  $-0.5$  and  $0.5$  Å are attempted. A RxMC step has been tried every five steps with equal probability for simulation box A and simulation box B and for the forward reaction and the backward reaction.

The run length varied between several runs of 10 million steps each for one data point and up to 10 runs of hundred million steps. The computational effort needed depended upon the duration of the equilibration and the adjustment of the concentration ratios between the species in the gas phase (box A).

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.9b04494>.

GEMC for adsorption; chemical reaction of  $NO_x$ ,  $N_2O_4$ , and  $NO_2$  molecule; chemical reaction of  $NO_x$  in gas phase; RxMC; equilibrium constant for  $N_2O_4$  dissociation, interaction parameters, potential, and combining rule; atoms in guest molecules; and atoms in lattice of MIL-127 (PDF)

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### Notes

The authors declare no competing financial interest.

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