

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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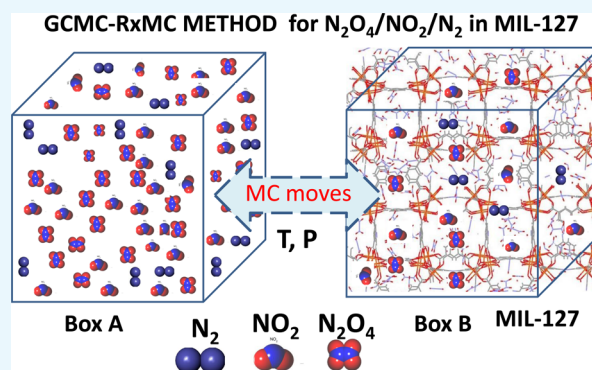


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ABSTRACT: A high selectivity of NO_x over N_2 (simulating air) is found in silico when studying the adsorption of the ternary mixture $N_2O_4/NO_2/N_2$ on the metal–organic framework MIL-127(Fe) by molecular simulations under consideration of the recombination 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.¹ 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 reduction² 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.^{3–12} 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.^{7,8,10,11} Instead, N_2 was sometimes only used to determine the porosity.⁶ 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.*⁷ and Matito-Martos *et al.*¹² mention and examine this chemical reaction that permanently happens among the NO_x under ambient conditions. In the paper of Han *et al.*,⁷ 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.*⁸). 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.*⁷ 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.⁸ 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.*¹⁰ 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.*¹¹ 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.*,¹² 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.*,¹³ 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.¹² 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.^{3,7} 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-workers⁸ 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.*¹² 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.¹⁴ 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.^{14,15} 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,¹⁴ both NO_2 and N_2O_4 must now be considered.

Because of their size, N_2O_4 molecules cannot penetrate into those ZIFs,¹⁴ 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^{14–18} or NO_2 capture.^{3,4}

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).¹⁹ 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.²⁰ MIL-127(Fe) has, for example, been used already to examine the separation of CO_2 from CO .¹⁷

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.

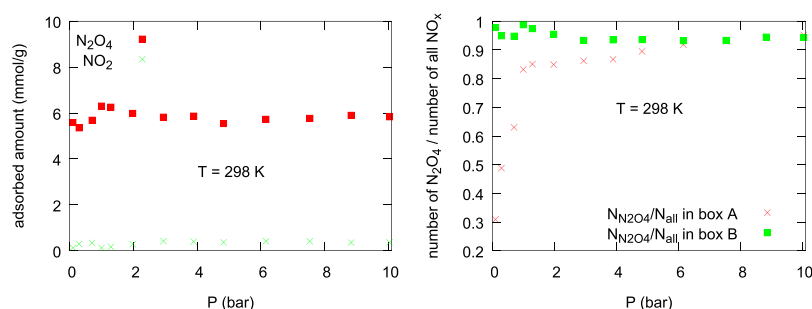


Figure 1. Left: adsorption/reaction isotherm of pure NO_x in MIL-127 at 298 K. Note that the majority of the adsorbed NO_x is present as N_2O_4 , and the saturation region of the isotherm is reached at low pressures. Right: ratio of N_2O_4 molecules to all NO_x molecules in box A (gas phase) and in MIL-127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

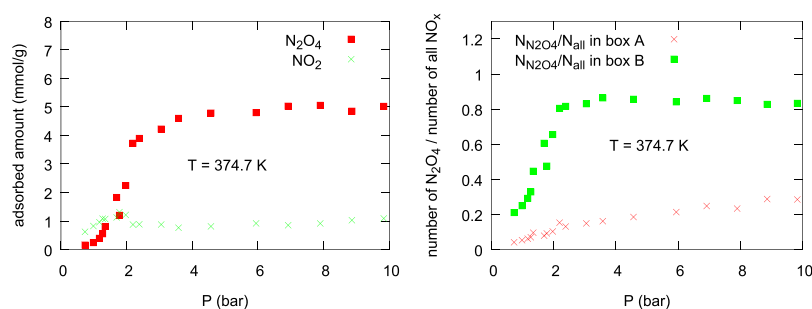


Figure 2. Left: adsorption/reaction isotherm of pure NO_x in MIL-127 at 374.7 K. Note that because of the endothermal splitting of N_2O_4 , the NO_2 concentration is enhanced at higher temperatures as compared to the one shown in Figure 1 (left). Right: ratio of N_2O_4/NO_x in MIL-127 in box A and in 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.¹² 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.¹² 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.¹²

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

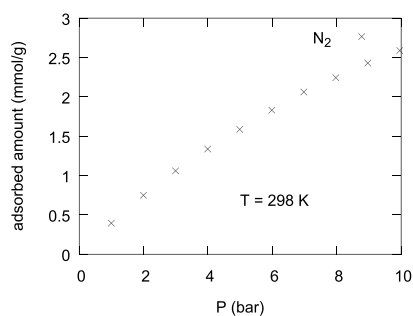


Figure 3. Amount of adsorbed N_2 as a function of pressure at 298 K for pure N_2 .

smaller. In order to see whether there are adsorption sites for N_2 , the RDFs of N_2 in the single component case have been examined.

Figure 4 shows the RDFs and number integrals of N_2 with the lattice atoms for which the RDF reaches the largest values. The case $N[N_2]-CN$ is the RDF of the N atom of 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 N_2 . For $N[N_2]-O[Fe]$, 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 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 N_2 and 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 $N_2O_4/NO_2/N_2$. The aim of this paper is to investigate the adsorption under the condition of simultaneously happening chemical reactions for the ternary mixture $N_2O_4/NO_2/N_2$. The equilibrium constant from studies of Chao *et al.*¹³ and Roscoe *et al.*²¹ 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 NO_x as well as for the mixture with 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 NO_x to N atoms in N_2 in box A was 1:20. Interestingly, a straight line fitted to the first points of the N_2O_4 curve would not point to the origin. This means that for low pressure, the adsorbed amount of N_2O_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 N_2O_4 with new ones enhances adsorption. Interestingly, the amount of N_2O_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 N_2 molecules. In the case of pure NO_x , it was about 6 mmol/g which is only 20% more than for the mixture with N_2 . Hence, the presence of N_2 does not reduce very much the amount of N_2O_4 within the porous solid except at very low pressure where the adsorption of pure N_2O_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 N_2O_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 N_2 is much lower than for the pure 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 N_2O_4 molecules to the number of 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 NO_x molecules in the gas phase are present as N_2O_4 molecules. Because one N_2O_4 molecule requires less space than two NO_2 molecules, this effect can also increase the amount of adsorbed NO_x , thus supporting a high selectivity of $NO_2:N_2O_4$ in the paper of Matito-Martos *et al.*¹² and of NO_x/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_{ar} as defined in eq 1 at 298 K and at different pressures. The ratio of N atoms in the NO_x to N atoms in N_2 has been chosen to be 1:20 or 1:40. The selectivity S_{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

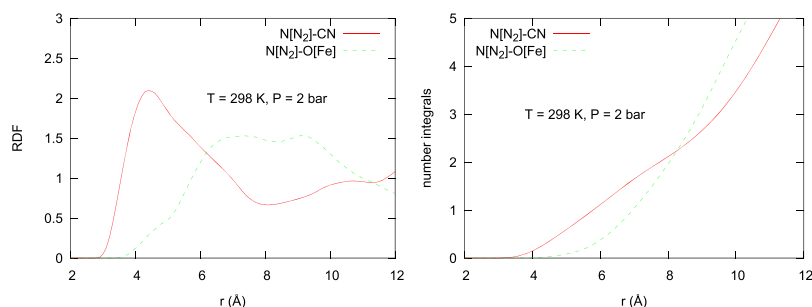


Figure 4. RDFs and number integrals of a single component N_2 adsorbed in MIL-127 at $T = 298$ K, $P = 2$ bar with two selected lattice atoms.

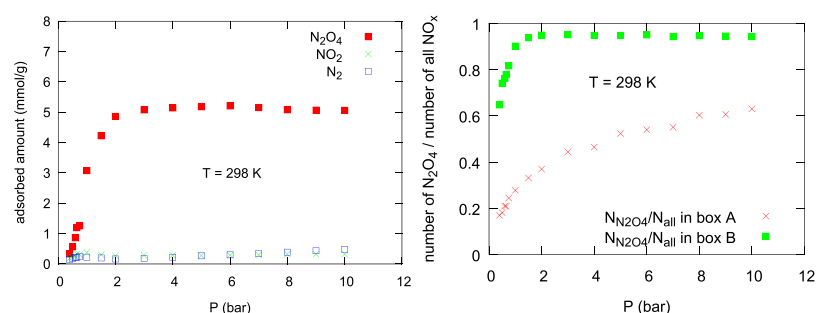


Figure 5. Left: amount of the adsorbed species in the ternary mixture $\text{N}_2\text{O}_4/\text{NO}_2/\text{N}_2$ in mmol/g as a function of pressure at 298 K at a ratio of 1:20 of N molecules in NO_x to N molecules in N_2 . Right: equilibrium ratio of the numbers of N_2O_4 molecules to the number of all NO_x molecules as a function of pressure in box A (gas) and box B (adsorbed) at 298 K.

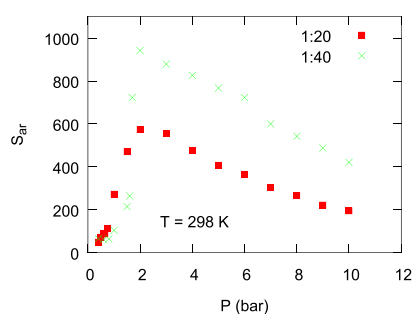


Figure 6. Adsorption/reaction selectivity S_{ar} resulting from both adsorption and NO_x reaction at 298 K at ratios 1:20 and 1:40 of N atoms in NO_x ($\text{N}_2\text{O}_4 + \text{NO}_2$) to N atoms in N_2 .

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 NO_x to the N atoms in 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 N_2O_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

	N_2O_4	NO_2	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
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. 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 N_2O_4 is the same within the range of fluctuations in all considered cases. Only in the case without N_2 , the potential energy of N_2O_4 may be somewhat lower but the difference is still comparable with the fluctuations of the calculations. The potential energy of NO_2 in the fictive case is lower than in the real ternary mixture. However, it is somewhat higher than in the case without N_2 . The negative average potential energy of the adsorbed N_2O_4 is almost twice that of NO_2 and 3 times that of N_2 . This explains the strong adsorption of N_2O_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 N_2O_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 N_2O_4 does not depend much upon the concentration of NO_x in the gas phase. Thus, lower concentration of NO_x in the gas phase means higher selectivity, according to eq 1. The fact that the maximum adsorbed amount of N_2O_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 NO_x and N_2 found within the MIL at 374.7 K and at various pressures. These

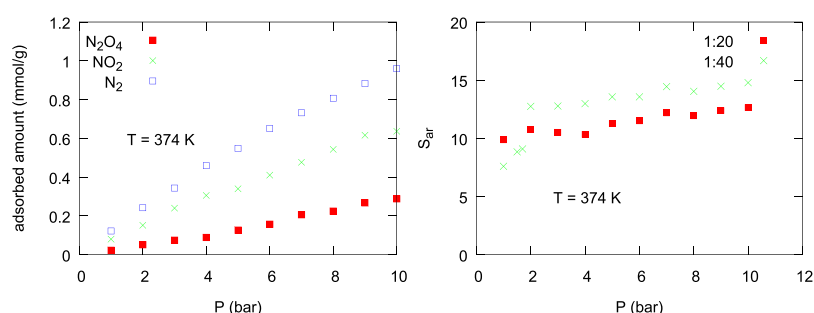


Figure 7. Left: the amount of molecules found in the MIL for the three particle sorts at 374.7 K as a function of pressure. The ratio of N atoms in NO_x ($\text{N}_2\text{O}_4 + \text{NO}_2$) to N atoms in N_2 is 1:20 in this case. Right: the adsorption/reaction selectivity S_{ar} resulting from simultaneous adsorption and reaction at 374.7 K at ratios 1:20 and 1:40 of N atoms in NO_x to N atoms in N_2 .

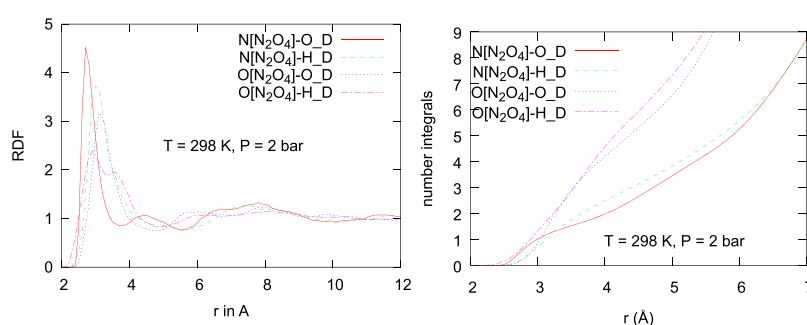


Figure 8. Left: RDFs of the N and O atoms of N_2O_4 with the strongest adsorption centers of the lattice, the O_{D} and H_{D} lattice atoms. Right: number integrals of the N and O atoms of N_2O_4 with the strongest adsorption centers of the lattice, the O_{D} and H_{D} lattice atoms.

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 NO_x to the N in 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 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 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 N_2O_4 with a lattice atom was found for the lattice atoms O_{D} and H_{D} . Hence, we checked these RDFs and the corresponding coordination numbers. Figure 8 shows that the atom-type O_{D} is attractive

for N_2O_4 . The peak of the N is higher and somewhat closer to the O_{D} than the peak for the O atom of N_2O_4 indicating the favorite geometrical arrangement. For more information, we checked also the number integrals.

For N_2O_4 with O_{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 N_2O_4 are situated close to each O_{D} atom. This corresponds to 0.9 N_2O_4 molecules because each N_2O_4 molecule contains two N atoms. For the O atom in N_2O_4 , the inflection with respect to O_{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 N_2O_4 , this corresponds also to 0.9 N_2O_4 molecules within the first shell of neighbors. Hence, these lattice atoms are not really adsorption centers.

For the N in N_2O_4 with H_{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 N_2O_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 N_2O_4 molecule. For the O in N_2O_4 with H_{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 NO_2 with the O_{D} and H_{D} lattice atoms. Interestingly, the probability density to find the N atom of NO_2 close to the O_{D} is much smaller than 1.0, which is in contrast to the N atom in N_2O_4 . This is obviously because these sites are mostly occupied by N_2O_4 molecules. For NO_2 , no such strong peaks are found in the RDFs as those for N_2O_4 shown in Figure 8. The evaluation

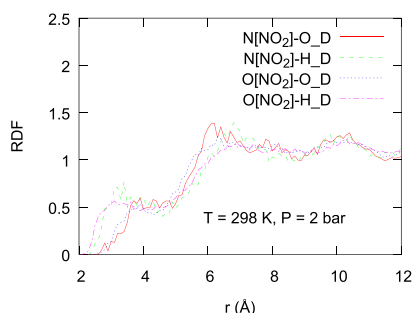


Figure 9. RDFs of the N and O atoms in NO_2 with the O_D and H_D lattice atoms.

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 N_2O_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 N_2O_4 with all other atoms in guest molecules in order to see whether some of them, particularly NO_2 , form clusters with the N_2O_4 .

As shown in Figure 10, left side, the RDFs of the N atom of N_2O_4 with all atoms in guest molecules are given. Of course, the RDF of N in N_2O_4 with N in N_2O_4 is the RDF with N of another N_2O_4 molecule, not those of the same one. The highest peaks, as shown in Figure 10, correspond to the N atoms in N_2O_4 , in NO_2 , and even to the N in 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 N_2O_4 with the atoms of another N_2O_4 is not very strong. Thus, clustering between N_2O_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 N_2O_4 is that with N in NO_2 and also the one between the N atoms in different N_2O_4 has almost the same height and position in spite of the large size of the

N_2O_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 NO_2 and N_2 can be seen. For example,

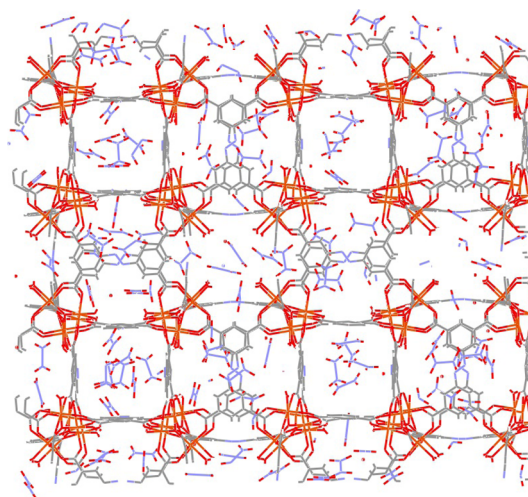


Figure 11. MIL-127 with adsorbed molecules. The molecules and lattice bonds are indicated by sticks. NO_2 molecules have the shape of a V. The N_2O_4 molecules have the shape of two connected Y, and N_2 is linear.

there is one N_2 and one NO_2 in the rightmost part in the middle of the picture. N_2O_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 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 NO_x over N_2 . A selectivity, defined with respect to the number of N atoms in both NO_x and in N_2 , can reach

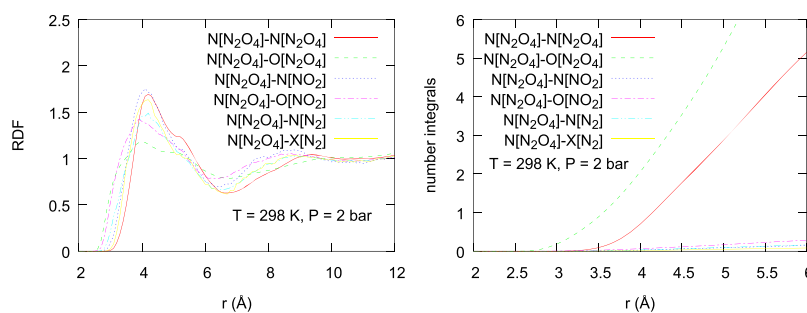


Figure 10. Left: the guest–guest RDFs of the N atom of N_2O_4 with all kinds of atoms in guest molecules. Right: number integrals of the N atom of N_2O_4 with all kinds of atoms in guest molecules.

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 NO_x exists mainly as 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 NO_2 into N_2O_4 , which is in accordance with the principle of Le Chatelier.

The N_2O_4 molecules are strongly attracted by the lattice, much more than NO_2 . The strong attraction of N_2O_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 N_2O_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 NO_x in the mixture. This may be explained by the finding that the maximum of the adsorbed amount of N_2O_4 does not depend much upon the concentration of NO_x in the gas phase. Thus, the lower concentration of NO_x in the gas phase means higher selectivity, according to eq 1.

The uptake of NO_x is strongly depending on the temperature. Thus, the 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 NO_x/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,¹² similar high NO_x/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 NO_2 and N_2O_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^{14,16,17,22–24} for the treatment of adsorption equilibria. The RxMC method has been introduced in pioneering studies,^{25,26} and a good description of both techniques, GEMC and RxMC, is given in the overviews,^{27,28} 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.*²⁹ For example, the combination of adsorption in a restricted geometry (different zeolites and slit pore) and chemical reaction has been investigated by RxMC methods.^{12,30,31} In a work of Fetisov *et al.*,³¹ the reactive adsorption of H_2S and CO_2 in Na^+ -exchanged zeolites has been examined. The simulations show that the presence of 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.*,¹² the same chemical reaction between N_2O_4 and NO_2 is considered which is the subject of the present paper. However, in the work of Matito-Martos *et al.*,¹² the NO_x reaction and adsorption are treated without the presence of other guest molecules such as N_2 . A high selectivity between the two species of NO_x by combined adsorption and reaction has been found. Because almost only N_2O_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.³² 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.*,¹² 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 NO_x , namely NO_2 and N_2O_4 , can be separated from N_2 . However, these two 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 NO_x from the gas mixture. The ratio $\text{NO}_2/\text{N}_2\text{O}_4$ in the ternary mixture with 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 NO_x molecules. Therefore, we decided to consider the total amount of N atoms in all NO_x and calculate their ratio to the number of N atoms in all N_2 molecules. We define a selectivity S_{ar} (the subscript ar 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 NO_2 and N_2O_4 in box A or in box B, respectively. $N_{\text{N}_2, \text{A}}$ is the number of N atoms in 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.³³ 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,^{34–37} 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,^{18,22,38–41} must not appear. Whether or not they appear can be examined, for example, by MD.

The common concentration of 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 NO_x divided by the number of N atoms in 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 NO_x content of air is usually much less than 1:40; however, in the simulations, very small numbers of 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.*⁴² 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.⁴³ 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 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.*¹³ 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 N_2 to those in 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 N_2 to those in 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 N_2O_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 N_2O_4 within the 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.¹² The authors defined a selectivity between NO_2 and N_2O_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.⁴³ However, material constants (e.g., critical data) are needed for this. Under ambient conditions, NO_2 and N_2O_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.*,⁴⁴ 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.⁴⁵

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

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