

A molecular dynamics study of the diffusion of a hydrocarbon in $\text{AlPO}_4\text{-5}$ molecular sieve

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RESUMEN: En este trabajo se presenta un estudio a partir de técnicas de Dinámica Molecular de la difusión de etano en el tamiz molecular tipo aluminofosfato $\text{AlPO}_4\text{-5}$. Los cálculos se realizaron a diferentes temperaturas y cantidades de moléculas de etano por celda unitaria. Las simulaciones se realizaron en condiciones de enrejado rígido y de enrejado vibrante. De acuerdo a los resultados obtenidos la difusión molecular del etano en una estructura de $\text{AlPO}_4\text{-5}$ libre de defectos sigue un régimen normal. Este resultado coincide con los experimentos de Dispersión cuasielástica de Neutrones (QENS por sus siglas en inglés). Se obtuvo además la energía de activación para una cantidad fija de moléculas de etano por celda unitaria. Los cálculos realizados en condiciones dinámicas muestran la influencia de las vibraciones del enrejado cristalino en la difusión molecular. Particularmente, las vibraciones del enrejado pueden ser un factor a considerar cuando las dimensiones moleculares son del orden del diámetro del canal. No obstante, de acuerdo a los resultados obtenidos en nuestro estudio este hecho no provoca un cambio cualitativo en el régimen de difusión de las moléculas de etano (con un diámetro molecular de ~ 3.8 Å) en el canal de 12-miembros del $\text{AlPO}_4\text{-5}$.

ABSTRACT: In this paper a computational study of the ethane diffusion in $\text{AlPO}_4\text{-5}$ molecular sieve by classical molecular dynamics techniques is presented. Calculations were performed at different temperatures and loading of ethane molecules per $\text{AlPO}_4\text{-5}$ unit cell. Static and dynamics $\text{AlPO}_4\text{-5}$ framework conditions in the calculations were analyzed. According to the results of the simulations the molecular diffusion of ethane in a defect-free $\text{AlPO}_4\text{-5}$ crystal structure occurs *via* a normal regime and not as single-file diffusion in agreement with the quasi-elastic neutron scattering (QENS) experiments. The simulated activation energy for a particular loading of the ethane molecules is calculated. Moreover, the calculations performed in dynamical conditions show the influence of the framework vibrations on the molecular diffusion. Particular, the framework vibrations can be a factor to take into account when the molecular dimensions are close to the channel diameter. However, according to our calculations this fact does not produce a qualitative

change in the diffusion regime of the ethane molecules (with a molecular diameter ~ 3.8 Å) in the 12-member channel of the $\text{AlPO}_4\text{-5}$ unit cell.

INTRODUCTION

The diffusion of hydrocarbon molecules inside the channel of zeolites is an essential phenomenon in many industrial applications of these materials.^{1,2} One type of diffusion, the single-file diffusion (sfd), has recently received a particular attention.³⁻¹² Single-file diffusion occurs in zeolite with a one dimensional pore structure as soon as the guest molecules are too large to be able to pass each other within the channels^{6, 13}. The best known feature of the single-file diffusion is that the time-dependent mean-square displacement of the tracer particle, $\langle \Delta z^2(t) \rangle$, is proportional to $t^{0.5}$ at long times, in contrast with the usual Einstein relation, $\langle \Delta z^2(t) \rangle \propto t$. This fact was predicted over 20 years ago¹⁴, but was experimentally verified much more recently.¹³

Much of the modeling of single-file diffusion in zeolites has been based on lattice-gas model (LG)^{1, 8, 14}. The main assumption about these LG models is that all the molecular

diffusion occurs *via* hops of the individual molecules between adjacent binding sites. Also, several theoretical studies⁹⁻¹² have shown that diffusion could be dominated by concerted events in which multiple molecules move together. This fact is possible because of the strong mismatches between the distance of the binding sites along the pore and the distance between adsorbed molecules that minimize the adsorbate-adsorbate potential.

The intracrystalline diffusion of ethane in the aluminophosphate $\text{AlPO}_4\text{-5}$ has been extensively studied.⁶⁻¹³ The $\text{AlPO}_4\text{-5}$ unit cell presents approximately cylindrical pores parallel to the *c* crystallographic axis of nominal diameter 7.3 Å. The molecular diffusion essentially occurs in the one-dimensional channel of 12 members. Experimental results¹³ using Pulsed Gradient Field (PGF)-NMR confirmed the existence of a *sfd* diffusive regime. However, a recent

paper of Jobic *et al.*⁵ reported a quasi-neutron scattering (QENS) study and they observed that the ordinary 1-D diffusion is in disagreement with the previous pulsed-field gradient results obtained by Gupta *et al.*¹³ Both methods are complementary because the molecular migration is followed over a few unit cells with QENS (time scale ≈ 1 ns) and over whole crystal with PGF NMR (time scale ≈ 1 ms). The apparent contradiction between both experimental results is explained by assuming that different $\text{AlPO}_4\text{-5}$ structures have been used in the experiments.

In this paper, a study of the ethane diffusion in $\text{AlPO}_4\text{-5}$ by semiclassical Molecular Dynamics techniques is presented. Diffusion coefficients at different loading of ethane molecules and temperatures are calculated. The paper attempts to obtain evidence of a single-file diffusion mechanism for the ethane molecules in $\text{AlPO}_4\text{-5}$. A com-

parison between the results with rigid and vibrating models of the $\text{AlPO}_4\text{-5}$ framework is presented.

COMPUTATIONAL METHODOLOGY

Calculations were performed in the hexagonal P6cc unit cell with parameters $a=b=13.7707$ Å and $c=8.3789$ Å. In Fig. 1 the structure running along *c* is shown. The diffusion of ethane occurs in the 12 member channel. With the aim of studying the influence of the vibrations on the diffusion both static and dynamic models for the crystal lattice were considered. The vibrating model assumes the harmonic approximation¹⁵ for (Al, P)-O and O-O interactions and only first neighbors were considered as interacting atoms. Likewise, P-Al contacts were included. The potential parameters used¹⁵ are shown in Table 1.

Figure 1. The $\text{AlPO}_4\text{-5}$ crystal structure running along *c* is shown.

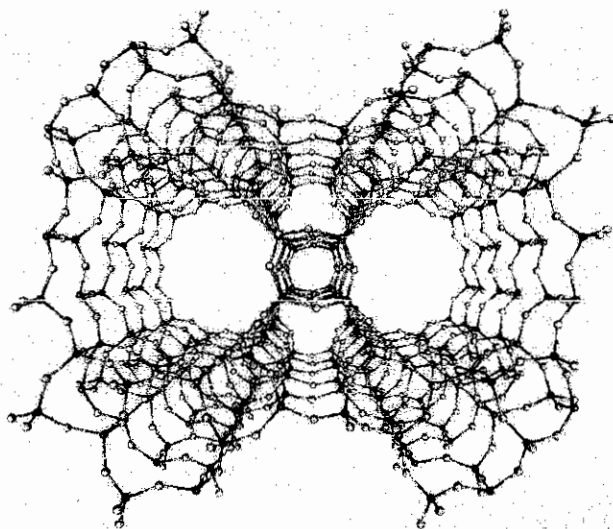


Table 1. Parameters for the effective harmonic potential for aluminophosphates molecular sieves (Energy in kJ mol^{-1} , Distances in nm)*

	Al - O	P - O	O - Al - O	O - P - O	Al - P
K	299880	367560	92048	92048	2092
r_0	0.1720	0.1516	0.280873*	0.247560*	0.32

* AlO_4 and PO_4 are assumed to be perfect tetrahedral structures at equilibrium, so these parameters are not independent

As for zeolites, the initial topology of the framework bonds was retained during the molecular dynamics simulation. The directional character of (Al, P)-O bonds was ensured by the O-O potential functions which do not correspond to a chemical bond but takes the place of a potential, depending on an angle between bonds, and makes calculations simpler. Recently, this model, with the potential parameters reported in Table 1, has been used for studying the ethane diffusion in $\text{AlPO}_4\text{-5}$.¹⁶

In earlier calculations, ethane molecules were modeled as spherical Lennard-Jones (LJ) particles in an $\text{AlPO}_4\text{-5}$ static framework.⁶ We modeled ethane molecules with two oscillating

interaction sites, considering the CH_3 group as a single interaction center. To preserve the possibility of full guest-host dynamical coupling, a Morse potential describes the intramolecular bond, with parameters derived from spectroscopic data.¹⁷ For the interaction ethane- $\text{AlPO}_4\text{-5}$ the site-to-site Lennard-Jones potential was adopted.¹⁸ Moreover, the Kisieliev model¹⁹ was employed. This model considers that the contributions of the Al and P atoms to the external potential are negligible. Thus, only the interaction ethane-oxygen ($\text{AlPO}_4\text{-5}$) was considered. The guest-host potential parameters used in the calculations are shown in Table 2.

A molecular dynamics box with $1 \times 1 \times 12$ -unit cells was considered

and the number of sorbed ethane molecule has been changed according to the loading: 4 molecule for a loading of 0.33 molecules per unit cell, 3 molecules for a loading of 0.25 molecule per unit cell, 2 molecules for a loading of 0.165 molecule per unit cell and 1 molecule for a loading of 0.082 molecule per unit cell. All the simulated systems were thermalized in the microcanonical ensemble by scaling the atom velocities at running temperatures (100, 300, 400 and 500 K) for 1 ns. Production runs of 10, 20 and 35 ns were then carried out using a time step of 1 fs. Finally, the center of mass coordinates and the velocities of ethane molecules were stored every 32 fs.

Table 2. Guest-host and guest-guest potential parameters used in the calculations

Parameter	Value a)	Value b)
$\sigma/\text{\AA}$	3.775	3.461
$\epsilon/\text{kJmol}^{-1}$	0.867	1.0

a) Lennard-Jones 12-6 guest-guest potential parameters¹⁸

b) Lennard-Jones 12-6 guest-host potential parameters¹⁸

RESULTS AND DISCUSSION

First, we performed molecular dynamic simulations assuming the $\text{AlPO}_4\text{-5}$ rigid framework and at low loading (0.082 ethane molecules per unit cell). After an equilibration MD run, productive runs of 10-20 ns were recorded. In Fig. 2, the dependence of the ethane center-of-mass (CM) mean square displacement (MSD) with the observation time at 300 K is presented. The behavior of the (CM) MSD is in agreement with a normal diffusion regime. With the objective of preventing the possible influence of the loading on the diffusive regime, simulations at higher loadings were performed. In Table 3 the diffusion coefficients and the exponent of the time are reported for different numbers of ethane molecules per unit cell. The exponents are in all the cases very

close to one which means that the diffusion for these loadings is according to a normal regime. Also, for the experimental loading (~ 0.7 molecules per unit cell)⁵ a very long trajectory (50 ns) was performed but no essential difference with the more shortest runs was observed. The simulated coefficient of diffusion at this temperature and loading ($1.8 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$) is very similar to the experimental value⁵ ($1.4 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$). This result supports the quality of the proposed potential model.

More information about the diffusion process can be obtained from the ethane-ethane center-of-mass distribution function (rdf) calculated at different loadings (Fig. 4). The peaks correspond to the most probable positions of two ethane Molecules in the channel. The intensity of the peaks increases with

the loading. This fact could suggest the existence of a concerted motion of the ethane molecules during the diffusion process. However, this fact does not seem to affect the diffusion regime at short-time scale. The simulated results are in agreement with the quasi-elastic neutron scattering (QENS) experiments.⁵

Subsequently, the dependence of the diffusion coefficients on the temperature was studied. The range of the temperature was $100 \text{ K} \leq T \leq 500 \text{ K}$. In this respect, Fig. 3 shows a log-log graph with the dependence between the diffusion coefficients and $1/T$ (for a loading of 0.33 ethane molecules per unit cell). Because of the diffusion in microporous materials is an activated process, diffusion coefficients are fitted according to the Arrhenius function:

$$D = D_0 \exp [-E_a/RT] \quad (1)$$

Here E_a is the activation energy and R is the constant of the gases

The activation energy obtained by fit of the Arrhenius equation was 250 K. This value is very similar to the reported by Sholl *et al.*¹⁰ considering a stepwise dimer diffusion model. Finally, a simulation with vibrating framework was performed. In Fig. 5 the (CM) mean square displacement (MSD) on the observation time at 300 K and with a loading of 0.33 molecules per $\text{AlPO}_4\text{-5}$ unit cell is presented. At long times the curve goes away from the results with fixed framework. However, the MSD can not be fitted by a $t^{0.5}$ type relation. Two aspects

can be commented with respect to the latter result:

- 1) the influence of the interaction guest molecule-framework in the molecular diffusion. This fact has been recently discussed by different authors^{20, 21} and is an essential factor to take into account when the molecular dimensions are close to the channel diameters. Ethane has a molecular diameter ~ 3.8 Å, approximately, the half of the 12 members effective diameters, ~ 7.3 Å
- 2) the normal diffusive behavior of the ethane diffusion in a defect-free

$\text{AlPO}_4\text{-5}$ crystal structure according to the QENS experiments⁵.

Particularly, in the latter point, the existence of defects in the crystalline structure of the $\text{AlPO}_4\text{-5}$ (vacancies, impurities, etc.) could affect the diffusive regime of the ethane molecules in the channel. However, this mechanism is only appreciable at longer time scale ($\sim 1\text{-}300$ ms) as reported by the (PFG)-NMR experiment.¹³ The behavior of the rfd of the ethane molecules (Fig. 4) obtained from the dynamics calculations supports this possibility.

Table 3. The diffusion coefficients and time exponent are reported for different loading

Loading/ molecules per			
Temp./K	unit cell	$D/\text{\AA}^2\text{ ps}^{-1\text{ a)}}$	$\alpha^{\text{ b)}}$
100	0.333	1.48	1.00
200	0.333	6.60	0.99
300	0.333	9.25	0.99
400	0.333	13.25	0.987
500	0.083	43.3	0.970
300	0.167	37.5	0.975
300	0.250	22.5	0.970

a) Linear fit of the MSD in the range between 1000 and 2000 ps

b) $\langle z^2(t) \rangle = At^\alpha$

Figure 2. The dependence of the ethane center-of-mass (CM) mean square displacement (MSD) on the observation time at 300 K is shown

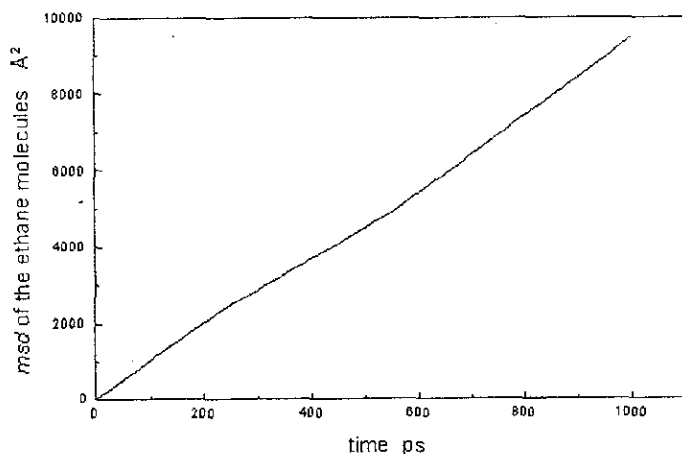


Figure 3. Diffusion coefficients at different temperatures. Continuum line represents the Arrhenius function fit. The activation energy obtained from the calculation is 254.33 K. A loading of 0.33 ethane molecules per unit cell was used.

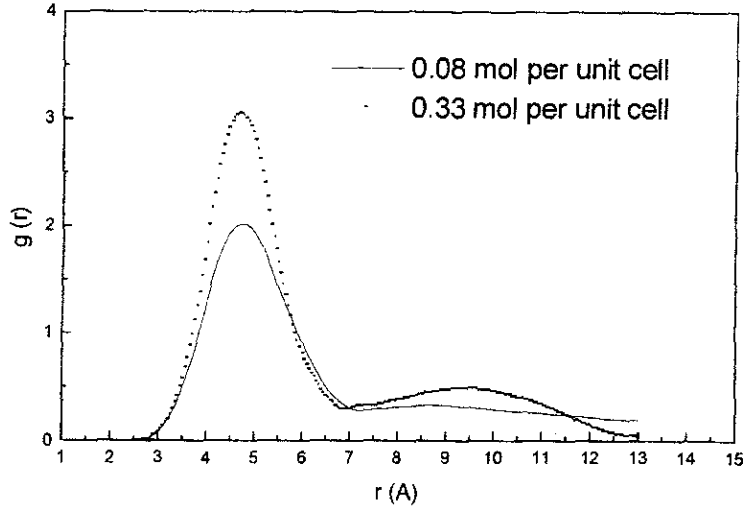


Figure 4. The radial distribution function (rdf) for the ethane molecules at different loadings.

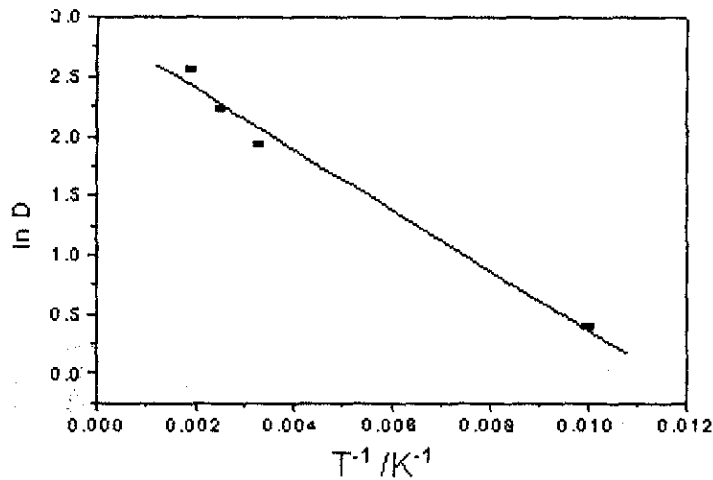
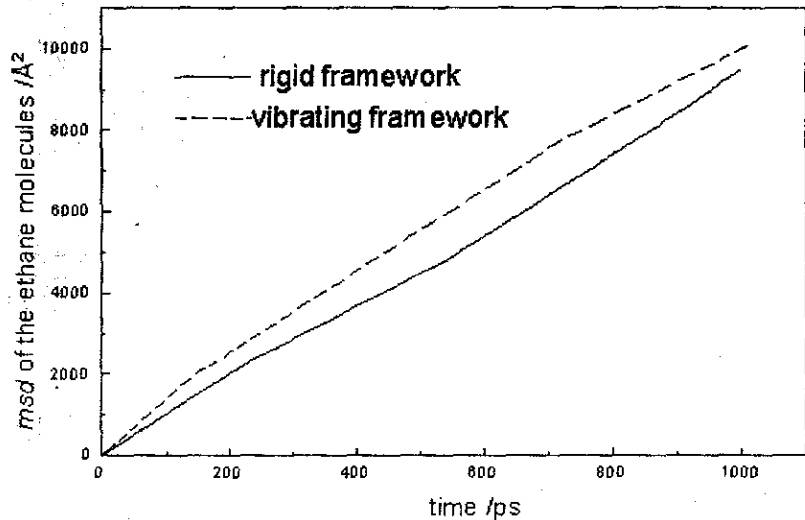


Figure 5. The dependence of (CM) MSD of the observation time at 300 K and with a loading of 0.33 molecules per $\text{AlPO}_4\text{-5}$ unit cell. A vibrating $\text{AlPO}_4\text{-5}$ framework was considered.



CONCLUSIONS

The most important conclusion is that the molecular diffusion of ethane in a defect-free $\text{AlPO}_4\cdot 5$ crystal structure occurs *via* a normal regime and not a single-file diffusion. The results were obtained for different loadings of the ethane molecules per $\text{AlPO}_4\cdot 5$ unit cell and in a broad temperature range. The simulated normal diffusion of ethane is in agreement with the quasi-elastic neutron scattering (QENS) measurement of Jobic *et al.*⁵. Also, we study the influence of the framework vibrations on the diffusion of ethane and we have found that it is an essential factor to take into account when the molecular dimensions are close to the channel diameters.

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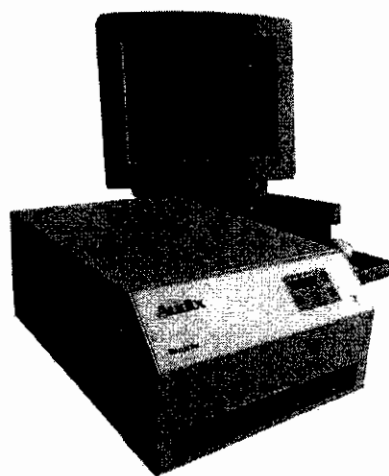
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