THEORETICAL STUDIES ON THE AFFINITY OF CO_2 AND N_2 MOLECULES TO SOLID SURFACES

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Abstract - Materials suitable for inorganic membranes with high efficiency for the gas separation process were studied by means of computational chemistry. It was shown that the difference in affinities of molecules to surfaces estimated from adsorption energies on model clusters is an important factor in making an effective membrane. Magnesia and alumina were shown to be effective in CO_2/N_2 separation system while silica and titania should not be selective materials.

1. INTRODUCTION

Much attention has been recently given to membrane gas separation technologies at high temperatures with respect to environmental protection and chemical reactions. Since inorganic membranes are highly thermal and chemical resistant, they would be usable under extreme conditions where the well-established organic polymer membranes cannot function [1]. Thus prospective application of inorganic membranes to direct removal of CO_2 from exhaust gases discharged from power station or factory would make separation system with low energy loss .

In general, gas separation by inorganic membranes can be described by three transport mechanisms: Knudsen diffusion, surface diffusion, and molecular sieving. Knudsen flow separation is based on the inverse square root ratio of the molecular weights of separated molecule. In the case of CO_2/N_2 separation, N_2 molecules can permeate easier than CO_2 and the expected separation factor is 0.8. As pore size decreases, other transport mechanisms may be involved. Molecular sieving separation [2] which is performed by microporous materials like zeolite is primary based on much higher diffusion rates of the smallest molecule. Surface diffusion mechanism is based on the affinity difference where diffusion selectivity favors the molecule with the strongest affinity for the membrane surface. The surface diffusion is a suitable mechanism for the separation system of molecules of similar weight or size and has already been proposed to explain the separation of CO_2 and N_2. Kusakabe *et al.* [3] reported that the $BaTiO_3$ membranes show high performance in CO_2 separation due to their strong affinity for CO_2. Uhlhorn *et al.* [4] doped an MgO cluster on a γ-alumina membrane and confirmed an increase in CO_2 adsorption, but they could not get high permeation rate of CO_2. They supposed that too strong affinity of CO_2 for MgO prevented it from smooth mobility over the surface.

However, no systematic theoretical study utilizing affinity difference has been reported so far on the gas permeation through inorganic membranes. In the present study, we apply the quantum chemical Density Functional Theory (DFT) method and Computer Graphics (CG) [5] technique to evaluate the affinity between various materials and surfaces, and to find factors characterizing surfaces with the affinity strong for CO_2 and weak for N_2, which is a key function in designing an efficient membrane.

2. MODELS AND METHODOLOGY

We have investigated the materials which are well known substrates for inorganic

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membranes: MgO, α-Al$_2$O$_3$, SiO$_2$ and TiO$_2$ (rutile). In order to study theoretically adsorption energies of CO$_2$ and N$_2$ molecules on these materials, clusters modeling these surfaces have been constructed on the basis of experimental structural data [6]. For MgO and α-Al$_2$O$_3$ the clusters consisted of a M$_2$O$_2$ (M=Mg, Al) unit while for SiO$_2$ and TiO$_2$ (rutile) a MO$_4$ (M=Si, Ti) unit has been selected, with geometrical parameters taken from the experimental structure. In the case of Al$_2$O$_3$, SiO$_2$ and TiO$_2$ where the covalent bonding prevails, dangling external oxygen bonds were saturated with hydrogens, which positions were optimized. Two modes of adsorption were considered on magnesia and alumina, namely on-top and bridging positions, whereas only the on-top position was assumed on silica and titania. Figures 1 to 6 show the considered adsorption geometries for the CO$_2$ molecule. Equivalent models were used in the case of nitrogen molecule adsorption.

The calculations of the electronic structure and energetically parameters were performed by means of the quantum chemical density functional methodology [7] which already proved to be a very good tool for investigation of metal oxides [8]. Computational results were obtained using software programs from Biosym Technologies of San Diego, DFT calculations were done with the DMol program [9] and graphical displays were printed out from Insight II molecular modeling system. All computations were held within local density approximation with Janak-Moruzzi-Williams functionals and double numerical plus polarization basis sets [10].

In order to calculate surface-molecule affinities, a potential energy curve with respect to variable surface-molecule distance was computed for each case, from which the optimum distance and energy were evaluated. Other geometrical parameters were kept constant during the calculations. The appropriate adsorption energies were then calculated as the total energy difference between the adsorption system and the bare cluster.
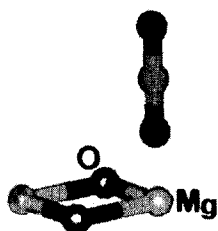

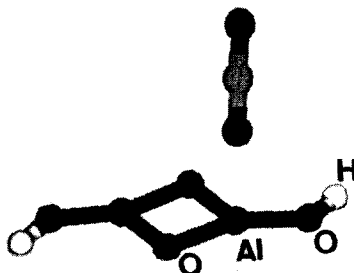Fig. 1 On-top adsorption geometry for the CO$_2$ molecule and MgO.

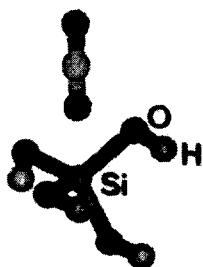Fig. 2 On-top adsorption geometry for the CO$_2$ molecule and α-Al$_2$O$_3$.

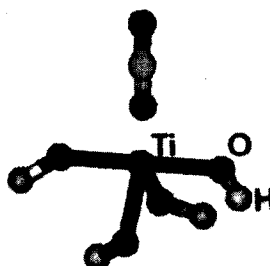Fig. 3 On-top adsorption geometry for the CO$_2$ molecule and SiO$_2$.

Fig. 4 On-top adsorption geometry for the CO$_2$ molecule and TiO$_2$ (rutile).

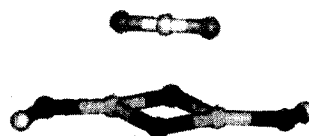Fig. 5 Bridging adsorption geometry for the CO$_2$ molecule and MgO.

Fig. 6 Bridging adsorption geometry for the CO$_2$ molecule and α-Al$_2$O$_3$.

3. RESULTS

The calculated potential energy curves for the on-top adsorption model on studied surfaces are shown in Fig. 7.a for CO_2 and in Fig. 7.b for N_2 molecule, respectively. The energy scale has been shifted assuming the bare cluster total energy as the zero energy reference level in each case thus the minimum on each curve defines directly the appropriate surface-molecule affinity. It may be easily seen that the CO_2 molecule was strongly bound on titania, alumina and magnesia with only weak adsorption on silica. The same holds for the nitrogen molecule. Similar curves were obtained for the case of the bridging adsorption models. There appeared, however, much bigger difference in behavior of CO_2 and N_2 in this case: carbon dioxide was found to be adsorbed much stronger on magnesia and alumina whereas bridging adsorption of nitrogen on these materials was very weak.

Numerical results of the calculations are displayed in Tables 1 for CO_2 and N_2 adsorption. In the tables the following properties are given: optimum adsorption distance R [Å], adsorption energy E [kcal/mol] and the molecule - surface charge transfer ΔQ. It can be seen from the table that the largest affinity was found for the adsorption of carbon dioxide in the bridging position on magnesia surface, with the binding energy of -18.7 kcal/mol. Nitrogen binds to the magnesia surface in the on-top position, but the adsorption energy is significantly lower (-12.6 kcal/mol). On alumina both molecules are adsorbed with moderate strength, however, the affinity difference was found to be significant in this case. On silica either of the studied molecules undergoes only weak adsorption. The discussed trends in surface affinities are confirmed by inspecting optimum adsorption distances and the charge transfer. In the case of silica and bridging position of nitrogen on magnesia or alumina, the adsorption distance is large and the charge transfer negligible, which indicates only weak, physical adsorption.
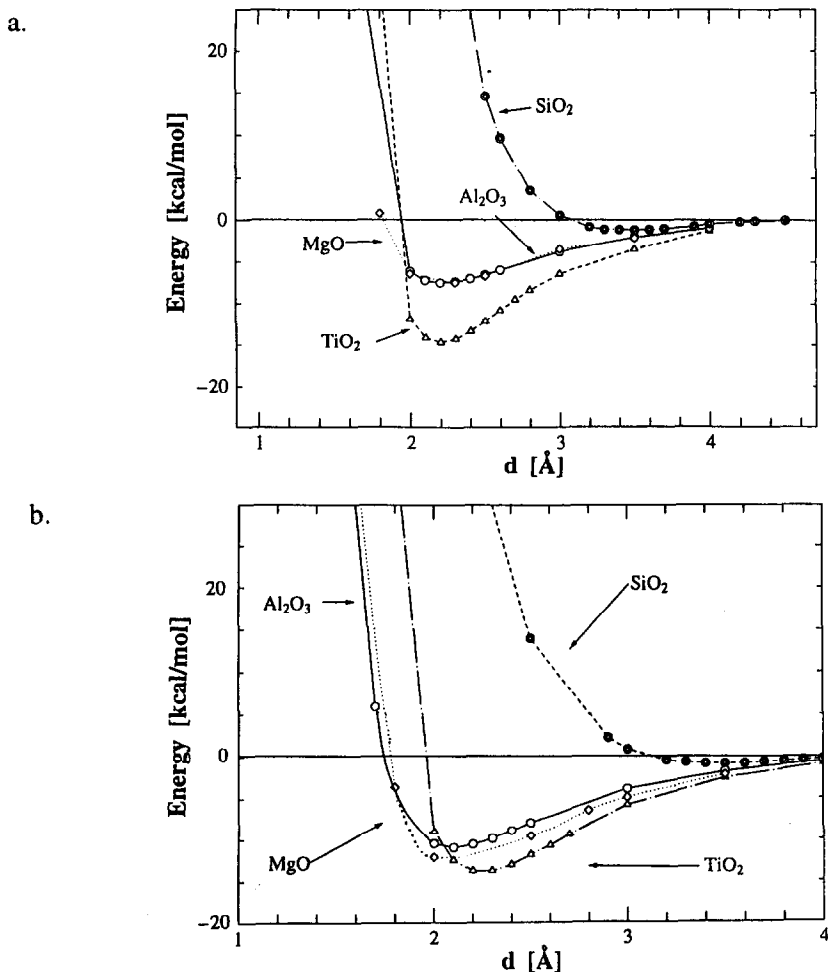
a.

b.

Fig. 7   The calculated potential energy curves for the on-top adsorption model on studied surfaces for CO_2 (a) and for N_2 (b).

Table 1. Optimum adsorption energies, distances and molecule - surface
charge transfer for carbon dioxide molecule and nitrogen molecule.

Cluster model		R [Å]		E [kcal/mol]		ΔQ [e]	
		CO_2	N_2	CO_2	N_2	CO_2	N_2
MgO	on-top	2.3	2.0	-7.44	-12.56	-0.012	-0.184
	bridging	2.3	2.7	-18.74	-3.49	-0.118	-0.054
Al_2O_3	on-top	2.2	2.1	-7.44	-11.40	+0.117	+0.176
	bridging	2.4	2.3	-13.19	-3.22	+0.123	+0.045
SiO_2	on-top	3.4	3.5	-1.44	-1.37	+0.006	+0.012
Ti O_2	on-top	2.2	2.3	-14.66	-14.20	+0.115	+1.132

4. DISCUSSION

Table 2 makes the basis for the discussion of adsorption properties and surface diffusion mechanism of CO_2 and N_2 molecules on studied materials. In column 2 of the table the difference of the adsorption energies for the best position of the two molecules is shown for each material. This value provides an estimate of the difference of CO_2 and N_2 affinities to the membrane surfaces, rendering the efficiency of the separation process. According to the surface diffusion mechanism magnesia and alumina should show significant selectivity in the $CO_2/N2$ separation

Table 2. Affinity differences and adsorption energies of CO_2 for studied materials

Material	ΔE [kcal/mol]	E (CO_2) [kcal/mol]
MgO	-6.18	-18.74
Al_2O_3	-1.79	-13.19
SiO_2	+0.23	-1.14
TiO_2	-0.46	-14.66

while pure silica and titania should be inactive. Column 3 of the table gives the best adsorption energy of carbon dioxide on studied oxides which is the second important factor in the mechanism. At the moment we are not in a position to discuss the absolute adsorption strength since this would require more elaborate calculations with better, nonlocal potentials or suitable model. However, the two factors should be taken into consideration while discussing the surface diffusion mechanism, thus both, silica and titania, should be excluded because of small affinity difference. There exists no extensive experimental material yet to fully support the presented results, a qualitative agreement, however, can be already established with the experimental trends discussed in the Introduction. According to our results regarding both, the difference in affinity and the adsorption strength, the expected efficiency in the separation process of N_2/CO_2 should follow the ordering: MgO > Al_2O_3 > TiO_2 > SiO_2.

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