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Al ionic radius influence on molecular dynamics simulations of γ-Al_2O_3

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Molecular dynamics (MD) simulations of γ-Al_2O_3, using a pairwise additive interaction potential of Pauling's type with four different radii for aluminum atoms, were analysed in order to determine the influence of the radius on the modification of coordination numbers of Al relative to the ideal structure, at two different temperatures of 300 and 1500 K. It is found that the best choice is the radius of penta-coordinated aluminum, reproducing structural and vibrational properties of the compound in excellent agreement with experimentally observed properties.

Keywords: γ-Al_2O_3; alumina; aluminum; molecular dynamics

1. Introduction

Due to the experimental difficulties associated with surface analysis techniques, computer simulations of catalytic systems based on alumina, have recently been used as an alternative way to investigate their dynamic and structural properties. The molecular dynamics (MD) method of simulation is the most suitable way to carry out studies of detailed mechanisms of ionic migration which are responsible for some of the most interesting and puzzling phenomena in catalysis, such as surface reconstruction and adsorption.

However, MD simulations only account for cation size and charge to determine cation coordination. Since only radius may be used for a given species using a simple simulation scheme, one could think that results of simulations would be biased by the selection of radius. In particular, aluminum atoms may occur in two different coordinations in the γ-alumina structure, on the other hand, according to Shannon and Prewitt [1] aluminum atoms may have different radii as a function of their coordination number. Therefore, it would be desirable to find the extent of the effect of Al radius in the final coordination environment for each cation. In order to do so, several MD runs were performed to elucidate the extension of the influence of radii on the structural characteristics predicted by this simulation technique.

In the present work, a theoretical analysis of the influence of the selection of radius for aluminum atoms in MD simulations at room and high temperatures is presented. The analytical form of the interaction potential is the same as the one used in a previous work [2] in order to compare the new results with the ones already obtained.

2. Calculations

2.1. INTERACTION POTENTIAL

In our simulations a Pauling's type function was used, which includes a Coulombic term and a steric repulsion term given by

$$V(r_{ij}) = \frac{q_i q_j e^2}{r_{ij}} \left[1 + \mathrm{sign}(q_i q_j) \left(\frac{\sigma_i + \sigma_j}{r_{ij}} \right)^n \right],$$

where r is the interatomic distance, q are the effective charges, and σ are the effective ionic radii. The exponent n was taken to be 9 following Adams and McDonald [3]. The values of charges and ionic radii used in the simulations are shown in table 1. This function is the same as used in a previous work [2] on the structure of γ-alumina.

2.2. MOLECULAR DYNAMICS SIMULATIONS

Molecular dynamics simulations in the microcanonical ensemble were performed in γ-Al_2O_3. The system consisted of 576 aluminum atoms and 864 oxygen atoms arranged in a cubic box with periodic boundaries taken from the previous work already mentioned. The electrostatic part of the potential was handled by the Ewald summation method and the calculation of the corresponding forces was carried out through spline interpolation and numerical derivatives. A set of MD runs were carried out to test four different radii for aluminum atoms at temperatures of 300 and 1500 K. In all cases, an equilibration run at constant temperature was performed for 5.5 ps followed by a production run of 10 ps. This procedure is the same as the one used in ref. [2], in order to compare the new results with the ones previously reported. An integration time step of 10^{-15} s was used and temperature fluctuations were of the order of 5 K and total energy variations were less than 0.1% around the mean value.

Table 1
Potential parameters

	q/e	σ(Å)			
Al	1.65	0.53	0.6025	0.62	0.675
O	−1.10	1.20	1.20	1.20	1.20

3. Results and discussion

3.1. STRUCTURE

The initial configuration was built from Lippens' model [4] removing the extra aluminum atoms and relaxing the system through MD simulations at constant temperature of 300 K. In this way the defects introduced by the removal of extra aluminum atoms essentially disappear approximately preserving the predicted [5] occupation percentages of tetrahedral (10%) and octahedral (47%) sites.

Table 2 shows the coordination numbers for both aluminum and oxygen atoms in the alumina structure, as a function of Al radius for two different simulation times of 10.5 and 15.5 ps at temperatures of 300 and 1500 K. The column labelled IN shows the coordination numbers for the initial configuration, and the following columns correspond to the four different radii used in the simulations. The column labelled 0.62 is the one which corresponds to the reproduction of simulations per-

Table 2
Coordination numbers as a function of radius (r in Å) and temperature. IN: initial configuration after randomly removing the aluminums in excess and relaxed with molecular dynamics

Coord. num.			Time = 10.5 ps				Time = 15.5 ps			
		IN	r = 0.53	0.6025	0.62	0.675	r = 0.53	0.6025	0.62	0.675
T = 300 K										
Al	4	164	172	164	161	37	171	165	162	37
	5	–	1	–	1	94	–	1	–	106
	6	412	403	412	412	439	405	410	414	425
	7	–	–	–	–	6	–	–	–	8
O	2	6	4	6	4	2	4	6	5	1
	3	329	349	329	330	216	342	330	329	222
	4	517	502	517	518	588	510	516	517	589
	5	12	9	12	12	58	8	12	13	52
T = 1500 K										
Al	3	–	1	1	–	–	2	–	–	–
	4	164	192	142	119	7	192	132	129	12
	5	–	51	33	56	155	43	50	46	158
	6	412	332	400	401	369	339	394	400	365
	7	–	–	–	–	43	–	–	1	41
	8	–	–	–	–	2	–	–	–	–
O	2	6	10	6	8	5	8	5	7	11
	3	329	425	344	319	203	423	336	326	209
	4	517	422	478	496	566	427	491	497	555
	5	12	7	36	41	89	4	32	31	88
	6	–	–	–	–	1	–	–	3	1

formed in ref. [2]. Due to thermal vibrations these coordination numbers may fluctuate from one simulation to another, since they are taken from instantaneous configurations; however, these variations are less than one percent. From the table it can be observed that when $r_{Al} = 0.53$ Å, in all runs there is a tendency of aluminum atoms to occupy tetrahedral sites, whereas when $r_{Al} = 0.675$ Å is used the tendency is to occupy octahedral sites.

The selection of the mean Al radius, $r_{Al} = 0.62$ Å, has been shown, from our simulations, to properly reproduce the occupation percentages predicted by neutron diffraction techniques, as well as radial distribution functions of γ-Al_2O_3. However, since the number of tetrahedral aluminums increase when $r_{Al} = 0.53$ Å and octahedral ones increase with $r_{Al} = 0.675$ Å, one could expect that the cationic migration would be inhibited by the separate treatment of tetrahedral and octahedral aluminums in the MD simulations. In order to find this out, an extra set of MD runs were carried out at the same temperatures as the previous ones, plus one more run at 1000 K, considering tetrahedral and octahedral aluminum atoms as different species in the MD program; the radii being $r_{Al} = 0.53$ Å for tetrahedral aluminums and $r_{Al} = 0.675$ Å for octahedral ones. Table 3 shows the coordination numbers for the three "species" considered in these runs. At 300 K there is essentially no difference between the results of this run and the one with $r_{Al} = 0.62$ Å; at 1000 K an exchange of coordination positions takes place and at 1500 K this exchange is enhanced as can be seen from table 3. This process in which some octahedral aluminums migrate to tetrahedral sites and some tetrahedral ones migrate to octahedral positions, giving a net balance of almost no migration at all, may

Table 3

Coordination numbers as a function of temperature when tetrahedral and octahedral aluminums are treated as different species, at two different simulation times (t in ps). IN: initial configuration after randomly removing the aluminums in excess and relaxed with molecular dynamics at 300 K

Coord.			$T = 300$ K		$T = 1000$ K		$T = 1500$ K	
		IN	$t = 10.5$	15.5	$t = 10.5$	15.5	$t = 10.5$	15.5
Al_t	4	164	164	164	154	152	129	121
	5				2	2	9	7
	6				8	10	26	36
Al_o	4		2	2	9	12	29	31
	5		2	2	7	8	32	24
	6		408	408	395	392	349	356
	7				1		2	1
O	2	6	5	5	4	3	5	4
	3	329	335	335	339	344	372	354
	4	517	513	513	508	505	460	478
	5	12	11	11	13	12	27	28

imply that the transformation from γ to δ, θ and finally α alumina may be more complicated than just the migration of aluminums from tetrahedral to octahedral sites as was previously suggested.

Although the occupation of both tetrahedral and octahedral sites changes as a function of radius, the average structural characteristics do not produce considerable changes in the radial distribution functions, as can be seen from table 4, where the positions of the main peaks of $g(r)$ have been tabulated to compare with the experimental ones. The variations of positions of the main peaks are at most tenths of angstroms, except in the case in which tetrahedral and octahedral aluminums have been considered separately in the molecular dynamics program. However, these differences are due to the fact that when no distinction is made, the positions of the peaks are averaged, especially for the pairs Al–Al and Al–O. This can be inferred from the last three columns of table 4.

3.2. VIBRATIONAL SPECTRA

The experimental spectrum [6] obtained in KBr shows a band at 1020 cm^{-1} and a broad absorption band ranging between 900 and 400 cm^{-1}. The velocity autocorrelation functions and their Fourier transforms, for aluminums and oxygens, were obtained in order to analyse the vibrational spectra, for the different radii used in the molecular dynamics simulations, shown in fig. 1. When $r_{Al} = 0.53$ Å, a broad band between 400 and 900 cm^{-1} is obtained, however the high frequency band centred at 1020 cm^{-1} is not present. For $r_{Al} = 0.6025$ Å, a broad band is present between 380 and 1050 cm^{-1} showing some peaks at 380, 573 and 912 cm^{-1}

Table 4

Positions of the main peaks of $g(r)$ for different aluminum radii in Å. The last three columns correspond to simulations where tetrahedral and octahedral aluminums are treated as different species

	EXP	0.53	0.6025	0.62	0.675	Al_t–Al_t	Al_o–Al_o	Al_t–Al_o
Al–Al	2.793	2.8194	2.8194	2.8194	2.8698	2.9193	2.8194	–
	3.275	3.2666	3.2666	3.2884	3.101	3.4583	–	3.2666
	3.950	–	3.7751	3.9603	–	–	3.8502	4.2058
						Al_o–O	Al_t–O	
Al–O	1.869	1.8345	1.8732	1.8732	1.9110	1.9110	1.7134	
	3.333	3.3531	3.3744	3.3744	3.4375	3.4166	3.2884	
	4.379	4.4054	4.4054	4.4054	4.3891	4.4216	4.2566	
						O–O		
O–O	2.793	2.7939	2.7939	2.7939	2.6894	2.7682		
	3.950	3.8316	3.8316	3.8316	3.8502	3.8873		
	4.838	4.8392	4.8244	4.8244	4.7946	4.8244		

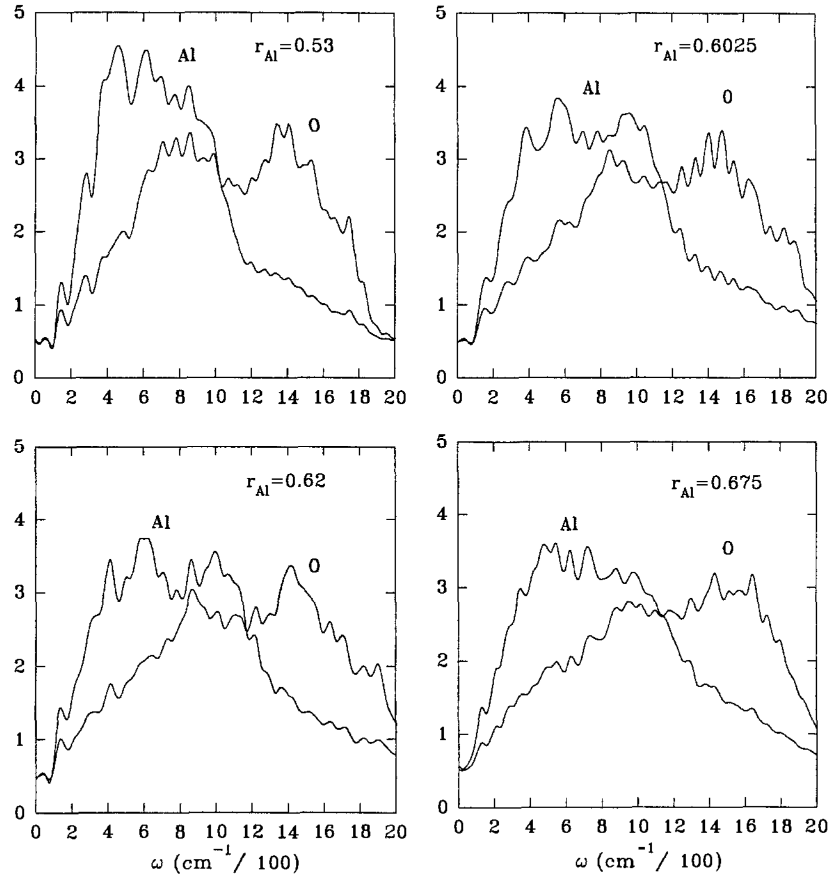

Fig. 1. Vibrational spectra, for the different radii used in the molecular dynamics simulations.

and, as in the previous case, the peak at 1020 cm^{-1} is not present. For r_{Al} = 0.62 Å, there are two bands centred at 580 and 1000 cm^{-1} approximately, agreeing well with the experimental data. For r_{Al} = 0.675 Å, there is a broad band between 470 and 1000 cm^{-1}, whose main features are at low frequencies. The power spectrum of oxygen shows a band centred at 860 cm^{-1} for the radii of 0.53 and 0.6025 Å, 886 cm^{-1} for 0.62 Å, and 964 cm^{-1} for 0.675 Å.

In order to interpret these changes in the vibrational spectra, it is useful to look at the spectra calculated for tetrahedral and octahedral aluminums separately. Fig. 2 shows the velocity autocorrelation functions obtained from the simulation with r_{Al} = 0.62 Å (labelled B), and the corresponding functions when tetrahedral (T) and octahedral (O) aluminums are treated as different species. The curve labelled A is the velocity autocorrelation function of aluminums without distinguishing between them in the same run. After Fourier transforming these functions (see fig. 3), the spectrum of tetrahedral aluminums shows a clear peak at around 600 cm^{-1} and no signal at higher frequencies, whereas the octahedral spectrum has

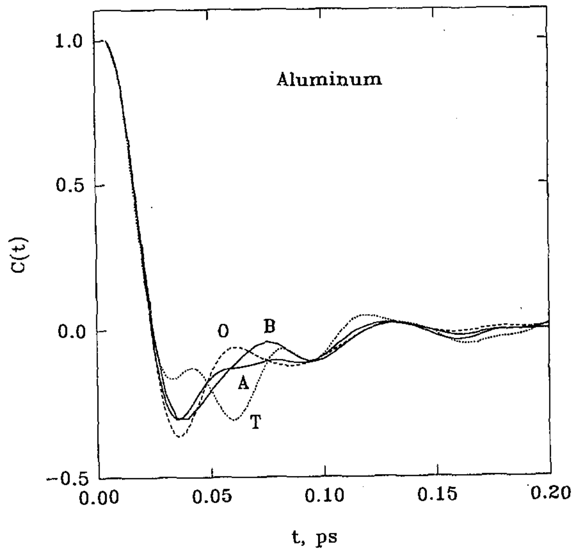

Fig. 2. Velocity autocorrelation functions obtained from the simulation with $r_{Al} = 0.62$ Å (labelled B), and the corresponding functions when tetrahedral (T) and octahedral (O) aluminums are treated as different species. Curve labelled A is the velocity autocorrelation function of aluminums without distinguishing between them in the same run.

two bands, one ranging between 300 and 650 cm^{-1} and another one between 850 and 1200 cm^{-1}. Our calculations confirm that the low frequency vibration is due to Al–O–Al bending, since for the tetrahedral aluminums there is a very well defined peak and for the octahedral ones a band is observed. This is due to the fact that octahedral aluminums have more vibrational modes than tetrahedral ones since the coordination number and Al–O bond distance are larger. The high frequency band of octahedral aluminums is probably due to the high number of collisions with oxygen atoms, which tetrahedral ones do not have, because they are confined in a low coordination sphere.

In the light of the previous discussion we can draw some conclusions about the spectra when different radii are used for aluminum atoms. For the aluminum radii lower than 0.62 Å the high frequency vibrations are inhibited because of the migration of aluminums from octahedral to tetrahedral positions. The vibrations of octahedral aluminums contribute less to the vibrational modes of the whole system, and the effect of the tetrahedral ones is enhanced. On the other hand, when the radius is that of octahedral aluminums, their number increases and the spectrum becomes a wide band over the interval (470–1000) cm^{-1}. Probably because the number of octahedral aluminums increases there is not a clear distinction between the tetrahedral and octahedral vibrational modes. The shift of the main peak of the oxygen spectrum towards higher frequencies described before, is due to a vibrational coupling of oxygens with an increasing number of octahedral aluminums.

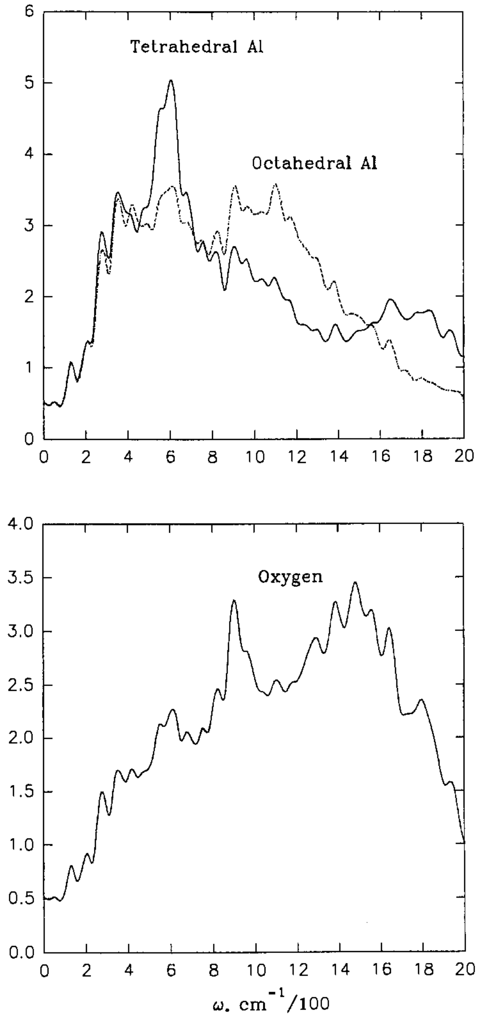

Fig. 3. Vibrational spectra of tetrahedral and octahedral aluminum atoms, when treated as different species in the molecular dynamics simulations.

4. Conclusion

Our results suggest that, using mean charges and radii for both aluminum and oxygen is the best approximation to model some important features of alumina based compounds, and that structural phase transitions and surface reconstruction mechanisms have to be studied in the future with more sophisticated simulation methods which include variations of radius as well as charge as a function of coordination.

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References

[1] R.D. Shannon and C.T. Prewitt, Acta Cryst. B 25 (1969) 925.
[2] L.J. Alvarez, J. Fernández Sanz, M.J. Capitán and J.A. Odriozola, Chem. Phys. Lett. 192 (1992) 463.
[3] D.J. Adams and I.R. McDonald, Physica B 79 (1979) 159.
[4] B.C. Lippens and J.J. Steggerda, in: *Physical and Chemical Aspects of Adsorbents and Catalysis*, ed. B.G. Linsen (Academic Press, New York, 1970) p. 171;
H. Knözinger and P. Ratnasamy, Catal. Rev. 17 (1978) 31.
[5] E.J.W. Vewy, Z. Krist. 91 (1935) 317.
[6] H.W. van der Marel and H. Beutelspacher, *Atlas of Infrared Spectroscopy of Clay Minerals and Their Mixtures* (Elsevier, Amsterdam, 1976).