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Thermodynamic study of NO thin films adsorbed on MgO(100)

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Adsorption isotherms of NO on uniform MgO(100) surface have been measured in a wide range of temperature 92K ≤ T ≤ 138K and a coverage corresponding to two first layering transitions. Thermodynamic properties of the first and the second nitrogen monoxide layers have been reported. Particularly, adsorption heat measured for the first layer adsorbed on MgO $Q_{st}^{(1)} = 5.47$ kcal.mol^{-1}, is 18% greater than that measured on the hexagonal graphite basal plane surface, indicating the large stability of the NO first layer adsorbed on MgO. This suggestion is supported by the bi-dimensional critical temperature which is displaced to the height temperatures range $T_{2C}/T_{3C} = 0.67$. By comparison to NO adsorbed on other substrates, the original result in the present study is the absence of bi-dimensional polymorphism in the explored range of temperature. We suggest a configuration where molecules are laying on the MgO(100) surface.

Keywords: Adsorption isotherms, Bi-dimensional polymorphism, Surface thermodynamics, Magnesium oxide

1 Introduction

Nitric oxide, NO has been recognised as an atmospheric pollutant. The derivative oxides NO_x are the result of multiple processes. The principal ones are automotive engines, industrial combustion system and the burning of oil-derived fuels with N-containing impurities. When released into the atmosphere the NO_x species undergo further oxidation and react with water producing the acid rain that acidify lochs and kills vegetation.

Adsorption of NO on metal and metal oxides surfaces has importance in terms of both practical application and fundamental surface science[1-7]. Moreover, the adsorption of NO on graphite and boron nitride and on lamellar halides have been studied by Matecki[8] and Enault[9], respectively.

Almost complete thermodynamic studies of the NO-adsorbent systems have been investigated[8,9]. Two dimensional critical temperature $T_{2C}^{(n)}$ are determined and thermodynamic values including differential enthalpy $\Delta H^{(n)}$, differential entropy $\Delta S^{(n)}$, free energy excess $\Delta F^{(n)}$ and isosteric heat of adsorption $Q_{st}^{(n)}$, where n represents the order of the adsorbed layer, are given.

In the previous mentioned systems, the measured isotherms are composed of two steps of equal height indicating the condensation of NO in two layers with the same density. But at temperatures lower than 90 K the first step is divided in two sharp steps of different height. The last steps have been interpreted as the adsorption of the dimer $(NO)_2$ parallel (α-phase) and perpendicular (β-phase) to the surface of the adsorbent[8], respectively. It is well established that the rate of NO dimerisation is elevated in dense phases. The adsorption of NO on MgO has been undertaken in order to investigate the influence of the square symmetry of the surface well potentials and the strong electric field of the MgO(100) surface on the thermodynamic and structural properties of the NO condensed phases.

2 Experimental Details

The sample used to measure NO isotherms is composed of MgO powders, prepared by burning Mg ribbons of 99.5% purity in air, as described in Ref. 10. Care should be taken to minimise the time between the beginning of the Mg combustion and to put the powder in the vacuum system at a pressure $P \approx 10^{-3}$ torr. In order to remove chemisorbed impurities, the powder is then baked at a temperature about 960°C, during 10 h and under a secondary vacuum $P \approx 10^{-6}$ torr. The baking temperature is gradually reached (~5 h). The powders so prepared are composed of well-crystallised micro-cubes presenting (1 0 0) facets. To check the homogeneity of the substrate, an isotherm of Kr is measured at 77.3 K (Fig. 1). This isotherm is also used to determine the specific surface area of the MgO sample, which is about 12 m^2 g^{-1} for

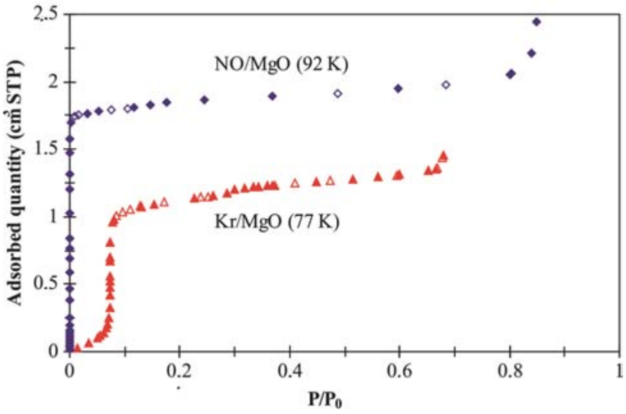

Fig. 1 — Adsorption isotherms of Kr at 77.35 K and NO at 91.77 K measured separately on the same sample of MgO. The area occupied by a Kr atom, at the completion of the first layer, is equal to 14.8Å^2 (Ref. 17). In this figure as in the following ones, two different symbols are used: full symbols indicate adsorption data and empty symbols indicate desorption data

our substrate. The nitric oxide used in this study has 99.97% purity. In addition, damping a glass finger of the gas container in liquid nitrogen and pumping the impurities present in the gaseous state carries out systematic purification before each isotherm. The dynamical pressure is of the order of 10^{-6} torr. The sample temperature that can be lowered to 30 K using a closed cycle cryocooler (CTI cryogenics) is measured by a platinum resistor (100 Ω at 273 K). But a more precise value of the isotherm temperature is given at the end of each isotherm by measuring the NO vapour pressure P_0. The variation of P_0 with the temperature is given in the literature Ref. (11). Temperature control is obtained by a temperature controller that provides a stability $\Delta T \approx 0.05$ K. To measure pressure in the introduction system and the adsorption cell we use a differential Baratron gauge ‘‘type MKS’’. The gauge head is kept at constant temperature (T = 50°C) which is quite different than the introduction volume one (room temperature). Pressures lower than 1 torr are corrected of the thermal effusion using Takaishi and Sensui[12] formulae.

3 Results and Discussion

Adsorption isotherms of NO condensed on MgO (100) powder have been measured in the temperature range 92-138 K by the standard volumetric method. Isotherms are formed of a succession of at least two steps indicating the condensation layer by layer of NO on MgO. Each step corresponds to a transition from a dilute (2D) phase to a (2D) dense one. Figure 2 shows the isotherms corresponding to the first layer of NO

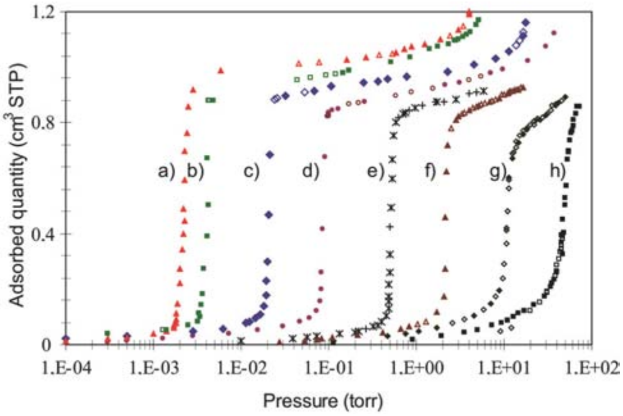

Fig. 2 — Set of adsorption isotherms of NO on MgO (100) powder sample at coverage corresponding to the first layer. The temperatures of isotherms are: (a) 91.77 K, (b) 93.66 K, (c) 99.23 K, (d) 104.84 K, (e) 112.58 K, (f) 119.68 K, (g) 128.86 K and (h) 138.75 K, respectively

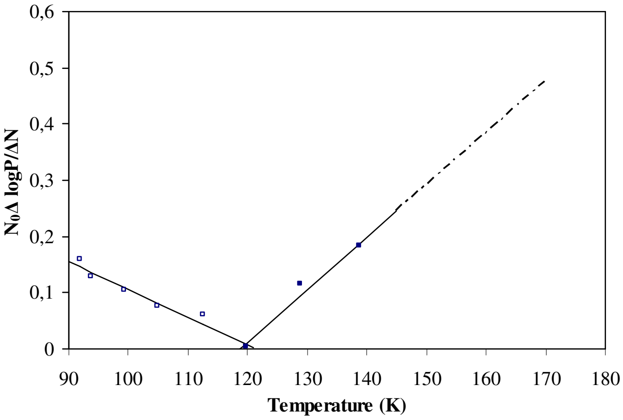

Fig. 3 — Variation with temperature of the inverse slope of the steps: (2D) critical temperature corresponds to the break of the curve.

adsorbed on MgO. In addition, Fig. 2 shows a sub-step which represents a fine transition, see especially isotherms (f) and (g) measured at 119.68 K and 128.86 K, respectively. Such sub-steps are a signature of the high homogeneity of the MgO sample used here and their interpretation needs more investigation, especially structural one.

The (2D) critical temperature is derived from Fig. 2. Such temperature characterizes crossing from a domain where transition from a dilute phase to a dense one is first order to a domain where this transition is continuous. Fig. 2 shows a loss of the step verticality in the isotherms as the temperature increases. To localize critical temperature, the inverse slope of steps versus temperature is shown in Fig. 3. When crossing the critical point, the curve shows a sharp break. The corresponding value of T_{2C} = 121±2 K is remarkably higher than those determined on other substrates.

In Table 1, critical temperatures (2D) measured for NO adsorbed on different substrates are summarized and the ratio T_{2C}/T_{3C} is also given. The high value measured on MgO indicates the effect of MgO (100) surface on the NO adsorbed phase. In the explored domain of temperature $92 \leq T \leq 138$ K, only one sharp transition corresponding to the first layer condensation is observed. By comparison of adsorption isotherms of Kr and NO measured separately on the same sample of MgO (Fig. 1), we have determined the area occupied by a $(NO)_2$ molecule adsorbed at the monolayer completion $\sigma \approx 20 \text{Å}^2$ corresponding to a dimer adsorbed parallel to the MgO (100) surface compared to 13 Å^2 when the dimer is adsorbed upright to the surface. It seems that the MgO (100) surface – NO molecules interaction is so important to prevent NO molecules to stand up as the pressure increases. Nevertheless, we remind here that NO isotherms recorded on other substrates and showing two sharp transitions corresponding to the first layer condensation are measured at temperatures lower[8,9] than 90 K. So it was not completely excluded that isotherms measured on MgO at temperature lower than 90 K will present a bi-dimensional polymorphism.

Figure 4 shows the isotherms corresponding to the second layer of NO condensed on MgO (100) surface. The almost equal height of the steps shown in Figs 2 and 4 suggests the same density for the two condensed layers. It is important to note here that the second layer has been condensed only on graphite and MgO. The coefficients $A^{(n)}$ and $B^{(n)}$ of the linear regressions $\log_{10}P^{(n)}(\text{Torr}) = -[A^{(n)}/T(K)]+B^{(n)}$ of the two layers stabilised on MgO depend on the temperature range and are given in Table 2.

The thermodynamic quantities $\Delta H^{(n)}$, $\Delta S^{(n)}$, $\Delta F^{(n)}$ and $Q_{st}^{(n)}$, obtained from the experimental data by application of Larher formalism[13,14] are summarised in Table 3 and will be compared to those measured on other substrates and corresponding to the α-phase, given in the same table, since the area occupied by an adsorbed molecule in α-phase is almost equal to that measured on MgO. The examination of such table reveals important properties. First the comparison of

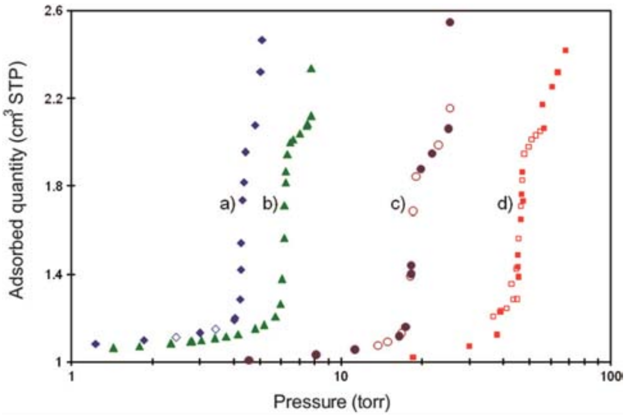

Fig. 4 — A set of adsorption isotherms of NO on MgO (100) powder sample at coverage corresponding to the second layer. The corresponding temperatures are: (a) 91.77 K, (b) 93.66 K, (c) 99.23 K and (d) 104.84 K

Table 1 — Two dimensional critical temperature of the first transition of the NO monolayer adsorbed on various substrates

Adsorbent	T_{2C}	T_{2C}/T_{3C}	Reference
Graphite	87	0.48	[8]
Boron nitride	87	0.48	[8]
$CdBr_2$	100	0.56	[9]
MgO	120	0.67	Our results

Table 2 — The coefficients $A^{(n)}$ and $B^{(n)}$ of the linear regressions $\log_{10}P^{(n)}(\text{Torr}) = -[A^{(n)}/T(K)]+B^{(n)}$ of the two NO layers stabilised on MgO

Temperature	$A^{(1)}$	$B^{(1)}$	$A^{(2)}$	$B^{(2)}$
$T<T_t(3D)=109.5$ K	1194.70	10.37	759.62	8.90
$T>T_t(3D)=109.5$ K	1173.75	10.14		

Table 3 — Thermodynamic properties of the first and the second layers of NO adsorbed on different substrates (Q_{st} is the adsorption heat, ΔH, ΔS and ΔF are respectively the differential enthalpy, the differential entropy and the free energy excess of the adsorbed NO layers)

Adsorbent	n layer order	Temperature range (K)	$\Delta H^{(n)}$ cal/mol	$\Delta S^{(n)}$ cal/mol.K	$\Delta F^{(n)}$ cal/mol	$Qst^{(n)}$ kcal/mol	reference
MgO	1	92-105	−1438	−0.4	−1394	5.47	Our results
		112-139	−2256	−7.8	−1283	5.37	
	2	99-105	554	6.2	−54.7	3.479	
Graphite	1	78-92	−454.9	4.5	−837.4	4.48	[8]
	2	77-85	69	1.2	−33.7	3.966	
BN	1	77-90	25.6	6.6	−525.5	4.00	[8]
CaI_2	1	85-90	448.5	5.4	−22.25	3.54	[9]
MgO	1	109-148	−2101	−6.5	−1262	5.22	[15]

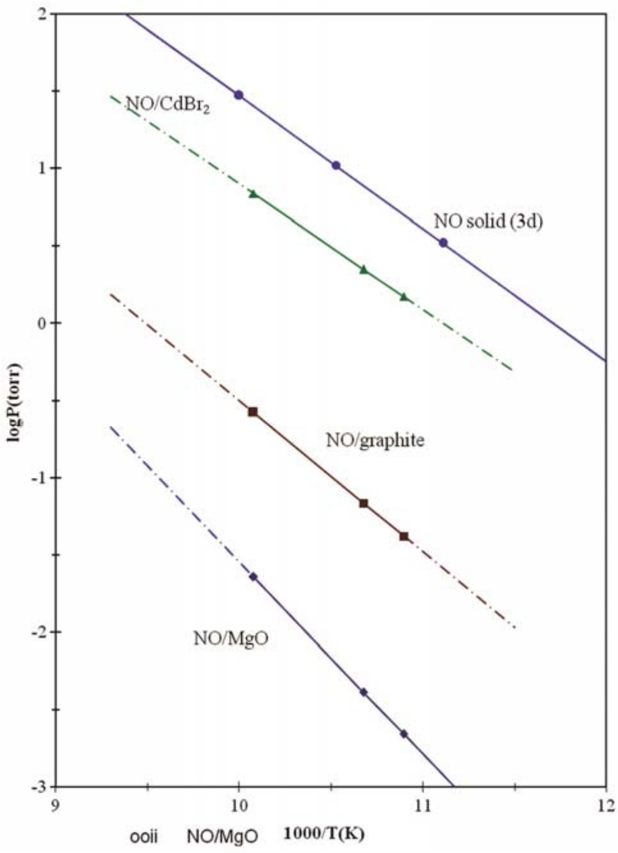

Fig. 5 — Clapeyron lines relative to the (2D) first transition observed in the monolayer film of nitric oxide adsorbed respectively on graphite, $CdBr_2$ and MgO. The line corresponding to the (3D) solid phase is also represented

the free energy excess $\Delta F^{(n)}$ shows a better adherence of the two adsorbed layers on MgO than on other substrates. Second, the isosteric heat of adsorption $Q_{st}^{(n)}$ measured for the first layer adsorbed on MgO was superior to those measured on other substrates. In fact, $Q_{st}^{(1)}$ represents the energy of interaction, including adsorbate-adsorbate and adsorbate-substrate contributions.

These two results are clearly shown in Fig. 5 where Clapeyron lines corresponding to the first layer adsorbed on different substrates and to the (3D) solid phase are represented. $\Delta F^{(n)}$ is represented by the interval at a given temperature, between the lines corresponding to the 1st layer and the (3D) solid phase whereas $Q_{st}^{(1)}$ is the slope of the corresponding line.

A previous study of the NO adsorbed on MgO has been performed by Furuyama *et al*[15]. The thermodynamic values deduced from their isotherms and reported in Table 3, are found to be in agreement with the values obtained by the authors. Another important result concerns the condensation pressure of the first layer. In fact, the relative pressure of the first layer condensation $P^{(1)}/P_0$ where P_0 is the vapour pressure of the (3D) dense phase at the temperature of the isotherm, is lower in the case of NO compared to that of inert gases and the corresponding values are 0.001 for NO and 0.1 for Kr adsorbed on the same substrate of MgO at comparable relative temperature T/T_C(3D) where T_C(3D) is the (3D) critical temperature. Such behaviour has been attributed to the electrostatic interaction including the NO quadric polar moment with the gradient of the electrostatic field of the MgO(100) surface and the NO dipolar moment with the MgO(100) surface electric field. A similar interpretation has been evoked when studying adsorption[16] of CO on MgO.

4 Conclusions

Adsorption isotherms of nitric oxide on MgO have been measured in a wide range of temperature 92-138 K. A detailed thermodynamic analysis has been carried out. The thermodynamic values, deduced from the measured isotherms are of great interest to elaborate the phase diagram of the NO thin films adsorbed on MgO. Two dimensional critical temperature is deduced, it is remarkably greater than those determined on other substrates. Another important component is the condensation pressure of the first layer. The NO monolayer is condensed at lower relative pressure and is more stable when adsorbed on MgO (100) surface compared to the other adsorbents.

The effect of the square symmetry of the MgO surface potential on the thermodynamic properties of NO adsorbed phases is evident. There is no two dimensional polymorphism in the explored range of temperature but such phenomenon is not excluded at lower temperature.

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