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CO ADSORBED ON Ni(001): EFFECTS OF THE INTERPLAY OF "ON-TOP" AND "BRIDGE" ADSORPTION COMPLEXES ON HEAT CAPACITY *

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ABSTRACT

The effects of the adsorption-complex isomerism on the standard thermodynamic terms characterizing gas–solid interactions have been studied. It has been shown that in terms of the localization concept of this interaction, it is possible, as is the case with gas-phase molecular complexes, to separate out the isomerism contributions to thermodynamics which enable the study of the isomerism effects in their explicit form. Special attention is given to the isomerism contribution to heat capacity at constant pressure; it has been shown that this term can exhibit a relatively distinct local maximum on its temperature-dependence curve. These general relationships are investigated with respect to the thermodynamics of the interaction of CO(g) with the Ni(001) plane.

INTRODUCTION

Descriptions of the thermodynamics of gas–solid interactions follow either the mobile or the immobile (localization) approach depending on the nature of this interaction [2–6]. The latter approach is especially relevant for chemisorption at low coverage. This approach has become increasingly appropriate in the light of more recent quantum-chemical studies of heterogeneous catalysis and sorption in terms of the cluster treatment [7–11], a well-established way of obtaining a more detailed insight into the adsorption process at molecular level. Energetic, structural and vibrational characteristics of the adsorption complex from theoretical calculations are very useful in completing the information obtainable from observation. In principle,

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quantum-chemical studies of gas–solid interactions using the cluster approach within the representation of the corresponding potential energy hypersurfaces by their isolated stationary points make it possible to describe the thermodynamics of these processes in terms of the localized concept and the harmonic description of vibrational motions; such a computational treatment requires no additional data from observation, being of a non-empirical nature [12–16].

The cluster approach is the leading modelling concept of quantum chemistry applicable to studies of the problems of heterogeneous catalysis [7–11]. Applications of this type of modelling soon showed that the complex formed by the interaction of substrate with cluster need not be unique, but can often be represented by a whole series of formally isomeric structures, i.e. if the cluster itself is substituted by the whole corresponding surface. Two types of this adsorption complex isomerism have been differentiated [14]; the site-caused isomerism (see, for example, refs. 17–21) and the adsorbate-caused isomerism (see, for example, refs. 22–24). However, it has been shown that both types of isomerism can be treated in a unified way under certain simplifying conditions [12,14].

The heat capacity of a system is a parameter which is frequently observed and is a means of its characterization. Hence, it is logical to investigate the effects of the adsorption complex isomerism on the heat capacity. This problem is dealt with in the present communication, being illustrated by the interaction of CO(g) with the Ni(001) plane.

ISOMERISM CONTRIBUTION TO THE HEAT CAPACITY FOR GAS–SOLID INTERACTION

Let us consider an interaction between the species A(g) and a solid phase M(s)

$$A(g) + M(s) \rightarrow A \cdot M^{(i)}(s) \qquad (1)$$

where ($i = 1, \ldots, n$) and n different types of adsorption complexes are being formed. It has been shown [12,14] that if the adsorption takes place at sufficiently low coverage (i.e. in the region of Henry's law) then the populations of individual structural types are proportional to their weight factors w_i

$$w_i = \frac{s_i q_i \exp\left(-\Delta H_{0,i}^{\ominus}/RT\right)}{\sum_{j=1}^{n} s_j q_j \exp\left(-\Delta H_{0,j}^{\ominus}/RT\right)} \qquad (2)$$

where q_i is the vibrational partition function of the ith adsorption complex, $\Delta H_{0,i}^{\ominus}$ is the enthalpy change for the ith realization of process (1) at absolute zero and s_i represents the steric factor giving the number of relevant adsorption sites per unit area of the solid phase surface.

If the energetic, structural and vibrational characteristics are available for A(g) and all $A \cdot M^{(i)}(s)$, then it is possible to determine, in the conventional way [2–6], the standard changes of enthalpy $\Delta H_i^{\ominus}$, entropy $\Delta S_i^{\ominus}$ and heat capacity at constant pressure $\Delta C_{p,i}^{\ominus}$ corresponding to particular examples of process (1), i.e. the so-called partial terms corresponding to the individual structures of the adsorption complex. In addition to these partial terms it is also meaningful to consider the overall terms $\Delta H^{\ominus}$, $\Delta S^{\ominus}$ and $\Delta C_p^{\ominus}$ which comprise contributions from all the structures in proportion to their weight factors. From these overall terms, it could be useful to extract the isomerism contributions $\delta H_1^{\mathrm{iso}}$, $\delta S_1^{\mathrm{iso}}$ and $\delta C_{p,1}^{\mathrm{iso}}$ with respect to the isomer with index 1 (usually the structure which is the most stable at low temperatures). For the isomerism contributions it can be shown that in the case of gas-solid interaction the formulae analogous to those for gas-phase molecular complexes are valid [25,26]

$$\delta H_1^{\mathrm{iso}} = \sum_{i=1}^{n} w_i \, \Delta H_i^{\ominus} - \Delta H_1^{\ominus} \tag{3}$$

$$\delta S_1^{\mathrm{iso}} = \sum_{i=1}^{n} w_i \left(\Delta S_i^{\ominus} - R \ln w_i \right) - \Delta S_1^{\ominus} \tag{4}$$

$$\delta C_{p,1}^{\mathrm{iso}} = \sum_{i=1}^{n} w_i \, \Delta C_{p,i}^{\ominus} + \frac{1}{RT^2} \left[\sum_{i=1}^{n} w_i \left(\Delta H_i^{\ominus} \right)^2 - \left(\delta H_1^{\mathrm{iso}} + \Delta H_1^{\ominus} \right)^2 \right] - \Delta C_{p,1}^{\ominus} \tag{5}$$

APPLICATION TO THE CO(g) AND Ni(001) SYSTEM

The adsorption of CO at the metal surface Ni(001) was studied theoretically several times [27–29], and, in accordance with observation, it was stated that there exists a two-fold isomerism of the adsorption complex, namely that CO can be bound either on a top site above a Ni atom or on a bridge site between two Ni atoms (the "on-top" and "bridge" positions, respectively). The basic characteristics of these two isomeric adsorption complexes are presented in Table 1. Substantial values are those of five inter-system vibrational frequencies which are due to the interaction of CO with the surface. These frequencies are deduced from two theoretical calculations: according to Richardson and Bradshaw (RB) [27] and to Parra and Micha (PM) [29]. Compared with the free CO(g) molecule, a certain shift in the value of its single vibrational mode (2143.2 cm^{-1}) is associated with the interaction [29]. On the other hand, however, because of lack of information it must be presumed that the characteristics of the solid surface remain

TABLE 1

A survey of the basic characteristics of the "on-top" and "bridge" adsorption complexes in the interaction of CO(g) with Ni(001) surface

Species	ΔE_i (kJ mol^{-1}) [a]	s_i (10^{20} m^{-2}) [b]	Source	Vibrational frequencies [c] (cm^{-1})	
"On-top"	−129.3	0.162	RB [27]	2088, [d]	437, 411(2), 82(2)
			PM [29]	2088, [d]	431, 389(2), 131(2)
"Bridge"		0.323	RB [27]	2099, [d]	457, 572, 76, 649, 184
			PM [29]	1981, [d]	366, 569, 71, 764, 397

[a] Potential energy change upon adsorption [28].

[b] Number of the adsorption sites on a unit surface area.

[c] Number in parentheses denotes degeneracy.

[d] The frequency corresponding to the harmonic vibrational frequency of the free CO(g) molecule: 2143.2 cm^{-1} [29].

intact despite the interaction with CO. At present only the $\Delta H_{0,i}^{\ominus}$ term for the "on-top" approach is known [28]. Therefore, the present study is an investigation into the "bridge" $\Delta H_{0,i}^{\ominus}$ parameter, which provides review of the possible types of behaviour depending on the relative energetics of the isomers. The free parameter of this treatment was the difference ΔE between the potential energies of the "bridge" and "on-top" structures. The other parameters for construction of the partition functions of the free CO(g) molecule were taken from ref. 30.

Table 2 gives a survey of the weight factors of the two types of adsorption complexes. If $\Delta E = 0$ (i.e. the same potential energy value for both types of

TABLE 2

Weight factor w_i of the "on-top" structure of the adsorption complex for selected temperatures T and potential energy differences [a] ΔE between both structures

T (K)	Source	w_i (%) [b]					
		$\Delta E = 0$	−1	−2	−3	−4	−5
50	RB	99.9	98.9	89.5	43.4	6.5	0.6
	PM	100.0	99.5	94.7	61.6	12.6	1.3
83.15 [c]	RB	98.3	93.2	76.2	43.0	15.1	4.0
	PM	98.6	94.4	79.9	48.4	18.1	4.9
200	RB	84.9	75.5	62.8	48.1	33.7	21.8
	PM	82.0	71.3	57.7	42.8	29.1	18.3
298.15	RB	78.6	71.0	62.1	52.3	42.2	32.8
	PM	73.8	65.3	55.6	45.6	35.9	27.2
500	RB	73.9	69.0	63.6	57.9	51.9	45.9
	PM	68.3	62.8	57.1	51.1	45.1	39.3

[a] ΔE denotes the difference: "bridge" − "on-top"; ΔE terms in kJ mol^{-1}.

[b] Here, i means "on-top"; the relationship $w_1 + w_2 = 1$ always holds.

[c] The normal boiling point of CO.

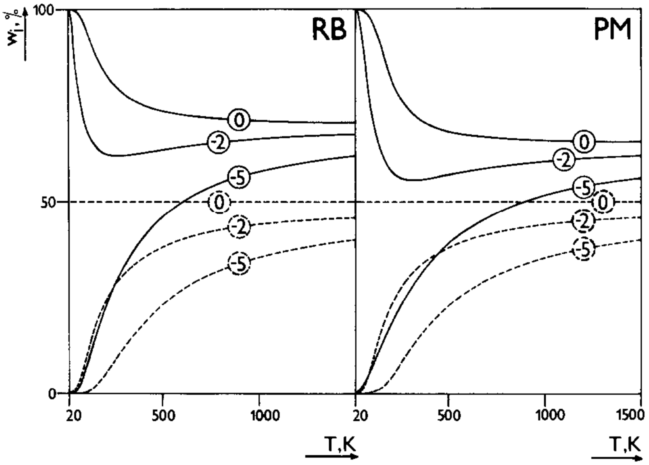

Fig. 1. Temperature dependences of the weight factors w_i (solid lines) and the simple Boltzmann factors (broken lines) of the "on-top" adsorption complex structure for selected values of the potential energy difference ΔE (indicated in kJ mol^{-1}), cf. Table 2; left, based on RB data [27], right, based on PM data [29].

structures), the "on-top" structure is always more populated, although at the high temperature limit its content decreases to about 71% and 66% in the RB and PM approximations, respectively. Generally, the RB population of the "on-top" structure is always somewhat higher than the corresponding PM value. However, a relatively small decrease of the potential energy of the "bridge" structure by 4–5 kJ mol^{-1} results in the inversion of the stability order, and the "bridge" structure becomes relatively more stable at low and medium temperatures; nevertheless, the "on-top" structure is more populated at the high temperature limit (Fig. 1). If the steric factors s_i were omitted from eqn. (2), the partition functions q_i neglected and the ground-state energies $\Delta H_{0,i}^{\ominus}$ replaced by mere potential energy terms, then the so-called Boltzmann factors would result; these are, in fact, used in some contexts. Figure 1 shows that their agreement is far from satisfactory in this particular case.

Table 3 presents the isomerism contributions $\delta H_1^{\mathrm{iso}}$, $\delta S_1^{\mathrm{iso}}$, and $\delta C_{p,1}^{\mathrm{iso}}$ related to the structure which is relatively more stable at low temperatures (i.e. "on-top" for the ΔE values nearer to zero, and "bridge" for more negative ΔE). As can be seen in Table 3 and, over a wider temperature range in Fig. 2, the $\delta C_{p,1}^{\mathrm{iso}}$ terms exhibit a temperature dependence with a local maximum whose position and height depend on the ΔE parameter. For example, in the PM approach, for $\Delta E = -2$ kJ mol^{-1} this maximum is somewhat greater than 7 J K^{-1} mol^{-1} and lies near 60 K. Obviously, the isomerism contribution to the heat capacity term can be more distinct than that to the entropy term. In addition, in contrast to the entropy term there exists no trivial upper limit for $\delta C_{p,1}^{\mathrm{iso}}$, and with varying values of the

TABLE 3

Isomerism contributions [a] to enthalpy δH_1^{iso}, entropy δS_1^{iso} and heat capacity $\delta C_{p,1}^{iso}$

T (K)	Source	δH_1^{iso} [b] (kJ mol^{-1})	δS_1^{iso} [b] (J K^{-1} mol^{-1})	$\delta C_{p,1}^{iso}$ (J K^{-1} mol^{-1})		
				$\Delta E = 0$	-2	-5
50	RB	0.003	0.07	0.43	4.77	1.13
	PM	0.002	0.04	0.28	6.03	1.24
83.15	RB	0.050	0.74	2.45	1.89	3.00
	PM	0.048	0.69	2.85	5.61	2.00
200	RB	0.359	3.15	1.36	−1.90	4.70
	PM	0.493	4.12	1.94	−2.83	3.72
298.15	RB	0.406	3.37	−0.09	−1.60	4.26
	PM	0.539	4.34	−0.47	−2.66	3.96
500	RB	0.335	3.19	−0.41	−0.72	2.63
	PM	0.377	3.93	−0.78	−1.18	2.82

[a] Related to the isomer indexed as 1, i.e. the isomer that is more stable at low temperatures: "on-top" and "bridge" structure for $\Delta E = 0$, -2 kJ mol^{-1} and $\Delta E = -5$ kJ mol^{-1}, respectively.

[b] Data for $\Delta E = 0$ only are presented.

parameters involved this contribution can attain substantially higher values (see ref. 26) than those reported in Table 3.

The existence of a local maximum in temperature dependence is a distinct qualitative feature. Nevertheless, the $\delta C_{p,1}^{iso}$ term itself is not easily accessible for measurement. It is more appropriate to consider the values of overall standard change $\Delta C_p^{\ominus}$. Table 4 presents the values of partial and overall

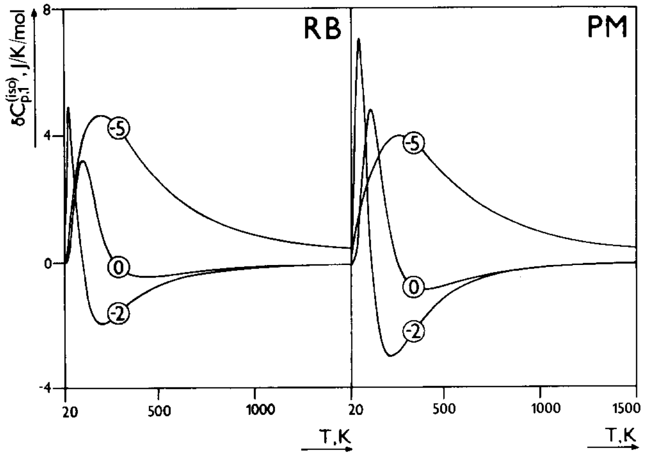

Fig. 2. Temperature dependences of the isomerism contributions to heat capacity $\delta C_{p,1}^{iso}$, related to the isomer more stable at low temperature (see Fig. 1 and Table 3) for selected values of the potential energy difference ΔE (indicated in kJ mol^{-1}); left, based on RB data [27], right, based on PM data [29].

TABLE 4

Partial and overall standard [a] changes in heat capacity at constant pressure for the adsorption process $CO(g) + (001)Ni(s) = CO \cdot (001)Ni(s)$

T (K)	Source	$\Delta C_p^\ominus$ (J K^{-1} mol^{-1}) [b]		
		"on-top"	"bridge"	overall [c]
50	RB	−18.4 (−18.4)	−22.3 (−22.3)	−18.0 (−18.0)
	PM	−23.4 (−23.4)	−23.1 (−23.1)	−23.1 (−23.1)
83.15	RB	−14.1 (−14.1)	−17.8 (−17.8)	−11.6 (−11.6)
	PM	−16.9 (−16.9)	−20.7 (−20.7)	−14.1 (−14.1)
200	RB	−0.67 (−0.67)	−6.06 (−6.06)	0.70 (0.70)
	PM	−0.71 (−0.71)	−8.32 (−8.32)	1.23 (1.23)
298.15	RB	5.24 (5.23)	1.00 (1.00)	5.15 (5.15)
	PM	5.36 (5.36)	−0.64 (−0.64)	4.89 (4.89)
500	RB	9.65 (9.61)	7.41 (7.47)	9.24 (9.20)
	PM	9.73 (9.69)	6.81 (6.77)	8.95 (8.91)

[a] Ideal behaviour, standard-state choice irrelevant.

[b] Evaluated for harmonic approach to the free CO(g) molecule. Data with inclusion of anharmonicity correction [30] for the latter species are presented in parentheses.

[c] Underlying weight factors evaluated for $\Delta E = 0$.

$\Delta C_p^\ominus$ terms for the process investigated and shows that in the particular case of the system studied, the local maximum noted above is overshadowed by the other contributions, although this need not be true in general.

In conclusion it can be stated that a correct description and interpretation of the behaviour of the CO(g) and Ni(001) system must accordingly consider the simultaneous presence of both structures, especially if the conditions of thermodynamic equilibrium are studied. The mutual proportions of the populations of both structures are, of course, very sensitive to their energy difference ΔE, which stresses the importance of its correct computational evaluation. The values of the isomerism contribution to heat capacity $\delta C_{p,1}^{\mathrm{iso}}$ appear to be significant, although their interesting extreme behaviour reported here need not be apparent in the values of standard overall changes following the corresponding chemical reaction. Studies of this type form a wider background for the newly formulated fluxional concept of the heterogeneous catalysis suggested by Simonetta [31].

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