Journal of Thermal Analysis and Calorimetry, Vol. 91 (2008) 1, 167–172

ENTROPY OF ADSORPTION OF CARBON MONOXIDE ON ENERGETICALLY HETEROGENEOUS SURFACES

X. Xia[*]*, R. Naumann d'Alnoncourt and M. Muhler*

Laboratory of Industrial Chemistry, Ruhr-University Bochum, 44780 Bochum, Germany

Standard entropies of adsorption (Δs^0) of CO on different materials (Cu catalysts, Au catalysts, ZnO and to TiO_2) are obtained from static adsorption microcalorimetry, adsorption isobars and temperature-programmed desorption, based on the thermodynamics of adsorption on energetically heterogeneous surfaces. Vibrational entropies of the surfaces $s^{\sigma}_{\mathrm{vib}}$ are normally between the rotational and the standard translational entropy of CO in gas phase, and decrease with increasing adsorption energy, which agrees with the explanation of statistical thermodynamics. Δs^0 reflects both the mobility of adsorbates and the specific adsorbate-adsorbent interaction. Limits for reasonable values of the entropy of adsorption are proposed.

Keywords: *entropy of adsorption, microcalorimetry, temperature-programmed desorption*

Introduction

The knowledge of adsorption entropy is important to understand adsorbate-adsorbent interactions. In previous studies on adsorption entropy, attention was paid to the mobility of surface species. Kemball [1] distinguished 'mobile' and 'localized' adsorption based on the adsorption entropy. Boudart *et al.* [2] proposed that the boundary of the negative of adsorption entropy is between 10 cal mol^{-1} K^{-1} and 12.2 cal mol^{-1} K^{-1}–0.0014 $\mathrm{K}^{-1}\cdot\Delta H$. Knox *et al.* [3] suggested two limits, one is that the adsorbates act as two-dimensional gas on the surface, the other is that the adsorbates are completely localized. Lopatkin [4, 5] studied entropies of adsorption of hydrocarbons on carbon blacks and found that the entropies of adsorption for aromatic hydrocarbon agreed with the loss of one translational degree of freedom, while there was a difference between this loss and the adsorption entropies of aliphatic hydrocarbons.

Most of the entropies of chemisorption were derived from calorimetrically measured heats of adsorption and adsorption isotherms [6–15]. It can also be derived from several isotherms at various temperatures [1], from temperature-programmed desorption (TPD) under free-readsorption conditions with known flow rate and amount of adsorption sites [16, 17], from kinetic experiments [2], and from gas chromatography [4, 5]. The first three methods are generally applied in the studies on solid surfaces and heterogeneous catalysis.

The Langmuir model is the basis for these studies, and the various entropy concepts within this model have been explained [18].

In the Langmuir model, the standard entropy of adsorption (Δs^0) is defined as

$$\Delta s^0 = s^{\sigma,0} - s^{g,0} = s^{\sigma}_{\mathrm{vib}} - s^{g,0} \tag{1}$$

where $s^{\sigma,0}$ is the standard mean integral entropy of an adsorbed mole of molecules referring to the standard state (fractional coverage θ=1), which is proved to be equal to the vibrational entropy of the surfaces $s^{\sigma}_{\mathrm{vib}}$ [18]; and $s^{g,0}$ is the molar entropy of adsorptive gas at standard pressure.

The Langmuir isotherm can be written as

$$\theta^{\mathrm{eq}} = \frac{Kp^{\mathrm{eq}}}{1+Kp^{\mathrm{eq}}} \tag{2}$$

where p^{eq} is equilibrium pressure and θ^{eq} is fractional coverage. Following this expression, Δs^0 is related to the Langmuir coefficient K by

$$K = \frac{1}{p^0}\exp\left(-\frac{\Delta H}{RT} + \frac{\Delta s^0}{R}\right) \tag{3}$$

$$\Delta s^0 = \frac{\Delta H}{T} + R\ln\frac{\theta^{\mathrm{eq}}}{(1-\theta^{\mathrm{eq}})\,p^{\mathrm{eq}}/p^0} \tag{4}$$

where ΔH is the adsorption enthalpy, p^0 is the standard pressure, R is the ideal gas constant, and T is the temperature. Therefore, Δs^0 can be derived by fitting Eq. (4) to the isotherm with known ΔH.

---

[*] *Author for correspondence: xinyu_xia@berkeley.edu
Current address: Department of Chemical Engineeering, University of Calirofrnia at Berkeley, 94720 Berkeley, USA

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Rouquérol *et al.* [10, 11] described the prerequisite to obtain Δs^0 from adsorption calorimetry: the adsorption should be close to equilibrium. If ΔH is not measured, from at least two adsorption isobars, Eq. (2) with Eq. (3) can be fitted and Δs^0 is still obtainable.

Additionally, Δs^0 is also related to the kinetic parameters by

$$\Delta s^0 = R\ln\left(\frac{A_a p^0}{A_d}\right) \qquad (5)$$

where A_a and A_d are the pre-exponential parameters for adsorption and desorption in the Wigner–Polanyi equation, respectively:

$$\frac{d\theta}{dt} = A_a \exp\left(-\frac{\varepsilon_a}{RT}\right)p(1-\theta) - A_d \exp\left(-\frac{\varepsilon_d}{RT}\right)\theta \qquad (6)$$

where t is time, ε_a and ε_d are the activation energies for adsorption and desorption, respectively. Therefore, from TPD measurements under a condition where re-adsorption happens freely [19], the adsorption entropy (instead of A_d) can be derived, with the following expression:

$$\beta\frac{d\theta}{dT} = -\frac{p^0\dot{V}}{N_m R T_a}\exp\left(\frac{\Delta H}{RT} - \frac{\Delta s^0}{R}\right)\frac{\theta}{1-\theta} \qquad (7)$$

where β is the heating rate, $\dot{V}$ is the flow rate, N_m is the molar amount of adsorption sites on the sample surfaces, and T_a is the ambient temperature.

Compared with the extensive study on heats of adsorption of small probe molecules (CO, H_2,CO_2 and NH_3) on catalyst surfaces, very few adsorption entropy values have been reported in literature. The reasons may include the following: (1) an evaluation method is lacking to study adsorption on energetically heterogeneous surfaces, with accurate consideration of entropy; (2) the error bars of heats of adsorption on supported materials are large, especially when there is perturbance by surface reactions; (3) the amount of adsorption sites of a single layer of porous materials is often uncertain; (4) for strong adsorption at room temperature, the equilibrium pressure is too low to be measured.

In this work, we present the adsorption entropies of CO on different materials. Kinetics and thermodynamics of adsorption on energetically heterogeneous surfaces have been studied in our previous work [20–22], Δs^0 can be derived with these theoretical results from many adsorption measurements. Here, we focus on CO adsorption, because, as a commonly applied probe molecule, CO has a low boiling point and a low vapor pressure, thus there is basically no interference of physisorption. In addition, adsorption of CO on many materials is not activated, nor very strong, thus the volumetric change is easy to reach equilibrium and the equilibrium pressure is easy to measure. CO adsorption may be accompanied by some redox reactions, but the interference of these surface reactions can be avoided by repeated adsorption measurements. Therefore, compared with that of other small probe molecules such as H_2,H_2O, NH_3 and CO_2, more measurements of CO adsorption are available for a reliable derivation of Δs^0.

Adsorption thermodynamics on heterogeneous surfaces

The distribution of adsorption sites corresponding to adsorption energy is evaluated by the following uniform distribution:

$$f(\varepsilon) = \begin{cases} 1/\varepsilon_\delta, & \text{for } \varepsilon \in [\varepsilon_m - \varepsilon_\delta, \varepsilon_m] \\ 0, & \text{elsewhere} \end{cases} \qquad (8)$$

where ε_m is the adsorption energy ε of the most active sites, ε_δ and f are the scale parameter and probability density of this distribution, respectively. The Temkin isotherm, which is commonly applied in catalysis studies, can be obtained from this model with some approximations [20, 23, 24]. By integrating Eqs (2) and (6) over ε, thermodynamics and kinetics of adsorption on heterogeneous surfaces are derived [20, 21].

Here s^σ_{vib} is assumed to be independent of ε (thus Δs^0 is also independent of ε). There are both theoretical and practical reasons for this assumption:

(1) Theoretically, for chemisorption, the variation of s^σ_{vib} on different adsorption sites is much smaller than ε. It is a function of vibrational frequency [25]:

$$s^\sigma_{vib} = R\sum_j\left\{\frac{h\nu_j/k_B T}{\exp(h\nu_j/k_B T)-1} - \ln\left[1-\exp\left(\frac{h\nu_j}{k_B T}\right)\right]\right\} \qquad (9)$$

where h is the Planck constant; k_B is the Boltzman constant; ν_j is the frequency of the j-th vibration. Figure 1 illustrates the vibrational contribution to entropy on the surfaces as a function of vibrational frequency according to Eq. (9), the vibrational entropy comes mainly from the low-energy vibration (wave number <1000 cm^{-1}). Moreover, the difference of adsorption entropy caused by the difference vibration wave number of about 200 cm^{-1} is only several J mol^{-1} K^{-1}, considerably smaller than the absolute value of Δs^0.

(2) Practically, a model concerning the dependence of s^σ_{vib} on ε not only increases the difficulty of the mathematical treatment, but also becomes too flexible. The assumption of identical Δs^0 is also ap-

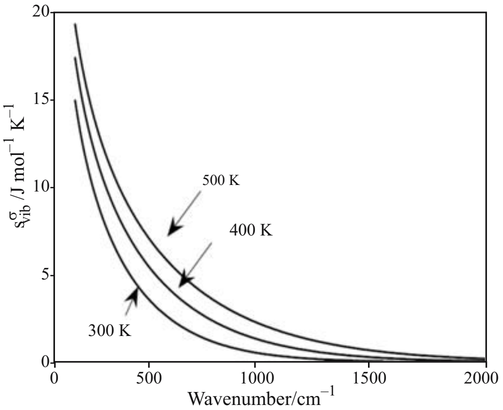

Fig. 1 Vibrational contribution to entropy on the surfaces as a function of vibrational frequency calculated from Eq. (9)

plied in the derivation of the adsorption isotherms (Temkin isotherm and Freundlich isotherm) on energetically heterogeneous surfaces [23].

Derivation from calorimetric measurements

Thermodynamics of adsorption on heterogeneous surfaces described by Eq. (8) is expressed by the following two equations [20]:

$$\Theta=\frac{RT}{\varepsilon_\delta}\ln\frac{1+\exp(\varepsilon_m/RT+\Delta s^0/R)p^{eq}/p^0}{1+\exp[(\varepsilon_m-\varepsilon_\delta)/RT+\Delta s^0/R]p^{eq}/p^0} \qquad (10)$$

$$q^{diff}= \\ =\varepsilon_m-\frac{[\exp(\varepsilon_\delta/RT)-1]\Theta-[\exp(\varepsilon_\delta\Theta/RT)-1]}{[\exp(\varepsilon_\delta\Theta/RT)-1]\{\exp[\varepsilon_\delta(1-\Theta)/RT]-1}\varepsilon_\delta \qquad (11)$$

where Θ is the fractional coverage on energetically heterogeneous surfaces, and q^{diff} is the differential heat of adsorption. By fitting Eqs (10) and (11) to the isotherm and q^{diff} in a static isothermal adsorption microcalorimetric measurement, Δs^0 is obtained [20].

Equation (10) alone can also be fitted to isobars, without direct measurements on q^{diff}. In this case, the change of Δs^0 as a function of T should be considered:

$$\Delta s^0(T)=s^\sigma_{vib}(T)-s^{g,0}_{vib}(T)-s^{g,0}_{rot}(T)-s^{g,0}_{trans}(T) \qquad (12)$$

The change of Δs^0 with T is mainly due to the variation of standard translational entropy of the gas phase ($s^{g,0}_{trsnas}$), which can be calculated from the Sackur–Tetrode equation [25]. Thus Eq. (12) changes to

$$\Delta s^0(T)=\Delta s^0_{vib}-s^{g,0}_{trans}(T) \qquad (13)$$

where $\Delta s^0_{vib}=s^\sigma_{vib}(T)-s^{g,0}_{vib}(T)-s^{g,0}_{rot}(T)$, its change with T is omitted. By fitting Eq. (10) with Eq. (13) and Sackur–Tetrode equation to several isobars, all the parameters of ε_m, ε_δ and Δs^0_{vib} can be obtained, and Δs_0 can be derived from Δs^0_{vib} at a given T with Eq. (13).

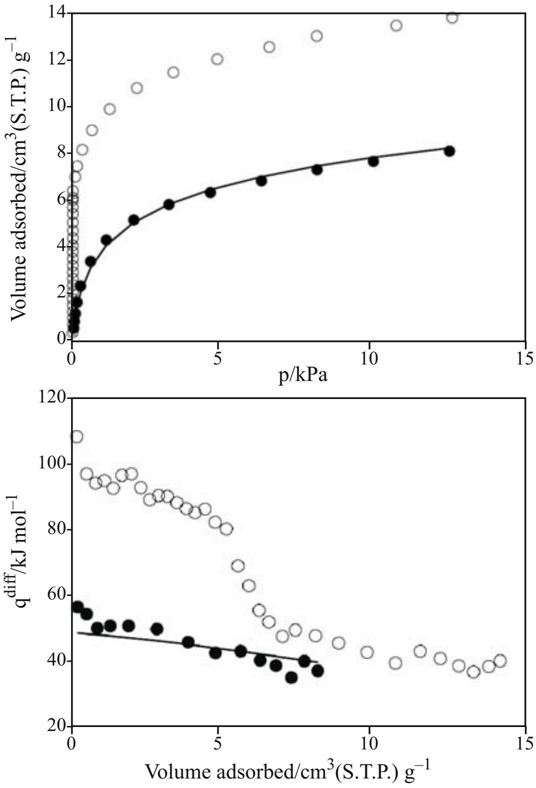

Fig. 2 Fitting Eqs (10) and (11) to isotherm and q^{diff} of the second adsorption measurement (filled circles) of CO on copper ion-exchanged ZSM-5 at 301 K. Open circles represent the first adsorption processes. Solid line: theoretical value with $\Delta s^0=-123$ J mol^{-1} K^{-1}, $\varepsilon_m=53$ kJ mol^{-1}, and $\varepsilon_d/V_m=1.35$ (kJ/mol)/(cm^3/g). Data source: Kuroda *et al.* [26]

Figure 2 presents an example of fitting Eqs (10) and (11) to the isotherm and differential heat in calorimetric measurements to obtain the adsorption entropy. The adsorption system is CO on a copper ion-exchanged ZSM-5 sample at 301 K studied by Kuroda *et al.* [26]; as the authors pointed out, the difference between the first and the second adsorption indicates that adsorption is not totally reversible. The second measurement reflects a stable surface, on which the adsorption can be well described by the above model. Since V_m was not given, fitting results are not sensitive to ε_δ, but to the ratio of ε_δ/V_m. The best fitting gives $\Delta s^0=-123$ J mol^{-1} K^{-1} (thus $s^\sigma_{vib}=75$ J mol^{-1} K^{-1}), $\varepsilon_m=53$ kJ mol^{-1}, and $\varepsilon_\delta/V_m=1.35$ (kJ/mol)/(cm^3/g).

The value of s^σ_{vib} or $s^{\sigma,0}$ is smaller than that of the translational contribution of entropy ($s^\sigma_{trans}=151$ J mol^{-1} K^{-1}). This is reasonable, because the movement of adsorptive molecules is restricted to two-dimension. s^σ_{vib} is larger than the rotational contribution of entropy of CO ($s^{g,0}_{rot}=47$ J mol^{-1} K^{-1}), such a value indicates the contribution of low-energy vibrations with $\nu<300$ cm^{-1} (Fig. 1). It could be attributed to the low-energy vibrations of the bending and rocking mode, therefore CO should be adsorbed on-top without obvious π-backbonding. This result agrees with the IR measurement by Kuroda *et al.* [26].

The data of the first adsorption in Fig. 2 infer the prerequisite of deriving adsorption entropy from a calorimetric measurement: the adsorption should not be too strong, otherwise the equilibrium pressure would be below the measurement limit, and Δs^0 could not be obtained. Such strong adsorption systems include CO adsorption on VIII-B metals and hexane adsorption on zeolites [27, 28]. This problem can be overcome by increasing temperature or by using isobars or TPD measurements, but at a higher temperature surface reconstruction and adsorbate rearrangements may also become strong and make the model invalid.

Derivation from TPD

TPD from surfaces of porous materials are often carried out in a flow set-up under a 'free-readsorption' condition [19]. In this case, TPD spectra can be evaluated with the following equation for associative adsorption [22]:

$$\beta\frac{\mathrm{d}\Theta}{\mathrm{d}T}=-\frac{p^0V}{n_\mathrm{m}RT_\mathrm{a}}\exp\left(\frac{\varepsilon_\mathrm{max}}{RT}-\frac{\Delta s^0}{R}\right)K_\delta \tag{14}$$

the nomenclature is similar to Eq. (7), except that K_δ is a coefficient reflecting the diffusion equilibrium between adsorbates on the sites with different desorption barrier (ε_d):

$$K_\delta=\exp\left(\frac{\varepsilon_\delta}{2RT}\right)\frac{\sinh(\Theta\varepsilon_\delta/2RT)}{\sinh[(1-\Theta)\varepsilon_\delta/2RT]} \tag{15}$$

Figure 3 shows the TPD spectra of CO from ZnO with co-adsorbed CO_2. The purpose of this measurement is to compare with a similar calorimetric measurement, from which it is found that the existence of surface carbonate enhances the interaction between CO and the adsorption sites on ZnO which is not totally occupied by CO_2.

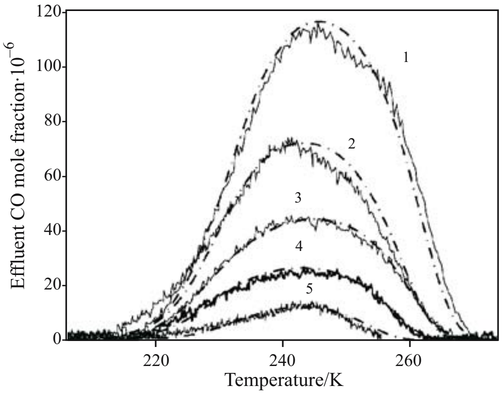

Fig. 3 TPD spectra of CO on Nanotek ZnO with co-adsorbed CO_2. 1, 2: first group, β=8.6 and 5.2 K min^{-1} respectively; 3–5: second group, β=8.7, 5.1 and 2.5 K min^{-1} respectively. Solid line: experimental data; dotted-dashed line: theoretical value, using parameters in Table 1

The experimental configuration of the flow TPD set-up was introduced elsewhere [29]. The composition of effluent gas (at ambient temperature) was monitored by a calibrated quadrupole mass spectrometer. Gas flow rate was 10 NmL min^{-1}. A ZnO sample with co-adsorbed CO_2 was obtained as following: 0.200 g of ZnO (ZnO Nanotek, from Nanophase Company) was pretreated at 450°C in diluted helium flow (purity: 99.9999%) for 4 h, then was exposed to 4% CO_2/He (purity: CO_2 99.9995%, He 99.9999%) gas flow at room temperature for 30 min, and to helium flow at room temperature for 1 h. The first measurement of TPD was achieved by the following procedures: CO is pre-adsorbed at 300 K in a flowing mixture of 10% CO in He (purity: CO 99.997%, He 99.9999%). Then the sample was cooled to 78 K rapidly in flowing CO/He by pouring liquid nitrogen into the heating block, followed by purging with pure helium flow for 10 min at the same temperature. Afterwards the sample was heated in helium flow with a heating rate of 5.2 K min^{-1}, until all CO desorbed (in the meantime, the desorption of CO_2 is negligible). The second measurement followed the first one and repeated the same procedure, but with a different heating rate (8.6 K min^{-1}). After this first group of TPD, the sample was heated up to 450°C to desorb all CO_2 and then adsorbed CO_2 again at room temperature, followed by a second group of CO TPD with three various heating rates.

Table 1 presents the thermodynamic parameters for the best-fitting to this two groups of TPD, with comparison to those fitted from the microcalorimetry measurement. The consistence between these results proved the reliability of these measurements. Compared with adsorption of CO on ZnO without CO_2 (ε_max=40 kJ mol^{-1} and Δs^0= −102 J mol^{-1} K^{-1}) [30], not only the adsorption energy becomes higher, but the adsorption entropy is more negative. Therefore, the interaction between CO and ZnO is stronger in the presence of CO_2. The value of Δs^0 still indicates a mediate on-top adsorption of CO, no overlapping surface reactions can be indentified from this value.

Table 1 ε_max and Δs^0 for best fitting to CO adsorption on ZnO with co-adsorbed CO_2

Measurements	ε_max/kJ mol^{-1}	Δs^0/J mol^{-1} K^{-1}
TPD 1st group	62	–114
TPD 2nd group	61	–114
Microcalorimetry	65	–114

Table 2 Δs^0 (303 K) and ε_m of CO adsorption on different surfaces

Adsorbates	Δs^0	ε_m
$Cu/ZnO/Al_2O_3$[a] [20]	–116	66
$Cu/ZnO/Al_2O_3$[b] [22]	–116	64
Cu/Al_2O_3[c] [31]	–110	71
Cu(I) exchanged ZSM5[a] [26]	–123	53
ZnO[b] [30]	–102	38
ZnO (CO_2 pretreated)[a]	–114	65
ZnO (CO_2 pretreated)[b]	–114	62
TiO_2[a] [32]	–104	40
TiO_2 (with 1 mass% Au)[c] [33]	–104	41
TiO_2 (sulfate-doped)[a] [34, 35]	–152	58
Au (100)[c] [36]	–84	46
Au/Al_2O_3[a] [37]	–120	59
Au/TiO_2[a] [37]	–150	77
Au/TiO_2[c] [33]	–146	83

Measurement methods: [a] microcalorimetry; [b] TPD; [c] isobars

Entropy of adsorption of CO on different materials

Table 2 summarizes the entropies of adsorption of CO on different materials derived with above methods. For a better understanding of the specific interactions on the surfaces, the relation of $s^{\sigma}_{\mathrm{vib}}$ *vs.* $\varepsilon_{\max}$ is plotted in Fig. 4.

In Fig. 4 it can be found that $s^{\sigma}_{\mathrm{vib}}$ of CO on different Cu catalysts measured with different methods are quite identical, which is typical for mediate or weak adsorption. The weak adsorption of CO on ZnO, on TiO_2 and on metallic gold is reflected not only by small $\varepsilon_{\max}$, but also by large $s^{\sigma}_{\mathrm{vib}}$. Similar to the effect of carbonate on ZnO surfaces, on sulfate doped titania, higher $\varepsilon_{\max}$ and lower $\Delta s^{\sigma}_{\mathrm{vib}}$ indicate stronger surface Lewis acidity due to the existence of acid anions. For the gold catalysts, Au/TiO_2 is found to be more active for CO adsorption compared with pure gold and Au/Al_2O_3; $\Delta s^{\sigma}_{\mathrm{vib}}$ may indicate an obvious π-backbonding, thus Ti^{3+} may exist, which can provide *d*-electrons through Au to CO.

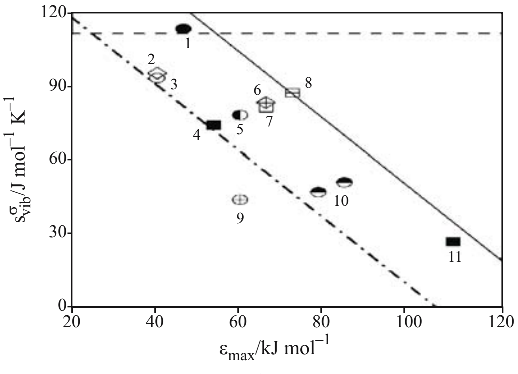

Fig. 4 Relation between $s^{\sigma}_{\mathrm{vib}}$, Δs^0 and ε_m of CO on different materials: 1 – Au(100); 2 – ZnO; 3 – TiO_2; 4 – CuZSM-5; 5 – Au/Al_2O_3; 6 – $Cu/ZnO/Al_2O_3$; 7 – ZnO pretreated with CO_2; 8 – Cu/Al_2O_3; 9 – TiO_2 doped with sulfate; 10 – Au/TiO_2. Data point 11 – is CO_2 adsorption on ZnO [38]. Solid line: limit of Eq. (17); dotted and dashed line: limit of Eq. (16); dashed line: limit of Eq. (18)

The data presented in Fig. 4 also indicate some limits of $s^{\sigma}_{\mathrm{vib}}$. The decrease of $s^{\sigma}_{\mathrm{vib}}$ with increasing $\varepsilon_{\max}$ means clearly that the vibration energy of adsorbates becomes higher for stronger adsorption. The limit proposed by Boudart *et al.* [2] is valid as the lower limit for most of these examples, which can be written as

$$s^{\sigma}_{\mathrm{vib}} > 146\ \mathrm{J\ mol^{-1}\ K^{-1}} - 0.0014\ \mathrm{K^{-1}}\varepsilon_{\mathrm{m}} \qquad (16)$$

Only one point (CO adsorption on sulfate doped TiO_2) is beyond this range. Due to the lack of results of other characterization methods, the reason of this deviation cannot be discussed here. With the same slope as Eq. (16), the upper limit concerning these data is estimated as

$$s^{\sigma}_{\mathrm{vib}} < 186\ \mathrm{J\ mol^{-1}\ K^{-1}} - 0.0014\ \mathrm{K^{-1}}\varepsilon_{\mathrm{m}} \qquad (17)$$

All of $s^{\sigma}_{\mathrm{vib}}$ values are smaller than $s^{\mathrm{g},0}_{\mathrm{trans}}$ (151 J mol^{-1} K^{-1}). This is reasonable, because they are corresponding to two-dimensional and three-dimensional movements, respectively. Most of $s^{\sigma}_{\mathrm{vib}}$ values are larger than $s^{\mathrm{g}}_{\mathrm{rot}}$ (47 J mol^{-1} K^{-1}) of CO at 303 K, due to the disorder of bending and rocking of CO on the surface. For stronger adsorption a narrow range of $0 < s^{\sigma}_{\mathrm{vib}} < s^{\mathrm{g}}_{\mathrm{rot}}$ can be estimated, in case that derivation from absorption measurements is difficult. With these limits, surface reactions can be distinguished, which often bring about entropies beyond this range.

The two-dimensional gas model provides other limits of reasonable adsorption entropy. According to this model, the adsorbate is regarded as two-dimensional gas which moves freely on the surfaces, and the entropy of the surfaces is considered as localized translation and rotation of adsorbates [3]. This is the extreme case of weak adsorbate-adsorbent interaction, consequently the following upper limit of $s^{\sigma}_{\mathrm{vib}}$ is obtained:

$$s^{\sigma}_{\mathrm{vib}} < s^{\mathrm{2D},0} \qquad (18)$$

where $s^{\mathrm{2D},0}$ is the standard entropy of two-dimensional gas. With Eq. (18) in Ref. [3], for CO adsorbates at 303 K, $s_{\mathrm{2D},0}$=111 J mol^{-1} K^{-1}, therefore $\Delta s^0 < s^{\mathrm{2D},0} - s^{\mathrm{g},0} = -87$ J mol^{-1} K^{-1}. Basically all the data in Fig. 4 agree with this limit.

The other limit proposed in Ref. [3], $\Delta s^0 > -95$ J mol^{-1} K^{-1} for localized CO adsorbates [3], is not suitable for both the data in Fig. 4 and the data gathered in that work (Fig. 2 in Ref. [3]). The reason may be due to that vibration frequency could not be well considered in Eq. (15) of Ref. [3]. From Fig. 1, it is seen that if the adsorbate-adsorbent binding is extremely strong, then $s_{\mathrm{vib}}^{\sigma}$ is close to 0. Therefore, the reasonable lower limit of $s_{\mathrm{vib}}^{\sigma}$ is

$$s_{\mathrm{vib}}^{\sigma}>0 \qquad (19)$$

Equations (16) to (19) formed the limits for reasonable value of entropy of chemisorption. Within this range, $s_{\mathrm{vib}}^{\sigma}$ can be well explained by Eq. (1). For example, with the known vibration frequencies inside and outside of CO adsorbates on copper (ν_{CO}=2076 cm^{-1}, ν_{CuC}=345.2 cm^{-1}, ρ=284.7 cm^{-1} and δ=32.8 cm^{-1}) [39], $s_{\mathrm{vib}}^{\sigma}$=68 or 98 J mol^{-1} K^{-1} is obtained concerning the degeneracy number for bending and rocking modes, and this value is very consistent to that derived from microcalorimetric measurement. From this point of view, entropies of chemisorption reflect more the specific adsorbate-adsorbents interaction than the localization of adsorbates.

Conclusions

Standard entropies of adsorption of CO on different heterogeneous surfaces are derived reliably from static adsorption microcalorimetry, adsorption isobars and temperature-programmed desorption based on the thermodynamics of adsorption on energetically heterogeneous surfaces. They reflect the specific interaction between adsorbates and adsorbents and are reasonable according to statistical thermodynamics.

References

1 C. Kemball, Adv. Catal., 2 (1950) 233.
2 M. Boudart, D. E. Mears and M. A. Vannice, Int. Chim. Belge 32 special issue, (1967) 281.
3 D. Knox and D. B. Dadyburjor, Chem. Eng. Commun., 11 (1981) 99.
4 A. A. Lopatkin, Ross. Khim. Zh., 40 (1996) 5.
5 A. A. Lopatkin, Zh. Fiz. Khim., 71 (1997) 916.
6 M. M. Dubinin, A. A. Isirikjan, A. I. Sacharov and V. V. Sepinskij, Izv. Akad. Nauk SSSR, Ser. Khim., 11 (1969) 2355.
7 M. Nagao and T. Motimoto, J. Phys. Chem., 73 (1969) 2355.
8 R. W. Glass and R. A. Ross, J. Phys. Chem., 77 (1973) 2751.
9 H. Blank, M. Bülow and W. Schimmer, Z. Phys. Chem., 256 (1975) 581.
10 E. Garrone, F. Rouquérol, B. Fubini and G. Della Gatta, J. Chim. Phys., 76 (1979) 528.
11 F. Rouquérol, J. Rouquérol, G. Della Gatta and C. Letoquart, Thermochim. Acta, 39 (1980) 151.
12 E. Garrone, G. Ghiotti, E. Giamello and B. Fubini, J. Chem. Soc. Faraday Trans. 1, 77 (1981) 2613.
13 N. Cardona-Martinez and J. A. Dumesic, J. Catal., 125 (1990) 427.
14 P. Cartini, A. Gervasini and A. Auroux, J. Catal., 150 (1994) 274.
15 P. Cartini, A. Gervasini and A. Auroux, Langmuir, 17 (2001) 6938.
16 M. Sawa, M. Niwa and Y. Murakami, Zeolites, 10 (1990) 307.
17 A. M. Efstathiou and C. O. Bennett, J. Catal., 124 (1990) 116.
18 N. Cardona-Martinez and J. A. Dumesic, Adv. Catal., 38 (1992) 149.
19 R. J. Cvetanović and Y. Amenomiya, Adv. Catal., 17 (1967) 103.
20 X. Xia, S. Litvinov and M. Muhler, Langmuir, 22 (2006) 8063.
21 X. Xia, R. Naumann d'Alnoncourt, J. Strunk, S. Litvinov and M. Muhler, Appl. Surf. Sci., 253 (2007) 5851.
22 X. Xia, J. Strunk, S. Litvinov and M. Muhler, J. Phys. Chem. C., 111 (2007) 6000.
23 F. C. Tompkins, Chemisorption of Gases on Metals, Academic Press, London 1978, p. 101.
24 W. Rudzinski and T. Panczyk, J. Phys. Chem. B, 104 (2000) 9149.
25 D. A. McQuarrie, Statistical Thermodynamics, University Science Books, Mill Valley, 1985, p. 81.
26 Y. Kuroda, Y. Yoshikawa, R. Kumashiro and M. Nagao, J. Phys. Chem. B., 101 (1997) 6497.
27 L. Li, X. Wang, J. Shen, L. Zhou and T. Zhang, J. Therm. Anal. Cal., 82 (2005) 103.
28 V. Rac, V. Rakić, S. Gajinov, V. Dondur and A. Auroux, J. Therm. Anal. Cal., 84 (2006) 239.
29 M. Muhler, L. P. Nielsen, E. Törnqvist, B. S. Clausen and H. Topsøe, Catal. Lett., 14 (1992) 241.
30 X. Xia, J. Strunk, R. Naumann d'Alnoncourt, W. Busser, L. Khodeir and M. Muhler, 'Probing the Surface Heterogeneity of Polycrystalline Zinc Oxide by Static Adsorption Microcalorimetry, Part I: The Adsorption of Carbon Monoxide', J. Phys. Chem. C. submitted.
31 O. Dulaurent, X. Courtois, V. Perrichon and D. Bianchi, J. Phys. Chem. B, 104 (2000) 6001.
32 X. Xia, W. Busser, J. Strunk and M. Muhler, Langmuir, 23 (2007) in press.
33 S. Derrouiche, P. Gravejat and D. Bianchi, J. Am. Chem. Soc., 126 (2004) 13010.
34 V. Bolis, B. Fubini, E. Garrone, C. Morterra and P. Ugloengo, J. Chem. Soc. Faraday Trans., 88 (1992) 391.
35 E. Garrone, V. Bolis and C. Morterra, Langmuir, 5 (1989) 892.
36 J. M. Gottfried, K. J. Schmidt, S. L. M. Schroeder and K. Christmann, Surf. Sci., 536 (2003) 206.
37 X. Xia, M. Comotti, J. Strunk, W. Busser, F. Schüth and M. Muhler, 'Comparison of CO oxidation over gold catalysts supported on different oxides studied by static adsorption microcalorimetry', in preparation.
38 X. Xia, J. Strunk, W. Busser, R. Naumann d'Alnoncourt and M. Muhler, 'The Influence of Surface Hydroxyl Groups on the Adsorption of CO_2 on Nanocrystalline ZnO Powders', J. Phys. Chem. submitted.
39 G. Witte, Surf. Sci., 502–503 (2002) 405.

DOI: 10.1007/s10973-007-8440-x