ELSEVIER

Catalysis Today 70 (2001) 73–82

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Site-specified and complex-specified formation of geminal species during adsorption of small molecules on cationic sites

Konstantin Hadjiivanov*, Elena Ivanova, Dimitar Klissurski

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

---

Abstract

The geminal complexes formed after adsorption of small molecules on cationic sites may be divided into two main groups: *site*- and *complex-specified*. Complex-specified formation always occurs during the interaction of definite cations with certain molecules. Typical examples are the $Co^{2+}(NO)_2$ species. A peculiarity, in this case, is that the geminal complexes are more stable than the respective linear species. The site-specified formation of geminal complexes is determined by the low co-ordination number of the cation serving as adsorption centre. Typical examples are the geminal species formed on metal cations exchanged in ZSM-5 zeolite: $Cu^{+}(CO)_2$ and $Na^{+}(N_2)_2$. In this case, the linear complexes are more stable than the geminal species. Mathematical expressions describing the adsorption isotherms as well as the ratios between the linear and geminal species at different coverages are proposed. The co-adsorption of two gases is also considered. Simultaneous adsorption of three molecules on one centre is illustrated by the formation of $Cu^{+}(H_2O)_2CO$ adducts on Cu-ZSM-5. Finally, the possibility of formation of species that are site- and complex-specified is discussed.

Keywords: Adsorption; Adsorption isotherms; Carbon monoxide; Co-adsorption; Co-ZSM-5; Cu-ZSM-5; Dinitrogen; Geminal species; IR spectroscopy; Na-ZSM-5; Nitrogen monoxide

---

1. Introduction

Heterogeneous catalysis involves reactions between adsorbed molecules. In many cases, e.g. dimerisation, elementary reaction steps require two molecules to be attached simultaneously to one surface centre. That is why detailed knowledge of the ability of the adsorption centres to co-ordinate two or more molecules is of great importance. When the co-adsorbed molecules are identical, geminal complexes of $M(L)_2$ type are formed. One can expect that, if such species can be produced on a given centre, mixed ML_1L_2 species would also be formed easily. However, many results imply that this does not occur in all cases.

Analysis of the data from the literature shows that geminal complexes can be divided into two main groups. The first group involves the cases when the geminal species are much more stable than the respective linear complexes. Moreover, linear species are often not observed at all. Typical examples are many surface di-nitrosyl species. It is known that NO in the condensed state forms dimers and in many cases NO adsorption on systems containing d^n metal cations results exclusively in formation of di-nitrosyls, e.g. $V^{4+}(NO)_2$ [1,2], $V^{3+}(NO)_2$ [1,2], $Cr^{3+}(NO)_2$ [3], $Cr^{2+}(NO)_2$ [4], $Mo^{4+}(NO)_2$ [5], $Fe^{2+}(NO)_2$ [6], $Co^{2+}(NO)_2$ [7] and $Rh^{+}(NO)_2$ [8]. Carbon monoxide also forms multi-carbonyls with some metal cations. Here the $Rh^{+}(CO)_2$ [9], $Ir^{+}(CO)_2$ [10], $Ru^{n+}(CO)_x$

---

* Corresponding author. Tel.: +359-2-9793598;
fax: +359-2-705024.
E-mail address: kih@svr.igic.bas.bg (K. Hadjiivanov).

0920-5861/01/$ – see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S0920-5861(01)00408-4

[11], $Os^{n+}(CO)_x$ [12], $V^{3+}(CO)_2$ [13], $Cr^{2+}(CO)_3$ [14], $Mo^{4+}(CO)_3$ [15] and $W^{4+}(CO)_2$ [16] species should be mentioned. An important peculiarity of all these cases is that the geminal species are produced irrespective of the kind of the support which could affect the stability of the species but would not influence the number of ligands. In this case, mixed complexes although sometimes produced are not typical. In what follows, we shall refer to those species as complex-specified geminal complexes.

The second group of geminal complexes concerns the cases when the linear species are more stable than the respective geminal complexes. At high equilibrium pressures of the adsorbate and/or at low temperatures, a second (third) molecule can be co-ordinated to the same centre. In these cases, the formation of geminal complexes is caused by the low co-ordination number of the central metal cation. As a result, mixed complexes are easily produced. Further on, we shall refer to those species as site-specified geminal complexes.

To the best of our knowledge, the first well-documented example of a site-specified geminal complex is $Ca^{2+}(CO)_2$ formed at low temperature and under a CO atmosphere on CaNaY [17]. With decreasing pressure these species lose one CO ligand and are transformed into Ca^{2+}–CO carbonyls. A similar phenomenon was proposed some years later for co-ordination of CO to Na^+ cations in Na-ZSM-5 [18]. Many researches have observed conversion between mono- and di-nitrosyls [19] and between mono- and di-carbonyls of Cu^+ ions in Cu-ZSM-5 [20–23] and in other zeolites [24,25]. Recently, conversion between mono- and geminal species was reported in the following cases: CO on Ag^+ from Ag-ZSM-5 [26–28]; CO on Na^+ from NaY [29,30], Na-ETS-10 [31] and Na-EMT [32]; CO on K^+, Rb^+ and Cs^+ from Me-EMT [32]; CO on Cu^{2+} from Cu-ZSM-5 [33]; N_2 on Na^+ from NaY [29], Na-ETS-10 [31] and Na-EMT [32]; N_2 on K^+, Rb^+ and Cs^+ from Me-EMT [32]; H_2 and NO on Na^+ from Na-ETS-10 [31]. In all these cases, the geminal species were observed at low temperature only. Also note that all of the above examples concern cations exchanged in zeolites or other molecular sieves. Indeed, it is well known that cations in a zeolite matrix are usually characterised by a low co-ordination number [34].

Adsorption equilibria have been widely described by different adsorption isotherms. Among them, the Langmuir's isotherm, concerning uniform active sites, is the basic one [35]. For a long time, there have been no isotherms describing the simultaneous occupation of one active centre by two or more molecules. Some years ago, we proposed such isotherms for the case of formation of di-carbonyls [36]. More recently, it was found that the equations proposed describe very well the experimental results in the case of $^{15}N_2$ adsorption on Na^+ cations from NaY [29].

Conventional adsorption techniques allow one to obtain experimentally the dependence of the total coverage on the adsorbate equilibrium pressure. The changes in concentration of the mono- and di-species, however, can easily be followed by IR spectroscopy, since both types of complexes are normally detected at different wavenumbers [13]. Considering diatomic ligands, in most cases, geminal species manifest symmetric and antisymmetric stretching modes [1–16,20–26] which facilitate their spectral identification. However, when adsorption is weak, both ligands behave as independent oscillators and the geminal species possess one stretching mode only [17,18,29–32].

The aims of this work are: (i) to propose a theoretical background of formation of geminal species, namely equations describing the adsorption equilibria; (ii) to illustrate, by different examples, the applicability of IR spectroscopy to the study of these processes. All examples are based on cation-exchanged ZSM-5 zeolites, since, among the cations in solids, the cations in a ZSM-5 matrix are believed to be characterised by the highest co-ordinative unsaturation [23,26,27]. In addition, since ZSM-5 is a highly siliceous zeolite, the exchanged cations can be regarded as isolated, which facilitates the theoretical considerations (see below).

2. Experimental

The preparation of Co-ZSM-5 [7] and Cu-ZSM-5 [33] samples was described elsewhere, whereas Na-ZSM-5 was a commercial product. The IR spectra were recorded on Nicolet Avatar 320 (CO and NO adsorption) and Bruker IFS-66 ($^{15}N_2$ adsorption) spectrometers. Prior to the experiments, the samples were activated by 1 h oxidation treatment at 400°C followed by 1 h evacuation at the same temperature. Carbon monoxide (>99.5) and nitrogen monoxide

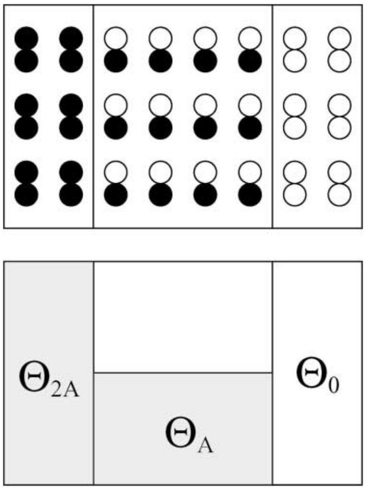
(>99.0) were purchased from Merck. Labelled nitrogen ($^{15}N_2$) was provided by Isotec, A. Matheson (USA) and had an isotopic purity of 99.7%.

3. Simultaneous adsorption of two equal molecules on one centre

The adsorption isotherms illustrating the simultaneous occupation of one centre by two molecules are proposed in Ref. [36]. Here the main points will be briefly recalled and some new consequences and applications will be proposed.

Let us consider a case when the surface centres are isolated and energetically homogeneous. Each centre can co-ordinate up to two adsorbate molecules and can thus be formally regarded as consisting of two sites. After co-ordination of one molecule to one site of the centre, the energetic characteristics of the neighbouring pair-site are changed. When a second molecule is co-ordinated, both adsorbed molecules become equal. Scheme 1 presents a picture, illustrating the occupation of the sites at a moderate coverage.

Here Θ_A is the fraction of sites where only one site from a centre is occupied by an adsorbate molecule and Θ_{2A}, the fraction of sites where both sites from a centre are occupied. The total coverage, Θ, is a sum of Θ_A and Θ_{2A}.



Scheme 1. Occupation of the sites at a moderate coverage. The opened circles correspond to free sites and the filled circles, to occupied sites.

The following correlations will be valid in the presence of equilibrium:

$$(1-2\Theta_A-\Theta_{2A})P = a\Theta_A \tag{1}$$

$$\Theta_A P = b\Theta_{2A} \tag{2}$$

where P is the adsorbate equilibrium pressure, and a and b are equilibrium constants having a pressure dimension.

From the above equations, the following adsorption isotherms can be derived easily:

$$\Theta_A = \frac{bP}{P^2+2bp+ab} \tag{3}$$

$$\Theta_{2A} = \frac{P^2}{P^2+2bP+ab} \tag{4}$$

$$\Theta = \Theta_A + \Theta_{2A} = \frac{P(P+b)}{P^2+2bP+ab} \tag{5}$$

Analysis leads to the following conclusions:

$$\text{when } P=(ab)^{1/2},\ \text{we have} \quad \Theta = 0.5 \text{ and } \frac{\partial\Theta_A}{\partial P} = 0 \tag{6}$$

i.e. Θ_A reaches a maximum with the above values of P and Θ,

$$\text{when } P=b,\ \text{we have } \Theta_A = \Theta_{2A} \tag{7}$$

i.e. at the cross-point of the Θ_A and Θ_{2A} curves. Eqs. (6) and (7) allow calculation of the coefficients a and b if one obtains experimentally the adsorption isotherms.

Plots of these isotherms with different ratios between the coefficients a and b are presented in Fig. 1. Panel A concerns a case when the adsorption of the first molecule is much stronger than the adsorption of the second molecule, i.e. $a \ll b$. This is illustrated with an a/b ratio of 1/60. It is seen that, at very low pressures, almost all sites are occupied by one molecule and the dependence of Θ_{2A} on the equilibrium pressure almost follows a Langmuir-type curve. Simultaneously, the concentration of the linear species decreases with pressure.

Using Eqs. (3) and (4), we simulated the IR spectra of adsorbed species. The positions and the FWHM of the bands were conformable to some cases observed with real systems. The absorption coefficients of all

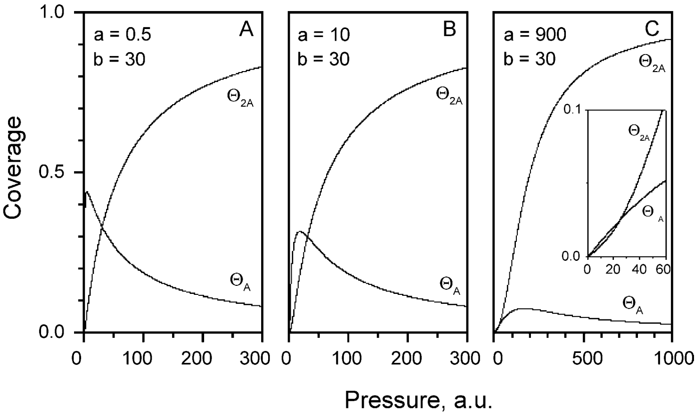


Fig. 1. Adsorption isotherms illustrating the case when up to two molecules can be simultaneously adsorbed on one centre: change in the concentrations of mono- and geminal species as a function of the adsorbate equilibrium pressure. Plots A, B and C illustrate the isotherms at different *a*/*b* ratios (for details see text).

bands were considered to be equal, although small differences were expected. The results of the case when the adsorption of the first molecule is much stronger (ratio $a/b = 1/60$) are presented in Fig. 2A. The inset demonstrates that, in this case, a clear isosbestic point exists. Fig. 3 presents the spectra of different equilibrium pressures of CO adsorbed on Cu-ZSM-5. According to data from the literature [20–24], the band at 2157 cm^{-1} is due to Cu^{+}–CO species, whereas the corresponding geminal Cu^{+}(CO)$_2$ complexes are characterised by a set of bands at 2177 and 2151 cm^{-1}. It is seen, from the inset in Fig. 3, that a clear isosbestic point exists between the bands at 2157 and 2151 cm^{-1}. The good coincidence between the simulated and the registered spectra is evident and supports both the assignments of the bands and the validity of the proposed isotherms. However, an additional isosbestic point between the 2157 and 2177 cm^{-1} bands is observed at low CO equilibrium pressures only. A possible explanation of this phenomenon is that vibrations of another species contribute to the 2177 cm^{-1} band, especially at high equilibrium pressures. Indeed, we have demonstrated recently that linear carbonyls formed with the participation of Cu^{2+} ions from Cu-ZSM-5 give rise to a band at 2178 cm^{-1} [33].

The second case we shall consider refers to weak interaction between the adsorbed molecules. Here the

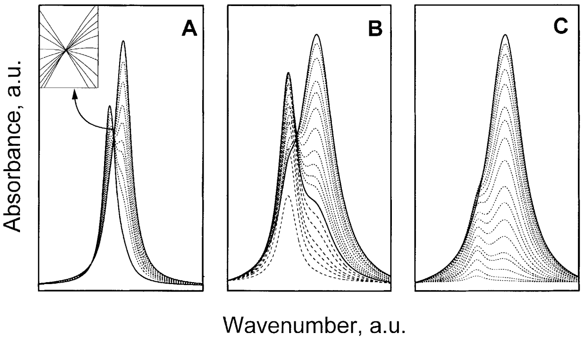


Fig. 2. Simulated spectra of mono- and geminal species at different coverages. Panels A, B and C illustrate the spectra at different *a*/*b* ratios and correspond to the same panels in Fig. 1.

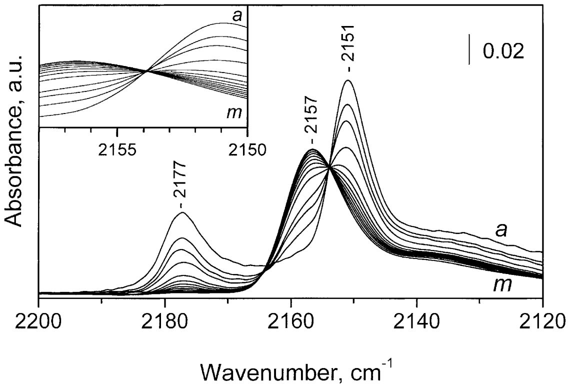


Fig. 3. FTIR spectra of CO adsorbed at ambient temperature on Cu-ZSM-5. Equilibrium CO pressure decreasing from 3 kPa (a) to 150 Pa (l) and after evacuation (m).

adsorption of the first molecule slightly affects the energetic characteristics of the neighbouring site from the centre, i.e. the values of the a and b coefficients are of the same order of magnitude. Consequently, this is valid for weak adsorption and one can expect this case to be realised, above all, at low temperatures. The adsorption isotherms in the case when $a/b = 1/3$ are presented in Fig. 1B. It is evident that both, Θ_A and Θ_{2A}, start to increase simultaneously at low pressures, although Θ_A does it with a higher rate.

Simulated spectra for this case are presented in Fig. 2B. Since simultaneous increase of Θ_A and Θ_{2A} occurs even at low pressures, no clear isosbestic point is found. However, at higher pressures, when Θ_A has already reached its maximum and started to decrease, an isosbestic point can be observed. Illustration of this case is provided in Fig. 4 which presents the spectra of $^{15}N_2$ adsorbed at 85 K on Na-ZSM-5. By analogy with $^{15}N_2$ adsorption on Na-EMT [32], the band at 2254.5 cm^{-1} is assigned to $Na^+(^{15}N_2)_2$ geminal complexes which, with the coverage decrease, are converted into linear $Na^+–^{15}N_2$ species (2257 cm^{-1}). The weak band at 2248.5 cm^{-1} is not due to surface species but arises from nitrogen adsorbed on the outer side of the cold cell windows. Because of the weak interaction between the adsorbed molecules, no splitting of the N–N stretchings into symmetric and antisymmetric modes is observed. The good coincidence between the experimental and simulated spectra is evident in this case again.

The third case refers to the situation when the geminal complexes are more stable than the mono-species. This is a complex-specified formation of geminal species. In principle, the strong interaction between the adsorbed molecules supposes a strong adsorption. Indeed, complex-specified geminal species are generally stable. The adsorption isotherms describing this case ($a/b = 30$) are presented in Fig. 1C. It is seen that a weak predomination of the concentration of the mono-species can be expected at very low coverages only. Note that with the increase of the a/b ratio the maximal value of Θ_A decreases. This is the reason that very often mono-species are not detected at all when a complex-specified formation of geminal species occurs. Another consequence of the strong adsorbate–adsorbate interaction is the splitting of the stretching vibrations of the diatomic adsorbate molecules into symmetric and antisymmetric stretches. In this case, the frequency of the linear species is, as a rule, observed between the frequencies of the geminal complexes.

The simulated spectra are presented in Fig. 1C. It is evident that there is no isosbestic point in this case. The complex-specified formation of geminal species is illustrated by the spectra of NO adsorbed on Co-ZSM-5 (Fig. 5). Introduction of NO to Co-ZSM-5 results in the appearance of two intense bands at 1894 and 1812 cm^{-1} assigned to the ν_s and ν_{as} of $Co^{2+}(NO)_2$ geminal species, respectively [7,37–42]. The spectra are hardly affected by evacuation at 150°C. However, evacuation at higher temperatures results in a gradual intensity decrease of both bands, and a weak band

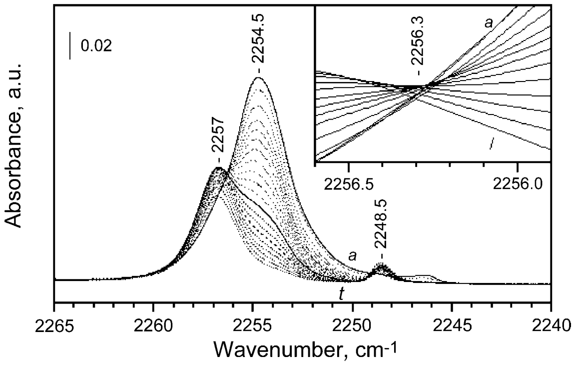


Fig. 4. FTIR spectra of $^{15}N_2$ adsorbed at 85 K on Na-ZSM-5. Equilibrium $^{15}N_2$ pressure of 10 Pa (a) and at gradually decreasing pressures (b–t).

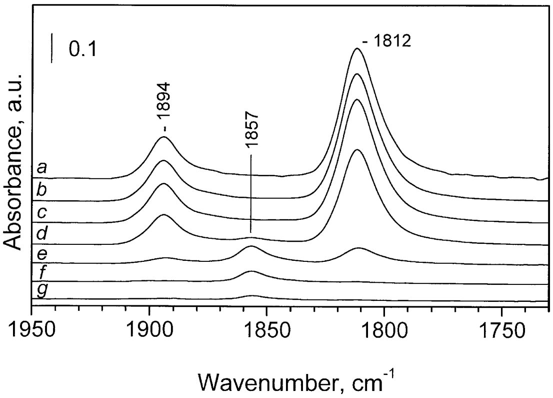


Fig. 5. FTIR spectra of NO adsorbed on Co-ZSM-5. Adsorption of NO (1330 Pa equilibrium pressure at ambient temperature), followed by evacuation at 20 (a), 150 (b), 200 (c), 250 (d), 300 (e) and 350°C (f).

at 1857 cm^{-1} emerges. This band reaches maximum intensity after evacuation at 250°C and almost disappears from the spectrum after 350°C evacuation. Based on the position and the behaviour of the band, it is assigned to Co^{2+}–NO species. As predicted by the adsorption isotherms (see Fig. 1C), the maximal concentration that the linear species can reach is much lower than the maximal concentration of the geminal complexes. Note that this example is not very precise, because the values of the *a* and *b* coefficients normally depend on temperature. However, we infer that the presented spectra correspond to different equilibrium conditions and the general picture is described well by the model. Unfortunately, at this stage we do not dispose of a more appropriate illustration, but one should expect that direct registration of the spectra at high temperatures could provide a better example.

As mentioned above, complex-specified formation of geminal species is hardly affected by the support. This means that $Co^{2+}(NO)_2$ di-nitrosyls should also be observed with other Co^{2+}-containing systems. Indeed, analysis of data from the literature shows that NO adsorption on different supported cobalt catalysts (CoX [37], CoY [38], Co–ferrierite [39], Co/SiO_2 [40], Co/SnO_2 [41], Co/Al_2O_3 [42]) results mainly in the formation of geminal $Co^{2+}(NO)_2$ complexes.

Very often the conversion between geminal and linear species proceeds under pressures that are too low to be measured accurately. As a result, the exact adsorption isotherms cannot be plotted. That is why, we propose other expressions that do not include the pressure as a parameter, namely $\Theta_A = f(\Theta)$ and $\Theta_{2A} = f(\Theta)$. From Eqs. (1) and (2) and putting $m = a/b - 1$ one can derive:

$$\Theta_A = -\frac{1}{2m} - \left[\frac{1}{4m^2} - \frac{\Theta^2 - \Theta}{m}\right]^{1/2} \quad (8)$$

for the case when $a < b$, i.e. $m < 0$

$$\Theta_A = \Theta - \Theta^2 \quad (9)$$

for the case when $a = b$, i.e. $m = 0$

$$\Theta_A = -\frac{1}{2m} + \left[\frac{1}{4m^2} - \frac{\Theta^2 - \Theta}{m}\right]^{1/2} \quad (10)$$

for the case when $a > b$, i.e. $m > 0$. The respective values for Θ_{2A} can be easily obtained knowing that $\Theta_{2A} = \Theta - \Theta_A$.

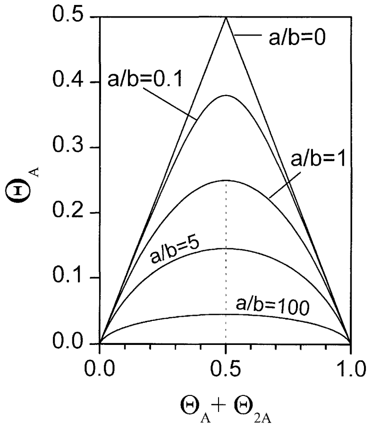


Fig. 6. Theoretical dependence of the concentration of mono-species (Θ_A) on the total coverage (Θ) for the case of formation of geminal species. The different curves correspond to different values of the *a*/*b* ratio.

Plots of Eqs. (8)–(10) are presented in Fig. 6. The Θ_A curve is symmetric and passes through a maximum at $\Theta = \frac{1}{2}$. Knowing the absorption coefficients, one can easily draw these dependencies using the IR spectra of adsorbed molecules. Thus, it appears that the plots Θ_A vs. Θ can be reliable criteria for the formation of geminal species. Analysis of the literature data shows that a similar plot (using the values of the integral absorbances) has been obtained in the

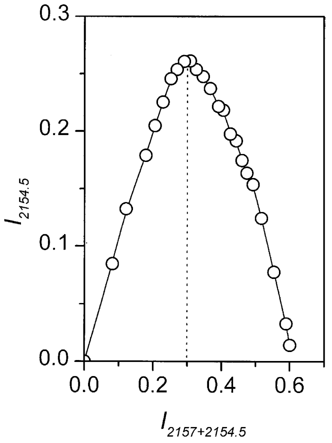


Fig. 7. Low-temperature $^{15}N_2$ adsorption on Na-ZSM-5. Dependence on the integral intensity of the 2154.5 cm^{-1} band (Na^+–$^{15}N_2$ species) on the sum of the intensities of the 2154.5 and 2157 cm^{-1} bands (Na^+–$^{15}N_2$ and $Na^+(^{15}N_2)_2$ species).

case of CO adsorption on Na-ZSM-5 [18]. Assuming close absorption coefficients, this supports the idea of co-ordination of maximum two CO molecules to one Na^+ site in this case. In Fig. 7, we report our data concerning $^{15}N_2$ adsorption on Na-ZSM-5. Evidently, the plots imply that again di-species are formed. It will be shown further on that the Θ_A vs. Θ dependencies possess another shape if three molecules can be bound to one site.

4. Simultaneous adsorption of three equal molecules on one centre

A very low co-ordination of a surface cation can provide the possibility of simultaneous co-ordination of three molecules on one centre. Indeed, formation of $Cu^+(CO)_3$ species at low temperatures and under CO equilibrium pressure has been reported for low-temperature CO adsorption on Cu-ZSM-5 [21,22]. The formation of these complexes is site-specified. A typical example of complex-specified formation of $M(L)_3$ species are $Ru^{n+}(CO)_3$ carbonyls [11,43,44], and excellent illustration of the transformation of $Ru^{2+}(CO)_3$ species at first to $Ru^{2+}(CO)_2$ and then to Ru^{2+}–CO has been recently reported [44].

Using the suppositions already applied to the co-ordination of two molecules, one can derive the following adsorption isotherms:

$$\Theta_A = \frac{bcP}{P^3 + 3cP^2 + 3bcP + abc} \tag{11}$$

$$\Theta_{2A} = \frac{2cP^2}{P^3 + 3cP^2 + 3bcP + abc} \tag{12}$$

$$\Theta_{3A} = \frac{P^3}{P^3 + 3cP^2 + 3bcP + abc} \tag{13}$$

where c is a constant describing the equilibrium for Θ_{3A}. These isotherms are presented in Fig. 8. Analysis of Eqs. (11)–(13) shows that

$$\Theta_A = \Theta_{2A} \text{ when } P = \tfrac{1}{2}b \tag{14}$$

$$\Theta_A = \Theta_{3A} \text{ when } P = \left(\frac{b}{c}\right)^{1/2} \tag{15}$$

$$\Theta_{2A} = \Theta_{3A} \text{ when } P = 2c \tag{16}$$

$$\Theta_A \text{ reaches its maximum when } \Theta = \tfrac{1}{3} \tag{17}$$

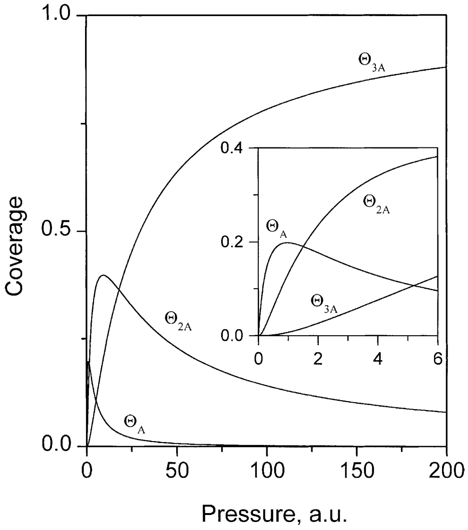


Fig. 8. Adsorption isotherms illustrating the case when up to three molecules can be simultaneously adsorbed on one centre. Change in the concentrations of M–L, $M(L)_2$ and $M(L)_3$ species as a function of the adsorbate equilibrium pressure: $a = 1$, $b = 3$ and $c = 9$ (for details see text).

$$\Theta_{2A} \text{ reaches its maximum when } \Theta = \tfrac{2}{3} \tag{18}$$

Thus, an important conclusion based on the above equations is that, if up to three molecules can be simultaneously co-ordinated to one centre, Θ_A from the plot Θ_A vs. Θ shall pass through a maximum at a Θ-value of $\frac{1}{3}$. Thus, as suggested above, the plots Θ_A vs. Θ can be reliable criteria for establishing the maximal number of molecules adsorbed on one centre.

5. Simultaneous adsorption of two gases

When two gases (A and B) are adsorbed, each of them being able to form site-specified geminal species, mixed complexes are also to be expected. Using the same premises as those applied to deriving Eqs. (3)–(5), the adsorption equilibria will be described by

$$(1 - 2\Theta_A - 2\Theta_B - \Theta_{2A} - \Theta_{2B} - \Theta_{AB})xP = k_1\Theta_A \tag{19}$$

$$(1 - 2\Theta_A - 2\Theta_B - \Theta_{2A} - \Theta_{2B} - \Theta_{AB}) \times (1 - x)P = k_2\Theta_B \tag{20}$$

$$\Theta_A x P = k_3 \Theta_{2A} \tag{21}$$

$$\Theta_B (1-x) P = k_4 \Theta_{2B} \tag{22}$$

$$\Theta_B x P = k_5 \Theta_{AB} \tag{23}$$

$$\Theta_A (1-x) P = k_6 \Theta_{AB} \tag{24}$$

where x is the mole part of one of the adsorbates. From the above equilibria,

$$\Theta_A = \frac{k_2 k_3 k_4 x P}{M} \tag{25}$$

$$\Theta_{2A} = \frac{k_2 k_4 x^2 P^2}{M} \tag{26}$$

$$\Theta_B = \frac{k_1 k_3 k_4 (1-x) P}{M} \tag{27}$$

$$\Theta_{2B} = \frac{k_1 k_3 (1-x^2) P^2}{M} \tag{28}$$

$$\Theta_{AB} = \frac{(k_2 k_3 k_4 / k_6)(1-x) x P^2}{M} \tag{29}$$

where $M = k_2 k_4 x^2 P^2 + k_1 k_3 (1-x)^2 P^2 + (k_2 k_3 k_4 / k_6)(1-x) x P^2 + 2 k_2 k_3 k_4 x P + 2 k_1 k_3 k_4 (1-x) P + k_1 k_2 k_3 k_4$.

The equations obtained are rather complex, but one could be interested in knowing the maximal value of Θ_{AB} because in this case the possible interaction between the A and B molecules will proceed with the highest rate. Evidently, Θ_{AB} will reach a maximum at high pressures and Eq. (29) can be transformed into

$$\Theta_{AB} = \frac{(k_2 k_3 k_4 / k_6)(1-x) x P^2}{k_2 k_4 x^2 P^2 + k_1 k_3 (1-x)^2 P^2 + (k_2 k_3 k_4 / k_6)(1-x) x P^2} \tag{30}$$

Differentiation shows that the maximum of Θ_{AB} is attained when:

$$\frac{x}{1-x} = \left(\frac{k_1 k_3}{k_2 k_4}\right)^{1/2} \tag{31}$$

Analysis of Eq. (31) indicates that, in general, if one of the gases is adsorbed much more strongly, its pressure has to be much lower. Intuitively, similar conditions have been applied to prepare mixed $Me^+(CO)(N_2)$ species on NaY [30].

The case of adsorption of two gases when site-specified formation of $M(L)_3$ species can occur, will be briefly discussed. Although the mathematical expressions are very complex, one can, based on the above discussion, deduce the general trends. We shall illustrate this example with the interconversion between Cu^+–CO, $Cu^+(H_2O)CO$ and $Cu^+(H_2O)_2CO$ species. Note that the Cu^+–CO species are very stable and resistant to evacuation at ambient temperature. We have reported [23] the conversion between the former two species. Recently, Zecchina et al. [22] have suggested the formation of $Cu^+(H_2O)_2CO$ complexes at high H_2O equilibrium pressures. Fig. 9 presents the spectra of Cu^+–CO species exposed to different pressures of water vapour. Evidently, the 2116 cm^{-1} band characterises the CO stretching modes from $Cu^+(H_2O)_2CO$ species. With the decrease in the water equilibrium pressure these species lose one H_2O ligand, thus being converted into $Cu^+(H_2O)CO$ adducts (2130 cm^{-1}). The further decrease in the water equilibrium pressure is accompanied by releasing of one more H_2O ligand, and Cu^+–CO complexes are formed (2157 cm^{-1}). Since the total concentration of these copper mono-carbonyls has decreased after the treatment with water vapour, it is evident that water-induced desorption of CO has also taken place. Inspection of the spectra presented in Fig. 9 suggests that this occurs mainly during the transformation between $Cu^+(H_2O)_2CO$ and $Cu^+(H_2O)CO$ complexes, since no clear isosbestic point is observed in this case. Evidently, water co-ordination to the copper cations

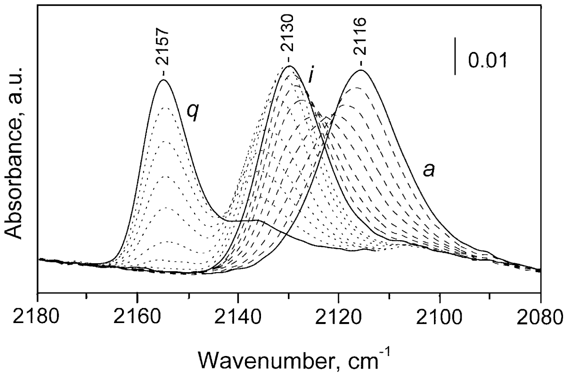


Fig. 9. FTIR spectra of CO and H_2O co-adsorbed at ambient temperature on Cu-ZSM-5. Adsorption of 1 kPa CO, followed by evacuation and introduction of 1.5 kPa equilibrium pressure H_2O (a); gradual decrease of the equilibrium pressure to 250 Pa (b–i) and to 10 Pa (j–p) and after evacuation (q).

from the Cu^+–CO species results in weakening of the Cu^+–CO bond as proposed earlier [23].

6. Site- and complex-specified adsorption of more than one molecule on one centre

Finally, we shall discuss a case when conditions for both site- and complex-specified formation of geminal species are realised. A typical example is adsorption of CO on Rh^+ exchanged zeolites. Indeed, CO adsorption on Rh^+ always leads to the complex-specified formation of the well-known $Rh^+(CO)_2$ gem-di-carbonyls [9,45–48]. Attempts have been made to detect carbonyls containing more than two CO ligands. Wang and Yates [46] have proposed that at low temperature and under CO equilibrium pressure, a negligible part of the rhodium gem-di-carbonyls on Rh^+/Al_2O_3 can be converted into $Rh^+(CO)_3$ species. The bands due to these species, however, are extremely weak and observable in the difference spectra only. Keyes and Watters [47] have also observed $Rh^+(CO)_3$ species on a Rh/SiO_2 sample but at a very high CO equilibrium pressure only (600 Torr). However, Miessner et al. [48], performing low-temperature CO adsorption on a RhY sample, have easily detected $Rh(CO)_4$ and $Rh(CO)_3$ species and their assignment was proved by co-adsorption of ^{12}CO–^{13}CO isotopic mixtures. Evidently, the combinations of the factors allowing site- and complex-specified formation of geminal species provides the possibility of co-ordination of up to four molecules to one centre.

7. Conclusions

- Geminal species are of two kinds: site- and complex-specified. In the former case, the simultaneous co-ordination of more than one molecule to one centre is determined by the low co-ordination number of the cationic centre, and the linear species are more stable than the geminal complexes. The complex-specified formation of geminal species is determined by the nature of the complex formed, and the linear species are not typical.
- IR spectroscopy is an appropriate technique for monitoring both kinds of geminal species. Moreover, this technique can provide additional and unique information about the energetic characteristics of the adsorbed molecules.

Acknowledgements

The authors thank Professor H. Knözinger for providing the possibility of performing the low-temperature $^{15}N_2$ adsorption and Mr. A. Milushev for his help with some calculations. KH is also indebted to the Alexander-von-Humboldt Foundation.

References

[1] A. Davydov, Kinet. Katal. 34 (1993) 333.
[2] K. Hadjiivanov, P. Concepcion, H. Knözinger, Top. Catal. 11–12 (2000) 123.
[3] V. Indovina, D. Cordischi, S. De Rossi, G. Ferraris, G. Ghiotti, A. Chiorino, J. Mol. Catal. 68 (1991) 53.
[4] A. Zecchina, E. Garrone, C. Morterra, S. Colluccia, J. Phys. Chem. 79 (1975) 978.
[5] J.B. Peri, J. Phys. Chem. 86 (1982) 1615.
[6] K. Segawa, Y. Chen, J. Kubsch, J. Dumesic, W.K. Hall, J. Catal. 76 (1982) 112.
[7] K. Hadjiivanov, B. Tsyntsarski, T. Nikolova, Phys. Chem. Chem. Phys. 1 (1999) 4521.
[8] H. Miessner, I. Bukhdart, D. Gutshick, J. Chem. Soc., Faraday Trans. 86 (1990) 2329.
[9] P. Basu, D. Panayotov, J.T. Yates Jr., J. Am. Chem. Soc. 110 (1988) 2074.
[10] I. Bukhardt, D. Gutschick, H. Landmesser, H. Miessner, Zeolite Chemistry and Catalysis, Elsevier, Amsterdam, 1991, p. 215.
[11] K. Hadjiivanov, J.-C. Lavalley, J. Lamotte, F. Mauge, J. Saint-Just, M. Che, J. Catal. 176 (1998) 415.
[12] H.K.Y. Zhao, B. Tesche, R. Barth, R. Epstein, B.C. Gates, J. Scott, Faraday Discuss. Chem. Soc. 72 (1981) 53.
[13] A. Davydov, IR Spectroscopy Applied to Surface Chemistry of Oxides, Nauka, Novosibirsk, 1984.
[14] S.D. Kohler, J.G. Ekerdt, J. Phys. Chem. 98 (1994) 4336.
[15] C.C. Williams, J.G. Ekerdt, J. Phys. Chem. 97 (1993) 6843.
[16] S.D. Kohler, J.G. Ekerdt, J. Phys. Chem. 98 (1994) 1276.
[17] E. Paukshtis, R. Soltanov, E. Yurchenko, React. Kinet. Catal. Lett. 22 (1983) 147.
[18] S. Bordiga, E. Escalona Platero, C. Otero Arean, C. Lamberti, A. Zecchina, J. Catal. 137 (1992) 179.
[19] E. Giamello, D. Murphy, G. Magnacca, C. Morterra, Y. Shioya, T. Nomura, M. Anpo, J. Catal. 136 (1992) 510.
[20] T. Pieplu, F. Poignant, A. Vallet, J. Saussey, J.-C. Lavalley, Stud. Surf. Sci. Catal. 96 (1995) 619.
[21] G. Spoto, A. Zecchina, S. Bordiga, S. Ricchiardi, G. Martra, G. Leofanti, G. Petrini, Appl. Catal. B 3 (1994) 151.
[22] A. Zecchina, S. Bordiga, G. Turnes Palomino, D. Scarano, C. Lamberti, M. Salvalaggio, J. Phys. Chem. B 103 (1999) 3833.

[23] K. Hadjiivanov, M. Kantcheva, D. Klissurski, J. Chem. Soc., Faraday Trans. 92 (1996) 4595.
[24] V. Borovkov, H. Karge, J. Chem. Soc., Faraday Trans. 91 (1995) 2035.
[25] C. Lamberti, S. Bordiga, A. Zecchina, M. Salvalaggio, F. Geobaldo, C. Otero Arean, J. Chem. Soc., Faraday Trans. 94 (1998) 1519.
[26] K. Hadjiivanov, Micropor. Mesopor. Mater. 24 (1998) 41.
[27] K. Hadjiivanov, H. Knözinger, J. Phys. Chem. B 102 (1998) 10936.
[28] S. Bordiga, G. Turnes Palomino, D. Arduino, C. Lamberti, A. Zecchina, C. Otero Arean, J. Mol. Catal. A 146 (1999) 97.
[29] K. Hadjiivanov, H. Knözinger, Catal. Lett. 58 (1998) 21.
[30] K. Hadjiivanov, H. Knözinger, Chem. Phys. Lett. 303 (1998) 513.
[31] A. Zecchina, C. Otero-Arean, G. Turnes-Palomino, F. Geobaldo, G. Spoto, S. Bordiga, Phys. Chem. Chem. Phys. 1 (1999) 1649.
[32] K. Hadjiivanov, P. Massiani, H. Knözinger, Phys. Chem. Chem. Phys. 1 (1999) 3831.
[33] K. Hadjiivanov, H. Knözinger, J. Catal. 191 (2000) 480.
[34] G. Vayssilov, M. Staufer, T. Belling, K. Neyman, H. Knözinger, N. Rösch, J. Phys. Chem. B 103 (1999) 7920.
[35] J.M. Thomas, W.J. Thomas, Introduction to the Principles of Heterogeneous Catalysis, Mir, Moscow, 1969, p. 37.
[36] K. Hadjiivanov, D. Klissurski, React. Kinet. Catal. Lett. 44 (1991) 229.
[37] J. Lunsford, P. Hutta, M. Lin, K. Windhorst, Inorg. Chem. 17 (1978) 606.
[38] K. Windhorst, J. Lunsford, J. Am. Chem. Soc. 97 (1975) 1407.
[39] Y.J. Li, T. Slager, J.N. Armor, J. Catal. 150 (1994) 388.
[40] B. Djonev, B. Tsyntsarski, D. Klissurski, K. Hadjiivanov, J. Chem. Soc., Faraday Trans. 93 (1997) 4055.
[41] Ph. Harrison, E. Thornton, J. Chem. Soc., Faraday Trans. 74 (1978) 2703.
[42] N.Y. Tøpsoe, H. Tøpsoe, J. Catal. 75 (1982) 354.
[43] M. Kantcheva, S. Sayan, Catal. Lett. 60 (1999) 27.
[44] H. Miessner, K. Richter, J. Mol. Catal. 146 (1999) 107.
[45] J.-C. Lavalley, J. Lamotte, R. Breault, J.P. Hindermann, J. Phys. Chem. 94 (1990) 5941.
[46] H. Wang, J.T. Yates Jr., J. Catal. 89 (1984) 79.
[47] M.P. Keyes, K.L. Watters, J. Catal. 100 (1986) 477.
[48] H. Miessner, I. Burkhardt, D. Gutschick, A. Zecchina, C. Morterra, G. Spoto, J. Chem. Soc., Faraday Trans. 86 (1990) 2321.