Infrared Study of ZnO Surface Properties

II. H$_2$–CO Interaction at Room Temperature

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Carbon monoxide adsorption on hydrogen-covered surfaces gives rise to well-defined mixed CO–hydrogen structures in the adsorbed state. The centers adsorbing hydrogen and CO are formed by a triplet of exposed zinc ions and at least one reactive oxygen ion. These active groupings of ions are mutually interacting and grouped to form a bidimensional array which is similar to a patchy reconstructed 0001 face.

INTRODUCTION

Carbon monoxide adsorption on hydrogen-saturated surfaces has been already studied (1, 2) and is known to modify the ν(Zn–H) and ν(O–H) bands of type I adsorbed hydrogen (3). In particular the narrow ν(Zn–H) band at 1708 cm^{-1} is replaced by a characteristic triplet at lower frequencies, and the ν(O–H) band at 3498 cm^{-1} is shifted to higher values. These data have been considered as a proof of CO/H$_2$ interaction in the adsorbed state but no detailed description of the surface mixed structures has been attempted. Such a description, however, is of vital importance for a better understanding of the active site structure and of the grouping of active sites in patches. As a consequence, in this paper the CO/H$_2$ interaction is investigated in detail. The CO/H$_2$ interaction is also important from a practical point of view, as it is connected with the industrial development of Fischer–Tropsch catalysts.

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EXPERIMENTAL

The samples, infrared equipment, and the vacuum manifold were fully described in part I of this series.

RESULTS

Figure 1 shows the band due to reversibly chemisorbed CO on a hydrogen-covered sample. The experiment was carried out as follows. On a hydrogen-saturated sample (i.e., in equilibrium with 100 Torr of H$_2$), CO was allowed to bleed in, in steps, to give gaseous mixtures characterized by increasing P_{CO}/P_{H_2} ratios, and the effect on the ir spectra was monitored at each step. A band initially located at 2192 cm^{-1} is observed whose intensity grows with the pressure following a Langmuir curve and is characterized by fairly constant half-width and shape. The peak position, on the other hand, undergoes a small shift ($\Delta\nu = 4$ cm^{-1}) to lower frequencies as the coverage increases.

Figure 2 shows the effect of a similar experiment in the O–H stretching region.

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The band due to surface OH groups of type I reversibly chemisorbed hydrogen is gradually shifted by CO chemisorption from 3498 cm^{-1} (characteristic of the CO-free hydrogen-saturated surface) to higher values, the integrated intensities and the half-width being fairly constant.

Figure 3 shows the effect of the same experiment in the Zn–H stretching range. A shifting towards lower frequencies and an intensity decrease of the band at first placed at 1708 cm^{-1} (Band I) is observed. Simultaneously a band initially located at ∼1694 cm^{-1} (Band II) starts growing and reaches its maximum intensity at a CO pressure of 60 Torr. Further CO pressure increases cause band II to decline, while

Fig. 2. Effect of adsorbed CO on the OH stretching band (percentage transmission vs wavenumber). $P_{CO}/P_{H_2} = 0.25, 1.2, 1.8$; $P_{H_2} = 100$ Torr.

another band (Band III), initially located at 1677 cm^{-1}, becomes evident. As for Band I, the positions of both Bands II and III continuously decrease with the CO pressure and coverage.

Figure 4 illustrates the effect of the same experiment in the 850 to 750-cm^{-1} region [δ(OH) and δ(ZnH)]. The effect of increasing the CO pressure was to shift the maximum initially located at 850–845 cm^{-1} to 830 cm^{-1}, while the maximum at 817 cm^{-1} is shifted to 804 cm^{-1}.

The series of spectra reported in Fig. 3 was deconvoluted in terms of three bands of Gaussian or Lorentzian shape by means of a computer program which can consider the band positions and widths as fixed or variable parameters (4). The recorded spectra were all analyzed independently of one another. The best agreement was observed with Gaussian-shaped curves with
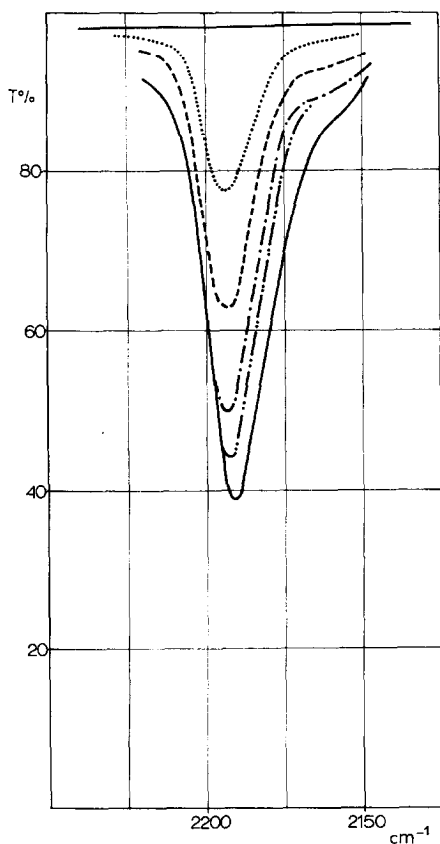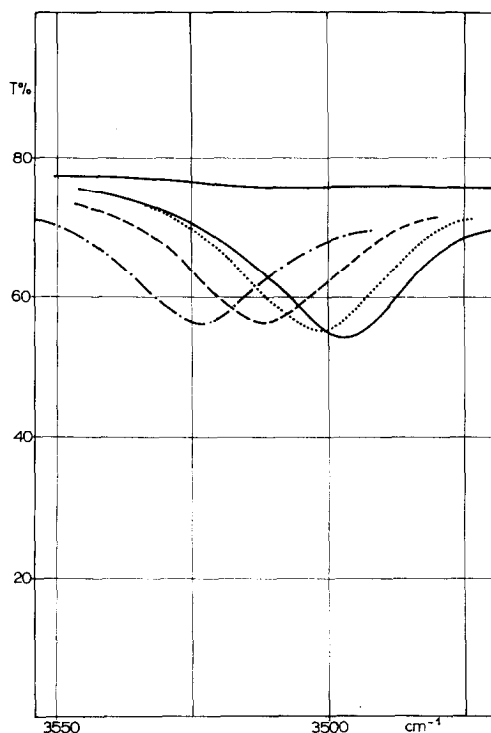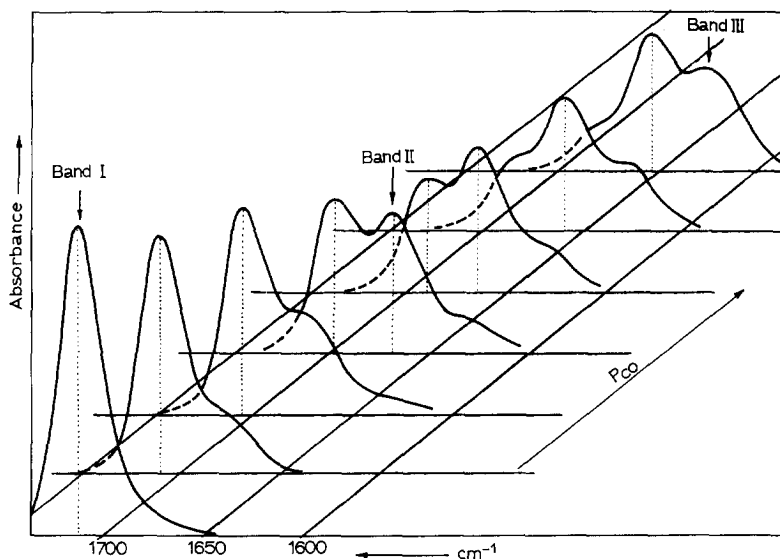

Fig. 1. The ir spectrum of CO adsorbed on H₂-covered ZnO. (Percentage transmission vs wavenumber). $P_{CO}/P_{H_2} = 0.2, 0.5, 0.8, 1.4, 1.8$; $P_{H_2} = 100$ Torr.

FIG. 3. Effect of increasing CO pressure on the Zn–H stretching bands (P_{H_2} = 100 Torr)(absorbance vs wavenumber).

peak position and width as variable parameters.

Frequency and integrated intensity of the three bands, as obtained by the deconvolution, at seven different CO pressures are listed in Table 1; in the first column of the table the optical densities of the CO peak are also reported, as these can be considered to be a rough measure of the CO coverage. Band I shows a continuous decrease, Band II reaches a maximum at $(OD)_{CO}$ = 0.200 (corresponding to 60 Torr of CO pressure) then slowly decreases, while Band III is always increasing. Finally the total integrated intensity (I + II + III) is fairly constant in a large CO optical density range. This observation implies that the extinction coefficients of Bands I, II, and III are almost the same and that no hydrogen displacement by CO is taking place. However, at higher CO optical densities (high CO pressures), the total integrated intensity begins to decrease slightly; this might be due to a side reaction leading to surface formate species (5).

In Fig. 5 the frequencies of the ν(OH), ν(ZnH) (I), ν(ZnH) (II), and ν(ZnH)

(III) bands are plotted against the CO coverage (optical density on the maximum of the CO peak). In all cases a good linear relationship is observed. The slope of the ν(OH) straight line is about twice that of the ZnH Bands I, II, and III. However, the slopes of Bands I, II, and III are slightly different and ordered as follows: I > II > III.

Some additional experiments have also been performed which will be briefly summarized. The effect of CO on H_2 and D_2 samples is fairly similar. In particular the Zn–D band at 1233 cm^{-1} is replaced, upon CO adsorption, by the usual triplet. The effect of CO adsorption on samples in contact with 1:1 H_2–D_2 mixtures (showing the bands at 1708 and 1233 cm^{-1} due to ν(ZnH) and ν(ZnD) modes) causes the appearance of two triplets with components in the same position observed for fully hydrogen- and deuterium-covered samples.

DISCUSSION

(a) The Structure of Adsorbed CO

The high-frequency value for the CO stretching adsorbed on the H_2- or D_2-covered surface is evidence for adsorption
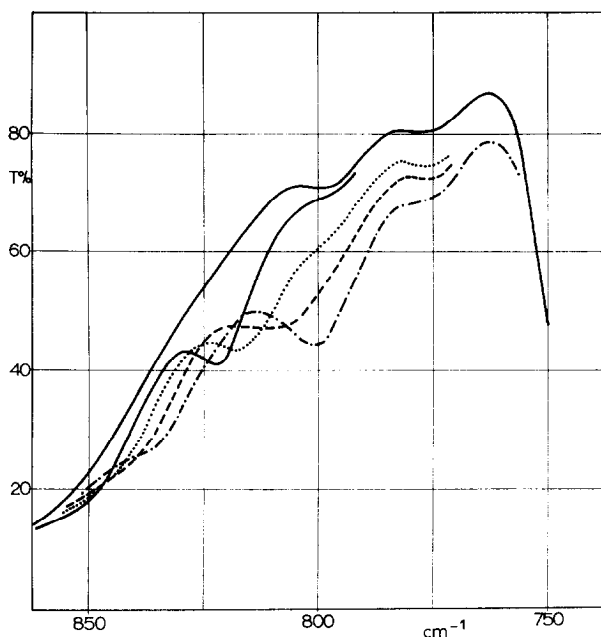
FIG. 4. Effect of adsorbed CO on the OH and Zn–H bending bands (percentage transmission vs wavenumber). $P_{CO}/P_{H_2} = 0.25, 1.2, 1.8; P_{H_2} = 100$ Torr.

via oxygen at an anion site or via carbon at a cation site (6). However, as the CO species is displaced by pyridine, which is known to form stable adducts with sites having Lewis acid character, the former hypothesis must be ruled out. As a consequence, we can conclude that CO is adsorbed on exposed Zn ions and that the lone pairs at the carbon and at oxygen atoms, respectively, extend and contract along the Zn–C–O axis. In other words, the molecule is strongly polarized with the negative and positive ends on the carbon and oxygen atoms, respectively.

TABLE 1

Frequencies and Integrated Intensities of Bands I, II, and III

P_{CO}(Torr)	(OD)$_{CO}$[a]	Band I		Band II		Band III	
		ν	Integrated intensity (a.u.)[b]	ν	Integrated intensity (a.u.)	ν	Integrated intensity (a.u.)
0	0	1708.0	8.69				
6	0.05	1707.2	6.03	1692.2	2.33	1671.6	0.19
10	0.07	1704.0	5.44	1688.3	3.06	1670.8	0.41
50	0.18	1701.1	4.57	1685.7	3.53	1670.2	1.25
80	0.23	1697.4	3.16	1683.2	3.65	1668.2	1.59
176	0.33	1695.2	2.01	1681.8	3.14	1666.6	2.48
241	0.37	1693.3	1.22	1679.6	3.16	1662.3	3.64

[a] Optical density measured on the maximum.
[b] a.u. = arbitrary units.

(b) Evidence for Well-Defined Mixed CO–Hydrogen Structures in the Adsorbed State

The formation of two new bands (II and III) is a feature which cannot be explained in terms of a nonspecific adsorbate-adsorbate interaction. In fact, on this basis, only continuous frequency shifts can be explained. The formation of Bands II and III appears to be the result of a strong perturbation of the Zn–H stretching band due to CO adsorption on the same zinc atom carrying the hydrogen or on its nearest neighbors.

The following reaction schemes can be envisaged:
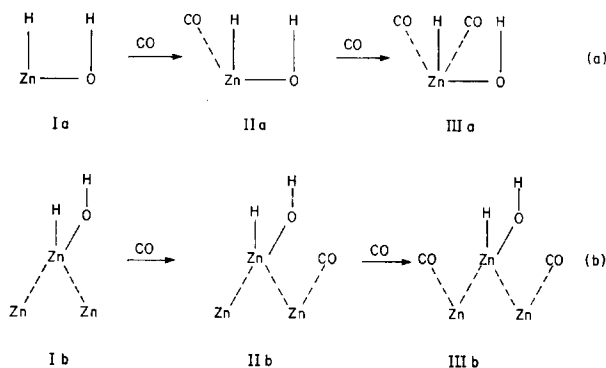
where Bands II and III are due to the stretching modes of Zn–H groups in structures II_a and III_a or II_b and III_b, respectively. In both schemes, by raising the CO coverage, Band I is expected to decline, Band II to grow to a maximum value and then to decline, and Band III to be always growing, in agreement with the data of Table 1. On these grounds, a choice between the reaction equilibria (a) and (b) cannot be made. However, as a surface zinc ion covalently bonded to a hydrogen atom can hardly have enough positive charge and sufficiently low coordination to polarize strongly one and/or two CO molecules, we strongly favor the second scheme characterized by an active center formed by a Zn–H group closely interacting with two equivalent or nearly equivalent nearest zinc ions.

The occurrence of consecutive reactions can also be proved by means of simple thermodynamic considerations. The equilibrium constants of the consecutive reactions of scheme (b) can be expressed in terms of surface coverages of species I_b, II_b, III_b and the CO pressure. We obtain:

$$K_1 = \frac{[II_b]}{[I_b]P_{CO}}, \qquad K_2 = \frac{[III_b]}{[II_b]P_{CO}}.$$

As the sum of the integrated intensities of Bands I, II, and III is constant or nearly constant, we assume that $\epsilon_{I_b} = \epsilon_{II_b} = \epsilon_{III_b} = \epsilon$ (integrated extinction coefficients). Hence, the surface coverage of each species is proportional to the integrated intensity. The equilibrium constants K_1 and K_2 (and the standard free energies of the two reactions) can consequently be easily calculated from our data, as they are the inverse of the CO pressures at which $[II_b] = [I_b]$ and $[II_b] = [III_b]$. We obtain:

$$K_1 = 11.4 \text{ atm}^{-1}, \quad K_2 = 3.7 \text{ atm}^{-1},$$

$$\Delta G_1^0 = -1.44 \text{ kcal},$$

and

$$\Delta G_2^0 = -0.78 \text{ kcal}.$$

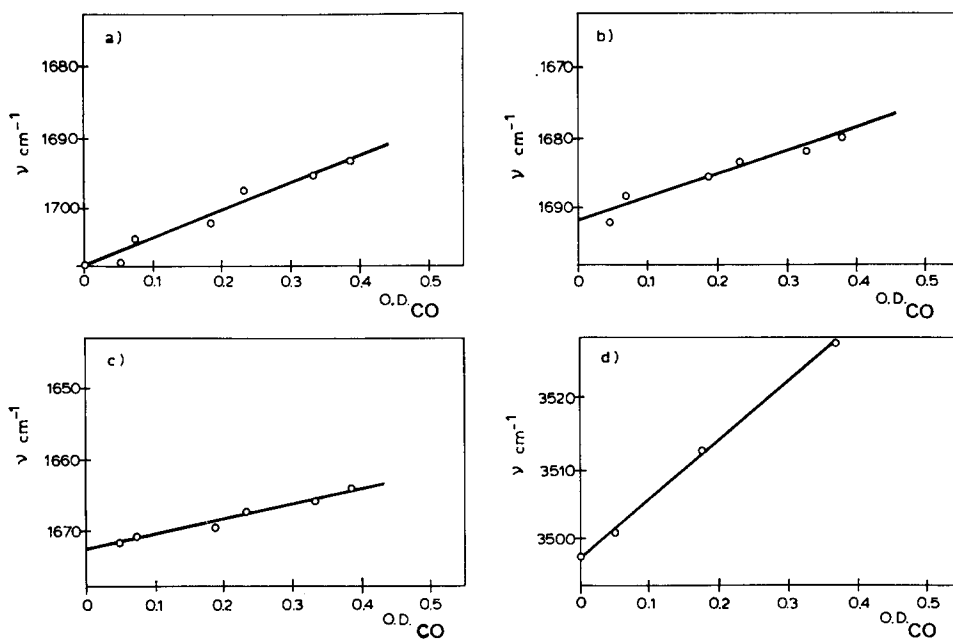The correctness of the K_1 and K_2 values

FIG. 5. Effect of CO coverage on the Zn–H (Bands I, II, and III) and OH frequencies. Band frequencies vs optical density of adsorbed CO: (a) Band I, (b) Band II, (c) Band III, (d) OH stretching band.
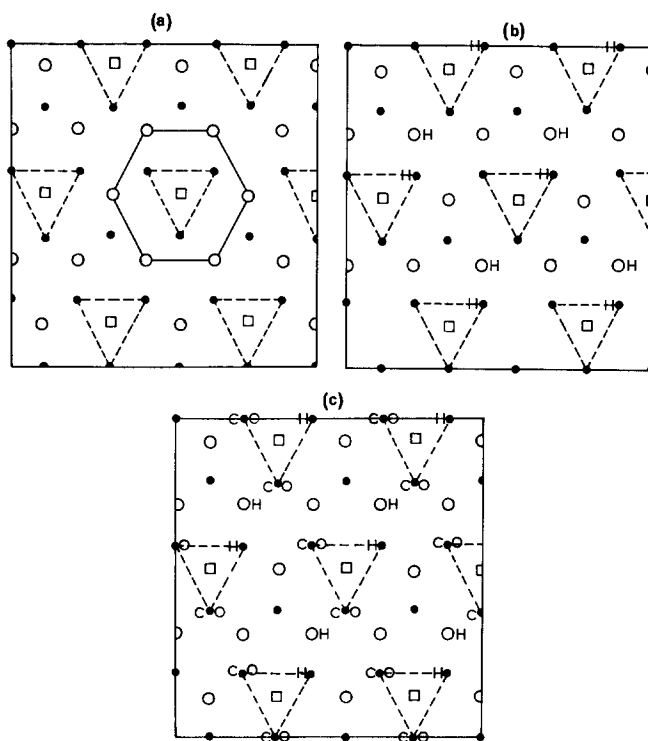

FIG. 6. Models of 2 × 2 reconstructed patches: (a) clean condition; (b) full H₂ coverage; (c) full H₂ and CO coverage.

has been further checked by inserting the obtained values into the expressions,

$$[I_b] = \frac{1}{1 + K_1 P_{CO} + K_1 K_2 P_{CO}^2},$$

$$[II_b] = \frac{K_1 P_{CO}}{1 + K_1 P_{CO} + K_1 K_2 P_{CO}^2},$$

$$[III_b] = \frac{K_1 K_2 P_{CO}^2}{1 + K_1 P_{CO} + K_1 K_2 P_{CO}^2},$$

where $[I_b]$, $[II_b]$, and $[III_b]$ are proportional to the integrated intensities of Bands I, II, and III. Three curves are obtained in this way which fit very well all the experimental data (optical densities of Bands I, II, and III vs CO pressure or CO band optical density). It is most interesting to notice that the difference between the free energy values of the two consecutive equilibria is near to $RT \ln 2$, which is the configurational contribution to the entropic term for one molecule in an active center containing two equivalent sites.

Finally, it can be seen here that the ir study of the interaction of CO with preadsorbed hydrogen gives information about the nearest neighbor situation of the Zn–O

$$\begin{matrix} H & H \\ | & | \end{matrix}$$

groupings. As in other cases, the CO molecule acts as an excellent surface probe.

(c) Frequency Changes of the Zn–H and OH Stretching Modes Induced by Adsorbed CO

The shift of the Zn–H frequency upon CO adsorption can be ascribed to two effects. The first one (the "discrete effect") causes the Zn–H frequency to change abruptly because of the formation of mixed complexes, while the second one (the "continuous effect") is responsible for the continuous shift due to the interaction with more distant groupings of atoms. As the two effects are simultaneously operat-

ing, the shifts on the Zn–H band due to the first effect can be obtained only by extrapolating to zero CO coverage.

The extrapolated Zn–H stretching frequencies of extremely diluted complexes II_b and III_b are found to be at 1691 and at 1672 cm^{-1} (Fig. 6). As a consequence, the shifts caused by the insertion of one or two CO groups in structure I_b are 17 and 36 cm^{-1}, respectively, which is again very consistent with the adopted model involving two nearly equivalent zinc atoms adjacent to the Zn–H groups. Abrupt frequency shifts (with appearance of new well-defined bands) are not observed for the OH stretching band. This fact implies that the "discrete effect" is no longer acting here, in agreement with the proposed structure of the adsorbing centers (where the OH groups are not in the nearest position with respect to the active Zn ions) and with the nature of the perturbation forces which are strongly distance dependent.

As the shifts caused by formation of mixed complexes and by interaction with more distant groupings of atoms have the same direction and comparable magnitude, they can be discussed together. CO dipoles in the adsorbed layer (with the positive and negative ends in the field of the surface positive and negative ions) increase the local coordination state of the surface ions, decrease the Zn ion polarizing power and the oxygen polarizability (7), and contribute with extra charges to the increase of the coulombic interaction with the ions of the solid.

Due to the simultaneous action of all these effects the Madelung energy is increased and the surface covalent character is decreased. Hydroxyls and hydride groups of the surface respond to this decrease in covalence becoming more polar in agreement with the observed shifts. Hence they can be considered as excellent probes of the surface ionicity.

The perturbation caused by each ad-

sorbed CO molecule is expected to be maximum on the nearest ions and to decay to small values within a limited number of ZnO spacings. On this basis the so-called "discrete effect" is associated with the interaction of an adsorbed CO with ZnH groups in adjacent positions, while the "continuous effect" is due to the interactions with groups located at more distant positions. If the perturbations caused at each given site by equivalent groupings at distant positions are additive, the linear dependence of the Zn–H and O–H stretching frequencies on the CO coverage is well explained (see part I of this series).

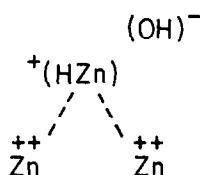### (d) A Model for the Adsorbing Patches

From the results discussed in both parts I and II of this series, the conclusion has been reached that the "adsorbing patches" contain the following (mutually interacting) grouping of ions:
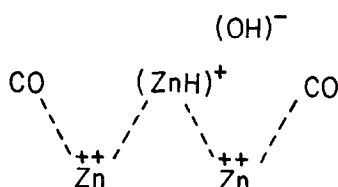
(a) clean surface,

$$\begin{array}{c}\overset{=}{O}\\ \overset{++}{Zn}\\ \overset{++}{Zn}\diagdown\overset{++}{Zn}\end{array}$$
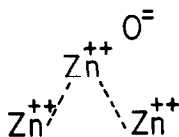
(b) hydrogen-covered surface,

$$\begin{array}{c}(OH)^-\\ {}^+(HZn)\\ \diagup\ \diagdown\\ \overset{++}{Zn}\quad\overset{++}{Zn}\end{array}$$

and (c) hydrogen- and CO-covered surface

$$\begin{array}{c}(OH)^-\\ CO\quad(ZnH)^+\quad CO\\ \diagdown\ \diagup\ \diagdown\ \diagup\\ \overset{++}{Zn}\quad\overset{++}{Zn}\end{array}$$

As the (a)–(a), (b)–(b), and (c)–(c) interaction forces decay to negligible values within a limited number of ZnO spacings, the patch structure on a clean ZnO surface

must be a kind of two-dimensional array of groupings (a). The morphology of ZnO prepared by combustion of metallic zinc is known (8), the more commonly observed faces being (0001), (000$\bar{1}$), (10$\bar{1}$1), (10$\bar{1}\bar{1}$), and (10$\bar{1}$0). According to Nosker et al. (9), polar wurtzite faces must be reconstructed in order to satisfy the "charge compensating criterion." In particular on the (000$\bar{1}$) face, one oxygen ion in every four should be missing.

Figure 6a shows a picture of a 2 × 2 reconstruction satisfying the previous conditions. It can easily be seen that in correspondence with each oxygen vacancy, there is a triplet of uncoordinated zinc ions, which is surrounded by a hexagon of oxygen ions in the outermost layer. The center of gravity of the negative charge of this hexagon is ~0.7 Å above the positive center of gravity of the three underlying Zn ions. A strong field gradient is consequently present in correspondence with the oxygen vacancies. A colliding hydrogen molecule should be strongly polarized on these sites and hence heterolytically dissociated to give hydride and hydroxyl groups. Figure 6b shows the result of hydrogen dissociation on these sites. It can be seen that, after H$_2$ chemisorption, two equivalent Zn ions still remain coordinatively unsaturated and hence they can act as CO adsorption centers. Figure 6c shows the situation at full H$_2$ and CO coverage.

This representation must be considered as largely ideal. In fact, on these low-temperature pretreated samples, some disorder is expected due to (a) more random distribution of oxygen vacancies, (b) presence of residual OH and carbonate-like impurities, and (c) finite dimensions of the reconstructed areas (patchy reconstruction). Patchy reconstructions on ZnO single crystal polar faces normally occur for more severe thermal treatments (10). Their appearance on these microcrystalline samples can be explained in terms of the

extremely different pretreatment conditions. In fact, our starting material is initially covered by OH and carbonate-like groups and the cleaning process mainly involves surface dehydration and surface decomposition reactions with loss of water and carbon dioxide. The small crystallite size is probably another factor capable of increasing the ionic mobilities (*11*). The proposal that the active patches are located on 2×2 patchy reconstructed $(000\bar{1})$ faces is not unique. In fact other polar faces (i.e., $10\bar{1}\bar{1}$) can show bidimensional arrays of similar unsaturated groupings of ions. However, it has been discussed here because of its simplicity.

CONCLUSIONS

The utilization of the CO molecule as a probe of the hydrogen-covered surface has led us to a further exploration of the structure of the adsorbing centers. They have been found to contain a triplet of highly uncoordinated zinc ions and at least one reactive oxygen ion in an adjacent position. These ion clusters give rise to well-defined mixed CO–hydrogen structures.

The active centers are mutually interacting and are grouped together, forming a bidimensional array (adsorbing patches). The reconstructed $(000\bar{1})$ face is shown to possess a regular array of similar ion clusters.

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