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Infrared Study of Lateral Interactions between Carbon Monoxide Molecules Adsorbed on Oxide Catalysts

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An infrared study of $^{12}C^{16}O$ and $^{13}C^{16}O$ adsorbed at 77 K on ZnO, TiO_2, BeO, Al_2O_3, and SiO_2 has provided details on two kinds of interactions between the adsorbed molecules which account for the dependence of the spectra on surface coverage. The observed ν_{CO} values, which for coordinatively bonded molecules are 50–100 cm^{-1} higher compared with gaseous CO, are lowered significantly (up to 30 cm^{-1}) on increasing coverage as a result of a "chemical" effect, namely the weakening of the electron-donating ability of metal ion after occupation of the adjacent sites with adsorbed molecules. The fine structure of the CO/ZnO spectrum reflects the stepwise character of this process. The second type of interaction is dipole coupling. This causes a comparatively weak upward shift (up to 6 cm^{-1}), partly counteracting the "chemical" effect.

INTRODUCTION

Application of IR spectroscopy to the investigation of catalytic systems usually includes the measurement of the frequency shifts caused by the adsorption of certain test molecules suitable for characterizing the strength of surface sites, and also the qualitative analysis of the adsorbed products of surface reactions with a view to establishing mechanisms. Only a few works deal with the spectral manifestations of lateral interactions between the adsorbed molecules, despite the possible role of such interactions in catalytic processes.

Boccuzzi *et al.* (*1*) have demonstrated that the influence of CO on the spectrum of preadsorbed hydrogen provides information on the nature and disposition of surface active sites. Lavalley and co-workers (*2*) used data on the interaction of CO with preadsorbed CO_2 to develop a model of the ZnO surface. Interaction between identical adsorbed molecules, which reveals itself in the dependence of band positions on surface coverage, has been studied almost exclusively for CO adsorbed on metals (*3, 4*). However, the same effect has been observed also for oxides (*5, 6*), and in the spectrum of CO adsorbed on ZnO at 77 K a fine structure caused by lateral interactions has been discovered (*7*).

Our intention in the present work was to use the advantages of low temperatures to clarify the nature of the interaction between CO molecules adsorbed on oxide surfaces and to find out the role played by the solid. For this purpose the dependence of the spectra of CO adsorbed at 77 K onto ZnO, TiO_2, BeO, Al_2O_3, and SiO_2 surfaces on the CO coverage and isotopic content of the adsorbed molecules has been investigated.

EXPERIMENTAL

To combine spectroscopic and adsorption measurements, the IR cell, which was a simplified model of the previously described stainless-steel cell for work at liquid-helium temperatures (*8*), was equipped with a deformation PMGD-1 pressure gauge. For coverage measurements the sample was displaced from the cooled part of the cell into a quartz tube which was kept at room temperature. Since the amount of adsorbed CO at 300 K and pressures of several Torr was negligible, the pressure increase gave us the value of the surface coverage, taking into account that the effective

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† Deceased.

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volume of the cell and the mass and specific surface area of the samples were known.

In order to measure the isosteric heat of adsorption, spectra were registered at varying temperatures for several different initial amounts of adsorbate in the cell at known gas pressures. Then for certain values of the CO band intensity corresponding to the occupation of a certain fraction of the sites under examination, ln P was plotted against $1/T$, the slope of the plot giving us the heat of adsorption.

Batches of oxide powders, analogous to those used in our earlier studies (*5, 7*), were pressed into 10 × 30 mm pellets. These were treated in oxygen and then under vacuum at 720–1070 K before the adsorption measurements. Commercial CO with natural isotopic abundance and $^{13}C^{16}O$ containing 84.7% of the main product were used. To avoid organic contaminations the gases were admitted into the cell through a trap cooled with liquid nitrogen.

Spectra were registered on a Specord 75 IR spectrophotometer with a spectral slit width of 1–3 cm^{-1}, and the accuracy of the wavenumber determination for narrow bands was not worse than ±0.5 cm^{-1}.

RESULTS AND DISCUSSION

The data obtained for the frequencies (expressed as cm^{-1}) of adsorbed CO, as well as the values of the BET specific surface area of the samples, s, the pretreatment temperature t and the maximum surface coverage with coordinatively bonded CO molecules, θ_{max}, at 77 K are given in Table 1. For all the oxides except SiO_2 the drastic pretreatment conditions which were employed removed essentially all the surface hydroxyl groups, and the coordinatively unsaturated metal ions were the main adsorption sites. A pressure of about 1 Torr was enough to saturate the surface with coordinatively bonded CO. The bands of physically adsorbed molecules, which appear at higher pressures, are not presented in Table 1.

The band at 2158 cm^{-1} of CO adsorbed on SiO_2 is due to molecules which are hydrogen-bonded to the surface Si–OH groups, as was shown earlier by Ghiotti *et al.* (*9*). The position of this band does not depend on the coverage. Spectra of the coordinatively bonded molecules, on the other hand, are very sensitive to the

TABLE 1

Maximum Coverages (θ_{max}) and Infrared Spectral Data for CO Adsorbed at 77 K

Oxide	s ($m^2\ g^{-1}$)	t (K)	θ_{max} molec nm^{-2}	cm^{-1}				
				ν_0	ν_s	ν_a	$\Delta\nu_{ch}$	$\Delta\nu_{dyn}$
ZnO	10	770	2.0	2192	2168	2162	30	6
				2189	2178	2174	15	4
TiO_2	70	720	2.6	2212	2207	2207	5	0
(anatase)				2195	2179	2176	19	3
				2180	2176		4	
					2164	2161		3
					2151			
BeO	110	870	2.4	2207	2187		20	
				2200	2180		20	
				2188	2173	2173	15	0
η-Al_2O_3	70	1070	2.5	2235				
				2202	2176	2171	31	5
SiO_2	300	870		2158	2158	2158	0	0

[a] For definitions of ν_0, ν_s, ν_a, $\Delta\nu_{ch}$, and $\Delta\nu_{dyn}$, see text.

amount of adsorbed CO. As a rule, the bands observed for low coverages at higher wavenumbers (ν_0) shift downward on increasing the concentration of the adsorbed molecules, reaching at saturating coverages θ_{max} the lowest frequency values, denoted in Table 1 as ν_s.

If the bands are narrow enough, one can observe a stepwise character in this shift, resulting in the appearance of a fine structure at medium coverages. This effect is illustrated in Fig. 1, which shows for ZnO the development of the spectrum of adsorbed CO as coverage is increasing up to saturation. The first doses of CO give rise to weak bands at 2192 and 2189 cm^{-1}. At higher coverages they disappear, and new bands show up instead at low frequencies. After reaching their maximum intensities the latter bands also diminish, and others at even lower wavenumbers arise, until eventually at $\theta = 2.0$ molec nm^{-2} a sharp strong band at 2168 cm^{-1}, accompanied by a much less intense one at 2178 cm^{-1}, remains in the spectrum. Further addition of CO does not alter the positions and intensities of the bands of the coordinatively bonded molecules. Using a comparatively thin and more transparent sample and the cell for liquid-helium temperatures we tried to estimate the half-width of the 2168-cm^{-1} band. It was found to be about 0.5 cm^{-1} at 77 K and not more than 0.3 cm^{-1} at 4 K. Such an extremely low half-width is due, apparently, to a highly ordered site arrangement on the surface.

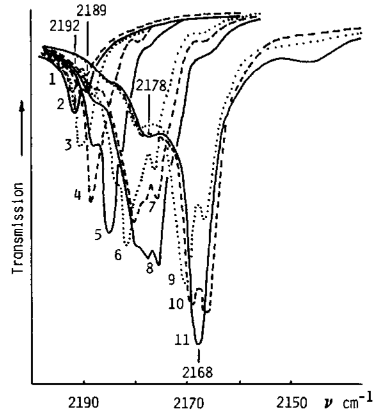

FIG. 1. Infrared spectra of CO adsorbed on ZnO, as observed on successive additions of CO at 77 K. Surface concentrations of adsorbed molecules are 0.11 (1), 0.22 (2), 0.43 (3), 0.54 (4), 0.60 (5), 0.86 (6), 1.00 (7), 1.36 (8), 1.60 (9), 1.97 (10), and 1.99 (11) molec nm^{-2}.

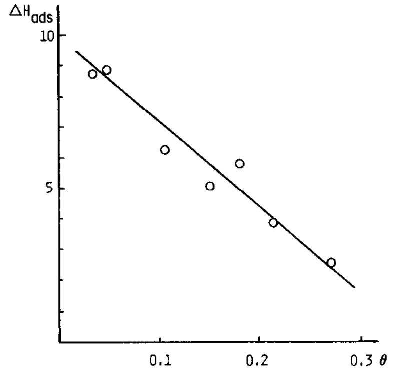

FIG. 2. Isosteric heat of CO adsorption on ZnO (kcal mole^{-1}), plotted against surface coverage θ. $\theta = 1$ corresponds to 6.0 molec nm^{-2}.

For several values of surface coverage, corresponding to certain intensities of the CO band, the isosteric heat of adsorption ΔH_{ads} was measured. As can be seen from Fig. 2, while the coverage of ZnO surface grows from about 0.2 up to 1.8 molec nm^{-2}, the heat of adsorption decreases almost in linear fashion from 10 kcal mole^{-1} (the limit obtained by extrapolation to $\theta = 0$) down to less than 3 kcal mole^{-1}; while the first doses of CO were completely adsorbed by the sample at 77 K, the saturating coverage, for which extrapolation gives a ΔH_{ads} value of about 1.5 kcal mole^{-1}, exists only in equilibrium with the gas phase. An analogous, although weaker, decrease of the CO/ZnO adsorption energy with increasing θ was found by Griffin and Yates (*6*) from the analysis of TPD spectra.

The fact that at the maximum as well as at the lowest coverages not more than two bands of coordinatively bonded CO can be observed implies the presence on the surface of not more than two different adsorption sites, one of which, namely that corresponding to the band at 2168 cm^{-1}, dominates. This means that under saturation conditions the majority of the adsorbed molecules occupy crystallographically identical sites and are uniformly surrounded by similar molecules. The 2178-cm^{-1} band may represent a small fraction of molecules adsorbed on another crystal face or on sites which in some other way are different from the rest. Sequential occupation of different surface sites cannot account for the diminution of the high-frequency bands on increasing the amount of adsorbed CO. Evidently, the frequency of coordinatively bonded CO molecules is affected by the occupation of the adjacent sites, and, as a result, the bands of both the previously adsorbed and the new molecules are shifted downward.

There is no doubt that the nearest molecules influence the CO frequency the most, and the fine structure at medium coverages indicates the surface heterogeneity induced by adsorption, reflecting the discrete character of site occupation. If the distinct CO bands correspond to different variants of the surrounding of the adsorbed molecule, when some of the adjacent sites are occupied and some remain vacant, it is possible to calculate the spectral changes with coverage for certain site arrangements on the surface. We have only to suppose that the process of site occupation is random enough and to postulate a law governing the weakening of the influence with the distance. Such a problem was analyzed by Nichols and Hexter (*10*) for a square net of sites, which was a model for the (100) face of silver with adsorbed Cl^- ions. The interaction was believed to decrease as r^{-3}. The histograms presented in that work have much in common with the spectra in Fig. 1.

For metals the influence of coverage on the CO frequency is brought about mainly by the effect of dynamic dipole coupling interaction (see, e.g., Ref. (*3*)). The coupling always shifts the observed frequencies to higher values and can be distinguished from other, static effects by means of isotopically substituted molecules. If ^{13}CO contains some admixture of usual ^{12}CO, the admixed molecules will not participate in the coupling interaction; if the latter is the only reason for the frequency shift, the position of the admixed molecule band, or the "dilution limit" of the ^{12}CO frequency, will coincide with the frequency of isolated CO molecules observed at low coverages. As shown by King and co-workers (*4*), this case occurs for Pt, while for Cu the coupling effect is almost completely cancelled by a downward "chemical" shift (*11*).

To determine the role of the dipole coupling effect in the case of oxides, we have studied the adsorption of ^{13}CO containing about 10% of ^{12}CO under conditions which guaranteed saturation of the surface with the coordinatively bonded molecules. The observed frequencies of the admixed ^{12}CO molecules ν_a are given in Table 1 in a separate column. As a rule, the ν_a values are somewhat lower than the frequencies of pure ^{12}CO at the same coverages, and the difference between ν_s and ν_a, denoted in the table as $\Delta\nu_{dyn}$, can be considered as a measure of the dynamic dipole coupling. The results presented in the table show that dipole coupling also exists for metal oxides and that it also shifts the frequencies upward, but unlike the situation with metals, this effect cannot explain the observed spectral alterations and only partly compensates the strong downward shift caused by static interaction. This shift, denoted as $\Delta\nu_{ch}$, is the difference between the frequency of isolated CO molecules as observed at low coverages, namely ν_0, and the frequency of the same molecules diluted by those of other isotopic content at saturating θ, namely ν_a.

Static shift can be a result of the direct influence of the electrostatic field of surrounding molecules. Griffin and Yates (*6*) tried to calculate this effect for the monolayer of molecules adsorbed on a reconstructed (0001) face of ZnO and obtained the value of +12 cm^{-1}, in contrast with the observed negative shift. Our estimate of this shift (*7*) was based on the dependence of ν_{CO} on the electrostatic field strength calculated by Hush and Williams (*12*). The shift, although downward, turned out to be too small to fit the experimental data. Even for a monolayer, i.e., for a coverage which is three times higher than the observed one, and after taking into account the sixfold increase of the CO molecule dipole after adsorption onto a ZnO surface, as reported by Gay *et al.* (*13*), it could not exceed 10 cm^{-1}.

Thus it must be concluded that the reason for the adsorption heat decrease and the downward static shift is the "chemical" inductive effect, that is the weakening of the electron-accepting power of a surface Zn^{2+} ion after occupation of the adjacent sites by other molecules. Comparison of the data presented in Table 1 shows that the $\Delta\nu_{ch}$ values vary over a wide range for different adsorbents, even though the saturation coverages θ_{max} are rather close to each other. In our opinion this means that the ability of different solids to transmit the influence of the adsorbed molecule from one site to the other is not the same. Measurement of these shifts for catalytic systems should provide semiquantitative information about possible changes in acidity or basicity of surface active sites as a result of the adsorption or introduction of promoting or inhibiting dopants.

Assuming that the two bands observed at low CO coverages in the spectrum of ZnO (Fig. 1) correspond to the bands at 2178 and 2168 cm^{-1} at θ_{max} in the way shown in Table 1, it is seen that the $\Delta\nu_{ch}$ values are different for different sites on the surface of the same oxide. The same effect is shown even more strikingly by the spectra of CO on TiO_2, where up to five narrow CO bands may be attributed to coordinatively bonded molecules on different surface sites (*5*) and which display different behavior with respect to coverage growth or isotopic dilution. The greatest $\Delta\nu_{dyn}$ and $\Delta\nu_{ch}$ values were found for the most intense band at 2195–2180 cm^{-1}.

Adsorption of isotopically substituted CO molecules on ZnO shows that both the chemical inductive and dipole coupling effects participate in the formation of the fine structure at medium coverages. At high coverages the appearance of a doublet at 2170–2167 cm^{-1} (Fig. 1, curve 10) is evidently caused by the dipole coupling, since at the same coverage the band of the admixed molecules of the other isotope is not split. Coverage-dependent structure in the spectrum of isotopically diluted molecules must contain direct information about the number of nearest surrounding sites, but the intensity of the band due to admixed molecules is too low. However, our data show that such a structure exists and contains at least four bands, corresponding to one band at θ_{max}. This means that every site is surrounded by not less than three identical sites.

The isosteric heat of CO adsorption on ZnO (10 kcal $mole^{-1}$ for low θ) is just a little lower than that of 10.5 kcal $mole^{-1}$ obtained calorimetrically at 300 K (*14*) or 12 kcal $mole^{-1}$ calculated from the TPD coverage dependence (*6*) and from photoelectron spectroscopy data (*13*). The main dissimilarity with the previously reported results is in the rate of decrease of ΔH_{ads} with increasing θ. Although the extrapolation of the CO coverage dependence observed at low θ for pumped-off samples to the saturation conditions (30 $\mu mol\ g^{-1}$) gave ΔH_{ads} = 7.4 kcal $mole^{-1}$ (*6*) or 5 kcal $mole^{-1}$ (*13*) for $\theta = 1$, our measurements at coverages close to saturation show that ΔH_{ads} must be about 1.5 kcal $mole^{-1}$ at $\theta_{max} = 2.0$ molec nm^{-2}, that is at $\theta = 0.3$ of a monolayer.

These results imply that attempts to obtain the distribution of surface site strength by measuring the differential heat of adsorption, as in Ref. (*15*), can lead to false information for systems with strong lateral interactions, since practically all nonspectroscopic methods of determination of ΔH_{ads} cannot distinguish the heat decrease caused by the site strength distribution from that produced by lateral interactions. Moreover, if the concentration of sites is high enough, the coverage with chemisorbed molecule may be limited by the interaction before all the sites are occupied, and hence in such a case even the total site concentration cannot be measured by the adsorption of test molecules.

In fact, the number of coordinatively unsaturated (cus) metal atoms for ideal dehydroxylated surfaces should be about 6 and 11 nm^{-2} for the $(10\bar{1}0)$ and (0001) faces of ZnO, respectively, 8.5 and 16 nm^{-2} for the same planes of BeO, 7 nm^{-2} for anatase (100) and 6.5 nm^{-2} for η-Al_2O_3 (100). Comparison of these figures with the θ_{max} values from Table 1 shows that the latter never reach even a half of the possible site concentration. It cannot therefore be excluded that it is not the number of sites, but the strong inductive interaction which actually determine the limit of chemisorption of CO. This statement, however, has to be proved by independent measurements of the surface site concentration.

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