JOURNAL OF CATALYSIS 68, 182–185 (1981)

NOTES

Transient ir Spectroscopic Investigation of Surface-Carbonyl Formation on a Supported Cobalt Catalyst

Carbon monoxide adsorption on supported metal catalysts has been the subject of extensive investigation by numerous spectroscopists (*1–3*). The reason for this is that CO is one of the best characterized diatomic molecules from experimental spectroscopy. Moreover, it is nondissociatively chemisorbed on a number of metal surfaces at ambient temperature yielding usually rather strong bands in the infrared, the assignment of which is facilitated by comparison with those of metal carbonyl complexes. Nevertheless, interpreting the spectra of this simple molecule adsorbed on supported transition metals has proved to be much more difficult than expected because of variation in the frequencies and intensities of the CO stretching bands (*2, 3*). In general there is a rough classification into bridged and linear species, and to CO attached to metal and oxygen ions in the case of incompletely reduced samples, or the alternative assignment to only linear species with different degrees of back-donation due to the coordination number of the adsorption sites (*4*). The distribution of the different kinds of adsorption sites, which is affected by particle size, nature of the support, sample preparation, pretreatment, and also by structural rearrangement during catalysis, has a substantial influence on the spectral features. In spite of the lasting uncertainty in the assignment, carbon monoxide is well suited as a probe for investigating the surface properties of catalysts.

Infrared studies on supported metal catalysts usually start with a complete *in situ* reduction of the impregnated and dried support in hydrogen at elevated temperatures. The observation of surface compounds is rarely performed during the course of a reaction. However, to elucidate the elementary steps and their sequence in reaction the dynamic ir spectroscopic concept, outlined by Tamaru (*6*) and Tamaru and Onishi (*5*), must be applied, enabling the determination of the different kinds of adsorbed species and the study of their dynamic behaviour under reaction conditions.

Applications of this concept have been reported, e. g., for the oxidation of carbon monoxide (*7, 8*) and for the hydrogenation of carbon monoxide to methane and higher hydrocarbons (*9, 10*). Although not yet practical, eventually, dynamic ir measurements may also be used in order to study the formation of supported metal catalysts. This can be done by following the course of the reduction of the deposited oxide by CO/H_2 via intermediate stages to the completely reduced metal. At the same time the CO molecule can be used as a probe, since it forms a number of changing surface species reflecting the respective stages of catalyst formation. This technique gives detailed information about CO surface species, which must be attributed to distinct intermediate stages. In addition, it should be possible to elucidate the formation of the catalyst.

For the first time this procedure has been applied to the system cobalt/silica, using carbon monoxide as a probe. The starting material containing 5.9 wt% cobalt was prepared by soaking silica (supplied from Merck AG, Darmstadt, article number 7754, specific surface area 320 m^2/g) in an aqueous solution of cobalt nitrate followed by drying. This powder was compressed into a thin self-supporting wafer

0021-9517/81/030182-04$02.00/0

of 8 mg/cm^2 and decomposed at 10^{-6} Pa, the temperature gradually being increased to 775 K in a UHV cell of the type employed in ordinary static ir studies and described elsewhere (*11*). After cooling to room temperature the sample consisted of CoO with a mean particle diameter of 3.5 nm, supported on silica. The investigations were made with a Perkin–Elmer 225 spectrometer, the ir beam of which gave rise to a sample temperature of about 345 K (*11*).

Upon admission of CO only very weak metal–CO bands appeared. Introduction of H_2, reaction for 24 h at 345 K, pumping-off, and subsequent admission of CO gave similar results. At zero time 13 kPa CO was introduced into the ir cell. Then 1000 min was allowed for reaching a largely steady state, as deduced from no significant further development of the ir bands. At this time 27 kPa H_2, purified by a palladium diffusion cell, was introduced and the spectra were recorded in rapid succession for 4 h. Figure 1 represents the change of the band positions and of the band intensities with respect to reaction time. A_{rel} means the relative absorbance $A(t)/A_{max}$, related to the maximum absorbance A_{max} reached in the course of reaction. The spectra pertaining to the different times indicated by the letters A, B, C, and D are shown in Fig. 2. As already stated, neither CO nor H_2 adsorbed separately gave rise to appreciable reduction under the conditions applied. It must be concluded that both gases cooperatively reduce the surface of the cobalt oxide under gradual formation of a supported cobalt catalyst, in the course of which a variety of CO surface compounds may be observed, resembling those already found in a previous investigation (*11*). As can be seen from the figures, the surface concentrations of the different species change with proceeding reaction, and the maximum intensity shifts from the high- to the low-frequency species with time. According to the assignment given in the literature (*3*), and depending on their time-resolved behaviour, the observed surface species may be classified into six groups, the details of which will be dealt with elsewhere (*12*), but which may be summarized as follows.

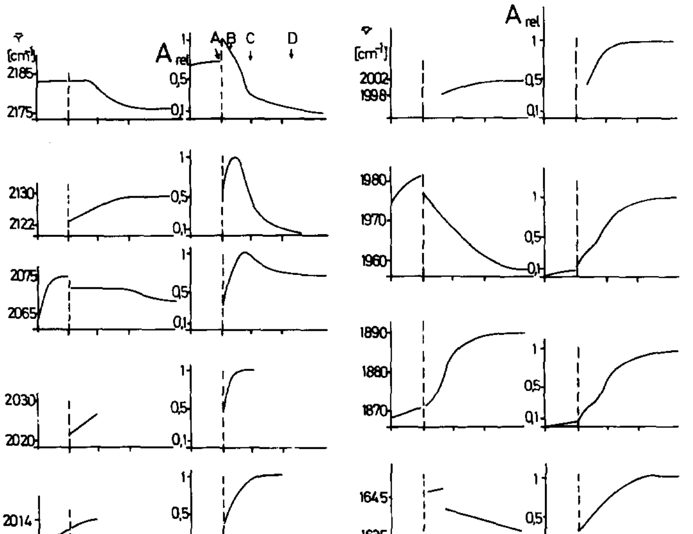

FIG. 1. Change of band position $\bar{\nu}$ and relative absorbance A_{rel} with time of CO adsorbed on silica-supported cobalt oxide after admission of CO at $t = 0$ and H_2 at $t = 1000$ min (dotted line).

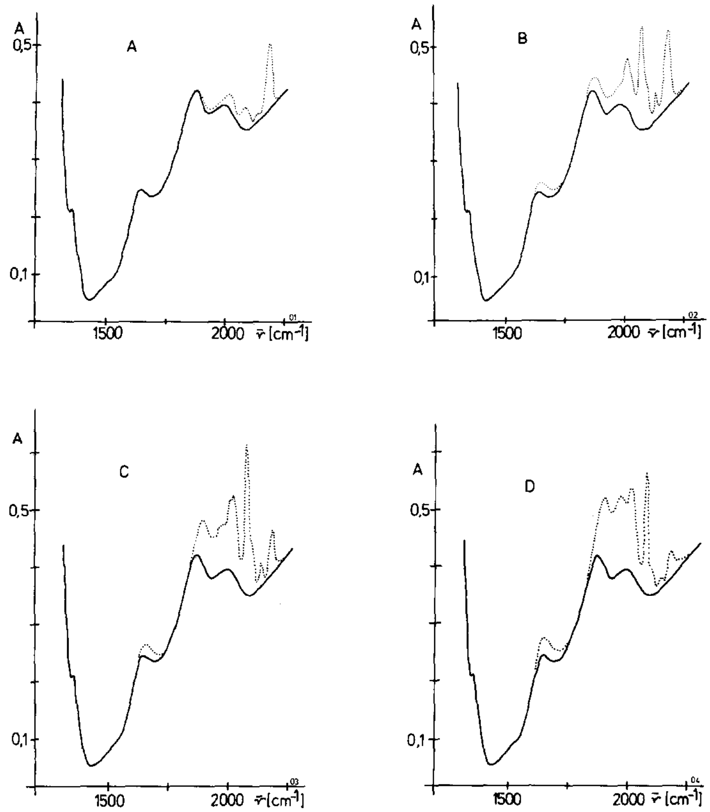

FIG. 2. Infrared spectra at different times of carbonyl formation belonging to the indicated points (A, B, C, D) in Fig. 1. (——) Background spectra, (· · ·) spectra during the course of catalyst reduction.

(i) Ionic carbonyls ($\bar{\nu} > 2143$ cm^{-1}). Species responsible for bands in this region arise from adsorption of CO on cobalt ions, resulting in a binding state similar to that for Ni^{n+} described by Politzer and Kasten (*13*).

(ii) Hydrocarbonyls ($\bar{\nu} \sim 2125$ cm^{-1}). In this case the joint adsorption of H_2 and CO on cobalt particles leads to the formation of complexes which may be assigned to hydrocarbonyls on the basis of comparing their frequencies with those of the well-known hydrocarbonyl compounds of cobalt (*14*).

(iii) Linear carbonyls in an oxygen-rich environment ($2100 > \bar{\nu} > 2050$ cm^{-1}). The different bands in this region arise from linear CO complexes with a varying extent of perturbation by oxygen in their environment. The unperturbed species give a band near 1960 cm^{-1}, which is in agreement with results of Bradshaw and Pritchard (*15*) and also Wojtczak *et al.* (*16*), who observed a similar band upon adsorption of CO on Co films.

(iv) Linear carbonyls with transient character ($2030 > \bar{\nu} > 1990$ cm^{-1}). In contrast to (iii), these bands show a transient behaviour, as there is a frequency jump (2014 cm^{-1}) or a disappearance (2025, 2008 cm^{-1}) with time or they arise somewhat after the start of the reaction (2000 cm^{-1}). According to Sheppard and Nguyen (*3*) they may be assigned to CO adsorption on Co atoms in different environments or sites where uncharged metal atoms are adjacent to charged ones. We believe that these complexes are intermediates not only between perturbed and unperturbed linear species but also between linear and bridged (multicentred) carbonyl complexes.

(v) Linear carbonyls in an oxygen-poor environment (near 1960 cm^{-1}). For comments see (iii) above.

(vi) Bridged carbonyls ($\bar{\nu} < 1900$ cm^{-1}). This assignment has been made in accordance with the results of transition metal carbonyl chemistry (*14*). In the present study the band at 1870 cm^{-1} is characteristic for a CO species on B_2 site (*3*). Also bands down to 1735 cm^{-1} associated with multicentred adsorption sites have been found (*12*).

Adsorbed water, which is produced during surface reduction of the cobalt oxide, is responsible for the band near 1640 cm^{-1}.

This brief survey shows that recording the spectra of carbon monoxide adsorption complexes during the course of reduction of supported oxides to metal catalysts provides valuable information about various surface compounds which only appear as intermediates in carbonyl formation. This can help to improve the assignment of the already known cobalt–carbonyl complexes and also give more insight into the formation of the catalytic surface.

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Received June 14, 1978; revised August 1, 1980