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Infrared Emission Study of the Reaction of CO with Ammonia Preadsorbed on MgO

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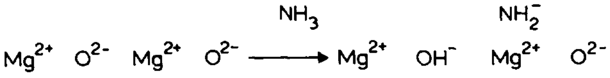
The reaction of CO with NH_2^- and OH^- groups on the surface of highly dispersed magnesium oxide has been studied by infrared emission spectroscopy in the temperature range 413–773 K. Formamide and formate ions are formed first and react to give isocyanate derivatives. Finally, simple $(NCO)^-$ ions are produced by decomposition of the isocyanate derivatives at higher temperatures. Reaction mechanisms are proposed on the basis of the spectroscopic evidence.

INTRODUCTION

High surface area MgO powder adsorbs ammonia at room temperature mostly in molecular forms (*1*). A small fraction (<10%) undergoes heterolytic dissociation on adjacent cations and anions in low coordination on the surface to give NH_2^- and OH^- groups (*1*) as indicated below:



$$Mg^{2+}\ O^{2-}\ Mg^{2+}\ O^{2-} \xrightarrow{NH_3} \overset{}{Mg^{2+}}\ OH^-\ \overset{NH_2^-}{Mg^{2+}}\ O^{2-} \qquad (I)$$

The presence of NH_2^- groups, and possibly NH^{2-} groups as well (*1*), enhances the basicity of the surface. It is of considerable interest to compare the reactivity of the clean surface (*2*) with the reactivity of the surface containing amino groups.

The aim of the present work was to study the interaction of MgO carrying presorbed ammonia with simple molecules (e.g., CO and CO_2) at elevated temperatures using infrared spectroscopy. For this purpose the emission technique is preferable to infrared absorption. Analysis of surface species by ir emission spectroscopy is generally limited by the low intensity of the radiation emitted (although Fourier Transform ir spectroscopy is now overcoming this handicap), but in the present case the intensity of the emission bands was sufficiently high to enable good quality spectra to be obtained in the temperature range of interest, namely 413–773 K, without the need to use FT ir spectroscopy.

EXPERIMENTAL

Reliable emission spectra were obtained in the system under study by making only small changes to a standard ir absorption spectrometer (Perkin-Elmer 521), as indicated in Fig. 1. This preserved the advantage of double-beam operation.

We measured the ratio E_T of the energy emitted by the sample at a given temperature in the 413–773 K range to the energy of a Nernst lamp at higher and constant temperature. Suitable base lines were obtained by screening the lamp by wire meshes.

As E_T is not the emittance, which would require the emission of a black body as reference, the recorded spectra cannot be di-

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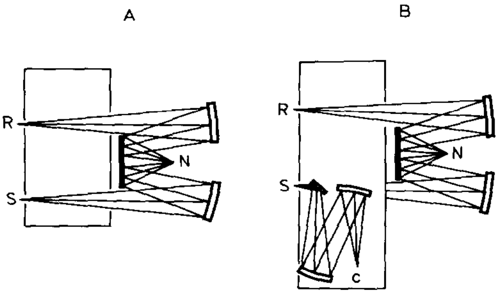


FIG. 1. Optical diagram of the Perkin–Elmer 521 spectrophotometer. (A) Standard arrangement for absorption measurements; (B) modified arrangement for emission measurements. N, Nernst lamp; R, reference beam; S, sample beam; C, emission cell.

rectly related to the absorption spectra according to the Kirchhoff law (*3*). In fact, the apparent intensities increase with temperature and, at a given temperature, decrease as the frequency increases.

The emittance could be derived by the Planck law assuming the emission of the lamp to be a good approximation to the black body emission at 1400 K and measuring some instrumental constants. However, this is not necessary in our case, as we are mainly interested in the change of each band with temperature as a probe of the changes in the surface species. Consequently the spectra were corrected only for the temperature dependence of E_T. The E_T values at the highest temperature taken as reference were calculated from the actual values measured at the various reaction temperatures following the curves of Fig. 2 and considering that the extinction coefficients do not vary significantly in the 413–773 K range in the absence of chemical reactions.

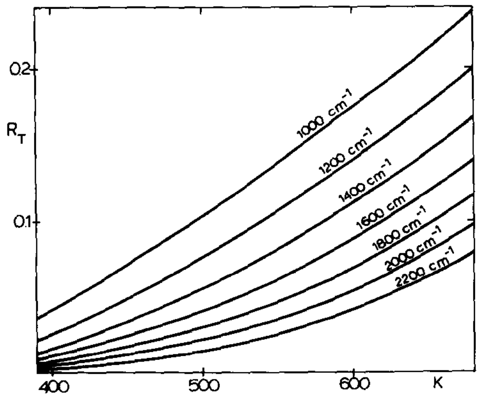


FIG. 2. Temperature dependence of R_T for various wavenumbers.

Let us now define a quantity R_T such that

$$R_T = \frac{W_T}{W_{1400}}$$

where W is the radiant power from a unit area of a blackbody in the wavelength interval dλ

$$W_T d\lambda = 2\pi h c^2 \bar{\nu}^5 \left(\frac{h\bar{\nu}c}{e^{kT}} - 1\right)^{-1} d\lambda.$$

The curves in Fig. 2 show the variation of R_T with temperature for various values of wavenumber $\bar{\nu}$. According to the above quoted hypotheses, and provided the same reference beam screen is used, it can be assumed that, for a given wavenumber:

$$\frac{E_T}{E_{T'}} = \frac{R_T}{R_{T'}}$$

where T and T′ are two different temperatures.

Figure 3 shows the jacket (right) and the

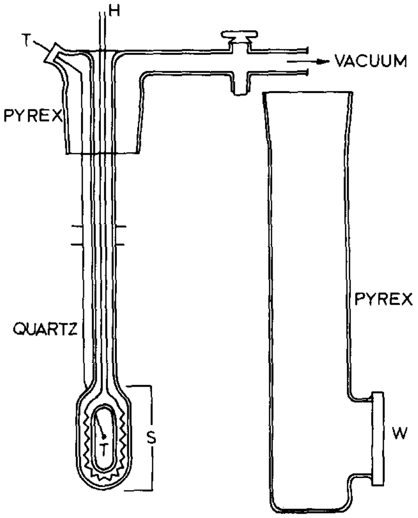


FIG. 3. Cell for infrared emission spectra. S, Sample holder; H, heater; T, thermocouple; W, CsI window.

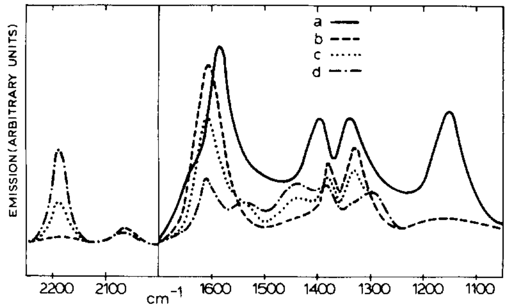


FIG. 4. Interaction of a MgO sample, after ammonia preadsorption, with CO (1.33 kN m^{-2}) at increasing temperature: (a) 413 K; (b) 453 K; (c) 553 K; and (d) 603 K.

internal part of the ir cell (left). This setup allows thermal treatments to be carried out *in situ* either *in vacuo* or in the presence of gases and vapors. The cell was permanently connected to a vacuum rig and not moved during the whole series of experiments. A 15-cm^2 piece of gold foil was wound around a quartz tube which contained the heater, and this gold foil faced the CsI window.

The sample was deposited onto the gold foil from a convenient suspension to obtain a homogeneous layer. The best results were obtained with layers 2–5 mg/cm^2 (*3–6*) thick. The gold support was chosen because of its low emissivity (*6*) and because it ensured a homogeneous heating of the sample as required by the Kirchhoff law (*7*).

High surface area MgO was obtained by thermal decomposition *in vacuo* (10^{-4} N m^{-2}) of $Mg(OH)_2$ which had been deposited onto the gold foil from acetone suspension. After a final outgassing at 900 K for 2 hr, the MgO specific surface area was 200 m^2 g^{-1}. The cell did not allow heating at higher temperature and, consequently, some surface hydroxyls were still present on the sample after the thermal pretreatment (*1*). Magnesium oxide was then contacted with 400 N m^{-2} ammonia (Matheson) for 1 hr at room temperature. After pumping off the excess NH_3 down to a pressure of 13 N m^{-2}, carbon monoxide (1.33 kN m^{-2}) was admitted into the cell at room temperature and finally the emission spectra were run at the desired temperature.

Because of the low emission intensity at high frequencies (*4*) and of the intrinsic emission of MgO at low frequencies, the useful spectral range was limited to the region 2250–1000 cm^{-1}.

The spectra presented below in Figs. 4–8 have been corrected for the E_T temperature dependence, as previously discussed.

RESULTS

Interaction of CO with Presorbed Ammonia

Figure 4 shows the effect of increasing temperature on the ir spectra which relate to the reaction of 1.33 kN m^{-2} CO with a MgO sample which had preadsorbed ammonia.

At 413 K four bands are observed at 1587, 1395, 1335, and 1150 cm^{-1} in the low frequency range ($\bar{\nu} < 1700$ cm^{-1}). A shoulder is also present at 1630 cm^{-1}.

At 453 K only three bands are observed, at 1604, 1380, and 1330 cm^{-1}. Their intensities decrease as the temperature is increased up to 603 K and new absorptions grow in at 1540, 1440, 1385, and 1300 cm^{-1}.

In the high frequency range ($\bar{\nu} > 2000$ cm^{-1}) a band is always present at 2060 cm^{-1}, but its intensity slightly decreases above 553 K. At 453 K a new band shows up at 2187 cm^{-1}. Its intensity is enhanced by increasing the reaction temperature and a linear relationship is found between such increments and the parallel decrements of the intensity of the band at 1604 cm^{-1}.

The above spectra were run after the sample had been 15 min at the desired temperature. By keeping the sample for longer times at 603 K in the presence of 1.33 kN m^{-2} CO (Fig. 5A), the intensity of the band at 2187 cm^{-1} increases, whereas that at 1604 cm^{-1} disappears (curve c). A weak emission, previously masked by the more intense companion at 1604 cm^{-1}, is now observed at 1590 cm^{-1}. Some variations are also observed in the intensities of the bands at 1540, 1440, 1385, and 1300 cm^{-1}.

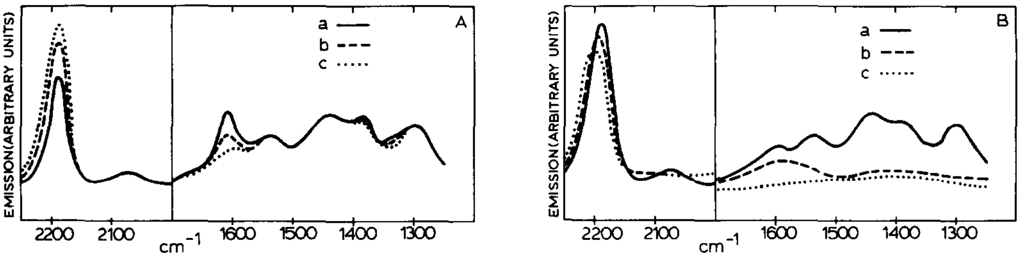


FIG. 5. (A) Effect of reaction time of CO (1.33 kN m^{-2}) at 603 K with a MgO sample, after ammonia preadsorption: (a) 15 min (the same as d in Fig. 4); (b) 30 min; (c) 60 min. (B) Effect of outgassing at increasing temperature: (a) the same as (c) in A; (b) outgassing at 603 K; (c) outgassing at 773 K.

Outgassing at 603 K leads to the disappearance of the latter bands and only emissions at 1590 (broad), 1400 (broad), and 2187 cm^{-1} are left in spectrum b of Fig. 5B. These bands are probably associated with the same surface species. As the outgassing temperature is further increased (Fig. 5Bc), the 1590 and 1400 cm^{-1} bands disappear, whereas the emission at 2187 cm^{-1} is progressively replaced by another at 2200 cm^{-1}; this latter band is the only one present in the high frequency region at 773 K. A very broad and weak emission is also observed at 1300–1500 cm^{-1}.

The surface species emitting at 2200 cm^{-1} is not affected by prolonged thermal treatment *in vacuo* at 773 K, but is destroyed by oxygen at that temperature; the products emit at 1500, 1400, and 1300 cm^{-1}. Methanol also reacts with the 2200 cm^{-1} surface species at 553 K (Fig. 6). The emission spectrum of the products shows intense bands at 1590 and 1100 cm^{-1} together with two weak and very broad bands in the 1500–1200 cm^{-1} region.

Interaction of CO_2 with Preadsorbed Ammonia

Fig. 7 shows the spectra relating to the interaction of 1.33 kN m^{-2} CO_2 with a MgO sample which had preadsorbed ammonia following the standard procedure. In this case, the emission at 2200 cm^{-1} already shows up at a temperature as low as 423 K (curve a) together with broad bands at 1630, 1540, 1400, and 1270 cm^{-1}. At 493 K the intensity of the 2200 cm^{-1} band increases and the intensity of the low frequency emission bands decreases (curve b). The former band is not affected by heating at higher temperature (553 K) whereas the latter ones are almost completely depleted, leaving very broad and weak emissions.

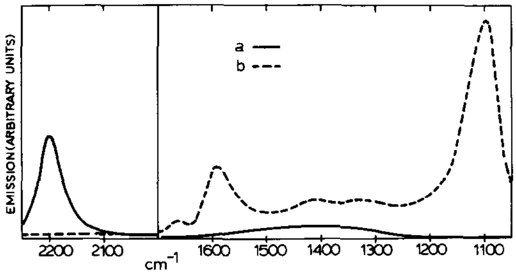


FIG. 6. Methanol interaction with surface isocyanate or cyanate species: (a) emission spectrum at 553 K of the $(NCO)^-$ species preformed at 773 K; (b) emission spectrum after subsequent admission of methanol (1.33 kN m^{-2}) at 553 K.

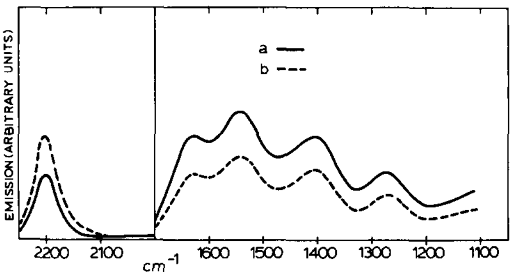


FIG. 7. Interaction of a MgO sample, after ammonia preadsorption, with 1.33 kN m^{-2} CO_2 at (a) 423 K and (b) 493 K.

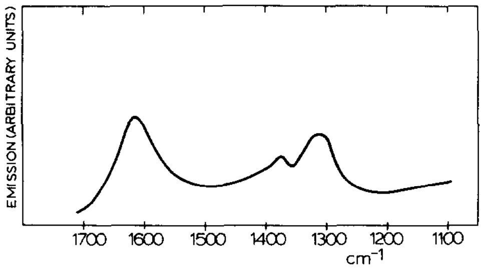


FIG. 8. Interaction of a hydroxylated MgO surface with 1.33 kN m^{-2} CO at 513 K.

Adsorption of Formamide

In a parallel experiment, formamide was allowed onto a MgO sample which, after standard outgassing at 900 K, had not been pretreated with ammonia. After 30 min at room temperature the excess formamide was pumped off at the same temperature. The emission spectra in the 413–523 K temperature range were similar, though weaker, to those shown in Fig. 4, except for the fact that only the band at 2060 cm^{-1} was present in the high frequency region. However, the band at 2187 cm^{-1} appeared when carbon monoxide was added to preadsorbed formamide.

Adsorption of CO on Hydroxylated MgO

Figure 8 refers to CO interaction with MgO sample which had been outgassed at 673 K, i.e., at a temperature much lower than that adopted in the standard pretreatment (900 K). This leaves a larger number of hydroxyl groups on the surface. Three bands at 1615, 1375, and 1320 cm^{-1} are present in the emission spectrum obtained at 513 K.

DISCUSSION

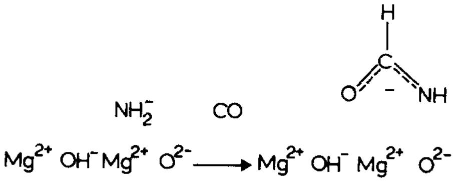
The ir emission spectra show that different species are present on the surface at the various temperatures.

Surface Species at 413 K

Two species or families of similar species are formed by the reaction of carbon monoxide at 413 K with a MgO surface which had preadsorbed ammonia: one is responsible for the low-frequency bands, which are strongly affected by increasing temperature, the other for the 2060 cm^{-1} emission.

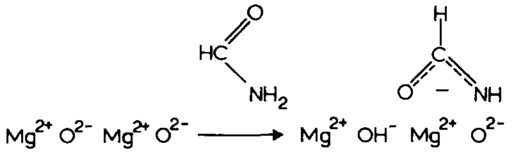
As for their nature, it is noticeable that the same bands are observed when formamide is admitted to the MgO surface. This suggests that either formamide itself or its derivatives must account for spectrum a in Fig. 4. We believe the latter to be the case for both surface species as the molecular formamide spectrum does not show any band in the 2100 cm^{-1} region and is also quite different in the low frequency range.

The 1700–1100 cm^{-1} bands could well be due to formamide ions produced *either* by CO addition to a surface containing NH_2^- groups as in the experiments of Fig. 4:



(II)

or by heterolytic dissociation of one of the N–H bonds when formamide itself is adsorbed:



(III)

Indeed, the bands at 1587, 1395, and 1335 cm^{-1} (Fig. 4a) resemble the absorptions shown in the same range by the formate ion, which is isoelectronic with the formamide ion, both in sodium formate (*8*) and when adsorbed on surfaces (*9*) (see Table 1). Moreover, the bands at 1587 and 1335 cm^{-1} agree well with those of the acetamide ions formed by heterolytic dissociation of acetamide on α-Fe_2O_3 (*10*) and δ-Al_2O_3 (*11*) and of formamide ions formed on α-Al_2O_3 (*11*) by reaction of HCN with surface hydroxyls. The 1630 and 1150 cm^{-1} bands are assignable to CNH deformation modes (*1*).

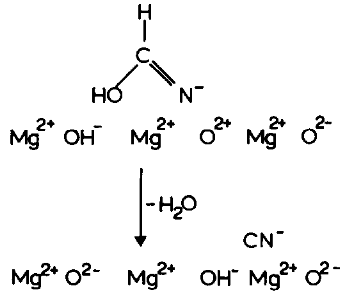
TABLE 1

Positions of Formamide and Formate Infrared Absorptions (cm^{-1})

Species formed at 413 K (formamide ions)[a]		Species formed at 453 K[a]	Sodium formate[b]		Surface formate[c]	Species of Fig. 8[a]
1630 sh	δ_{CNH}					
1587 s	NH C – as.str. O	1604 s	1567	O C – as.str. O	1630–1530	1615
1395 m	δ_{CH}	1380 m	1377	δ_{CH}		1375
1335 m	NH C – s.str. O	1330 m	1366	O C – s.str. O	1410–1320	1320
1150 m	δ_{CNH}					

[a] This work.
[b] Ref. (*10*).
[c] Ref. (*9*).

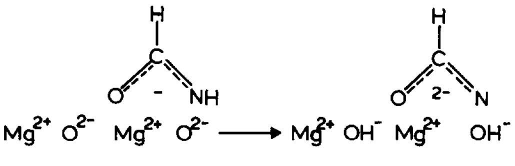
The band at 2060 cm^{-1} is probably due to cyanide ions, which in KCN and NaCN absorb at 2070 and 2080 cm^{-1}, respectively (*12*). In fact, CN$^-$ groups can be easily formed by dehydration of a fraction of preformed formamide ions:


(IV)

At temperature higher than 413 K the dehydration mechanism (IV) is in competition with the oxidation reaction to be described later, and the concentration of CN$^-$ ions does not vary significantly as the reaction temperature is increased up to 603 K (Fig. 4a,d).

Surface Species at 453 K

The ir spectrum of the surface species at 453 K (Fig. 4b) is simpler than the spectrum at 413 K (Fig. 4a) and shows three bands at 1604, 1380, and 1330 cm^{-1}. Such emissions are similar, though slightly shifted, to those at 1587, 1395, and 1335 cm^{-1} in the spectrum of Fig. 4a and may have the same origin, that is the symmetric and antisymmetric NCO stretchings (1330 and 1604 cm^{-1}) and the CH deformation (1380 cm^{-1}) of adsorbed formamide ion. However, the bands which had been assigned to NH deformation modes in the spectrum of Fig. 4a are absent in the spectrum of Fig. 4b. This suggests that further dehydrogenation of the formamide ion might have occurred at 453 K to give


(V)

The removal of the proton from an imido group is often observed in organic reactions (*13*) and may well be promoted on MgO, which is able to stabilize anionic surface species bearing two or more negative charges (*2*). The interaction with Mg^{2+} cations in low coordination on the surface is bound to reduce the actual charge of the adsorbed species.

The proposed structure for the surface species formed at 453 K (Scheme V), though reasonable, is only tentative, but it is justified by the changes in the spectra at higher temperature, as discussed below.

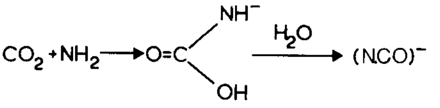
Surface Species at 453–773 K

The $(HCON)^{2-}$ ion is not stable at temperatures higher than 453 K and quantitatively produces new species as the sample is heated in excess CO up to 603 K (Fig. 4c,d). The spectrum at 603 K (Fig. 5A,c) is dominated by the emission at 2187 cm^{-1}. Such a high frequency band denotes the presence of "cumulated" double bonds and can be assigned to the antisymmetric stretching of isocyanate groups. Indeed, amides are well known to produce isocyanate derivatives by a number of reactions. Strong bands at 2164 and 2180 cm^{-1} have been observed in the infrared spectra of BrNCO and INCO (*14*), respectively. It is also relevant that similar bands, though at somewhat higher frequencies, have been observed following the adsorption of C_xH_yNCO and HNCO and in the NO + CO reaction on MgO and on magnesia-supported metal (*15*).

The formation of a species containing the (NCO) group is thus inferred. Other surface species, responsible for most of the emission bands in the low frequency range, are built up on the surface together with the isocyanate species. However, the former are readily eliminated by outgassing at 603 K, whereas the latter is not (Fig. 5B,b).

At higher temperature, the surface species characteristic of 603 K give place to different species characterized by a strong emission at 2200 cm^{-1}. This process does not require excess CO to be present and proceeds by heating the sample in vacuo to 773 K (Fig. 5B,c).

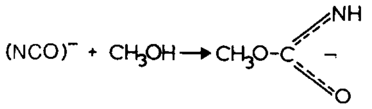
It is noticeable that the emission band at 2200 cm^{-1} appears at a lower temperature when carbon dioxide is admitted to MgO after ammonia preadsorption (Fig. 7). The spectrum of CO_2 adsorbed on a clean MgO (*16*) surface is very different and does not show any absorption at 2200 cm^{-1}. We conclude that the anion carbamic acid is firstly formed, followed by dehydration to give adsorbed $(NCO)^-$:



$$CO_2 + NH_2^- \longrightarrow O{=}C(NH^-)(OH) \xrightarrow{H_2O} (NCO)^- \qquad (VI)$$

The 1700–1100 cm^{-1} emission bands (Fig. 7) are associated with the intermediate carbamate ions. Their intensity decreases as the dehydration process is favoured by increasing the temperature, whereas the emission at 2200 cm^{-1} due to the final product is enhanced.

The species emitting at 2200 cm^{-1} is very reactive. For instance, it readily reacts with methanol, giving rise to bands in the region 1700–1000 cm^{-1} (Fig. 6b), which are easily assignable to a urethane ion produced by the following reaction



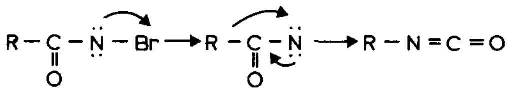
$$(NCO)^- + CH_3OH \longrightarrow CH_3O{-}C(NH)(O)^- \qquad (VII)$$

The overall spectroscopic evidence strongly suggests the formation of $(NCO)^-$ as the final product of the CO interaction with a MgO surface containing amino groups. This species is likely to be in ionic form, as with most of the species observed on the surface of MgO. The formal structure could be either $N{\equiv}C{-}O^-$ (cyanate) or $^-N{=}C{=}O$ (isocyanate). We are not able to decide whether it interacts with the surface via the nitrogen or the oxygen atom. A more detailed knowledge of the structures of the intermediate products requires a discussion of the mechanisms which might be operative at the successive stages of the reaction.

Mechanisms of Isocyanate Ion Formation

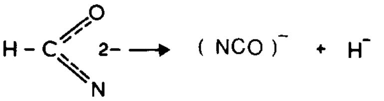
It has been shown that formamide anions are involved in two successive dehydrogenation processes. In a third step, isocyanate compounds form on the surface as a result of the decomposition of the formamide ions.

A well-known process leading to isocyanate derivatives from amides is the Hofmann reaction (*17*), that is an oxidation reaction via a nitrene intermediate



(VIII)

An alternative process could be operative on the MgO surface, that is a third step producing $(NCO)^-$ and hydride ions:



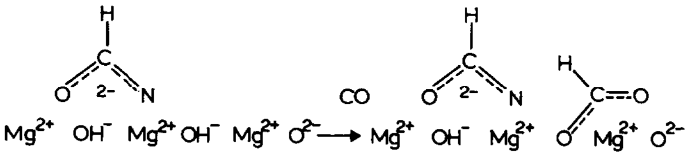
(IX)

MgO is in fact able to break the C–H bond in hydrocarbons and heterocycles (*18*).

However, Schemes VIII and IX are not satisfactory in this case, as they do not justify the need for excess CO to assist the production of isocyanate compounds from preformed formamide species. In fact, it has been shown that when formamide alone is admitted to MgO, the reaction stops after the two dehydration steps producing the dianion and no isocyanate compound is observed until CO is admitted into the cell. Analogously, when a MgO surface containing NH_2 groups is contacted with excess CO (1.33 kN m^{-1}), the formamide ions appear first, and then transform at higher temperature into isocyanate derivatives.

The experiment described in Fig. 8 refers to the reaction of CO with a hydroxylated surface and may suggest a possible role for the excess CO. The emission bands (Table 1) observed in the spectrum (Fig. 8) can be easily assigned to the vibrations of formate ions (*8*, *9*).

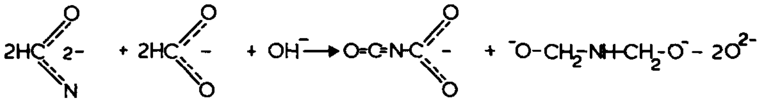
Hydroxyl ions are present on the MgO surface following the heterolytic dissociation of ammonia (Scheme I) and more are produced by dehydrogenation of the formamide species firstly formed upon CO addition (Schemes II–III). Such OH^- groups are bound to react with excess CO, so that surface formates are produced together with the formamide ions



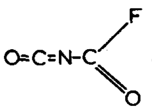
(X)

The emission bands due to formate and formamide ions overlap and cannot be distinguished in the spectra of Fig. 4.

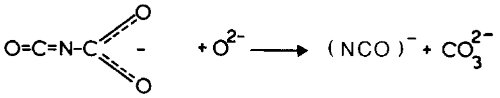
We propose that the two surface species react at temperatures higher than 453 K. Though no reference can be made to analogous process in the homogeneous phase, a plausible reaction, involving a surface hydroxyl, is the following:



(XI)

The oxidized compound is the ion of an isocyanato-carboxylic acid and is considered to be responsible for the emission bands at 2187 and 1590 cm^{-1} (Fig. 5B,b). The fluoro-derivative of this acid, namely , is known (*19*). The reduced species is regarded as responsible for the other emissions in the low frequency region and is either desorbed or decomposed upon outgassing at 603 K (Fig. 5b).

Finally, at the highest temperature the carboxylate species decomposes by the following reaction, which involves a surface O^{2-} ion:



(XII)

Accordingly, the 2187 cm^{-1} band is replaced by the emission at 2200 cm^{-1}. The 1590 cm^{-1} band also disappears and the broad and complex emission growing in at 1300–1500 cm^{-1} is probably due to the low frequency mode of the $(NCO)^-$ species and to the vibrations of the carbonate groups. However, at such a high temperature, carbon dioxide could be desorbed into the gas phase.

CONCLUSIONS

The reaction of CO with amino groups on the surface of MgO proceeds through several steps and finally produces $(NCO)^-$ ions. Infrared emission spectroscopy is shown to be a very informative technique in this study as it provides the spectra of the species present on the surface at the reaction temperature. As a consequence, the nature of intermediates and the changes they undergo can be determined unambiguously and plausible mechanisms can be proposed.

The relevant reaction steps as the temperature is increased up to 773 K are:

(a) formation of formamide and formate ions ($T \leq 453$ K);

(b) reaction between formamide and formate ions to give an isocyanato-carboxylate species ($453 \text{ K} < T < 603$ K);

(c) decomposition of the latter species to give $(NCO)^-$ ions ($603 \text{ K} < T < 733$ K).

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